EXPLOSIVES

(*Photo by E. H. Mills.*)

EXPLOSIVES

BY
ARTHUR MARSHALL
A.C.G.I., F.I.C., F.C.S.
Chemical Inspector, Indian Ordnance Department

SECOND EDITION

Vol. I
HISTORY AND MANUFACTURE

WITH 77 ILLUSTRATIONS

PHILADELPHIA
P. BLAKISTON'S SON & CO.
1012 WALNUT STREET
1917

Printed in Great Britain

DEDICATED

By Permission

To the Right Honourable

DAVID LLOYD GEORGE, M.P.

PRIME MINISTER

who during the great European War also served

his King and Country as

Chancellor of the Exchequer

Minister of Munitions

and

Secretary of State for War

"Arma Virumque Cano"
Virgil.

PREFACE TO SECOND EDITION

THE fact that a second edition of this work has been called for only a year after the publication of the first indicates that it was really wanted. The Great War has meantime completed the second year of its course, but has not caused the introduction of any very novel explosives, despite sensational statements of some journalists. Certain aspects of the manufacture of explosives have, however, become of greater importance, and have therefore been treated in greater detail in this edition. Picric acid, trinitrotoluene and other nitro-aromatic compounds were formerly merely by-products of the dye industry, and consequently their manufacture seemed only to call for brief notice in a work on explosives. Now, however, they are being made on a very large scale in factories specially erected, and their supply has become a matter of national importance in every country in Europe. Before the War nitric acid made from the air could hardly anywhere compete with that manufactured from sodium nitrate, but the blockade of Germany has altered this. Thus does history repeat herself, for in the Napoleonic wars England cut off the supply of potassium nitrate from India to France and caused a great development of the French saltpetre industry. The blockade has also caused Germany to pay more attention to chlorate and perchlorate explosives and those made with liquid oxygen.

The publication of *Les Poudres et Explosifs*, by L. Vennin and G. Chesneau, has enabled me to improve the description of French explosives and methods. As in the first edition, but little space has been given to explosive substances that have not any commercial, military or theoretical importance. A systematic account of all classes of explosives, organic and inorganic, will be found in the work of Vennin and Chesneau just mentioned.

I have spared no trouble to make the work as reliable and useful as possible to those engaged in making and dealing with the explosives used in this titantic struggle, and I hope that in this way I have assisted slightly, in spite of the fact that I am detained far from the principal theatres of war. There are of course some matters in connexion with explosives which cannot be published.

My best thanks are given to my former fellow student, G. C. Jones, for very kindly undertaking the revision of the proofs and the preparation of the index, thus not only relieving me of much work, but also greatly expediting the publication of this edition. My former colleague, William Barbour, has made a number of useful suggestions and supplied me with copies of some papers which I could not otherwise have obtained in time.

A. MARSHALL.

NAINI TAL, INDIA.
February, 1917.

PREFACE TO FIRST EDITION

SINCE the late Mr. Oscar Guttmann published his work on the *Manufacture of Explosives* in 1895 no comprehensive book on this subject has appeared in English. In the interval the explosives industry has undergone many changes: every branch of it has developed enormously—even that of black powder; and scientific investigations have thrown light on many of the problems that arise in the manufacture and use of explosives. Especially during the last few years many obscure points have been cleared up. It is hoped therefore that the present work will be found to supply a real want.

In a single book of moderate size it is not possible to treat in detail every point that arises in connexion with explosives. Consequently it has been necessary to restrict its scope in some directions. The methods of using explosives belong rather to the subjects of ballistics, blasting, etc., and their full discussion would alone require a larger work than this. Therefore they have only been referred to briefly. Details of manufacture, although often of much practical importance, can only be learnt properly in the factory: consequently they have been omitted in many cases. Proposals made in patent specifications have not been dealt with unless they possess practical or theoretical importance; for more detailed information concerning patents relating to explosives the reader should refer to works such as those of R. Escales. Subjects which are treated fully in the ordinary scientific or technical textbooks have only been dealt with in so far as they throw new light on problems connected with explosives.

On the other hand, an endeavour has been made to increase the usefulness of the book by collecting allied facts from scattered sources, and placing them in juxtaposition with one another. Some subjects, which are only mentioned briefly, or not at all, in other books have been treated more fully than their intrinsic importance would otherwise have called for. Numerous references to original papers, etc., have been given to assist those who require more detailed information concerning the subjects dealt with. Considerable space has been given to matters connected with the difficult and intricate question of the stability of nitro-cellulose and allied compounds.

I am indebted to my wife for her valued help in revising the book. My thanks are also due to Mr. W. Rintoul, Mr. J. Thorburn, and Mr. W. R. Moore for assistance in revising the proofs.

It is my earnest hope that the book may be of help to my country in the present time of emergency.

A. MARSHALL.

NAINI TAL, INDIA.

CONTENTS

PART II: BLACK POWDER

CHAPTER IV

MANUFACTURE OF SALTPETRE

CHAPTER V

MANUFACTURE OF CHARCOAL AND SULPHUR

CHAPTER VI

MANUFACTURE OF GUNPOWDER

PART III: ACIDS

CHAPTER VII

SULPHURIC ACID

CHAPTER VIII

NITRIC ACID

CHAPTER IX

MIXED AND WASTE ACIDS. MANIPULATION

PART IV: NITRIC ESTERS OF CARBOHYDRATES

CHAPTER X

THEORY OF NITRATION OF CELLULOSE

CHAPTER XI

CELLULOSE

CHAPTER XII

MANUFACTURE OF NITRO-CELLULOSE

CHAPTER XIII

THE STABILIZATION OF NITRO-CELLULOSE

PART V: NITRIC ESTERS OF GLYCERINE

PART VI: NITRO-AROMATIC COMPOUNDS

CHAPTER XIX

NITRO-DERIVATIVES OF AROMATIC HYDROCARBONS

CHAPTER XX

OTHER NITRO-AROMATIC COMPOUNDS

PART VII: SMOKELESS POWDERS

CHAPTER XXI

SLOW-BURNING SMOKELESS POWDERS

CHAPTER XXII

REQUIREMENTS OF A SLOW-BURNING SMOKELESS POWDER

CHAPTER XXIII

FAST-BURNING SMOKELESS POWDERS

PART VIII: BLASTING EXPLOSIVES

LIST OF PRINCIPAL ABBREVIATIONS

JOURNALS, ETC.

A. and E.	*Arms and Explosives.*
Ang.	*Zeitschrift für angewandte Chemie.*
A.R.	*Annual Reports of H.M. Inspectors of Explosives.*
Ber.	*Berichte of the German Chemical Society.*
Bull.	*Bulletin of U.S. Bureau of Mines.*
Chem. Ind.	*Die chemische Industrie.*
Chem. Trade. J.	*Chemical Trade Journal.*
Compt. Rend.	*Comptes Rendus.*
C.Z.	*Chemiker-Zeitung.*
J. Soc. Chem. Ind.	*Journal of the Society of Chemical Industry.*
P. et S.	*Mémorial des Poudres et Salpêtres.*
Phil. Trans.	*Philosophical Transactions of the Royal Society.*
Proc. R.S.	*Proceedings of the Royal Society.*
S.R.	*Special Reports of H.M. Inspectors of Explosives.*
S.S.	*Zeitschrift für das gesamte Schies- und Sprengstoffwesen*
Trans. Chem. Soc.	*Transactions of the Chemical Society.*

BOOKS

Chalon.	*Les Explosifs Modernes.*
Cundill and Thomson.	*Dictionary of Explosives.*
Hime.	*Gunpowder and Ammunition*, by Lieut.-Colonel Hime.
Manufacture.	*The Manufacture of Explosives*, by O. Guttmann.
Monumenta.	*Monumenta Pulveris Pyrii*, by O. Guttmann.
Twenty Years' Progress.	*Twenty Years' Progress in Explosives*, by O. Guttmann.
Rise and Progress.	*The Rise and Progress of the British Explosives Industry.*
Worden.	*The Nitro-cellulose Industry*, by Worden.
Zschokke.	*Militarische Spengtecknik*, by B. Zschokke.
Vennin and Chesneau.	*Les Poudres et Explosifs*, 1914.

OTHER ABBREVIATIONS

b.p.	boiling-point.	G/c.	guncotton.
c.c.	cubic centimetres.	m.p.	melting-point.
coll. cot.	collodion cotton.	N/c.	nitro-cellulose.
D/n/g.	dinitroglycerine.	N/g.	nitro-glycerine.
D/n/t.	dinitrotoluene.	sp. gr.	specific gravity.
g.	grammes.	T/n/t.	trinitrotoluene.

Temperatures are always in degrees Centigrade unless otherwise stated.

INTRODUCTION

Explosion : Explosive : Gas Evolution : Heat Liberation : Sensitiveness : Constituents of Explosives : Oxygen Carriers : Combustible Constituents : Nitro-aromatic Compounds : Nitric Esters : Smokeless Powders : Endothermic Compounds : Velocity of Explosion : Incomplete Detonation : Stability : Summary

Explosion.

WHEN gas or vapour is released so suddenly as to cause a loud noise an explosion is said to occur, as, for instance, the explosion of a steam boiler or a cylinder of compressed gas. Great and increasing use is made of explosive processes in gas, petrol, and oil engines for driving machinery of all kinds. In these engines the material that explodes is a mixture of air with combustible gas, vapour, or finely-comminuted liquid, and in the explosion these are suddenly converted into water vapour and the oxides of carbon, which latter are gases. Although all these things are liable to explode, none of them are called explosives; this term is confined to liquid and solid substances, which produce much more violent effects than exploding gaseous mixtures, because they occupy much smaller volumes originally.

Explosive.

An explosive is a solid or liquid substance or mixture of substances which is liable, on the application of heat or a blow to a small portion of the mass, to be converted in a very short interval of time into other more stable substances largely or entirely gaseous. A considerable amount of heat is also invariably evolved, and consequently there is a flame.

Gas Evolution.

That evolution of gas (or vapour) is essential in an explosion is rendered evident by considering thermit. This consists of a mixture of a metallic oxide, generally oxide of iron, with aluminium powder. When suitably ignited the aluminium is converted into oxide and the iron or other metal is set free in a short interval of time with the evolution of an enormous quantity of heat, but there is no explosion. It is indeed because no gas is evolved that thermit can be used, as it is, for local heating and welding.

Heat Liberation.

It is also an essential condition that heat should be evolved in an explosive reaction, otherwise the absorption of energy due to the work done by the explosion would cool the explosive and consequently slow down the reaction until it ceased, unless heat were supplied from without. Ammonium carbonate, for instance, readily decomposes into carbon dioxide, ammonia, and

VOL. I.

I

water, but in so doing it absorbs heat; consequently the reaction is much too slow to be explosive. Ammonium nitrate, on the other hand, is decomposed into oxygen, nitrogen, and water, with the evolution of heat, and is consequently liable to explode. A violent impulse is required to start the explosion, but once it is started the energy (or heat) liberated suffices to propagate the explosion, unless the conditions be such that the energy is dissipated more rapidly than it is liberated.

Sensitiveness.

Another essential for an explosive is that the reaction shall not set in until an impulse is applied. If the reaction set in spontaneously, it is obvious that its energy cannot be utilized in the form of an explosion. A mixture of sodium and water evolves hydrogen with the liberation of heat, but reaction sets in immediately the two substances come in contact with one another. Different explosives require impulses of very different strengths to cause them to explode. Some, such as diazobenzene nitrate, are exploded by a slight touch; these explosives are of no practical utility as they are too unsafe. Others, such as fulminate of mercury, are exploded by a moderate blow or a small flame; these are used principally for charging caps and detonators, a small quantity serving to explode a large amount of some other less sensitive explosive. Most of the explosives now used can be exploded by a blow only if it be extremely violent, and many of them cannot be exploded by a flame in the open in ordinary circumstances. The tendency is to use less sensitive explosives because they are safer to handle, but it should never be forgotten that the term "safe," when applied to an explosive, is only a comparative one. The duty of an explosive is to explode, and if it is not treated with proper respect it will, sooner or later, explode at the wrong time with extremely unpleasant results.

Before the subject of explosives was understood so well as it is now, inventors were very liable to think an explosive was very powerful, and therefore valuable merely because it was very sensitive, whereas too great a degree of sensitiveness is really a most objectionable feature. In the middle of the nineteenth century many such mixtures as potassium chlorate and picric acid were proposed through this want of comprehension of a fundamental condition.

Constituents of Explosives.

The explosive gaseous mixtures used in gas and oil engines to which reference has been made are composed of a combustible material, consisting largely of carbon and hydrogen, and air, the useful constituent of which is oxygen. Similarly, nearly all commercial explosives are composed partly of combustible elements, of which carbon and hydrogen are the most important, and partly of oxygen combined, but not directly with the hydrogen and carbon. On explosion the oxygen combines with the hydrogen to form water, and with the carbon to form carbon monoxide or dioxide, or a mixture of the two. It is the heat set free in this combustion that is the main or entire cause of the rise of temperature. The formation of these two oxides of carbon liberates very different quantities of heat; 12 grammes of carbon unite with 16 grammes of oxygen to form 28 grammes of carbon monoxide with the liberation of 29 large Calories, and the same quantity of carbon unites with 32 grammes of oxygen with the liberation of 97 large Calories.

Consequently an explosive is considerably more efficient if it contains sufficient oxygen to oxidize the carbon entirely to dioxide, but the effect is reduced to some extent by the relatively high specific heat of carbon dioxide. In some classes of explosives, however, a very high temperature is objectionable; this is the case with smokeless powders and explosives for use in coal mines. Smokeless powders, therefore, are generally made of such a composition that the greater part of the carbon is oxidized only to monoxide. But there is always some carbon dioxide formed, for it takes up some of the oxygen from the water vapour and liberates hydrogen, or if the total quantity of oxygen be very small there may even be free carbon produced. In the case of safety explosives for coal mines, the temperature of explosion is also sometimes kept low by restricting the proportion of oxygen, but this means is not free from objection because carbon monoxide is poisonous. Other methods are therefore adopted in some safety explosives to reduce the temperature.

Oxygen Carriers.

The oxygen may either be contained in a separate compound, such as saltpetre, which is mixed mechanically with the combustible material, or the two may be combined together in a single compound, as is the case with nitro-glycerine, trotyl, and many other modern explosives. The substances rich in oxygen are often referred to as "oxygen carriers"; those most used are nitrates, chlorates, and perchlorates, in which the oxygen is united to nitrogen and chlorine respectively. Ordinary gunpowder, or "black powder," belongs to the class of explosives that have separate oxygen carriers, in this case saltpetre. The table on page 4 shows the properties of the principal oxygen carriers.

It will be seen from this table that the proportion of available oxygen is about the same in the chlorates as in the corresponding nitrates, but whereas the chlorates decompose with the evolution of a small amount of heat, the nitrates require a considerable amount of heat to split them up, except in the case of the ammonium compound. Explosives containing chlorates are consequently much more powerful than those containing nitrates, but they are also very sensitive unless special measures are adopted to render them more inert. The perchlorates require considerably less heat to decompose them than the nitrates, and have more available oxygen. As they are now produced at quite low cost by electrolytic methods, it is not surprising to find that they are being used more and more for the manufacture of explosives. Ammonium nitrate and perchlorate decompose with the evolution of heat, this being due to the formation of water, but the available oxygen is diminished by the same cause. Ammonium nitrate can be detonated by itself, although only with difficulty, and then gives a large volume of gas at a comparatively low temperature. In consequence of this low temperature it has been found very useful as a constituent of safety explosives for use in coal mines, but it also forms part of many other high explosives. Ammonium perchlorate suffers under the disadvantage that amongst its products of explosion is the poisonous gas, hydrogen chloride, or hydrochloric acid.

Oxygen carrier	Molecular weight	Density	Reaction	Heat evolved		Oxygen available	
				per mol.	per 100 grams.	per 100 grams.	per 100 c.c.
Nitrates.							
Potassium.	101·1	2·08	$2KNO_3 = K_2O + N_2 + 5O$	−75·6	−74·8	39·5	82
Sodium .	85·0	2·26	$2NaNO_3 = Na_2O + N_2 + 5O$	−60·5	−71·3	47	106
Calcium .	164·1	2·36	$Ca(NO_3)_2 = CaO + N_2 + 5O$	−70·6	−43·0	49	115
Barium .	261·5	3·2	$Ba(NO_3)_2 = BaO + N_2 + 5O$	−94·4	−36·1	31	98
Lead . .	331·1	4·58	$Pb(NO_3)_2 = PbO + N_2 + 5O$	−54·6	−16·5	24	111
Ammonium	80·1	1·71	$NH_4NO_3 = 2H_2O + N_2 + O$	+27·6	+34·5	20	34
Chlorates.							
Potassium.	122·6	2·00	$KClO_3 = KCl + 3O$	+11·9	− 9·7	39	78
Sodium .	106·5	2·29	$NaClO_3 = NaCl + 3O$	+13·1	+12·3	45	1103
Barium .	304·3	3·18	$Ba(ClO_3) = BaCl_2 + 6O$	+25·9	+ 8·5	31·5	100
Perchlorates.							
Potassium.	138·6	2·54	$KClO_4 = KCl + 4O$	− 7·8	− 5·6	46	117
Sodium .	122·5	—	$NaClO_4 = NaCl + 4O$	−12·4	−10·2	52	—
Barium .	336·3	—	$Ba(ClO_4)_2 = BaCl_2 + 8O$	− 4·3	− 1·3	38	—
Ammonium	17·5	1·89	$2NH_4ClO_4 = 2HCl + 3H_2O + 5O + N_5$	+29·5	+25·1	34	65

Potassium permanganate and bichromate have also been used, but they possess no special advantages. Permanganate explosives are often inconveniently sensitive. Attempts have also been made to use liquid oxygen, which has the advantage of being cheap and containing 100 per cent. of available oxygen, but the difficulties of employing a liquid which boils at 200° C. below the ordinary temperature are so great that these attempts were given up. The Germans are, however, making great efforts to develop these explosives for work in mines, so as to set free a corresponding quantity of nitrates for military use. For the same reason the German authorities are encouraging the use of chlorates and perchlorates.

Combustible Constituents. In black powder the combustibles are charcoal and sulphur; in blasting explosives many sorts of organic matter have been used or proposed, and some inorganic substances, such as potassium ferrocyanide, ammonium oxalate, and antimony sulphide, but those in common use are not very numerous. For explosives containing nitroglycerin an absorbent material must be used, and of these wood meal is the most usual, but flour and starch are constituents of some nitro-glycerine explosives, and in a few cases such substances as tan meal and prepared horse-dung are present. Cork charcoal has great absorptive power, but its high cost prevents its use. Ordinary charcoal is a constituent of some explosives, as also is coal-dust. American dynamites often contain resin and sulphur, and these constituents are sometimes met with in other explosives. Oily materials, such as castor oil, vaselin, and paraffin wax, reduce the sensitiveness of an explosive, and one or other of them may usually be found in a chlorate blasting explosive. The addition of aluminium greatly increases the heat of explosion; it is present in the explosives of the ammonal type.

Nitro-aromatic-Compounds. Modern high explosives very frequently contain nitro-derivatives of the aromatic compounds obtained from coal tar, especially the mono- di- and tri-nitro-derivatives of benzene, toluene, and naphthalene. The nitro-groups in these compounds contribute oxygen for the explosive reaction. The trinitro-compounds of substances containing only one benzene ring are explosives in themselves; trinitrotoluene, for instance. Trinitrotoluene is not only a constituent of composite explosives, but is also very largely used by itself as a charge for shell and submarine mines, and for other military and naval purposes, for which its insensitiveness combined with its great violence render it suitable. Picric acid (trinitrophenol) is also much used for these purposes, and trinitrocresol to a less extent. Although they detonate with great violence, these trinitro-compounds do not contain sufficient oxygen to oxidize the whole of the carbon they contain even to the stage of carbon monoxide. Their power as explosives is, therefore, increased by mixing them with oxygen carriers. Commercial explosives containing trinitrotoluene always have also some other constituent which can supply the deficient oxygen.

Nitric Esters. Nitro-glycerine and the nitro-celluloses are the principal members of another very important group of substances that can be used as explosives without admixture. Strictly speaking, they are not nitro-derivatives, but nitric esters. The more highly nitrated celluloses, such as gun cotton, contain enough oxygen to convert all the hydrogen into water and the carbon into monoxide, and even some of it into dioxide. Nitro-glycerine, $C_3H_5N_3O_9$, not only has enough to oxidize entirely all its hydrogen and carbon, but also has a little oxygen left over. Nitro-glycerine is the most powerful explosive compound known, but its power is increased by dissolving in it a small proportion of nitro-cellulose, which utilizes the excess of oxygen and at the same time converts it into a gelatinous solid known as blasting gelatin.

Smokeless Powders.

All smokeless powders consist largely of nitrocellulose, which has been more or less gelatinized and converted into a compact colloid by means of a suitable solvent; many of them contain practically nothing else, but in others there is a considerable proportion of nitro-glycerine. Small percentages of mineral jelly, inorganic nitrates, and other substances are also added, in many cases to improve the ballistics or the stability. Powders for rifled arms are always colloided as completely as possible, whether they be for small-arms or ordnance, to make them burn slowly and regularly, but in shot-gun powders the original structure of the nitro-cellulose is not always destroyed entirely, as they are required to burn comparatively rapidly.

Endothermic Compounds.

There are some explosive compounds which do not depend for their action on oxidation or reduction. These are endothermic substances, which decompose with the evolution of gas and heat; they are usually rather sensitive. The only compounds of this class that are of commercial importance are fulminate of mercury, $Hg(CNO)_2$, and lead azide, PbN_6, both of which are used only for exploding other explosives.

Velocity of Explosion.

There are other endothermic explosive compounds in which the heat liberated on decomposing into their elements is only of minor importance compared with the larger amount set free by the redistribution of the oxygen. Such are tetryl and mono- and dinitro-naphthalene.

The heat and gas evolved are the two principal factors which govern the power of an explosive, i.e. the amount of work it can do in the way of displacing objects. But the time taken by the explosion is also a matter of great importance. The rate of explosion is measured by making a column of the explosive, confining it, if necessary, in a metal tube, and measuring the time that the explosive wave takes to travel a known distance. In black powder and similar nitrate mixtures the velocity of explosion is only a few hundred metres a second, but with modern high explosives the velocity of detonation is from two to seven thousand metres a second. This naturally makes them much more violent and destructive. Explosives of the gunpowder type are used when earth or soft rock is to be blasted, or when the material must not be broken up too much. Propellants for use in firearms are required to burn slowly; for rifled arms they must be slower even than gunpowder. They are not exploded by means of another high explosive, but merely lit by a powerful flame, and should then burn by concentric layers. The rate of burning increases with the pressure in the gun, but for completely gelatinized powders it is less than a metre a second.

Incomplete Detonation.

The more insensitive explosives, such as trinitrotoluene, if fired with a weak detonator are only partially decomposed. Not only is some of the explosive merely scattered, but the velocity of the explosive wave is low. Consequently the effect produced is comparatively small.

Stability. Another important property of an explosive is its stability. It should retain its properties and composition unchanged when stored even for a long period. Above all it should not be liable to explode or ignite spontaneously. Nitro-cellulose unfortunately is liable to this defect, and consequently special precautions have to be taken in the case of smokeless powders and other explosives containing it.

Summary. The most important properties of explosives are: power, sensitiveness, velocity of explosion, stability and temperature of explosion. The power depends upon the temperature of explosion and the quantity of gas and vapour evolved. The prices of the constituents and the ease and safety of manufacture are also of importance. All these factors are dependent on the composition of the explosive and some of them on its physical state.

PART I

HISTORICAL

CHAPTER I

EARLY HISTORY

Gunpowder : Confusion of terms : Incendiary mixtures : Greek fire : Wild-fire : Saltpetre : The Chinese : The Indians : Friar Bacon : The Arabs : Invention of firearms : Summary : Gibbon

Gunpowder

Since the very earliest times man has been searching for more and more effective means of killing his fellows and the beasts and birds that threatened his safety or provided his food or clothing, but there is reason to believe that the first explosive, gunpowder, was not known before the thirteenth century. This is a mixture of three substances, saltpetre, sulphur and charcoal, two of which have been known from time immemorial, for sulphur occurs native in a state of considerable purity in some volcanic districts, and charcoal is made by simply heating wood. The early history of gunpowder and explosives generally is therefore closely connected with the discovery of methods of preparing and purifying saltpetre.

Confusion of terms.

The investigation of this and other similar matters is rendered difficult not only by the scarcity of early records, but also by the great uncertainty as to their true interpretation. When saltpetre, gunpowder and guns were discovered or invented, new words were not made, but old terms were adopted which had previously been used for somewhat similar objects. Our word "powder," for instance, means any dust-like material, but the term smokeless powder is now used to denote a class of substances which have nothing in common with dust. "Gun" is from the old English "gonne," which was used to denote an instrument for throwing projectiles before the introduction of gunpowder. Similarly the Arabic "bunduq" (بندوق) now used for any rifle or sporting gun, formerly meant a pellet shot from a small catapult used for sporting purposes. Saltpetre (sal petræ) merely means salt of the rock, and the other Latin term for the same material, "nitrum" (nitron, nitre), formerly meant soda or any other white efflorescence. Both nitron and natron in late Latin were derived from the Arabic نطرون (Ntrun'), some of the vowels being usually omitted in writing that language as in shorthand. Similar difficulties occur with the terms in other languages. Nevertheless, considerable progress has lately been made in ascertaining the early history of gunpowder and fire-arms, and various wild statements as to the great antiquity of the knowledge of gunpowder in some countries are now quite discredited, as it is found that the evidence upon which these statements were made will not bear scrutiny.

rly Incen-
ry Mix-
es.

Long before the discovery of saltpetre, incendiary materials had been used in warfare, such as pitch, sulphur, petroleum and other oils. Burning brands were frequently attached to arrows or were thrown by means of engines (catapults), and the descriptions of the effects produced by these early "fire-arms" is often so fanciful and exaggerated that they have been thought to imply the use of gunpowder, with which they really have no connexion. A ball of burning pitch mixed with sulphur and naphtha thrown against a wooden building or ship would cause a fire, which if not quickly extinguished might prove disastrous. Such incendiary mixtures were known in England as "wild-fire." The prompt application of a bucket of water or some sand would, however, remove the danger. Hence, although isolated instances occur in ancient history where great success was achieved with these incendiary mixtures, they must generally have proved ineffective.

ek Fire
). 668.

The one notable exception to this is the "Greek-fire" or "sea-fire," the secret of which prevented the conquest of Constantinople and Europe by the Moslems for several centuries. About the year A.D. 668, some forty-six years after the flight of Mohamed from Mecca to Medina, the Arabs, still at the height of their conquering enthusiasm, commenced to beleaguer Constantinople by land and sea, when an architect named Kallinikos fled from Heliopolis in Syria to the Imperial city and imparted the secret of the "sea-fire." This repeatedly spread such terror and destruction among the Moslem fleet, that it was the principal cause of the siege being eventually raised after seven years. In A.D. 716 to 718, the Arabs again appeared before Constantinople with eighteen hundred ships, but again were defeated by the fire; so effectually, that after a stormy passage only five galleys re-entered the port of Alexandria to relate the tale of their various and almost incredible disasters.

Russian naval forces were similarly defeated in 941 and 1043, and the Pisans at the end of the eleventh century.

What, then, was the nature of this "sea-fire"? From the contemporary accounts we know that it was discharged from tubes or siphons in the bows of the ships, but its mode of preparation was kept a close secret and it was never used successfully by any but the Greek rulers of Byzantium. There appears to be no doubt that naphtha was the principal ingredient, and it may also have contained sulphur and pitch. Colonel H. W. L. Hime came to the conclusion that it must have been mixed with quicklime, the slaking of which by the sea-water raised the temperature to the ignition point of the sulphur.[1] I have made a number of attempts to produce ignition in this

---

[1] *Gunpowder and Ammunition*, London, 1904.

way, but although a fairly high temperature was reached the sulphur never caught fire. The heat set free by the slaking of the lime would be ample to raise the temperature to the ignition point if there were no loss of heat, but the reaction is a slow one compared with an explosion, for instance, and consequently much of the heat is dissipated. It seems more probable that the naphtha was simply discharged from a squirt or fire-engine (sipho), and that it was ignited by means of a flame in front of the orifice, and that the secret consisted in the method of constructing the squirt or pump, and of using it so as not to injure the users. If this be so, the Greek fire did not differ greatly from the flame-projectors now employed by the Germans.

Wild-fire.

Later the name "Greek fire" was given also to combustible materials which were ignited and then thrown by ballistæ or other machines, and were used on land. These compositions were semi-solid masses of sulphur, pitch, naphtha and other substances that burn readily, and when saltpetre had been discovered this also was added. Such mixtures may more correctly be called "wild-fire." They were much used by the Moslems in the Crusades. Thus Joinville, the faithful and devoted companion of St. Louis in the disastrous sixth Crusade (A.D. 1250), says that "it came flying through the air like a winged long-tailed dragon, about the thickness of a hogshead, with the report of thunder and the velocity of lightning; and the darkness of the night was dispelled by this deadly illumination." Nevertheless, the Greek fire on this occasion did very little damage. That men like St. Louis and Joinville, usually absolutely fearless, should have been terrified by such a cause and described it in such exaggerated language seems to have been due to the fact that they looked upon it as a product of the Devil. By 1250, however, the Arabs were acquainted with saltpetre, and it is quite likely that they mixed some with the incendiary, causing it to burn far more fiercely. Similar language is used in describing the incendiary missiles discharged by the Moors in Spain in battles and sieges of about the same date.

A.D. 1250.

Saltpetre.

Saltpetre (potassium nitrate) is formed in the decomposition of animal and vegetable matters. Under favourable conditions it forms an efflorescence on the ground. It must have been by the investigation of such efflorescences that saltpetre was first discovered. These efflorescences are never pure and seldom contain more than a small percentage of potassium nitrate. The ancients did not clearly distinguish such deposits of saltpetre from the similar ones of soda which are found in some localities. The first preparation of saltpetre of even moderate purity from such a deposit would require considerable chemical knowledge, and it could only have been done in a country where the deposits are plentiful, that is, in a country sufficiently warm to accelerate the decomposition of the organic matter and having a regular and prolonged dry season during which the deposit would collect and not be washed away. The climate of Western Europe is consequently not favourable, and moreover scientific knowledge and investigation were very backward in Europe in the early Middle Ages. The people who were most proficient in this branch of knowledge at that time were the Arabs or rather the Arabic-speaking people of Spain, Northern Africa and Syria, and many parts of these countries have climates suitable for the formation of saltpetre deposits. Consequently, it is not surprising that it is in Arabic that the first clear reference to saltpetre is to be found. This is in the writings of Abd Allah ibn al-Baythar, a Spanish Arab who died at Damascus in 1248. It seems probable that the Arabs and Egyptians knew saltpetre in a fairly pure state about 1225.

e Chinese.

The Chinese apparently became acquainted with saltpetre at about the same period, and it is possible that they were the original discoverers of saltpetre. The Egyptians called it "Chinese snow,"[1] and it is significant that Chingis, the Mongol conqueror, brought Chinese engineers with him in 1218 to reduce the fortifications of the cities of Persia.[2] The statements made by the early Jesuit fathers as to the great antiquity of the manufacture of gunpowder in China, have been shown to be inaccurate and founded on erroneous translations.[3] Marco Polo, who was in the Far East from about 1274 to 1291, says concerning the city of Chan-Glu in Part II., Chapter L., of his book: "In this city and the district surrounding it they make great quantities of salt, by the following process; in the country is found a salsuginous earth; upon this when laid in heaps, they pour water, which in its passage through the mass imbibes the particles of salt, and is then collected in channels from whence it is conveyed to very wide pans not more than four inches deep. In these it is well boiled and then left to crystallize. The salt thus made is white and good, and is exported to various parts." The material prepared in this way could not fail to contain a considerable proportion of saltpetre, moreover the soil in the province of Che-li, in which the city mentioned seems to have been situated, is known to be rich in saltpetre. But from Marco Polo's statement it is probable that the product was used as common salt. In fact, the Chinese appear to have used saltpetre as ordinary salt even at much later periods.

nese fire-
ks.

In the chronicles called *Tung-Klan-Kang-mu* there is an account of the siege of Pien-King (now Kai-fung-fu) in 1232, and this was translated into French by Reinaud and Favé in the *Journal Asiatique* for October 1849:

> "At that time use was made of the 'ho-pao' or fire pao, called 'Tchin-tien-loui' or 'thunder that shakes the sky.' For this purpose an iron pot was used which was filled with 'yo.' As soon as a light was applied, the pao rose and fire spread in every direction. Its noise resembled that of thunder

---

[1] Hime, *Gunpowder and Ammunition*, p. 17.

[2] Gibbon, chap. lxiv.

[3] Hime, chap. vii.

and could be heard more than 100 lis (thirty-three English miles); it could spread fire over more than a third of an acre. This fire even penetrated the breast plates on which it fell."

"The Mongols constructed with ox-hides a passage which enabled them to reach right to the foot of the rampart. They commenced to sap the walls, and made holes in them in which they could remain sheltered from the men above. One of the besieged proposed that they should hang fire-paos from iron chains and let them down the face of the wall. When they reached the places that were mined, the paos burst and shattered the enemies and the ox-hides, so as not to leave a vestige of them."

"In addition, the besieged had at their disposition some 'arrows of flying fire' (fei-ho-tiang): to an arrow was attached a substance susceptible of taking fire; the arrow flew suddenly in a straight line and spread flames over a width of ten paces. No one dared approach. The fire-paos and arrows of flying fire were much feared by the Mongols."

This arrow may have been a squib or a rocket, or merely an arrow to which a saltpetre mixture was attached. The effects described could hardly have been produced without the use of saltpetre, nor the great noise without an explosive, but we need not take literally the statement that it could be heard thirty-three miles away.

By A.D. 1259 the Chinese had made a further advance. The same annals state: "In the first year of the period Khai-King was made an appliance called 'tho-ho-tsiang,' that is to say, 'lance with violent fire.' A 'nest of grains' was introduced into a long bamboo tube, which was set light to. A violent flame came out and then the 'nest of grains' was shot forth with a noise like that of a pao, which could be heard at a distance of about 500 paces." This was evidently the device now known as a Roman candle.

The Indians.

Statements have been made with regard to the antiquity of gunpowder in India upon similarly incorrect evidence. It is improbable that the refining of saltpetre can have been discovered in India, as the habits of mind of the educated classes would prevent their interesting themselves in such matters, and the institution of caste would render it impossible for them to handle many of the materials involved. But the same institution has enabled the saltpetre industry to be developed very widely, when once the process had been discovered elsewhere and introduced, as a special caste of saltpetre workers was formed, and India still supplies a large proportion of the saltpetre used. The saltpetre at first must have been very impure, as the methods of refining it were crude.

Friar Bacon 1214 to 1294

About 1249 Roger Bacon wrote an account of the composition and manufacture of saltpetre and gunpowder in his *De Secretis* and *Opus Tertium*. Those in the former work are fairly full, but were concealed by means of

Fig. 1. Portrait of Roger Bacon.
(By kind permission of Lord Sackville, from a photograph by H. E. Corke.)

ciphers, which, however, have been deciphered by Colonel Hime with great ingenuity.[1] Bacon's statements, when not cryptic, are generally vague.

In his *Opus Tertium*, written about 1250, a clearer passage has recently been found by Prof. P. Duhem in a fragment discovered in the Bibliothèque Nationale, Paris. The following free translation has been published by Colonel Hime in the journal of the Royal Artillery for July 1911 :

> "From the flashing and flaming of certain igneous mixtures and the terror inspired by their noise wonderful consequences ensue. As a simple example may be mentioned the noise and flame generated by the powder, known in divers places, composed of saltpetre, charcoal and sulphur. When a quantity of this powder no bigger than a man's finger is wrapped up in a piece of parchment and ignited, it explodes with a blinding flash and a stunning noise. If a larger quantity were used, or if the case were made of some solid material, the explosion would of course be much more violent, and the flash and din altogether unbearable.
>
> "If Greek fire, or any fire of the same species, be employed, nothing can resist the intensity of its combustion.
>
> "These compositions may be used at any distance we please, so that the operators escape all hurt from them, while those against whom they are employed are suddenly filled with confusion."

The Arabs

There can be little doubt that soon after the discovery of saltpetre the Arabs introduced it into their "Greek fire" and other incendiaries. In Europe, saltpetre must have been more scarce than in Africa and Asia. Moreover, the chivalry of Western Europe looked upon such means of war with horror and perhaps were half aware that the use of them must eventually destroy the Order.

In the *Liber Ignium* of Marcus Græcus, which was probably translated into Latin from an Arabic source about 1300,[2] there are several references to such mixtures, but the translator does not appear to have understood the subject he was writing on, and consequently it is not now possible to be sure whether he is endeavouring to describe firebrands, rockets or other fire-works. One "flying fire" (ignis volatilis) is composed of :

Resin	1
Sulphur	1
Saltpetre	2

dissolved in linseed oil and put into a (hollow) reed or piece of wood. This was apparently an incendiary (wild-fire).

---

[1] *Gunpowder and Ammunition*, chap. viii. *See* also first edition of this work.

[2] *See* Hime, p. 103.

Another is made of

Sulphur	1
Vine or willow charcoal	2
Saltpetre	6

These were rubbed down together on a marble slab and put into a case (tunica) in different manners according to the effect to be produced. To make a loud noise the case was to be short and wide, and filled only half full, and was to be bound with strong iron wire. Evidently this was a cracker not unlike one described by Bacon. On the other hand, the "flying tunica" was to be thin and long, and filled with the above powder well rammed in. This was apparently an imperfect rocket or squib. The same work contains a second description of these fire-works (recipes 12, 13, 32, 33), but this does not help to clear up the uncertainties.

That the Arabs were probably using saltpetre in their firebrands in 1250, is shown by the passage in Joinville, quoted above (page 13). At the siege of Niebla, in Spain, in 1257, we are told that the Moors "launched stones and darts from machines, and missiles of thunder and fire."

Invention of firearms.

The Chinese do not appear to have developed explosives beyond this point, or to have made the next step, namely, of causing the powder to throw a heavy projectile instead of a ball of fire. Perhaps they made the attempt, but with disastrous results to themselves.

This step could only be taken by a nation which was at once progressive and well acquainted with the working of metals. For some time the development of gunpowder must have been impeded by the scarcity and poor quality of saltpetre. Before any great advance could be made, it was necessary for a considerable organization to grow up for collecting the saltpetre and refining it. In the meantime all the available supply was no doubt absorbed by the makers of warlike combustibles.

In the thirteenth century, therefore, saltpetre was known and used from China to Spain and England, but before the invention of fire-arms its utility can have been but small. No reliable fuse having yet been discovered, hand grenades or bombs can have been of little use and must have been more dangerous to those using them than to the enemy. The fire-works which have been alluded to must have been very uncertain in their action and not without risk to the fire-worker. It does not seem to have occurred to anyone to use explosives to blow up the walls of a besieged town by mining underneath and firing off a large quantity; the primitive powder was no doubt too uncertain in its action and its properties were not well enough known. There is evidence to show that, for getting minerals, gunpowder was not used until the seventeenth century.[1]

---

[1] *See* chap. ii.

The real development of gunpowder and its extensive use had to wait, therefore, for the invention of the gun. It is generally considered that this was accomplished by the German monk Berthold Schwartz, as he is named as the inventor in many old manuscripts. There is, however, a curious inconsistency about the dates mentioned. The year 1380 is given by Flavius Blondus, Æneas Sylvius, Baptista Saccus and many others living in the fifteenth century. Other writers have stated that the invention was made in 1354, 1390, and 1393.[1] But on the other hand, there is no doubt that guns were used much earlier. There is a manuscript in the Asiatic museum at Petrograd probably compiled by Shems ed Din Mohammed about 1320 which shows tubes for firing off both arrows and balls by means of powder.[2] In an illuminated manuscript entitled *De Officiis Regum*, written by Walter de Millemete in 1325 and preserved in Christ Church Library, Oxford, there is a drawing, reproduced in Fig. 2, of a rudimentary gun shaped like a bottle, and discharging a dart. A man is applying a light to the touch-hole. On February 11, 1326, the Republic of Venice ordered the provision of iron bullets and metal cannon for the defence of its castles and villages,[3] and in 1338 cannon and powder were provided for the protection of the ports of Harfleur and l'Heure against Edward III.[4]

In two frescoes in the church of the former monastery of St. Leonardo in Leccetto, near Siena, painted by Paolo del Maestro Neri in 1340 are shown a large cylindrical cannon discharging a spherical cannon ball, and many hand-guns.[5]

In 1331 cannon were apparently used by the Moors at the siege of Alicante,[6] and in 1342 in the defence of Algeciras against Alphonso XI of Castille.

The Counts of Derby and Salisbury were present with the Spaniards, and it is supposed that they introduced guns into England. In the following years there are several references in the accounts of the Wardrobe of Edward III of payments on account of saltpetre. Thus Thomas de Roldeston, Clerk of the King's Private Wardrobe in the Tower of London, gives an account for forty shillings for making powder and repairing various arms in the period 1344 to 1347: "Eidem Thomæ super facturam pulveris per ingeniis et emendatione diversarum armaturam XL sol."[7] And an account was discovered by Guttmann delivered by John Cok, Clerk of the King's Great Wardrobe for the date

---

[1] Guttmann, *Manufacture of Explosives*, 1895, vol. i., pp. 10–11.

[2] O. Guttmann, *Monumenta Pulveris Pyrii*.

[3] Libris, *Histoire des Sciences mathematiques en Italie*, vol. iv, p. 487; *P. et S.*, vol. vii., p. 33.

[4] *P. et S.*, vol. vii. p. 34.

[5] *See* Guttmann, *Monumenta Pulveris Pyrii*, 1906.

[6] Utescher, *S. S.*, 1914, p. 101.

[7] Guttmann, *Manufacture of Explosives*, vol. i., p. 13; Hunter, *Archæologia*, 1847 vol, xxxii.

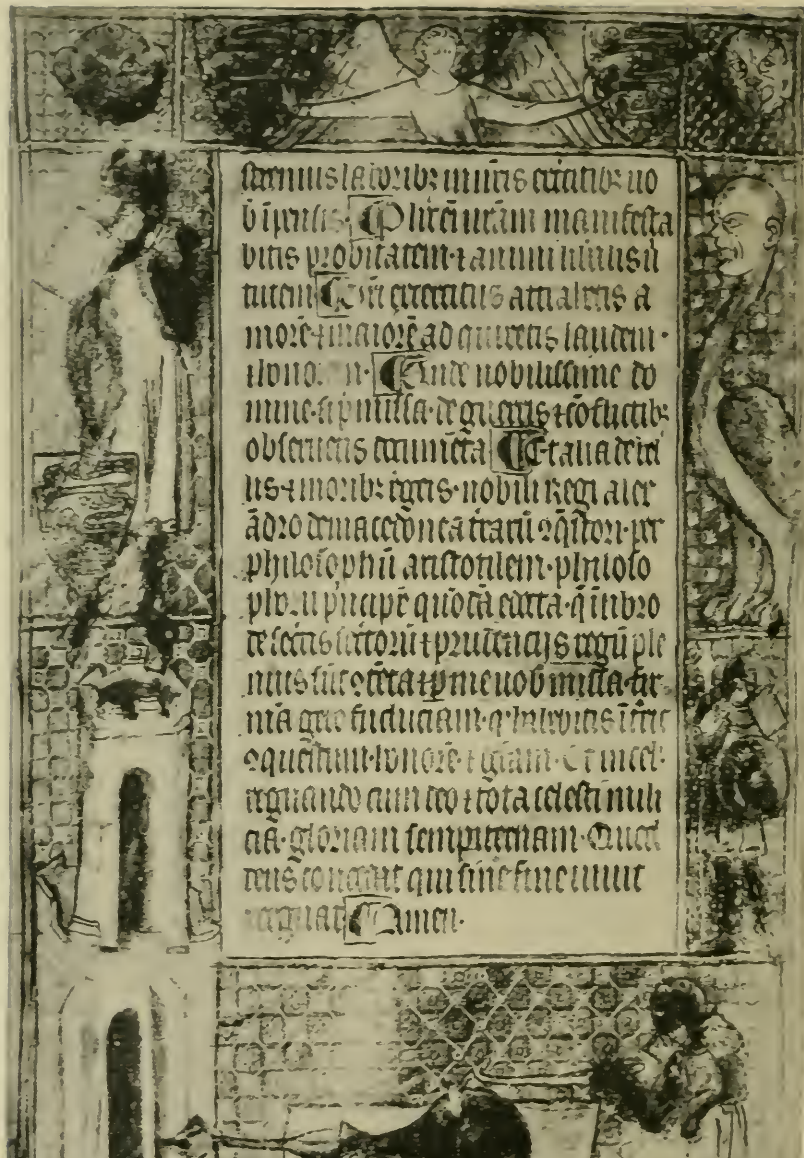


FIG. 2. From Walter de Millemete's Manuscript. A.D. 1326. (By kind permission of the Dean of Christ Church, Oxford.)

May 10, 1346, for 912 lbs. of saltpetre, and 886 lbs. of quick sulphur for the King's guns:[1] "Et eidem Thomæ de Roldeston per manus Willielmi de Stanes ad opus ipsius Reis pro gunnis suis $\overset{c}{\mathrm{I}}$ XXII lib. sal petræ et DCCC $\overset{xx}{\mathrm{IIII}}$VI lib. sulphur vivi per breve Regis datum X die Maii dicto anno XX^{o}." When all possible allowance has been made for alterations in the meanings of words, there can be no doubt that in 1346 King Edward had guns and powder. On November 25, 1346, and again on September 21, 1347, an official order was given to buy all available saltpetre in the country. On the first occasion 750 lbs. of saltpetre and 310 lbs. of sulphur were obtained; on the second, 2021 lbs. of saltpetre and 466 lbs. of sulphur. The price of the saltpetre was 18*d.* per lb., of the sulphur 8*d.*

At the battle of Crecy (August 26, 1346) guns were used by the English. The French are also believed to have possessed them, but apparently left them behind in order not to be encumbered with them in their pursuit of the English.

Summary. We see then that saltpetre became known about 1225 and that by 1350 fire-arms were in use to a considerable extent in Western Europe.

Saltpetre was apparently discovered by one of the Oriental nations, and was used for making fire-works and incendiary mixtures both in the East and West, but especially the East. The explosive properties of saltpetre mixtures must have been known to many people besides Roger Bacon, but they were of little use until the discovery of fire-arms, which apparently was made in Italy or Germany early in the fourteenth century.

The period of the first development of fire-arms was in many respects an important one. The division of the power in Italy, France and Germany among a great number of petty rulers had given the opportunity for the growth of the free cities on the one hand and the Papacy on the other. The latter had used its power to crush the Albigeois in Southern France, the most civilized and cultured people of the time, and by 1250 had extinguished them with fire and sword. The free cities were frequently richer than important countries, and it was in them that the skill and knowledge were developed which made it possible to construct ordnance and make gunpowder. Only in England did the king retain much power. In the East the prestige of Christianity and the "Franks" was then at its lowest ebb, but a steady advance was to come. The Christian religion had been extirpated from Africa and a great part of Spain, and in Syria the Crusaders had finally failed to retrieve the Holy Sepulchre. The Arabs had long since been obliged to resign most of their conquests to the Turks, who had reduced the Eastern Roman Empire to little more than the city of Constantinople, and that had become the spoil alternately of French, Normans, Venetians and Genoese.

---

[1] Public Record Office, London. L.T.R. Enrolled Wardrobe Account No. 4.

The final fall of the city was, however, postponed by the appearance of another race who came, like the Turks, from Central Asia. These were the Tartars or Moguls, the greatest conquerors known in human history. Under Chingis they conquered China in 1210 to 1214, Carizme, Transoxiana, and Persia in 1218 to 1224. The cities of the Middle East were reduced with the aid of a staff of skilful Chinese engineers, who perhaps brought with them the secret of saltpetre. Under the successors of Chingis fire and destruction were carried into Russia, Poland and Hungary. At the beginning of the fourteenth century the Mogul Empire declined under the civil wars which almost inevitably result on the death of a monarch in the East. The Turks regained their ascendancy for a time in Western Asia. In 1361 to 1405 Timour or Tamerlane usurped the whole of Chingis' Empire except China, and added to it Northern India, part of Syria and Asia Minor.

But already the forces were being born which were to revolutionize the world. In the cities of Italy, Germany, England and France a spirit of freedom in inquiry, adventure and culture was arising which now dominates the whole earth.

Gibbon

NOTE.—The account of the Greek fire is largely derived from Gibbon's *Decline and Fall*. Although this remarkable work was written in the eighteenth century, yet such is its accuracy that even upon such a difficult and technical matter as this, subsequent research has been able to find no errors in the statements. In a footnote relating to the discovery of gunpowder, Gibbon says:

"The vanity, or envy of shaking the established property of fame, has tempted some moderns to carry gunpowder above the fourteenth and Greek fire above the seventh century. But their evidence, which precedes the vulgar æra of the invention, is seldom clear or satisfactory, and subsequent writers may be suspected of fraud or credulity. In the earliest sieges some combustibles of oil and sulphur have been used, and the Greek fire has *some* affinities with gunpowder both in nature and effects."

It is impossible to sum the matter up better.

CHAPTER II

DEVELOPMENT OF GUNPOWDER

Early manufacture : Early powder-making machinery : Incorporating mill : Stamp mills : Additions to gunpowder : Corned powder : Pressed powder : Breaking down : Composition of gunpowder : Testing gunpowder : Fire-arms : Double-barrelled guns : Rifles : Cannon Projectiles : Incendiary missiles : Shell : Fuses : Hand-grenades : Infernal machines : Fire-works : Military mines : Blasting

Early manufacture.

In the fourteenth century gunpowder was only used on a small scale and was made in ordinary houses with pestle and mortar. We hear, for instance, that the Rathaus at Lübeck was destroyed by fire in 1360 through the carelessness of powder makers.[1] Berthelot has stated that there were powder mills at Augsburg in 1340, at Spandau in 1344 and Liegnitz in 1348,[2] but Feldhaus could find no confirmation of these statements in the archives of these towns. There is no mention of gunpowder or fire-arms in Augsburg before 1372 to 1373, and the first powder mill was erected at Spandau in 1578. The scale of operations gradually increased, and in 1461 we find the first mention of a "powder-house" in the Tower of London; powder was made there for many years, as also in Porchester Castle.[3] In the sixteenth century mills of considerable size were in existence: the Liebfrauenkirche in Liegnitz suffered at this time from the effects of explosions in a mill near by. In 1554 to 1555 a gunpowder mill is said to have been erected at Rotherhithe, and about 1561 George Evelyn, the grandfather of John Evelyn, the diarist, had mills at Long Ditton and Godstone, having learned the methods of manufacture in Flanders. A few years later he obtained from Queen Elizabeth a monopoly of the manufacture of gunpowder, which he and his sons were able to maintain more or less until 1636, when Samuel Cordewell obtained the monopoly, which was abolished by Parliament in 1641, the year before the outbreak of the Civil War. George Evelyn made a fortune out of gunpowder, and some of his sons did well, but it is doubtful whether

---

[1] F. M. Feldhaus, *S.S.*, 1909, p. 275.

[2] *Revue des deux Mondes*, Aug. 15, 1891, p. 817.

[3] *Brit. Exp. Ind.*, pp. 183 *et seq.* *See also History of the Evelyn Family*, by Helen Evelyn, 1915, pp. 19 and 26.

any one else made much money out of it in England. After the Restoration the monopoly of gunpowder, as of many other materials, was re-established for a time, but does not appear to have been maintained long.

In the reign of Charles I the contractors supplied to the Crown every year 240 lasts of gunpowder at 7*d.* or 8*d.* per lb., and the Crown sold it again at about a shilling, the retail price being about 16*d.* A last consisted of 24 barrels containing 100 lbs. each.[1]

Early powder-making machinery.

At first gunpowder was made by simply pounding up the constituents and mixing them together in a mortar. Often the pestle was suspended from a flexible wooden rod, which acted as a spring to assist the lifting. The very earliest known example of such an appliance is shown in an illustrated manuscript, the "Codex Germanicus," preserved in Munich (No. 600 of the Hof- und Staatsbibliothek). Guttmann assigns to this the very early date of 1350.[2] Similar pictures appear in later manuscripts, such as the "Rust und feuerwerck buych" of the fifteenth century, in the Stadtbibliothek at Frankfurt a/M. The latter also shows the next step in the adoption of machinery, the stamp mill. Guttmann, in his *Monumenta Pulveris Pyrii*, gives reproductions of many old drawings of such plant. In the fifteenth and sixteenth centuries there were generally two stamps working in each mortar. They were raised alternately by a cam projecting from an axle which was turned by hand. At a later date water wheels and treadmills were used as the motive power, and only one stamp worked in each mortar. Horses do not seem to have been used.

Incorporating mill.

There is a picture of an incorporating mill with an edge-runner in a book entitled *Corona e Palma Militare di Arteglicria* by A. Capo Bianco, and published at Venice in 1598. It has only one edge-runner, and the machine is apparently turned by a horse working in the same building.

Stamp mills.

Stamp mills were still used extensively on the Continent at the end of the nineteenth century, but in England they were forbidden. Tilt hammers were also used sometimes, especially in Switzerland, and in more modern times rotating drums containing hard wood balls have been employed.

At first the powder was used in the fine state. In this condition it burned slowly, as the interstices were very small; it was liable to foul the fire-arm very badly after a few rounds, and it was difficult to regulate the effect, which depended very much upon the ramming. Bourne, in his *Art of Shooting in Great Ordnance*, 1587, said: "The powder rammed too hard and the wad also, it will be long before the piece goes off. . . . The powder too loose . . . will make the shotte to come short of the mark. . . . Put up the powder with the rammer head somewhat close, but beat it not too hard." Other disadvantages of the fine powder were that it absorbed moisture very rapidly, and the constituents were liable to separate one from the other if the powder were subjected to much vibration. For although amorphous carbon has

---

[1] *Brit. Exp. Ind.*, p. 278.

[2] *Monumenta*, p. 19, Fig. 48.

much the same absolute density as saltpetre and sulphur, powdered charcoal contains many cavities which make it lighter than the other constituents.

Additions t
gunpowder.

It was partly to prevent this separation of the constituents that the early powder-makers added camphor, sal ammoniac and gum dissolved in spirit to their powder. Thus in the "Codex Germanicus" of the fourteenth century the following recipe is given: "Wiltu ein gut starck pulver machen So nym IIII lb Salniter und I lb swebel und I lb kol/1 uncz salpetri und I uncz salarmaniak Item und ainen XII tail campfer und stoz daz alls wol undeinand/ und tu gepranten wein darczu und stoss damit ab. und derre daz wol an der sunn/so hastu ein uberstarck beliwig pulver/ dez phunt mer tut denn sust III phunt getun möchten /und ist auch behaltig und wirt lenger pesser."

Translation: "If you want to make a good strong powder, take 4 lb. of saltpetre, 1 lb. of sulphur and 1 lb. of charcoal, 1 oz. of salpratica and 1 oz. of sal ammoniac and one-twelfth part of camphor. Pound it all well up together, and add spirit of wine and mix it in, and dry in the sun. Then you have a very strong powder, of which 1 lb. will do more than 3 lb. otherwise. It also keeps well and becomes better with time."

In another part of the same manuscript it is stated: "Wenn wa nicht gampfer pey ist daz pulver erwirt und verdirbt gern. Aber daz gamfer halt allez pulver auf/ und ist auch kreftig und prunstig in allem pulver wenn man in darin tut." Translation: "When there is no camphor, it crumbles and easily spoils. But the camphor holds all powder together, and is also strong and quick in all powder, if one puts it in."

"Salpratica" was a mixture of saltpetre, camphor and sal ammoniac, made by dissolving them all in spirit, placing the mixture in an unglazed earthenware vessel, and scraping off the efflorescence that was formed. The composition must have been very variable. These volatile materials were also supposed to improve the power of the explosive by increasing the amount of "air."

Corned
powder.

The separation of the ingredients was restrained at a later date by "corning" the powder, that is, breaking the cakes into small grains only, instead of to a fine powder. In order to get a hard mill-cake, which would give good grains, the contents of the mortar were moistened before the end of the stamping operation with water, wine or urine. After it had been broken down the grains of the required size were separated by sifting.

The earliest known reference to corned powder is in the "Firebook" of Conrad von Schongau dated 1425.[1] It left less fouling in the fire-arm and burned faster and more regularly than the very fine powder, but it developed greater pressure and consequently it could not be used in the ordnance of the time, but only in hand-guns. The fine powder came to be called "serpentine," apparently from the name of the small cannon.

---

[1] M. Jähns, *Geschichte des Kriegswesens*, Leipzig, 1880.

Whitehorne, in his *Certain Waies for the Ordering of Souldiers in Battelray*, 1560, says: "If serpentine powder should be occupied (used) in handguns, it would scant be able to drive their pellets a quoit's cast from their mouths; and if handgun (*i.e.* corned) powder should be used in pieces of ordnance, without great discretion, it would quickly break or mar them."

According to Guttmann, the French powder-mills began in 1525 to grain and classify their powder by passing it through sieves.[1] Apparently corned powder came gradually into use for small-arms and hand-grenades during the fifteenth century, and for big guns in the sixteenth, the construction of these being sufficiently improved by that time. In an engraving by Phillip Galle, after a drawing by John Stradanus, to which the date 1570 has been assigned,[2] the operations of casting and finishing guns are shown, and the manufacture had evidently reached a fairly high state of development by that time.

ssed
vder.

A really hard compact grain could not be made by this method, consequently after a time presses were introduced to compress the mill-cake before corning. According to Guttmann[3] presses were first used for this purpose in 1784. At Faversham in 1789 the powder was compressed by means of a screw press, shown in drawings in a contemporary note-book.[4] In the nineteenth century hydraulic presses were introduced.

aking
vn.

The cake was broken down by hand with wooden mallets, and then pressed through sieves to granulate and sort it. At one time wooden rollers were used to press it through the sieves, but later discs of lignum vitæ were placed in the sieves, which were suspended by means of cords and swung backwards and forwards. Colonel Congreve in 1819 introduced his granulating machine, which is described in Chapter VI.

nposition
unpowder.

Colonel Hime has given tables to show the development that took place in the composition of gunpowder in the course of time. With some alterations these are reproduced here:

ENGLISH GUNPOWDER

Date	Authority	Saltpetre	Charcoal	Sulphur
1250	Roger Bacon	41·2	29·4	29·4
1350	Arderne (Laboratory receipt) .	66·6	22·2	11·1
1560	Whitehorne	50·0	33·3	16·6
1635	Government contract . .	75·0	12·5	12·5
1670	Sir J. Turner	71·4	14·3	14·3
1742	Robins	75·0	12·5	12·5
1781	Bishop Watson . . .	75·0	15·0	10·0

---

[1] *Manufacture*, vol. i., p. 17.

[2] *Monumenta*, Fig. 8.

[3] *Manufacture*, vol. ii., p. 204.

[4] *Brit. Exp. Ind.*, Fig. 13 and p. 36.

Foreign Gunpowder

Date	Country	Saltpetre	Charcoal	Sulphur
14th Century	Germany	66·6	16·6	16·6
1560	Sweden	66·6	16·6	16·6
1595	Germany	52·2	26·1	21·7
1598	France	75·0	12·5	12·5
1608	Denmark	68·3	23·2	8·5
1697	Sweden	73·0	17·0	10·0
1882	Germany	78·0	19·0	3·0

The proportions 6 : 1 : 1, known as "as, as, six," were first adopted in France at the end of the sixteenth century and have been adhered to there more or less ever since.[1]

The fourteenth-century German powder has been substituted for a French powder of about the same date mentioned by Hime, as it is a more satisfactory example. The last item in the list is German cocoa powder, ballistically the best "black" powder ever made.

But in reality the composition was extremely variable. Every powder-maker had his own formula in early days, and in the absence of testing apparatus there was no means of judging which was best. With the invention of corned powder another variable was introduced, the size of the grains, and the confusion became still worse.

Testing gu powder.

In the Middle Ages the only tests applied to powder were to feel it to ascertain whether it was moist, and to burn a little to see whether much residue was left. The first instrument for testing powder, of which we have any knowledge, is that described by Bourne in his *Inventions and Devices*, published in 1578. It was a small metal cylinder with a heavy lid on a hinge. The lid was prevented from falling by a ratchet, and the angle to which it rose when powder was fired inside the box measured its strength. **1578.**

A much better instrument was that devised by Curtenbach and described by him in his *Halinitro Pyrobolia*, in 1627. This consisted of a heavy conical shot which rested on the mouth of a small mortar and could travel vertically upwards along a stretched wire. It was prevented from falling again by a series of catches. There is a copy of this in the Imperial Museum in Vienna, and Guttmann gives a reproduction of a photograph of it as Fig. 67 of *Monumenta Pulvis Pyrii*. **1627.**

Master-Gunner Nye, in his *Art of Gunnery*, 1647, described the same instrument, and also proposed that the strength of powder be measured by **1647.**

---

[1] Chalon, *Explosifs Modernes*, p. 228.

firing bullets from a pistol into clay, or by firing a heavy ball from a mortar and finding out how far it travelled. This last, the *mortar éprouvette*, was adopted by the French and other Governments, and led to considerable improvements in the powders. By the beginning of the eighteenth century the proportions of the constituents were fairly well fixed, and the powders for different guns differed only in the size of grain. In 1742 Robins placed the matter on a more scientific basis by the invention of the ballistic pendulum, by means of which the actual velocity of a projectile could be measured. By the end of the century, practically every country had come to use the proportions, 75 of saltpetre, 15 of charcoal, and 10 of sulphur.

-arms.

To trace in detail the development of fire-arms is beyond the scope of this work. Moreover it has depended far more upon the engineer than the powder-maker, who has nearly always been able to supply powder more powerful than the gun-maker has been able to use, through insufficient engineering skill. At first the chivalry of Western Europe was entirely opposed to the use of fire-arms, but it soon had to acquiesce in the employment of gunpowder in warfare, but made a longer struggle as regards the hunting of animals. Hawking and the chase were the only respectable forms of sport, but poachers were not governed by the same scruples, and laws were consequently passed to prevent the use of fire-arms by them. For instance, in 1555 the Elector Augustus, of Saxony, prohibited the possession of fire-arms by peasants and shepherds, and in 1562 small shot was absolutely prohibited throughout the Duchy of Mecklenburg.[1] Nevertheless, it was not possible to prevent the use of military muskets for sporting purposes. Italy, in this respect, as in so many others, was ahead of Northern Europe. Benvenuto Cellini (*b.* 1500, *d.* 1571) when a young man was very fond of shooting for sport, and made his own gunpowder. He shot with a single bullet and boasted of his skill as a marksman. He makes no mention of there being any prejudice or law against the use of fire-arms.[2]

ble-bar-
d guns.

It was not until the double-barrelled gun was introduced that there was any real difference between the military and sporting weapons. Double guns were first made sufficiently light to be practicable in the middle of the seventeenth century; in the eighteenth century the ribs were added, and the flint lock and hammer were introduced.

s.

Rifles were already known in the first half of the sixteenth century, and are said to have been invented by Augustus Kotter, of Nuremberg, in 1520, but for a long time the rifle was used principally for sporting purposes, because the necessity of ramming the bullet down the barrel with its spiral grooving made the loading very slow. Moreover, the powder left much fouling in the grooves, and consequently it was necessary to clean the arm after a few rounds.

---

[1] Greener, *Modern Shot Guns*, 2nd ed., p. 1.

[2] *Vita di Benvenuto Cellini*, part i.

With the old musket, on the other hand, the bullet was smaller than the bore, and this trouble did not arise to anything like the same extent. In the seventeenth century the rifle was tried in several continental armies, but in every case it was given up again.[1] For sporting purposes accuracy was of more importance than rapidity of fire, and the rifle was able to hold its own, especially in mountainous countries such as the Tyrol and Switzerland. In the American War of Independence the sporting rifle was necessarily used for military purposes, and the English Government found it advisable to enlist on the Continent a corps of " Jägers " to put against the colonial marksmen. Afterwards the Rifle Brigade was raised, and this proved a success from the first. Robins, the inventor of the ballistic pendulum, had already prophesied that wonderful effects would be produced by the State which could first make the military rifle a practical success.

Since then every part of the rifle has been further improved : the action, the rifling, the sights ; and magazines have been added to increase the rate of fire. In 1886 smokeless powder for rifles was introduced, and this has added greatly to the efficiency of the weapon. The final development is the introduction of automatic rifles and machine guns, such as that of Maxim, but this part of the evolution of small-arms is still in progress. The development of the pistol has proceeded on similar lines.

Cannon.

The first guns were tubes or pots, which could withstand only very slight pressures. Then they were made of strips of wrought iron welded together. By the sixteenth century they were being cast in bronze, and by the eighteenth in iron. Until the second half of the nineteenth century a gun consisted simply of a block of cast metal with a smooth bore machined out and a vent drilled near the breech. It is true that breech-loading guns were made at a much earlier date, for examples of them may be seen in the museums, but the crudity of the workmanship is sufficient to explain why they were given up again. In the Crimean war (1854) many of the guns used had seen service in the Napoleonic campaigns. In 1858 a committee recommended the introduction of rifled ordnance into the British naval service, and from that time there has been rapid and continuous improvement in all sorts of guns. The introduction of the buffer has made the guns much steadier ; breech-loading guns were re-introduced, and the mechanism of the breech has since then been improved enormously.

To meet the requirements of the longer and more accurate guns the grains of the powder were gradually increased in size so as to make them burn more slowly. In 1871 Pebble or P powder was made by cutting cubes from pressed slabs, and in 1881 Prism powder was made by moulding hexagonal prisms and pressing them in a special press. The Germans in 1882 made a brown prism powder, and in spite of attempts to keep the method of manufacture

---

[1] *Textbook of Small-Arms*, 1909, pp. 6, 7.

secret, it was being made at Waltham Abbey also two years later. This very large and dense powder was required on account of the great increase in the size of naval guns. In 1882 at the bombardment of Alexandria we had 80-ton guns of 16-inch bore, and in 1886 110-ton guns of 16¼-inch calibre. This powder did not retain its importance long, however, for in the nineties smokeless powder entirely displaced black powder as a propulsive explosive in cannon. With smokeless powder it is now possible to throw a shell weighing a ton a distance of twenty miles.

jectiles.

The first projectiles used were made more or less like arrows with metal "feathers" and arrow-heads,[1] just as the first railway carriages were built like stage-coaches. These were soon found to be unsuitable and were replaced by round shot made of iron, bronze, lead or stone. All these materials remained in use for several centuries, but stone was the most common for large guns, partly because its cost was only a fraction of that of a metal shot of the same size, and partly because the guns would not stand the strain of discharging the heavier materials. Lead and iron bullets were usually used for small-arms, but in an emergency any small handy article was made use of.

endiary
siles.

Attempts were made very early to throw from guns incendiary missiles such as had been discharged previously from machines, but some difficulty must have been experienced from the flames being extinguished by the rapid motion through the air. At the siege of Weissenburg in 1469 stone balls were used considerably smaller than the bore of the gun, and these were smeared over with incendiary matter and wrapped in a cloth soaked in the same mixture.[2]

ll.

Actual shell could not be used at that time, because it was not known how to cast them in metal. But a sort of weak shell was made of earthenware, or by joining two hemispheres of metal. These were filled with a slow burning powder well rammed in, or other incendiary matter, and were provided with an igniter, which was set light to by the flame from the gunpowder of the propelling charge, but there must have been considerable uncertainty about the ignition, and of course it was much too dangerous to introduce a lighted shell into the bore of a gun which had been charged with serpentine powder by means of a shovel. The difficulty was sometimes overcome by enclosing the powder in a paper cartridge, but this method did not find general acceptance. Red-hot shot could not be used for the same reason, until Stephen Bathory, King of Poland, in 1579 used a thick wet wad to prevent the fire spreading to the charge. Hot shot were used with great effect in the defence of Gibraltar by the English in 1782.

Solid shot are not used now except for practice and experimental purposes.

---

[1] *See Monumenta*, Plates 69, 70, 71 ; Hime, p. 199 ; *Rise and Progress*, Fig. 3,

[2] Hime, p. 220.

The shell for the early muzzle-loading rifled guns were provided with studs to fit into the rifling and with copper plates (gas-checks) over the base to prevent the escape of the gases past the shell. For some of the early rifled breech-loading guns the shell were coated with lead, but now they are provided with copper bands near the base to take the rifling and prevent the escape of the gases. Originally of course shell were filled with black powder, but now high explosives are used almost exclusively for common shell. Shrapnel shell were devised about 1784 by Lieutenant Shrapnel for use against troops in the open. They were adopted officially in 1803 and consisted of a round shell containing only a small charge of powder, just sufficient to break the envelope into fragments, which continued to travel more or less in the same direction and with the same velocity as the shell did before. After the introduction of rifled cannon the Shrapnel shell developed into a cylindrical missile filled with bullets embedded in rosin with a small charge of black powder, which, when ignited by a time fuse, expels the bullets. Against troops in the open its killing power is great, but it is ineffective against them when entrenched, and it has not the nerve shattering effect of common shell charged with high explosive.

Formerly case shot was used against troops at short range. It consisted of a case containing a large number of bullets, which spread out from the muzzle of the gun, the case being broken up in the bore. The principal sorts of case shot were grape, canister and spherical case. They are not used much now, as their place has been taken by shrapnel shell and machine guns. Chain shot was fired against the rigging of ships: it consisted of two balls or half balls united by a chain, and are said to have been invented by De Witt, Pensioner of Holland, about 1666.

Fuses. For explosive shell the difficulty was to make a satisfactory igniter or fuse. The earliest record of really successful explosive shell is in the accounts on the sieges of Wachtendonck and Bergen-op-Zoom in 1588, the master gunner being an Italian refugee from Parma in the employment of the Dutch. The fuses used were apparently tubes or pipes filled with slow-burning powder, which were driven into the fuse-hole of the shell, and this type was adhered to until the middle of the nineteenth century and later, when concussion and percussion fuses were invented.

The fuses were made to burn 14 to 20 seconds, corresponding to ranges of 1000 to 2000 yards in the mortars, which were always used instead of ordinary guns for throwing shell. The shell were used for the destruction of stone fortifications and ships; against men they were not effective, as there was usually plenty of time to get away from them before they exploded. Until after the introduction of watches, which were invented by Huygens in 1674, no convenient means existed of testing the time of burning of a fuse. In the middle of the eighteenth century fuses were made of beechwood with a hole down the middle filled with fuse powder. The fuse could be cut to any required length. Great accuracy was not demanded of them, until Captain Mercier during the siege of Gibraltar in 1779 proposed to fire shell from guns instead of howitzers or mortars. Short "calculated" fuses were then used so as to make the shell burst over the Spanish working parties. The effect produced was considerable.

Accurate fuses were also required for the Shrapnel shell, which was devised by Lieutenant Shrapnel, R.A., about 1784, and officially adopted in 1803, but they were made upon the same principle until the second half of the nineteenth century.

nd-
enades.

Hand-grenades seem to have been used to a considerable extent in the first half of the sixteenth century, at which time they were probably made of earthenware. They are said to have been used at the siege of Arles in 1536.[1] Whitehorne, writing in 1560, says that "earthen bottles or posses" had been formerly used, but he recommends "hollow balles of metal, as big as smal boules and ¼ in. thick, cast in mouldes and made of 3 partes of brasse and 1 of tinne." They were charged with "3 partes serpentine, 3 partes fine corne powder and 1 part rosen." A little fine corned powder was used as priming, and he directs that the grenades be "quickly thrown," as they will almost immediately "breake and flye into a thousand pieces."

In the seventeenth century the problem of the fuse for hand-grenades was fairly well solved, and regiments were formed of "Grenadiers," powerful men specially trained to throw grenades. Major Adye, writing in 1802, said grenades could be thrown twenty-six yards.[2]

fernal
achines.

The doubtful honour of having invented infernal machines is ascribed to a Nuremberg citizen in 1517, but there is a drawing of one by Leonardo da Vinci, who lived from 1452 to 1519. In 1645 attempts were made to blow up Swedish ships in Wismar harbour by means of clock-work bombs. The clock-work actuated a flint lock with a revolving steel wheel. Clock-work infernal machines containing a nitro-glycerine explosive were used also by the Irish-American Fenians in 1883 and 1884, but now clock-work is not generally applied in these criminal attempts.

re-works.

Fire-works seem to have been made soon after the discovery of gunpowder; references to them are found in the writings of Hassan-er-Rammah, Roger Bacon, Marcus Græcus, and Albertus Magnus in the thirteenth and fourteenth centuries. They were probably made first in China and introduced into Europe in the thirteenth century. They were used to celebrate peace at Vicenza in 1379.[3] The essential features were developed early, and later centuries have added nothing really novel. Improvements have been made in the artistic effects, precision of execution and safety, but the general prin-

---

[1] *Militär Wochenblatt*, Sept. 11, 1915.

[2] Hime, chap. x.

[3] A. Gnadewitz. *S.S.*, 1915, p. 273

ciples are the same. The introduction of chlorates at the end of the eighteenth century has been of some assistance, but their use has been restricted on account of the dangerous character of many chlorate mixtures. In the seventeenth and eighteenth centuries large sums were spent in Europe on fire-work displays to celebrate special events, but they were not much used in war. Carcasses containing incendiary composition, smoke-balls and light balls were used, however, in the Peninsula.[1] The Indians fired rockets in the defence of Seringapatam in 1792, but they do not appear to have done much damage. At the siege of the same town in 1799 explosive rockets seem to have been used with some effect.[2] Soon after this the Ordnance Office applied to the Royal Laboratory, Woolwich, for the services of some one who understood the manufacture of rockets. The Laboratory referred the Ordnance Office to the East India Company, who replied that they knew of no one who possessed such knowledge.

Colonel Congreve of the Hanoverian Army (afterwards Sir W. Congreve) was thus led to make experiments, and he devised the Congreve rocket, the most powerful thing of the kind that had been used in warfare. It proved very effective at Copenhagen and Walcheren in 1807, and at the passage of the Adour in 1813, but it was at the battle of Leipsic that it achieved the greatest renown, for a French infantry brigade in the village of Paunsdorf, unable to withstand their well-directed fire, surrendered there to the Rocket Brigade. At Waterloo also good service was rendered.

Since the Napoleonic wars the improvements in ordnance have been so great that the war rocket is no longer used. For military purposes rockets are only fired now as signals and to illuminate the enemy's position at night, and for the latter purpose they have been displaced to a great extent by star shell.

Military mines. The use of gunpowder for blowing up the enemy's walls and fortifications commenced in the fifteenth century. Mines charged with gunpowder were used in 1415 by the English at the siege of Honfleur.

Blasting. For blasting minerals gunpowder does not appear to have been used until the seventeenth century. The first recorded blasts were made by Gaspar Weindl at Schemnitz, in Hungary, and from there the method was introduced into Germany in 1627. Prince Rupert, son of the Queen of Bohemia and nephew of Charles I, is said to have brought the practice of blasting to England in 1629, but this is doubtful; 1670 is a more probable date.[3] In 1689 Thomas Epsly Senior started the use of gunpowder in the Cornish mines.[4] The late Mr. Oscar Guttmann, in his book on *Blasting*, published in 1906, gave the following concise account of the further progress:

"When bore-holes first came into use they were made with iron-mouthed

---

[1] *Rise and Progress*, p. 174.

[2] Hime, p. 129.

[3] *Brit. Exp. Ind.*, p. 255.

[4] Feldhaus, *S.S.*, 1908, p. 218.

borers, fairly large—nearly 3 inches in diameter, and then closed with a wooden plug, termed the 'shooting plug.'

"Henning Hutman in 1683 employed a kind of drilling-machine. In 1685 clay tampings, and in 1686 firing-tubes, began to be used. In 1689 paper cartridge cases were used to replace the older form of leather, and in 1717 bore-holes of smaller diameter came into vogue. The use of the chisel-borer dates from 1749, blasting the untouched breast from 1767 (first at Zinnwald)."

It is only by blasting operations that many of the engineering feats of modern times have been made possible. In constructing means of communication, such as roads, canals and railways, immense quantities of explosives have been used.

CHAPTER III

PROGRESS OF EXPLOSIVES IN THE EIGHTEENTH AND NINETEENTH CENTURIES

Berthollet, Chlorate : Igniters : Forsyth's detonator lock : Fulminates : Caps : Fuses : Gun-cotton : Nitro-glycerine : Ammonium nitrate explosives : Sprengel explosives : Coal-mine dangers : Cheddite : Inspection of explosives : Smokeless powders : Picric acid : Trotyl

IN the nineteenth century commenced the active application of science to explosives, with the result that this industry like so many others developed enormously. In this chapter no attempt will be made to give in detail the history of each invention ; only the principal discoveries will be mentioned, and an attempt will be made to show how one has led up to and assisted another.

Berthollet, chlorate.

When chemistry was put on a firm basis at the end of the eighteenth century, there was a great increase in the number of chemical compounds which could be made in the laboratory. No man had more influence upon chemical science than Count Claude L. Berthollet (1748-1822). Amongst the substances which he discovered was potassium chlorate, or at least he in 1786 first showed clearly how it could be prepared in the pure state, and he investigated and described its properties ; for it seems to have been known to Glauber (1603–1668). Berthollet found that potassium chlorate, if substituted for saltpetre, produced a more powerful (or violent) explosive, and proposed in 1788 to manufacture gunpowder with it. But the results were most disastrous. A party had been made up to see the first of the new powder made in the mills : M. and Mme. Lavoisier, M. Berthollet, the Commissary, M. de Chevraud and his daughter, the engineer, M. Lefort, and others. Whilst the mixture was being incorporated in a stamp-mill the party went to breakfast. Lefort and Mlle. de Chevraud were the first to return, and as they did so the charge exploded with great violence, throwing them to a great distance and causing them such injuries that they both died in a few minutes.

In spite of repeated attempts it has not been found possible to make a satisfactory propulsive explosive with chlorate ; the explosion is always liable to be too violent and uncontrollable.

Until the invention of Cheddite all the chlorate mixtures proposed were too sensitive to be used with safety even as blasting explosives. Cundill and Thomson's *Dictionary of Explosives* issued in 1895 includes the descriptions of 150 mixtures containing potassium chlorate, but with the exception of a few cap and fuse compositions none of these have proved to be of practical use.

Igniters.

The first fire-arms were set off by means of a lighted match, which was applied to a priming of fine powder. Rain or wind seriously interfered with the operation. In the eighteenth century the flint lock was devised and a lighted match was no longer necessary. In its best form the priming powder was contained in a small chamber which was uncovered only at the instant when the descending flint struck a spark from the steel. Although this was a great improvement it left much to be desired as regards ease of loading, rapidity of ignition, and fouling of the touch-hole. Hence the persevering attempts to devise an easier and simpler method.

orsyth's etonatorlock.

In 1805 the Rev. A. J. Forsyth, a Scotch minister, made a sporting gun with a detonator lock, and in the next year submitted his invention to the Master-General of Ordnance, who asked him to adapt it to the requirements of the Service. Forsyth's device consisted of a receptacle or magazine shaped like a scent-bottle, which was attached to the lock of the gun. It contained a detonating mixture of potassium chlorate, charcoal and sulphur. By rotating the magazine a small quantity of this was caused to fall into a small hole in a plug communicating with the touch-hole of the gun, and on again rotating the magazine it was brought into such a position that the portion of detonating priming could be set off by the fall of the hammer.

Forsyth spent some £600 in trying to produce a satisfactory device for military purposes, and he claimed to have succeeded, but the Government authorities were not convinced and did not adopt it. At the time they only paid Forsyth's expenses, but they granted £1000 to his relatives shortly after his death.

For sporting purposes Forsyth's invention had some success, but the profits must have been largely swallowed up by the numerous lawsuits that he instituted to protect it from 1811 to 1819. Before very many years had elapsed Forsyth's device was displaced by the copper tube or cap, containing fulminate of mercury.

ulminates.

Fulminates of gold and silver have long been known, and their discovery was ascribed to Basil Valentine, a fictitious person of the fifteenth century. They were perhaps invented by Cornelius Drebbel, a Dutchman, about 1600.[1] Pepys, in his diary for November 11, 1663, recounts a conversation with a Dr. Allen, who told him about *Aurum fulminans*, "of which a grain . . . put in a silver spoon and fired, will give a blow like a musquett and strike a hole through the silver spoon downward, without the least force upward."

---

[1] F. M. Feldhaus, *S.S.*, 1909, p. 258.

Mercury fulminate.

The fulminates of gold and silver are, however, too sensitive and dangerous for any practical use, but they have played their part as toys and scientific curiosities. Liebig, who was born in 1803, when a boy saw a quack in the market-place of Darmstadt make fulminating silver. The alcohol he recognized from the smell of a garment which the quack had cleaned with liquid from the same bottle. He went home and succeeded in making the substance. In 1823, when he was in Paris with Gay Lussac, he investigated the fulminates at the suggestion of the latter, and isolated fulminic acid. By that time the comparatively stable fulminate of mercury was well known, having been described by Edward Howard, F.R.S., in a paper before the Royal Society in 1800. It is stated that it was manufactured in France in 1819.

Fulminate cap.

There is some uncertainty as to who first invented the fulminate of mercury cap, but it seems that several people were working at the idea at the same time and contributed towards the final success. According to H. Wilkinson,[1] J. Shaw, of Philadelphia, invented a steel cap in 1814; in 1815 a pewter cap, and in 1816 a copper cap. The London gun-maker, Joseph Egg, seems to have adopted the idea from Shaw. The Paris gun-makers, Prélat and Deboubert, in 1820 patented caps filled with fulminates of silver and mercury respectively. E. Goode Wright, of Hereford, in 1823 published a paper[2] on the fulminate of mercury cap, and subsequent workers seem to have derived much information from it. Frederick Joyce was the first to make a real success of the percussion cap about 1824. The firm of Joyce and Co. claim an earlier date, but although experiments may have been made in previous years there appears to be no evidence of manufacture on a considerable scale.[3]

The capped cartridge.

The next important step was to combine shot, powder and cap in one cartridge, which could be inserted in the breech of the arm. Many attempts had been made from very early times to make breech-loading fire-arms, but workmanship and knowledge of engineering were not sufficiently advanced to make a success of it. In 1836 Lefaucheux introduced his pin-fire breech-loading shot-gun, the barrels of which were made to drop as in the modern shot-gun to allow the cartridges to be introduced. This gun, although it had many imperfections, combined all the principal features of those made at the present day. About 1853 the English and French gun-makers introduced the central fire hammer gun, which fired cartridges having a cap in the middle of the base of the cartridges, but the first really successful central fire gun was that made by Daw in 1861.[4]

Breech-loading rifle

In 1841 the Prussians adopted a breech-loading rifle, the "Zündnagel-

---

[1] *Engines of War*, p. 187.

[2] *Phil. Mag.*, vol. lxii., p. 203.

[3] The account of the discovery of the percussion cap is largely taken from the paper by E. Wyndham Hulme, B.A., in the *Rise and Progress of the British Explosives Industry*, London, 1909. *See also* Utescher, *S.S.*, 1914, p. 101.

[4] Greener, *Modern Shot Guns*, 2nd ed., 1891, p. 4.

gewehr," invented in 1838 by Dreyse. In this ignition was effected by a needle being driven right through the base of the cartridge into a disc of fulminating material. After a few rounds the rifle could not be fired from the shoulder in consequence of the escape of flame. The needles also rusted and broke. But in spite of its defects the gain in rapidity of fire caused it to be maintained as the general arm in the wars of 1848, 1866, and 1870.[1]

assepôt fle.

The French adopted the Chassepôt in 1866. This was a considerable improvement upon the Prussian rifle; escape of gas at the breech was prevented by means of a rubber washer. About the same time a committee sat in England to decide upon a rifle, and finally selected that of Mr. Jacob Snider, an American. But at the suggestion of Colonel Boxer the cartridge case was made of brass instead of thin paper as in previous rifles. This not only greatly improved the accuracy of shooting, but effectually prevented the escape of gas at the breech.[2]

fety fuse.

The old method of firing a blasting charge was to lay a train of powder up to it, or use a quill or rush filled with powder. The time taken by these to burn was very uncertain, however, and this caused numerous accidents in the mines. This led Mr. William Bickford, of Tuckingmill, Cornwall, in 1831 to devise his "miner's safety-fuse," wherein a continuous thin core of powder was contained in cable of jute and string.[3] This gradually came more and more into use, and the fuse was improved in quality as experience was gained in its manufacture. For use in wet places a special quality was made covered with tape and varnished. Soon after 1840 the Bickford fuse was adopted by the English military authorities. In 1836 a factory was started in America; in 1839 in France, and in 1844 in Germany. Before 1840 guttapercha-covered fuse had been adopted for blasting under water. Various modifications have since been invented, including fuse cased in metal, "Colliery Fuse," which emits no sparks,[4] and various sorts of "instantaneous fuse," which burn very rapidly and enable many shots to be fired simultaneously.

ell fuses.

As stated in the last chapter the fuses of shell were originally arranged to be ignited by the flash of the powder charge in the gun. The invention of the percussion cap, however, made it possible to start the action of the fuse in another and more certain manner. In 1846 Quartermaster Freeburn, R.A., invented the first English time fuse started by the concussion of the discharge; and in 1850 Commander Moorson, R.N., brought forward the first percussion fuse which was actuated by the shock of impact of the shell.[5] These two types of fuse are still in use and are made to screw into either the

---

[1] *Textbook of Small-Arms*, 1909, chap. ii.

[2] *Textbook of Small-Arms*, 1909.

[3] Eng. Pat. No. 6159 of 1831.

[4] Patented by Sir G. Smith in 1886.

[5] Hime, p. 245.

nose or base of the shell. Very often both methods are combined in a "time and percussion fuse." Shell were used with great effect by the Russian fleet against the Turkish at Sinope in 1853.[1]

Gun-cotton. 1846.

Gun-cotton was discovered in 1845–1846 by C. F. Schönbein, Professor of Chemistry at Basle, in the course of some experiments which he was making upon highly oxidized bodies, following up a train of thought suggested by his discovery of ozone in 1844. Pélouze had made an explosive in 1838 by the action of nitric acid on cotton, but he did not take the important step of mixing sulphuric with the nitric acid, and he did not make any practicable application of his explosive. Schönbein at once recognized its importance as an explosive and kept the method of preparation secret, whilst he endeavoured to sell the process to various Governments. He showed that when fired in a musket gun-cotton produced the same velocity as a much greater weight of gunpowder. Professor Böttger, of Frankfort-on-Main, discovered gun-cotton in 1846, independently of Schönbein, but he entered into an arrangement with him to share the profits of the invention. Several others, attracted by the great stir that was caused by the invention, endeavoured to make gun-cotton, and some of them succeeded, but Schönbein was able to maintain the start he had obtained. In the autumn of 1846 he came over to England and gave some very successful demonstrations at Woolwich and Portsmouth and before the British Association. In the name of John Taylor he took out a British Patent,[2] and he entered into an agreement for three years with John Hall and Sons that they should have the sole right to manufacture gun-cotton at their powder works at Faversham, and in return should pay one-third of the net profit with a minimum of £1000 down, and the same each year. But before a year had elapsed, on July 14, 1847, there was an explosion of the gun-cotton which destroyed the factory and killed twenty-one men. After this Hall and Sons refused to proceed with the manufacture. About the same time there were disastrous gun-cotton explosions at Vincennes and Bouchet, and these produced such an effect that no more gun-cotton was manufactured in England or France for some sixteen years.

Meantime Schönbein had offered his process to the German Union (Deutscher Bund) for 100,000 thalers, and a committee had been formed to consider the matter, on which Liebig represented the state of Hesse, and Baron von Lenk, who was secretary, represented Austria. This committee sat until 1852, but finally refused to buy the process, partly on political grounds. The individual members of the Union were then able to make separate negotiations, and at the suggestion of von Lenk, who had done most of the actual work of the committee, Austria acquired the process for 30,000 gulden.

von Lenk.

In 1852 the Emperor of Austria appointed a committee to inquire into the use of gun-cotton for military purposes, and with some interruptions this

---

[1] Rusch, *S.S.*, 1908, p. 189.

[2] No. 11407, October 8, 1846.

continued to sit until 1865. In 1853 a factory was erected at Hirtenberg to carry out von Lenk's method of making gun-cotton. In this the purification was somewhat more thorough than in Schönbein's original process, for instead of merely washing with water until neutral, von Lenk washed for three weeks, then boiled with dilute potash solution for fifteen minutes, washed again for several days, impregnated the yarn with water-glass, and finally dried. Von Lenk also constructed some batteries of 12-pounder guns to be fired with gun-cotton cartridges. These guns were so much damaged by firing, however, that no other nations adopted them. About 1860 von Lenk introduced bronze guns, which were less liable to burst than iron ones, and these not only had a propulsive charge of gun-cotton, but also had shells containing a bursting charge of the same explosive. It was found, however, that these often burst in the bore, and this was evidently due to the very sudden shock of the discharge exploding the shell charge, for when gunpowder was used to fire the gun-cotton shells, no bursts took place. On July 20, 1863, the magazine at Hirtenberg exploded, and this seems to have finally decided the Austrian authorities to give up gun-cotton as a propulsive explosive, and von Lenk was then allowed to communicate the method of manufacture to other Powers. In 1865 another magazine exploded on Steinfelder Heath, near Vienna, and on October 11, 1865, the manufacture was officially stopped in Austria.

The further development then took place in other countries. Von Lenk made communications to the Emperor Napoleon III, and experiments were started in France. In 1864 he took out an American patent.

In 1862 and 1863 von Lenk took out patents in England in the name of Révy to protect his methods of purification,[1] and in the latter year he came over with the permission of the Emperor to describe his process to a committee of the British Association. The same year Messrs. Prentice and Co. started to make gun-cotton at Stowmarket by von Lenk's process, but an explosion occurred there soon after.

bel.

Under the direction of Frederick Abel, the Chemist of the English War Department, manufacture was also started about the same time on a small scale in the Royal Gunpowder Factory at Waltham Abbey. This made it possible for Abel to carry out those experiments and researches which led to a revolution in the explosives industry, and have rendered gun-cotton one of the safest explosives in manufacture and use. In 1865 he took out a patent for pulping gun-cotton and pressing it into blocks,[2] and in 1866 and 1867 he published his *Researches on Gun-cotton*.[3] He showed that by pulping

---

[1] Eng. Pats. 1090 of 1862 and 2720 of 1863.

[2] Eng. Pat. No. 1102 of 1865. The pulping of gun-cotton had, however, been carried out at Le Bouchet in France (*see* Escales, *Schiessbaumwolle*, 1905, p. 15).

[3] *Phil. Trans. of Royal Society*, 1866, p. 269; and 1867, p. 181.

gun-cotton in the same way as is done with rags, etc., in the manufacture of paper, he not only got it in a more convenient state for pressing into blocks, but the violent mechanical treatment removed much of the impurity, and the gun-cotton was reduced to a condition in which it was much easier to wash it thoroughly. The object of compressing the pulped gun-cotton was to restrain the violence with which it exploded in the gun,[1] but although it was better than von Lenk's yarn it was still uncontrollable; it damaged the guns, and the accuracy of the shooting was unsatisfactory. It was not until some seventeen years later that a successful smokeless military powder was made. Gun-cotton was therefore only used for blasting purposes. Prentice and Co., of Stowmarket, adopted Abel's process of purification and have continued to use it ever since. In 1868 its utility was much increased by the discovery by Abel's assistant, E. A. Brown,[2] that dry compressed gun-cotton could be caused to explode very violently by a detonator containing fulminate of mercury, this appliance having been already used by Nobel [3] for detonating nitro-glycerine. Brown afterwards made the further discovery that a slab of wet gun-cotton could be exploded by means of a small primer of dry gun-cotton. This rendered it possible to store the greater part of the gun-cotton in the wet state, a great advantage for military purposes, and in this field gun-cotton as originally prepared under the superintendence of Abel still holds its ground to some extent.

Other uses nitro-cellulose.

In 1847 Maynard discovered that nitro-cellulose was soluble in a mixture of ether and alcohol, although it did not dissolve in either liquid alone, and this led to the invention of the collodion photography by Scott Archer in 1851, and to other uses of collodion. Celluloid, made by dissolving nitro-cellulose in camphor with the aid of heat and pressure, was patented by J. W. and I. S. Hyatt in 1870.[4] The artificial silk industry may be said to have started in 1884 when Count Hilaire de Chardonnet took out his first patent.[5]

Nitro-glycerine.

In 1846 nitro-glycerine was discovered by Sobrero, Professor of Chemistry at Turin, who had been assistant to Pélouze in 1838 when he made his first experiments on nitrating various bodies. But no practical application was made of it except that very small quantities were used in medicine as a cure for angina pectoris. People were no doubt deterred by the dangerous nature of the material and the inconvenience of dealing with a liquid explosive, as also by the difficulty in causing it to explode. In 1859 to 1861, however, Alfred Nobel and his father made experiments with it, and found that it could be exploded by means of a detonator containing fulminate, and in 1862

---

[1] *See Chem. News*, 1866, (4) p. 250, and 1871, (24) p. 141.

[2] Eng. Pat. No. 3115 of 1868.

[3] Eng. Pat. No. 1345 of 1867.

[4] Amer. Pat. 105,338, July 12, 1870. *See J. Soc. Chem. Ind.*, 1914, p. 225.

[5] French Pat. 165,345.

commenced to manufacture it at Heleneborg, near Stockholm. Many serious accidents occurred in the transport and use of the explosive, and in 1864 an explosion took place at the Heleneborg works, which destroyed them, killed the head chemist and Nobel's brother, and caused his father a paralytic stroke from which he never recovered. Nobel, however, was not deterred by this, and proceeded to re-erect his factory at Vintervikken, and build a new one at Krümmel in Germany. He was convinced that nitro-glycerine was the most powerful explosive known or likely to be discovered, and he allowed nothing to prevent him turning its properties to profitable account. The continual catastrophes, however, caused the various states to pass laws restricting or prohibiting the transport and use of nitro-glycerine. In consequence Nobel searched for means to make the material safer and more convenient to handle, and discovered that kieselguhr had the power to absorb three times its weight of nitro-glycerine.[1] This, combined with the fulminate detonator mentioned in the same specification, produced a very convenient and fairly safe explosive. Nobel then proceeded to exploit his inventions, and he did this with such success that by 1873 fifteen factories had been built or founded in the various countries of Europe and America. In 1875 he made another important invention,[2] that of blasting gelatine. The nitro-glycerine in this explosive was solidified by having about 8 per cent. of collodion cotton dissolved in it. As compared with kieselguhr dynamite this has two advantages: the nitro-glycerine is not liable to be displaced from it by water, a defect which in the case of dynamite has led to many accidents; and, secondly, the substance added is itself an explosive, and consequently blasting gelatine is 25 per cent. more powerful than dynamite. Gelatinized nitro-glycerine containing a small proportion of collodion has been made a constituent of many blasting explosives, the nature of the other constituents and the method of preparation being modified to produce explosives suitable for blasting different sorts of rock and other materials.[3]

monium
rate ex-
sives.

In 1867 the Swedish chemists, C. J. Ohlsson and J. H. Norrbin, took out a patent for explosives consisting of ammonium nitrate, either by itself or in admixture with other substances such as charcoal, sawdust, naphthalene, picric acid, nitro-glycerine or nitro-benzene. They were led to their invention by theoretical calculations, which showed that a very large amount of heat and gas was given off in the explosion of these mixtures. They selected the proportions so that all the carbon should be converted to carbon dioxide and the hydrogen to water. Considerable difficulty was, however, experienced in igniting the charges, and consequently they usually added some nitro-glycerine to assist the explosion. Afterwards they used the

---

[1] Eng. Pat. No. 1345 of 1867.

[2] Eng. Pat. No. 4179 of 1875.

[3] A very interesting account of Alfred Nobel and his inventions was contributed by de Mosenthal to the *J.S.C.I.* for 1899, p. 443.

fulminate detonator. The explosive was used to some extent in Sweden. Early in the seventies Alfred Nobel bought up the invention and took out further patents in connexion with it, but great difficulties were experienced in consequence of the very hygroscopic nature of ammonium nitrate. Soon after this Nobel invented blasting gelatine, and he did not take much active interest in ammonium nitrate explosives for some time.

Sprengel explosives.

In 1871 Dr. Hermann Sprengel, F.R.S., the celebrated inventor of the mercury vacuum pump, took out patents for a whole series of mining explosives to be made by mixing an oxidizing substance with a combustible one[1] "in such proportions that their mutual oxidation and de-oxidation should be theoretically complete." The essential feature was that the two constituents were to be mixed together on the spot just before the explosive was required, and the mixture was to be exploded by means of a fulminate detonator. As oxidizing agents he mentions amongst others nitric acid and chlorate of potash; as combustibles, a very large number of substances including nitro-benzene, nitro-naphthalene, carbon bisulphide, petroleum, picric acid. Liquid nitric acid is a most objectionable material to handle, nevertheless several inventors have taken out patents for Sprengel explosives containing nitric acid either enclosed in glass tubes or absorbed in fossil flour or other similar material.[2] Needless to say, they have never found favour. In addition to its other disadvantage there is the serious danger that the nitric acid may come in contact with the detonator and cause a premature explosion. This actually happened in 1884 to the inventor Punshon.

Sprengel explosives consisting of chlorate of potash and a liquid combustible material have, however, been used to a considerable extent. The American, S. R. Divine, took out a patent in 1880 for mixtures of this sort and several English patents in the following years.[3] One of these mixtures, under the name of Rackarock, was used on October 10, 1885, for the great blasting operation of Hell Gate in New York Harbour. On this occasion 240,399 lb. of Rackarock were used together with 42,331 lb. of dynamite.

There are considerable advantages in transporting separately two such inert substances as nitro-benzene and chlorate of potash, but against this must be put the difficulty and inconvenience of mixing the constitutents in the right proportions on the spot. If made up beforehand the cartridges are dangerously sensitive and become more so on keeping. Under the English Explosives Act this mixing is considered to constitute the manufacture of an explosive, and consequently may only be carried out in a duly licensed

---

[1] Brit. Pats. Nos. 921 and 2642 of 1871. *Jour. Chem. Soc.*, 1873, p. 796; *S.S.*, 1907, p. 184.

[2] Hellhoff, Brit. Pats. 1315 of 1879, 1285–87 and 2775 of 1880. Punshon, Brit. Pats. 2242 of 1880, 2428 of 1883. Bichel, French Pat. 171,169 of 1885.

[3] Eng. Pat. Nos. 5584 and 5596 of 1881, 1461 of 1882, 5624–25 of 1883.

factory. Therefore Sprengel explosives have never been used in the British Isles, but they were introduced by the Americans into China and Siberia when the first railways were built there, and one of them is now licensed in Italy.[1]

xyliquit.

A somewhat similar explosive Oxyliquit, invented by Linde, consisted of liquid oxygen absorbed in wadding, charcoal, or other organic material. It was found that these mixtures would not detonate readily, so kieselguhr was substituted as absorbent with an addition of liquid petroleum. This detonated all right, but was more sensitive to a blow or spark than dynamite. It was very inconvenient to use, as the cartridge had to be fired within five or fifteen minutes of its preparation, according to the diameter. The explosive was tried in 1899 by a commission in Austria, and on a fairly large scale in the building of the Simplon tunnel, but in spite of the low cost of liquid oxygen it was found that the practical difficulties were very great.

During the War, however, the use of explosives of this class is being encouraged in Germany in order that the available supply of nitrates may be used as far as possible for military purposes. The industrial use of chlorate explosives is being extended for the same reason.

icric acid.

Sprengel also drew attention to the fact that picric acid by itself could be detonated by a powerful detonator and was a very violent explosive, but no use was made of it in this way until many years later.

oal-mine
angers.

The revival of ammonium nitrate explosives was due to the demand for such as would not ignite the fire-damp in coal-mines. Numerous disasters due to the explosion of fire-damp led to the appointment of commissions in many of the countries of Europe to inquire into the matter and propose remedies. The nature of the danger was investigated in 1815 by Sir Humphry Davy, and one source of disaster was removed by the substitution of the Davy lamp for the naked light. As time went on gunpowder was used more and more for breaking the coal, and after 1870 dynamite was also used. About 1873 Macnab proposed to insert a cylinder filled with water in front of the charge. Others have suggested wet moss, jelly containing 90 per cent. water and sawdust saturated with a solution of alum and sal ammoniac. But these devices were found to be cumbersome and expensive and not very effective.

arcelin
erthelot.

In 1870, during the Siege of Paris, Professor M. Berthelot, who had hitherto devoted himself to pure science, was called upon to give his city and country the benefit of his scientific knowledge, and he was thus led to study the subject of explosives and especially to consider the amount of heat or energy liberated in the reactions which take place, for he had been working at thermochemistry for some years and was practically the founder of this branch of science. After the war was over Berthelot's services were still retained by

---

[1] Guttmann, *Twenty Years' Progress*, p. 10.

the State in connexion with all matters connected with explosives. On the recommendation of the French Academy of Sciences he was in 1876 appointed a member of the Committee on "Poudres et Salpêtres." In order to deal adequately with the many new inventions he recommended the formation of a special commission. This was done in 1878, and Berthelot was appointed president of the new "Commission des Substances explosives," a position which he occupied for many years.

In 1877 a commission was appointed in France to inquire into the question of ignitions of coal-damp. In the report which it made in 1880 it was obliged to admit that there was then no explosive known that would not ignite coal-damp. An English Commission which reported in 1886 was forced to come to an equally unsatisfactory conclusion.

Prussia. In 1885 the Prussian Government built at Neunkirchen the first testing station for investigating mining explosives and adopted a method of testing, which with slight modifications has been copied by the Governments of England and several other nations. A long iron cylinder was filled with mixtures of coal-damp. coal dust and air, and the explosives were fired. At first the explosive was simply suspended in the gas mixture, and it was found that the gas was ignited every time. Afterwards it was fired from a small mortar without tamping, and it was found that under these conditions kieselguhr dynamite was safe up to 100 grammes, and gelatine dynamite up to about 80.

It was now that ammonium nitrate explosives came to the fore again, as experience showed that considerably larger charges could be used without igniting the gaseous mixture. Two of the first of these were roburite and securite, mixtures of ammonium nitrate with dinitro-benzene. But it was also found possible by suitable admixtures so to alter the character of nitro-glycerine explosives that they can be used in coal-mines with comparative safety. In 1885 Schmidt and Bichel introduced carbonite, a mixture of nitro-glycerine, saltpetre and flour. This has been able to hold its own to the present day and is still considered one of the best safety explosives.

France. In 1887 another commission was appointed in France to inquire into the matter. Influenced by Berthelot's work and theories it directed its attention mainly to the question of the heat developed by an explosive and the resulting temperature of the products. Explosives having a high temperature of explosion, such as nitro-glycerine (3200°), gun-cotton (2600°) or collodion cotton (2060°), should be mixed with a substance having a low temperature of explosion such as ammonium nitrate (1130°). Three sorts of safety explosives were therefore introduced into France: Grisoutine, a mixture of ammonium nitrate and nitro-glycerine; Blasting Powder P, ammonium nitrate and collodion cotton; and Grisounite, ammonium nitrate and nitro-aromatic compounds such as nitro-naphthalene.

The great drawback to the use of ammonium nitrate is its hygroscopic nature, but the tendency to absorb water from the atmosphere has been overcome to a great extent by coating the grains with paraffin-wax or other waterproofing material, and by enclosing the cartridges in suitable envelopes.

England. In Germany and England it has long been recognized that the temperature of explosion is only one of the factors in making an explosive safe or dangerous to use in fiery mines, and consequently reliance has been placed more upon trials in testing galleries, which are intended to imitate as nearly as possible the conditions in a mine. The North of England Institute of Mining and Mechanical Engineers appointed a Committee in 1888 to inquire into this matter. Their trial gallery at Hebburn Colliery was completed in 1892, and after experimenting with various explosives until 1895 they recommended the use of several, the majority of which were ammonium nitrate explosives.

It was upon the results obtained by this Committee that the Coal Mines Regulation Act of 1906 was founded. This Act, which is still in force, authorizes the Home Secretary to prohibit the use of any explosive in coal-mines, and to appoint Inspectors of Explosives to administer the Act. A testing gallery was erected in Woolwich Arsenal, and there all explosives had to be tested before they were permitted to be used in coal-mines in the United Kingdom. More recently a larger testing gallery has been erected at Rotherham, where tests can be carried out on lines more nearly approaching those that have been adopted in Germany and Belgium.

Cheddite. In 1897 F. A. G. Street took out patents for explosives consisting of potassium chlorate mixed with castor-oil in which aromatic nitro-compounds are dissolved. The great sensitiveness of chlorate mixtures is thus overcome. The explosive thus produced is called Cheddite, and is used largely in England, France, and Germany.

Inspection of explosives. In 1875 was passed the English "Explosives Act," which has had such a great influence upon the development of the explosives industry. Its form was largely due to the late Colonel Sir V. D. Majendie, who was appointed the first permanent Inspector of Explosives to administer its provisions. The necessity for legislation was revealed by an explosion at Messrs. Ludlow's, at Birmingham, which caused the death of fifty-three persons. Colonel Majendie was instructed to report upon it. Previous to this there had been many other accidents large and small, including that of two powder magazines on the banks of the Thames at Erith, which killed thirteen people and did great damage to property.

The Inspectors of Explosives were given power to inspect all magazines and factories and see that operations are carried out in a reasonably safe manner. As a result the number of deaths in explosives factories has been very greatly reduced in spite of the fact that the number of people employed is several times as great:

	Average number killed per annum in explosives factories
1868–1870	43
1871–1874	32
1878–1887	7·5
1888–1897	5·2
1898–1907	6·9
1908–1914	9·0

By the wise and tactful manner in which they carried out their duties Colonel Majendie and his colleagues conferred this great benefit upon the employees in the explosive factories without in any way seriously interfering with the development of the industry. In fact, the precautions, which the inspectors insisted on, have been advantageous to the shareholders as well as to the workpeople and the general public. In 1898 Sir Vivian Majendie died in harness, but the work has been carried on in the same spirit by his successors, Colonel Ford, Captain J. H. Thomson, and Major A. Cooper-Key, and the other Inspectors of Explosives working under them. The provisions of the English Explosives Act of 1875 have been largely adopted in the legislation of foreign countries, British Colonies, and India.

Smokeless powders. It has already been pointed out that the early attempts of von Lenk and others to make a satisfactory smokeless powder from gun-cotton were unsuccessful because it was much too violent in its effects. The gun-cotton being in a state of fine fibre interspersed with air spaces the explosion travelled through it almost instantaneously. Black powder, on the other hand, being a mechanical mixture, the explosion can only start at the points where the particles of saltpetre are in actual contact with the particles of sulphur and charcoal, consequently the time of explosion is comparatively long.

Schultze powder. The first successful smokeless powder was that of Major Schultze, of the Prussian Artillery. First, he appears simply to have impregnated little grains of wood with saltpetre,[1] but afterwards he purified the wood to some extent by washing, boiling and bleaching it, and then nitrated it, and purified the nitrated lignose by much the same process as that used by von Lenk for gun-cotton. The grains thus obtained were then impregnated with saltpetre, alone or mixed with barium nitrate.[2] This was introduced about 1865. **1865.** According to an analysis published by Cundill in the *Dictionary of Explosives* the nitro-lignin contained more than 20 per cent. of unnitrated lignin. This and the different physical structure of wood as compared with cotton made the material burn more slowly in the gun, and the rate was still further reduced by the addition of the nitrates of potassium and barium. The explo-

---

[1] Sanford, *Nitro-Explosives*, 1896, p. 173.

[2] Eng. Pat. 900 of 1864.

sive was still too violent for rifles, however, but was found to be quite suitable for shot-guns. The Austrian rights to Schultze's invention were acquired by a firm called Volkmann's K.K. priv. Collodinfabriks Gesellschaft, H. Pernice and Co. Volkmann took out Austrian patents in 1870 and 1871, which were kept secret at the time, but Guttmann obtained copies of them and published translations in his *Twenty Years' Progress in Explosives* (Whittaker, 1909). From these it is seen that Volkmann had made the further step of partly gelatinizing the grains by treating them with a mixture of ether and alcohol, whereby the explosion would be restrained still more. This powder was made under the name of Collodin from 1872 to 1875, but then the Austrian Government stopped the manufacture on the ground that it was an infringement of their gunpowder monopoly. The nitro-lignin made as described by Volkmann must have been decidedly impure and, therefore, unstable, and difficulties were no doubt experienced in obtaining uniform results.

A company was formed in England in 1868 to work Schultze's invention, and a factory was established at Eyeworth, in the New Forest, in 1869, and this after a time achieved great success after the methods had been altered by Griffiths. By 1881 Schultze powder had become so popular with sportsmen on account of the light recoil and absence of smoke as compared with black powder, that the London gun-makers found irksome the restrictions upon the quantities they were allowed to store. The manufacturers of this powder have modified their methods from time to time to meet the demands of sportsmen and to keep abreast of the general advance in the technology of explosives, so that the Schultze powders are still amongst the best. In 1883 Schultze started a factory in partnership with Voltz and Lichtenberger at Hetzbach in Hesse-Darmstadt, and powder is still made there under Schultze's patents.[1]

E. C. powder 1882.

The next successful smokeless powder was invented at the works of the Explosives Company at Stowmarket, which formerly belonged to Thos. Prentice and Co. It was protected by patent No. 619, taken out in 1882 by Walter F. Reid and D. Johnson. This was called E. C. Powder (Explosives Company), and consisted of nitro-cotton mixed with the nitrates of potassium and barium with the addition of colouring-matter and small quantities of other organic compounds. It was made into grains which were hardened by being partially gelatinized by means of a solvent, ether-alcohol. A separate company was formed to work the invention, and a factory was started at Green Street Green, near Dartford, in Kent. This is still in existence, and E. C. Powder continues to be much used.

Gelatinized powders.

For use in rifled fire-arms these powders are too quick. For this purpose it has been found necessary to destroy entirely the structure of the original cellulose by thoroughly gelatinizing it. The first to produce a good smokeless

---

[1] A. Voigt, *Herstellung der Sprengstoffe*, i., p. 116.

rifle powder was the French engineer Vieille, working on behalf of the French Government in 1884. He incorporated the nitro-cotton with ether-alcohol in a machine such as is used for kneading bread. The resulting paste was rolled out into thin sheets and cut into small squares and dried. The powder was called Poudre B, after General Boulanger. In 1889 a gelatinized nitrocellulose flake powder was introduced in Germany.[1] In 1888 Nobel invented a powder called Ballistite, consisting of a nitro-cotton of low nitration gelatinized with nitro-glycerine, and in the same year an English committee adopted Cordite, a mixture of highly nitrated gun-cotton, nitro-glycerine and vaseline (mineral jelly), gelatinized by means of acetone. A nitro-glycerine powder of the cordite type was adopted in Austria-Hungary in 1893.[2]

Every nation now uses propellants consisting principally of gelatinized nitro-cotton either by itself or mixed with nitro-glycerine. These gelatinized powders when suitably ignited in the gun burn from the surface inwards, consequently the time of explosion can be increased by making the individual pieces of explosive bigger. Without altering the composition powders can be produced suitable for every sort of rifled fire-arm from a pistol to a 14-inch gun.

Picric aci

Picric acid has been used for a long time as a dye, and was in fact the first artificial dye to be discovered, for its formation was observed in 1771 by Woulfe by the action of nitric acid on silk. Laurent was the first to make it in 1843 by the nitration of phenol and dinitrophenol and to recognize that it is trinitrophenol. The fact that picric acid combines with metals and bases to form explosive picrates has also been known for a long time, and when its manufacture from phenol had reduced its price many mixtures containing them were proposed. Picric acid also was added to explosives as a combustible constituent. None of these mixtures were used to any great extent, however. In 1871 Sprengel demonstrated that picric acid by itself could be detonated by means of fulminate,[3] but this also led to no practical result until E. Turpin in 1885 pointed out the great advantages of using picric acid for filling shell,[4] in consequence of its stability, insensitiveness and violence. This was adopted by the French Government under the name of Melinite. Other high explosives are mostly too sensitive to use in shell : they are liable to explode in the bore of the gun from the shock of discharge. For this reason gunpowder only was previously used, and it still forms the bursting charge of shrapnel shell and other sorts which only require a moderate disruptive

---

[1] Von Neyman, *Jahrbuch der Armee und Marine*, Dec. 1914, *S.S.*, 1915, p. 145.

[2] Grotouski, *Mitt. Art.-und Geniewesen* through *S.S.*, 1914, p. 386.

[3] Eng. Pat. 2642 of 1871 ; *J. Chem. Soc.*, 1873, p. 796.

[4] French Pat. 167,512 of Feb. 7, 1885, with additions Oct. 17, 1885, and Sept. 1, 1892. Eng. Pat. 15,089 of 1885. Germ. Pat. 38,734 of Jan. 12, 1886.

power. Picric acid, however, is nearly as insensitive as black powder and can therefore be used with safety for shell. In fact, it requires a very powerful detonating primer to ensure complete detonation. With various modifications picric acid was adopted in almost every country for this purpose. It has the disadvantage, however, that it readily forms picrates if it comes in contact with metals or earthy materials, and these picrates are much more sensitive than picric acid. Its melting point also is inconveniently high.

In his patents Turpin pointed out that the sensitiveness could be reduced still further by compression, or by mixing the picric acid with heavy oils or with collodion. At first collodion was used in this way, but later the acid has generally been used by itself, either in compressed blocks or melted and cast directly into the shell. In 1911 the Civil Court in Paris granted Turpin 100,000 francs in compensation because he had not been permitted to utilize his invention to his own profit.[1] In 1888 picric acid was adopted by the German Army both for filling shell and for military blasting, and about the same date shell were filled in England with molten picric acid under the name of Lyddite, derived from Lydd, the place where the experiments were carried out.

Trotyl. In 1904 the Germans commenced to use trinitrotoluene, otherwise trotyl, instead, as it is free from the disadvantages of picric acid referred to above. This is now used very largely for high explosive shell, and is also often mixed with other substances to form complex explosives.

---

[1] *See S.S.*, 1912, p. 57.

PART II

BLACK POWDER

CHAPTER IV

MANUFACTURE OF SALTPETRE

Nitre deposits : French saltpetre industry : Artificial nitre beds : English saltpetre industry : Formation of nitrates : Berthelot's researches : Bacterial action : Indian saltpetre industry : Indian refinery : Chili nitrate deposits : "Conversion" saltpetre : Refining saltpetre : Saltpetre from the atmosphere

So far as is possible in the almost entire absence of all records, an account has been given in Chapter I of the first discovery of saltpetre.

Nitre depo

Until the middle of the nineteenth century all saltpetre was obtained by dissolving it from earth and deposits in cellars and caves and similar places, where it had formed naturally. In Europe there are very few localities where nitrate can accumulate in the soil to such an extent that a profit could be made by extracting it. There is no prolonged dry season during which deposits can form without being washed away again. Consequently saltpetre could only accumulate in sheltered places, such as cellars and stables, especially those in which there was much nitrogenous matter undergoing decomposition. As it was of the utmost importance in every country to have a sufficient supply of saltpetre, especially in time of war, its production formed the subject of royal decrees and orders at an early date. In France, officers (salpêtriers commissionés) were appointed in 1540 to search for and extract saltpetre, and no doubt the industry was in existence some time before.[1] This edict was confirmed and renewed in 1572, and again whenever France was waging a serious war. The saltpetre workers operated on the earth of stables, sheep-pens, cattle-sheds, cellars and pigeon-houses, and on the plaster and rubbish removed when houses were pulled down. They had the right to gather material everywhere, with scrapers and brushes in the houses, with picks and shovels in places not inhabited. No building or wall could be pulled down until notice had been given to the saltpetre workers, who stated which parts they wanted reserved.

**French sa
petre indu**

In the eighteenth century the saltpetre workers in France received many additional privileges. For instance, they could set up their vats and other plant in public halls, private courtyards or wherever they thought fit. The

---

[1] Berthelot, *Sur la Force des Matières explosives*, 1883, vol. i., p. 345 *et seq.*

local authorities had to supply the wood required for heating, and provide carts for transporting the plant and the saltpetre to the refinery. As a rule each locality was visited once every three years.

rtificial itre beds.

Saltpetre was also obtained from artificial nitre-beds, consisting of earth mixed with animal and vegetable matters, ashes, refuse of buildings, lime and marl. This was all placed in a large barn, and collected in heaps mixed with twigs and intersected with holes to allow access of the air. It was turned over also from time to time and watered with urine. Nitrate gradually formed in the mass and was extracted with water. There were many modifications of this process adopted in different places.

In the reign of Louis XIII (1610 to 1643) the annual crop of saltpetre amounted to 3,500,000 lb., but it gradually diminished in the eighteenth century largely on account of the strong objection the people naturally had to the presence of saltpetre workers in their houses and domains. In 1775 the quantity had fallen to 1,800,000 lb., and half the annual requirement was imported from India. If it had not been for the many privileges the nitrate workers enjoyed, the home product could not have competed at all with that imported from India. In 1789, the year of the fall of the Bastille, a great effort was made, however, to revive the industry, and 3,000,000 lb. were obtained. In 1791, however, the National Assembly proposed to abolish the privileges of the saltpetre workers, but war broke out, the harbours of France were blockaded, and it became necessary to produce in the country all the saltpetre for the powder required. The recent increase of chemical knowledge and the hearty co-operation of the greater part of the population made it possible to produce 16,000,000 lb. in a single year, and 5,000,000 in the next. The whole organization was placed under the control of the department of "Poudres et salpêtres," which still continues to regulate matters concerning explosives.

When peace was finally re-established, the renewed competition of Indian saltpetre dealt a severe blow to the industry in France, and in 1840 the bounties were abolished, but it struggled on until the exploitation of the sodium nitrate deposits in Chile and the potash deposits in Germany in the second half of the nineteenth century led to the production of artificial saltpetre. The consequent reduction of price almost entirely killed the French saltpetre industry, and in 1870, when a scientific committee was engaged in providing Paris with all stores necessary for its defence, Berthelot could find only one or two small producers in Champagne.

nglish salt- etre industry

Until the sixteenth century saltpetre seems mostly to have been imported into England, much of it coming from Spain, but in 1515 Hans Wolf, a foreigner, was appointed to be one of the King's gunpowder makers in the Tower of London and elsewhere. He was to go from shire to shire to find a place where there is stuff to make saltpetre of, and "where he and his laborers shall labor, dig or break in any ground." He is to make compensation to its owners. And in 1531 Thomas à Lee, one of the King's gunners, was appointed principal searcher and maker of gunpowder.[1]

As already stated gunpowder was only manufactured in England on a small scale until the second half of the sixteenth century, when George Evelyn started mills on a comparatively large scale. Consequently there was little difficulty before that time in obtaining sufficient saltpetre, but then it became necessary to grant the saltpetre men special privileges for digging up the floors of stables, dovecots and even private dwellings, and the kingdom was divided into a number of areas in which the collection and working of the saltpetre was assigned to various people. In 1561 Queen Elizabeth granted Gerard Honrick, a Dutchman, £500 (or £300) for teaching two of her subjects how to make saltpetre.[2] In 1588 she granted a monopoly for gathering and working saltpetre to George Evelyn, Richard Hills and John Evelyn. The monopoly extended over the whole of the South of England and the Midlands, except the City of London and two miles outside it. In 1596 Robert Evelyn acquired the rights in London and Westminster from the licensees there. As a rule, however, the Evelyns did not work saltpetre themselves, but bought it from the saltpetre men.

In the reign of Charles I there was considerable friction between the saltpetre men and the public, but it was probably due more to the weakness of the Crown than to any real difficulty in obtaining in England the quantity of saltpetre required, viz. 240 lasts per annum. There was also competition between the saltpetre men and the soap-boilers for wood ashes, which were then practically the only source of potash and were required for the conversion of sodium nitrate into the potassium compound. In 1834 the Lords of the Admiralty gave orders to the Governor and Company of soap-boilers that the saltpetre men were to have the pre-emption of wood ashes, on the ground that saltpetre was a commodity of such necessary use for the King and public that it ought to be preferred before the making of soap.[3] The monopoly of saltpetre was abolished in 1641 at the same time as the monopoly of gunpowder. It was revived for a time after the Restoration, but manufacture then was on a considerably larger scale.

The East India Company, then in its infancy, imported Indian saltpetre into England as early as 1625 and set up a powder mill in Windsor Forest, which, however, was stopped on the ground that it interfered with the King's deer. Next year the Company received a license to erect mills in Surrey, Kent and Sussex. At this time its importations were on a small scale, but when its charter was renewed in 1693 it was stipulated that 500 tons of saltpetre should be supplied every year to the Ordnance. Ever since then, Indian saltpetre has been used very largely in England for the manufacture of gunpowder.

[1] *Brit. Exp. Ind.*, p. 185.

[2] *Brit. Exp. Ind.*, pp. 210, 258.

[3] *Brit. Exp. Ind.*, p. 269.

ormation of itrates.

Whence come these large quantities of nitrates? The nitrogen of the atmosphere does not form chemical compounds at all readily. Under the influence of lightning, and high tension electricity generally, small quantities of nitric acid are formed and these are carried down by rain into the soil and rendered available for plant life. But Lawes and Gilbert in their researches at Rothamsted found that the amount of nitrogen removed with the crops was more than the total sum of that added as manure and brought down by the rain together with the loss of nitrogen from the soil. No plants can grow without absorbing nitrogen compounds from the soil; and when animal and vegetable matters decompose, a portion of the combined nitrogen is liberated as nitrogen gas, but in spite of this steady loss there is no indication that the surface of the earth as a whole is becoming poorer in combined nitrogen.

erthelot's esearches.

Berthelot investigated this matter about 1876 and discovered that nitrogen and oxygen also combined under the influence of electricity of quite low tension, such as that yielded by two or three electric cells, although only very slowly, and moreover that in the presence of carbohydrates such as dextrine the combination was considerably more rapid.[1] Although the quantities thus obtained in small laboratory experiments only amounted to a few milligrammes in several months, yet, as there are always differences of potential of this order over the whole surface of the globe between the earth and the air above it, he considered that this phenomenon was sufficient to account for all the nitrates and other compounds of nitrogen that are formed.

acterial ction.

Since then, however, it has been found that this is by no means the only cause of the formation of nitrogen compounds from the nitrogen of the atmosphere. There are bacteria in the soil, which can take up nitrogen from the air and cause it to combine with other elements to form nitrates and more complex bodies such as albuminoids. Some of these, such as Azobacterium Chroococcum Beijerinck, can live and act freely in the soil; others seem only to exist in the nodules that are found on the roots of certain sorts of plants. The Bacterium Radicicola is perhaps the most important of these; it is found on the roots of the leguminosæ (beans, peas), and renders it possible for these crops to grow on otherwise sterile soil, which afterwards is able to support other crops. Some other plants such as the alder tree have similar nodules on their roots. There are some soil bacteria also, which convert nitrates into nitrites, others carry out the reverse change, others again liberate nitrogen from nitrates or nitrites, and several of these actions may be going on simultaneously in the soil.

Bacterial action proceeds most rapidly in a warm moist climate like that of Bengal. The accumulation of nitrate to such an extent, that it can readily be collected in large quantities, also requires that there shall be regular seasons of the year when little or no rain falls. In this respect, Bengal and most other

---

[1] *Sur la Force des Matières Explosives*, 1883, vol. i., chap. vi.

parts of India satisfy the conditions. It was found by Leather that at Pusa in Behar the nitrification takes place mostly in the top 6 or 12 inches of soil and principally at the commencement of the rainy season. There is more nitrate in fallow soil than in that that is covered with crops. The mean quantity that was washed out of the soil into the drain gauges was 70 lb. of nitric nitrogen per acre from fallow soil and 13 lb. from cropped soil.[1] Headden has found that in Colorado soils are often rendered sterile by the presence of too much saltpetre, which at times amounts to 6 per cent. of the soil. It is formed by azobacter.[2]

Indian saltpetre industr

Bihar is the principal seat of the saltpetre industry in India, but considerable quantities also come from the United Provinces and the Punjab, and smaller amounts from other parts of India and from Burma. Except what is consumed in the country, the greater part is exported from Calcutta. Fifty or sixty years ago, the average quantity exported was over 30,000 tons per annum, now it is 18,000 to 20,000. In the places where the nitrous earth is collected the natural vegetation is scant, as the soil in many cases is too salt for crops to grow even during the rains. It is obtained in and around existing village sites and on the mud walls of houses and cow-sheds. In the rainy season, lasting from June to October, the process of nitrification goes on in the warm moist soil, assisted by the addition of nitrogenous refuse. The following account by R. W. Bingham [3] gives a clear picture of the industry in the last century :

" It is all made by a peculiar caste called 'nuniah,' and, so far as my experience shows, is principally in the hands of . . . 'mahajuns,' who make yearly advances, charging 12 per cent. for the same. The 'nuniahs' are a tolerably safe class, compared with the ordinary 'riot' (peasant), to deal with, and pay the 'zemindars' (landowners) a comparatively large price (if measured by the 'bigah') for the old walls and old sites in which they revel. The supply of saltpetre from these old sites appears to be practically inexhaustible ; for we find the 'nuniah' very busy making up his piles just after the setting in of the rains. This earth he exposes to the sun and rain, and takes care, by erecting walls, etc., that the precious stuff is not wasted away. A casual visitor would not be able to understand what he is after, but when the hot suns of April, May and June come on, then himself and his family boil merrily away, and eliminate saltpetre and salt from this apparently useless soil. Then the 'mahajan' is on the look-out and secures the saltpetre as it is made, and carries it to his own refinery for final manipulation ; while the salt which is

---

[1] J. W. Leather, *Mem. Dep. Agr. in India*, vol. ii., no. 2, Jan. 1912.

[2] W. P. Headden, Colorado Agr. Col. Expl. Station, *Bulletins* 155, 160, through *Nature*, 1911, p. 364. *J. Ind. Eng. Chem.*, 1914, p. 586.

[3] *Jour. Agricultural and Horticultural Soc.*, xii., p. 107, old series ; *Dict. Economic Products of India*, S. 686, vol. vi. part ii. p. 437.

always bitter, and I should say unwholesome, under the name of 'khari nimuk' is sold to the lowest classes of the community at a cheap rate. The business must be a profitable one, as the large bankers of Ghazipore, Patna and Benares are always ready to go into the trade, and to advance money to responsible middlemen. . . . Sometimes these men experience considerable trouble in recovering their advances, but in that case they quietly walk off with the bullocks of the 'nuniah' who . . . never dreams of making a complaint, but begs or borrows from his comrades and friends till he has got money enough to release them by paying back principal and interest : well knowing that he will get no more advances, and will, besides, be put out of caste by his castemates if he does not, at all events, pay the original advance. If, on the contrary, he makes more saltpetre than will cover his advance, and he has no particular ceremony going on, he will clandestinely sell his partially refined saltpetre to other petty purchasers, and get drunk while the money lasts, and

Fig. 3. Percolators for Extracting Indian Crude Saltpetre.

ask contemptuously, 'What, am I a poor man that I should work?' The trade is too hazardous a one, and the petty advances spread over too wide an extent of country, to make it worth the while of Europeans with capital to attend to; in consequence it is almost wholly in the hands of the large houses above named (who are connected with Calcutta native firms, and who in turn have their small branches in every petty town in the district)."

The industry is conducted on the same lines now as then, except that it is not as remunerative as it used to be. Hooper[1] made analyses of a large number of samples of the earth collected by the "nuniahs": the amount of nitrates in them varied from 1 to 27 per cent., but as a general rule they contain 3 to 5 per cent., also several per cent. of sodium chloride and sulphate. A description of the process of extraction has been given by Leather and Mukerji.[2]

[Fig. 4. Evaporating Liquor from Percolator.

---

[1] *Agricultural Ledger*, 1905, No. 3.

[2] *Bulletin* No. 24 of the Agricultural Research Institute, Pusa, 1911; *S.S.* 1912, 116 and 136.

The "nuniah" builds an earthen chamber called the "kuria" or "kothi" with wet mud, which is allowed to dry. This chamber (*see* Fig. 3) has either circular walls some 5 or 6 feet in diameter, or oblong walls, and a floor which slopes slightly from back to front. In the front wall is a hole at the level of the bed, which allows the nitrate liquor to drain away into a pot. Above the bottom of this earthen chamber a false bottom is laid, consisting of bamboos and matting placed on a few loose bricks. The nitrate earth is filled in on this with great care. Stones, etc., are removed from it as far as possible, and it is put in slightly moist and trodden down so as to leave no channels, through which the water would run too rapidly. Wood ashes are generally mixed with the earth, so that the potash in them may convert into saltpetre the nitrates of lime and magnesia. A small piece of matting is placed over the top of the earth and water is poured on cautiously. The liquor that percolates through first is fairly strong: it is transferred to shallow earthenware or iron basins and evaporated down (Fig. 4) by means of a fire of wood, leaves or twigs, or in the Punjab to shallow masonry trays in which the concentration takes place through the action of the very dry air and the heat of the sun. The weak liquor that percolates through afterwards, is thrown on to a heap of already extracted earth, where it evaporates: this earth is afterwards extracted again. The strong liquor is boiled down until crystals begin to appear, and then is allowed to cool: the crystals are then fished out, fresh liquor is added to the mother liquor and the concentration is carried out as before. The composition of the crude saltpetre thus produced varies considerably. Hooper gives the analysis of fifty-five samples, and of these the following have been selected by Leather as being typical:

	Farukhabad		Okara		Mozafferpore	Burhanpura
	I	III	I	III		
Potassium nitrate . . .	66·07	44·92	53·00	26·86	49·36	68·40
Calcium nitrate . . .	—	—	2·60	—	3·28	2·60
Magnesium nitrate. . .	2·54	4·80	—	12·24	7·44	2·12
Sodium chloride . . .	21·84	35·38	34·22	34·80	16·82	17·98
Sodium sulphate . . .	3·65	10·00	3·88	11·20	14·60	3·40
Insoluble matter . . .	·90	1·20	1·10	1·40	1·50	1·70
Water	5·00	3·70	5·20	13·50	7·00	3·80
	100	100	100	100	100	100

No attempt is made to separate the sodium chloride at this stage because there is an excise duty on it, and the salt department only allows the recovery to take place in the refineries, where a proper control can be kept. Some of the crude saltpetre is used as manure, but the greater part goes to the refinery.

Indian refinery.

In the refinery the processes are very similar to those carried out by the "nuniah." There is always a large heap of saltpetre earth, which is worked over and over again, the weak liquors being always thrown on to it. This is extracted in "kothias," but the strong liquors are not evaporated down by themselves; crude saltpetre is dissolved in them at the boiling-point. The quantity added is such that the potassium nitrate is all dissolved to form a boiling saturated solution, whereas the greater part of the sodium chloride remains undissolved (*see* Table of Solubilities on p. 63) together with the insoluble matter. The hot liquid is allowed to settle for a little while, and then run into wooden vats where it is allowed to cool slowly and deposit crystals of potassium nitrate. The residue in the dissolving tank is washed with water to recover the saltpetre in it, and the common salt may be purified by dissolving it in weak nitre liquor, decanting off and evaporating down. The insoluble matter and all weak liquors are added to the heap of earth, which steadily grows from year to year. The mother liquor from the crystallization of the saltpetre is also added to it after it has been used three or four times, as it is then too impure.

The refined saltpetre is in large crystals of a brownish colour. To purify it further and improve the colour it is sometimes subjected to a washing process: it is put in sacks over wooden tubs and cold water is poured through it. This of course dissolves some of the potassium nitrate as well as the impurities, and is consequently returned to the refinery process. Leather and Mukerji give the following analyses of refined saltpetre before and after washing:

	Burhanpura		Savan		Bakramau	
	Un-washed	Washed	Un-washed	Washed	Un-washed	Washed
Potassium nitrate . . .	90·70	94·91	81·98	91·55	88·63	94·70
Potassium sulphate . .	—	—	5·44	·93	·15	·15
Sodium sulphate . . .	·91	·03	—	—	—	—
Potassium chloride . . .	—	—	2·59	2·51	6·06	2·67
Sodium chloride . . .	5·40	3·12	7·05	1·68	·07	·10
Sand	·30	·20	·20	·35	—	—

Leather has designed a simple plant on more up-to-date lines to carry out the refining process, and is endeavouring to get the Indian refiners to take it up. This consists of a dissolving vessel provided with a stirrer, a filter in which the liquor is rapidly filtered at a high temperature, and a series of coolers in which the saltpetre is caused to crystallize rapidly. The crystals are then freed as far as possible from the mother liquor in a centrifugal machine. The saltpetre produced has a purity of 90 to 93 per cent.

Chili nitrate deposits.

The plain of Tamarugal in Chili is even more favourably situated than Bihar or Bengal. It lies between the Andes and the comparatively low Coast Hills at a height of about 3000 feet above the sea within the tropics. As a rule there is very little rain there, but about once in six or seven years the plain, which is about 45 miles wide, is flooded. The plain slopes gently towards the Coast Hills and as there is no outlet for the water, it collects there and evaporates, and all the nitrate it has dissolved from the entire plain is deposited in a comparatively narrow area. The entire product of the bacterial action upon many hundreds of square miles for many centuries is found in the Chili nitrate beds. As the soil contains sodium compounds and comparatively little potassium, it is principally sodium nitrate that has been desposited.[1]

The following gives the results of analysis of commercial Chili nitrate :

Sodium nitrate	94·20
Potassium nitrate	1·51
Sodium chloride	1·06
Sodium iodate	0·01
Potassium chlorate	0·26
Magnesium sulphate	0·26
Magnesum chloride	0·32
Calcium sulphate	0·07
Insoluble	0·16
Water	2·15
	100

During the Crimean War (1854–1855), the demand for saltpetre was so great that the existing sources of supply in Europe and India did not suffice, and considerable quantities were made from Chili nitrate, which had been supplied to Europe in constantly increasing quantities since 1830. The salt beds at Stassfurt, however, did not commence to yield potassium chloride (Carnallite) until about 1863, therefore other sources of potash had to be used to convert the sodium nitrate from Chili into the corresponding potassium salt. The only sources of potash then available were kelp, and the ash of wood, etc. When the war was over, saltpetre prepared in this way could no longer compete with the natural product from India. But shortly afterwards fresh sources of potash were found in "suint," the dried sweat of sheep, which is washed from the wool, and in the cinder of "vinasse"

---

[1] *See* Newton, *J. Soc. Chem. Ind.*, 1900, p. 408.

(Schlempekohle), which is obtained as a by-product in the refining of beet sugar. With the development of the Stassfurt potash industry these lost their importance however.

"Conversion" saltpetre.

Large quantities of potassium nitrate are now made by the interaction of Chili nitrate and commercial chloride of potash, which is made by lixiviating "carnallite," a double chloride of potassium and magnesium, occurring in immense deposits near Stassfurt in Germany. In the heated and concentrated mother liquor from a previous operation commercial sodium nitrate (about 95 per cent. purity) and potassium chloride (not less than 80 per cent. purity) are dissolved, the nitrate being in slight excess. Of the four salts that might be present in the solution thus formed, sodium chloride has the least solubility at a high temperature and potassium nitrate the greatest (*see* Table below). At a low temperature potassium nitrate has the lowest solubility. The figures are of course for pure salts dissolved in distilled water, and the presence of other substances in solution would alter the solubilities somewhat, but the figures given in the last two columns, the solubilities of sodium chloride and potassium nitrate in water which is simultaneously saturated with both salts, show that in this case the salts have little effect upon one another's solubility. Consequently in the hot concentrated solution of sodium nitrate and potassium chloride most of the sodium chloride is precipitated out :

$$NaNO_3 + KCl = KNO_3 + NaCl$$

TABLE OF SOLUBILITIES

Temperature	Gramme mols. per 1000 g. water					
	One salt only present				When water is saturated with KNO_3 and NaCl	
	NaCl	KCl	$NaNO_3$	KNO_3	KNO_3	NaCl
0° C.. . .	6·10	3·70	8·54	1·31	1·8	5·6
20 . . .	6·14	4·56	10·3	3·12	3·4	6·5
40 . . .	6·24	5·36	12·2	6·32	6·0	6·4
60 . . .	6·36	6·11	14·5	10·9	9·9	6·0
80 . . .	6·53	6·85	17·4	16·7	16·5	6·2
100 . . .	6·75	7·60	20·9	24·3	28·0	6·9
120 . . .	6·84	8·43	25·1	38·9	38·0	7·2

Calculated from figures in Seidell's *Solubilities of Inorganic and Organic Substances*, 1907. A "gramme-mol." is the molecular weight of a substance in grammes. To find the actual weight of the salts dissolved by 1000 parts of water, multiply the above figures by the corresponding molecular weights : for NaCl 58·5, KCl 74·6. $NaNO_3$ 85·1. KNO_3 101·1.

The solubilities of these different salts in the presence of one another have recently been investigated by J. W. Leather and J. N. Mukerji, whose results do not differ very greatly from the above. At temperatures below 30° C., however, they found that a small proportion of KCl is formed in a solution saturated with KNO_3 and NaCl, and a corresponding amount of solid $NaNO_3$ is deposited. At temperatures above 30° C. on the other hand KCl is deposited and $NaNO_3$ formed in solution, and as the temperature rises the quantities of these salts increase rapidly.[1]

The liquid is boiled for half an hour to complete the reaction as far as possible, then it is run through a filter into shallow cooling tanks; some more water may now be added with advantage to prevent sodium chloride separating out with the potassium nitrate.

The solution is kept stirred whilst it cools, so that the potassium nitrate may separate in small crystals, which do not contain so much mother liquor as large ones. The crystals are drained and then washed with the liquors from the next crystallization. This is best done in a centrifugal machine, as the quantity of washing liquor is thereby reduced to a minimum.

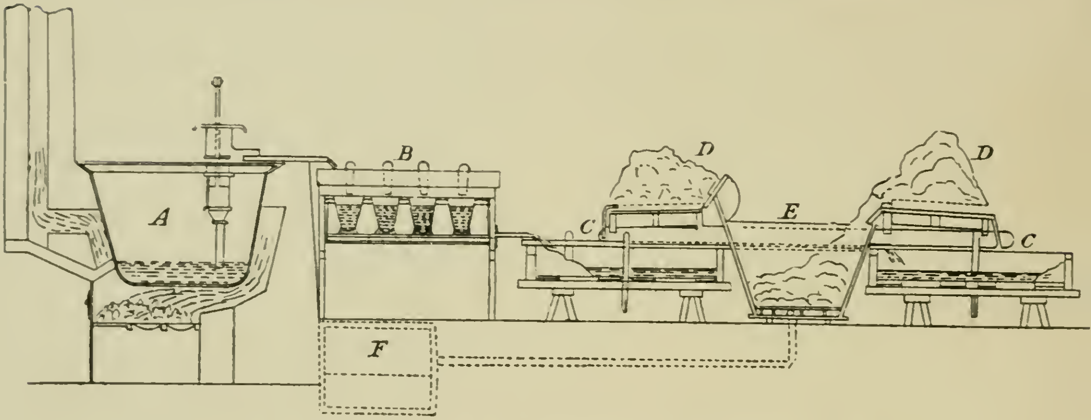


FIG. 5. Plant for Refining Saltpetre at Waltham Abbey.

The crude saltpetre thus obtained still contains several per cent. of sodium chloride and about a half per cent. of magnesium chloride. It is purified by dissolving in the washings of the purified salt, allowing it to crystallize, and washing with water, whereby the percentage of chloride is reduced to 0·05 per cent. or less, and the material is rendered practically free from all other impurities. Finally it is dried.

The sodium chloride formed in the conversion is washed on the filter with liquors containing gradually diminishing amounts of nitrate, until the solid contains only 0·8 per cent. or less. This "saltpetre salt" then contains about

---

[1] *Mem. of Dept. of Agriculture in India,* Chemical Series, vol. iii., No. 7, 1914.

98 per cent. of sodium chloride in the dry state. It is unsuitable for the manufacture of hydrochloric acid, because this would be contaminated with nitrous compounds, and moreover the plant would be strongly attacked. It is therefore either sold to farmers to put on the land or used in copper extraction or other metallurgical processes.

"Artificial" or "conversion" saltpetre made as above, is usually supplied by the chemical works to the explosives factory in such a state of purity that no further purification is necessary. Natural saltpetre from India on the other hand always contains a considerable amount of impurity and requires to be refined before use.

Although the quantity of black powder made is still very considerable, it is not nearly so large as it was twenty years ago. The black powder factories now being worked were all in existence at that time, and they mostly have large saltpetre refineries attached, which more than suffice to refine all the material that they require. It has not been found worth while to reconstruct the refineries, as they are still capable of turning out saltpetre of good quality. It would nowadays be possible, however, to erect up-to-date plant that would save much space and some fuel and labour.

Refining
dian salt

At Waltham Abbey, as at some other English powder factories, Indian saltpetre is used exclusively. The total quantity imported into England every year is, however, only 10,000 tons and the total consumption for making powder, etc., several times that amount. The balance is made up with "conversion" saltpetre.

Walthar
Abbey m

The method of refining still followed at Waltham Abbey is as follows: The crude or "grough" saltpetre is dissolved up in a large iron copper, *A* (Fig. 5), which has a capacity of 500 gallons, and is fitted with a perforated false bottom which prevents the saltpetre adhering to the vessel. For each charge, about 25 cwts. of grough saltpetre are taken, and 5 cwts. of crystals recovered from liquors, and 5 cwts. of crystals left in the crystallizing cisterns. This is all dissolved in about 280 gallons of the washings of the purified saltpetre, which also contains a considerable amount of the salt. The fire is lit under the copper, and in about two hours the saltpetre is dissolved and the liquid boiling. Just before it boils a thick scum rises to the surface consisting mostly of impurities. This is skimmed off and the false bottom is removed, and cold water is added from time to time to induce fresh scum to form, if it will. The fire is then withdrawn and the liquid is allowed to settle for two hours. Then a hand pump is lowered into the copper and the liquid is pumped into filters *B*, where it passes through linen cloth. From here it runs to shallow copper crystallizing troughs *C*. As it cools down, the liquid is kept stirred by a workman in order to make the saltpetre separate in small crystals, and the saltpetre "flour" as it forms is drawn up on to an inclined draining platform *D*, and from there is passed to a washing vat *E*. After the temperature has fallen to about 32° C. (90° F.) the solution is no longer stirred and any crystals that form after that are treated as grough nitre.

Vashing.

The washing vat *E* is about 6 feet long, by 4 feet wide, by 3 feet 6 inches deep, and is fitted with a false bottom made of wood with small holes bored in it. Below the false bottom is a plug which can be removed to allow the washings to flow away. First the charge is washed with 70 gallons of water sprinkled over it by means of a rose, the plug being left out so that the washings can drain away to a liquor tank *F*. After draining half an hour the plug is inserted and the saltpetre covered with fresh water, which after standing half an hour is also allowed to drain into *F*. Finally the salt is washed by sprinkling with 100 gallons of water, the plug remaining out. The saltpetre is now allowed to drain all night and is then removed to the store-house where it is allowed to dry spontaneously. In about three days the moisture has fallen to 3 or 5 per cent.

other liquor.

The mother liquors and other impure solutions are boiled down to about a quarter of their original volume. Any scum or deposit that forms during the boiling should be removed and water then be added. The solution is now filtered and allowed to crystallize. The crystals are treated as grough saltpetre and the mother liquor returned to the evaporating pots.

ontinental
ethods.

The methods of refining adopted in France, Germany and other countries are substantially the same as that at Waltham Abbey. A small proportion of size is, however, often added in the refining copper to assist the formation of scum.

altpetre from
ie atmo-
here.

Potassium nitrate could also be made from the calcium nitrate produced from atmospheric oxygen and nitrogen by processes such as that of Birkeland and Eyde as carried out at Notodden, but the calcium chloride obtained as a by-product would be of no value. Or the dilute nitric acid obtained in the Birkeland-Eyde process could be treated with limestone or chalk and potassium chloride :

$$CaCO_3 + 2KCl + 2HNO_3 = 2KNO_3 + CaCl_2 + CO_2 + H_2O.$$

In this case the carbonic acid could be collected and compressed into cylinders and sold. Up to the present, these methods do not appear to have been adopted, but nitric acid and ammonium nitrate are being made on a very large scale, especially in Germany.[1]

---

[1] *See* chap. viii.

CHAPTER V

MANUFACTURE OF CHARCOAL AND SULPHUR

Charcoal : Wood used : Distillation : Composition : Brown charcoal : Sulphur : Sicilian sulphur : By-product sulphur : Louisiana sulphur : Refining sulphur : Properties : Functions of sulphur

Wood use

At one time the charcoal for black powder was made almost exclusively from alder-wood, but later other soft woods were used, and straw charcoal was also introduced for the brown powders for heavy ordnance. Charcoal from soft woods is generally used, especially for the better qualities of gunpowder, because it is more easy to ignite. In England dog-wood is much used, especially for rapid burning powders of small grain ; for larger powders, alder and willow. In Germany alder and willow are the principal woods used ; in Austria, alder and hazel ; in Switzerland, hazel ; in France black alder is used for high class powders, for mining powders common white woods such as white alder, poplar, aspen, birch and hazel ; in Spain, the oleander, yew, willow, hemp stems, and vine ; in Italy, almost exclusively hemp stems.

Charcoal burnt in heaps or kilns has not been used very largely for gunpowder since even the very earliest days, for it was soon found that to produce good powder it was necessary to select the wood carefully and burn it very uniformly. It has therefore been heated in ovens or iron vessels, and the procedure of the present day does not differ materially from that of the fourteenth century.

The wood should be cut in the spring, as the sap in it at that time of the year contains much less inorganic matter, so that although the proportion of sap is larger, yet the percentage of ash in the wood is much smaller. Moreover, wood cut in the spring is much more easily freed from its bark, which also contains a large proportion of ash. The wood is kept at least eighteen months, and generally not less than three years, to allow the sap to dry out of it and other changes to take place. The practice varies considerably as regards protecting the wood from rain : at Dresden it is kept in sheds ; at Spandau in the open ; at Waltham Abbey also the wood is kept in the open, but the dog-wood is covered with thatch, whereas the alder and willow are not.

The wood is split if necessary into pieces about 1 inch thick, and these are placed in an iron cylinder about 2 feet in diameter and 3 feet 6 inches long. This cylinder is then raised by means of suitable tackle and placed in a furnace, which is heated as uniformly as possible. The higher the temperature and the longer the heating, the lower is the percentage of hydrogen and oxygen in the charcoal and the greater is its hardness and the difficulty with which it is ignited. At Waltham Abbey dog-wood for R.F.G. or M.G.^{1} powders is heated 4 hours, for R.F.G.^{2} 8 hours. Alder and willow for R.L.G.^{2} are heated 3½ hours, for R.L.G.^{4}, P., and Prism ^{1} Black 4 hours, for P ^{2} 6 hours.

Distillation. When the temperature of the wood attains about 280° C. volatile products of decomposition of the wood come off plentifully. These could be condensed by means of a suitable condenser, and worked up into acetate of lime and wood spirit. The charcoal plant of a powder mill is, however, on such a small scale as compared with the factories in which charcoal is produced for metallurgical processes with recovery of the by-products, that it is not usually considered worth while to do this. The volatile products are therefore simply led into the furnace by which the wood is being heated, and so some expenditure of fuel is saved. To enable the gases and volatile products to escape the cylinder has some holes bored in it at one end, and the furnace is provided with a pipe to lead away these products. When the carbonization has proceeded far enough, the flame of the burning gas becomes blue. The furnace is then opened, the cylinder taken out by means of the tackle, and a fresh cylinder of wood put in before the furnace has had time to cool. The cylinder that has been taken out is placed inside a larger cylinder, which has a closely fitting lid, and is there allowed to cool. It is necessary that the cooling should take place out of contact of the air, as otherwise the charcoal will catch fire. Even when cold it at first absorbs large quantities of oxygen from the air, and in so doing may become sufficiently hot to catch fire. Therefore oxygen must only be allowed gradual access to the charcoal: it should not be ground until a week after it has been burnt. Before use it is carefully picked over by hand to remove any that has not been properly burnt, as also any foreign matters that have got into it. Charcoal intended for powders for ordnance should be jet black in colour: its fracture should show a clear velvet-like surface: it should be light and sonorous when dropped on a hard surface, and so soft that it will not scratch polished copper.[1] The yield of such charcoal is 28 to 30 per cent. of the dried wood. For small-arms a more slackly burnt charcoal can be used, and the yield may be as much as 40 per cent. Such charcoal has a reddish-brown colour, which is perceptible in the powder until it has been glazed with graphite.

---

[1] *Treatise on Service Explosives*, 1907, p. 10.

Compositi

The composition of some typical charcoals is shown in the Table [1] below. Spanish hemp charcoal is usually burnt in pits holding ½ to 1 ton. When the carbonization has proceeded far enough the pit is covered with a woollen cloth on which earth is placed. This probably accounts for the high percentage of ash in the analysis below.

Description	Carbon	Hydrogen	Oxygen	Ash
From P. Powder, Waltham Abbey . .	85·26	2·98	10·16	1·60
From R.L.G., Waltham Abbey . .	80·32	3·08	14·75	1·85
From R.F.G., Waltham Abbey . .	75·72	3·70	18·84	1·74
From F.G., Waltham Abbey . . .	77·88	3·37	17·60	1·15
Curtis's and Harvey, Sporting . .	77·36	3·77	16·62	2·25
Curtis's and Harvey, Mining . . .	83·74	3·07	10·45	2·74
Spanish, Hemp Charcoal. . . .	76·29	3·31	14·87	5·53
German Sporting Powder. (B. & S.) .	68·8	3·7	27·5	Trace
Austrian Cannon Powder. (K.) . .	81·3	2·8	13·6	2·3
Austrian Small Arm Powder. (K.). .	82·6	2·9	12·5	2·0
Russian Powder. (F)	72·5	2·9	22·3	2·3

Brown charcoal.

The charcoal for brown or "cocoa" powder was made from rye-straw, which was only carbonized very slightly.[2] It was heated only about half an hour, then taken out of the furnace. The carbonization proceeded spontaneously a little further and then the charcoal cooled. The result was a soft charcoal containing a large percentage of oxygen and hydrogen. In the operation of pressing the powder this became a coherent colloid which bound the other constituents together to a dense impervious mass, which burnt comparatively slowly. The cocoa powder gave the best ballistics in heavy ordnance of any "black" powder ever produced, but it has now been entirely displaced by smokeless powders.

For cheap blasting powder and powder for scaring birds and supplying natives of Africa, etc., charcoal of an inferior quality can be used.

SULPHUR

Sicilian sulphur.

Sulphur occurs native in many volcanic districts, especially in Sicily, and until recent times practically the whole of the world's supply came from there. The sulphur in Sicily is mixed with limestone, the ores containing

---

[1] Noble and Abel, *Trans. Roy. Soc.*, 1875 and 1879; Noble, *Artillery and Explosives*, 1906, pp. 127, 129. "B. & S." means analysis by Bunsen and Schischkoff, "K" by Karolyi, "F" by Fedeow.

[2] Guttmann, *Manufacture*, vol. i., p. 90; Cundill and Thompson, p. 21; *Treatise on Service Explosives*, 1900, p. 110

usually from 20 to 40 per cent. of sulphur. Formerly the sulphur was recovered by the wasteful "calcaroni" process. The ore was piled in a large heap and covered over with moistened ash except for a small opening. Combustion was started with burning wood, but the combustion of part of the sulphur provided most of the necessary heat. The sulphur melted out and flowed down on to a prepared floor. Only about 60 per cent. of the sulphur in the ore was recovered by this process, and the large quantities of sulphur dioxide set free were very injurious to the surrounding vegetation. This method has been largely superseded by the introduction of recuperative furnaces invented by Gill and modified by Sanfillipo. About six large chambers are arranged in a series so that the hot gases from one can be made to heat the next. By this process the recovery is about 80 per cent. Attempts have been made to introduce more efficient methods whereby practically the whole of the sulphur could be recovered by melting it out with hot brine or steam, or distilling it with superheated steam. These methods have not attained any great success, however, the obstacles being the absence of any local supply of fuel and the backward state of the country. The sulphur is refined by distillation, the principal distilleries being situated in Marseilles. Some powder mills have small sulphur refineries of their own, as at Waltham Abbey for instance.

Two sorts of sulphur can be obtained by distillation: flowers and stick sulphur. The former consists of minute crystals, which have been deposited on the interior surface of a large chamber or "dome" into which the vapours have been passed. The flowers contain a small percentage of sulphuric acid formed by the action of the air on the sulphur, and consequently are not suitable for the manufacture of explosives. Stick sulphur, on the other hand, is very pure and only requires to be ground.

-product lphur.

For the manufacture of sulphuric acid elementary sulphur is but little used now, as it pays better to roast various ores in which it is combined with metals, such as copper pyrites and zinc-blende, but it does not pay to extract sulphur as such from these ores. A certain proportion of it comes on the market, however, as it is obtained as a by-product in the Leblanc soda process. The sulphuric acid used in that process is ultimately converted into calcium sulphide, CaS, and for many years this accumulated in great heaps, which were a public nuisance, no method being known by which it could be worked up except at a prohibitive cost. Eventually the Claus-Chance process was devised and perfected, which enabled this to be done. Kiln gas is passed over the "soda-waste," converting it into calcium carbonate and sulphuretted hydrogen: $CaS + H_2O + CO_2 = CaCO_3 + H_2S$. As the sulphuretted hydrogen is rather dilute and variable in concentration, the gas is led through a fresh quantity of the waste, by which it is absorbed, forming the bisulphide: $CaS + H_2S = CaH_2S_2$. When kiln gas is led through this the sulphuretted hydrogen is again given off, but is of double the previous concentration: $CaH_2S_2 + H_2O + CO_2 = CaCO_3 + 2H_2S$. This gas is collected in a gas-holder, and can be fed from there into the chambers where it is converted into sulphuric acid, or it can be mixed with gas from the pyrites burners, whereby sulphur is caused to deposit in accordance with the equation: $2H_2S + SO_2 = 2H_2O + 3S$. The sulphur thus obtained is of considerable purity.

Sulphur is also obtained in the purification of coal-gas from sulphuretted hydrogen and other sulphur compounds.

Louisiana sulphur.

Until recently the market was entirely controlled by an English association, the Anglo-Sicilian Sulphur Company, formed in 1895. Sulphur had been found in Louisiana in 1865, during some boring operations for petroleum, but it was situated underneath 500 feet of quicksand, and all attempts to work it commercially failed until the matter was taken up by Hermann Frasch in 1891, and even then years of work were required and a large amount of capital before success was achieved. The sulphur is mixed with a much smaller proportion of limestone than in Sicily, the ore containing about 70 per cent. sulphur. The method that has been adopted is to put down a pipe of 10 inches diameter until the sulphur deposit is reached, then the hole is continued with a 9-inch drill through the sulphur deposit, which is about 200 feet thick. A 6-inch pipe is passed to the bottom, and a 3-inch pipe through this, both being perforated near their lower ends. Superheated water is passed down the 6-inch pipe, but the sulphur passes up the 3-inch. At first it was raised by means of pumps, but now air is forced down: this mixes with the sulphur and reduces its density, and it is raised to the surface of the ground by the pressure of the water used for melting.

The "Union Sulphur Company" has been so successful that it has acquired the whole of the trade of the United States and also exports considerable quantities. The production amounts to several hundred thousand tons per annum.

The sulphur as it comes up from the well is said to have a purity of 99·93 to 99·98 per cent. It is simply run into great bins, which hold as much as 150,000 tons each. When it has cooled the sides of the bins are removed, the sulphur is broken up, and is then ready for shipment.

The Anglo-Sicilian Sulphur Company finding itself unable to contend with Frasch's Company finally retired from the business, but it had made enormous profits for many years. The Italian Government has formed a compulsory trust to control the marketing of Sicilian sulphur and ensure a living wage to the Sicilian workmen. This has proved very successful and the workers in Sicily are now better off than they have been for many years past.

On the occasion of the presentation to him of the Perkin Medal, Frasch gave a very interesting account of the various difficulties he had to contend with in working out his invention, and this is published in the *J. Soc. Chem. Ind.*, 1912, pp. 168–176.[1]

fining
phur.

Sicilian sulphur requires to be refined before it can be used, and this is done by distilling it. The crude or "grough" sulphur is placed in an iron pot, which is heated from below by a furnace until the sulphur boils. The vapour passes over into a chamber where the sulphur is deposited on the walls in the form of small crystals, which constitute "flowers of sulphur." If the walls of the chamber are allowed to get hot enough to melt the crystals the sulphur runs down and is tapped off and cast into sticks or rolls. The still is often so arranged that the waste heat from the furnace melts another charge of crude sulphur ready to run into the still as soon as the first charge has been distilled off. The refinery at Waltham Abbey is provided not only with a large chamber or "dome" but also with a condenser leading to a receiver. Only the first portion of vapour is admitted to the dome, then the vapours are turned into the condenser. Flowers of sulphur are not fit for making explosives because they contain a small proportion of sulphuric and sulphurous acids. The flowers from the dome are therefore redistilled.

operties.

Roll sulphur consists of pale yellow brittle crystals belonging to the rhombic system, having a density of 2·07 at 0°. It melts at about 113°, to an amber-coloured liquid, but when the heating is continued above 120° it gradually becomes darker and more viscous. Between 160° and 220° it is so viscous that the vessel containing it can be inverted without losing any. If this viscous amorphous mass be cooled rapidly part of it retains the amorphous condition and is insoluble in carbon bisulphide, which dissolves ordinary rhombic sulphur with ease. Flowers of sulphur always contain a proportion of this insoluble modification. Sulphur boils at 444·5°.

unctions of
lphur.

One reason why sulphur is added to black powder is that its temperature of ignition, 261° C, is low, and consequently it makes the powder burn more readily. But another reason is that under the influence of pressure, not only in the press but also in the incorporating mill, it flows and becomes colloidal, cementing together the particles of charcoal and the minute crystals of saltpetre. From the examination of microphotographs Cronquist[2] found that brown charcoal has a similar power of becoming colloidal under pressure. This is why brown gunpowders burn more slowly and regularly than black, and why the percentage of sulphur in them can be reduced or abolished altogether.[3]

Sulphur oxidizes slowly in the air, forming sulphur dioxide and a little sulphuric acid. If a chlorate be present chloric acid is liberated, and this accelerates the oxidation, and there is grave danger of spontaneous ignition occurring.

---

[1] *See also S.S.* 1911, p. 236.

[2] *S.S.*, 1906, p. 53.

[3] *See* p. 86.

CHAPTER VI

MANUFACTURE OF GUNPOWDER

Advantages and disadvantages : Composition : Grinding the ingredients: Weighing and mixing : Incorporating or milling : Automatic drenchers : Removing the mill-cake : Breaking down : Pressing : Granulating or corning : Dusting and glazing : Stoving or drying : Finishing and blending : Cut powders : Moulded powders : Blasting powders : Sprengsalpeter : Cahuecit : Petroklastit : Bobbinite : Water-soluble powder : Products of explosion

The invention of so many other blasting explosives and smokeless powders has greatly restricted the consumption of black powder, but it has been able to hold its own in certain fields in consequence of its advantages : its low price, the ease with which it can be ignited, its insensitiveness to shock, its stability at moderately high temperatures, its regular rate of burning, and the non-corrosive nature of the residue that it leaves in the gun. But against these must be placed its great disadvantages : its want of power and the great quantity of smoke that it evolves. For shot-guns its rate of explosion is suitable, only the recoil and smoke are disagreeable, but for rifles the rate of burning cannot be controlled sufficiently ; for driving the bullets out of shrapnel shell there is no better explosive, and it is still used for armour-piercing shell, because the high explosives used for other sorts of shell will not withstand the great shock of impact without exploding prematurely ; for filling the rings of time fuses for shell no satisfactory substitute has yet been found.

Composition

Guttmann, in his book on the *Manufacture of Explosives*, published in 1895, gave the following as the compositions of the principal powders made at that time :

	Saltpetre	Sulphur	Charcoal
(*a*) *Rifle Powders :*			
Austria-Hungary	75	10	15
Belgium	75·5	12	12·5
China	75	10	15
France [1]	75	10	15
Germany [2]	74	10	16

---

[1] *Vennin et Chesneau*, p. 322, give the proportions 75 : 12·5 : 12·5.

[2] The proportions afterwards used in Germany for rifle powder were 75 : 9 : 15.

	Saltpetre	Sulphur	Charcoal
(*a*) *Rifle Powders :*			
Great Britain	75	10	15
Holland	70	14	16
Italy	75	10	15
Persia	75	12·5	12·5
Portugal	75·7	10·7	13·6
Russia	75	10	15
Spain	75	12·5	12·5
Sweden	75	10	15
Switzerland	75	11	14
Turkey	75	10	15
United States	75	10	15
(*b*) *Cannon Powders :*			
Austria-Hungary	74	10	16
France [1]	75	10	15
Germany	74	10	16
Great Britain	75	10	15
Switzerland	75	10	15
(*c*) *Sporting Powders :*			
Austria-Hungary	76	9·4	14·6
France	78	10	12
Germany	78	10	12
Great Britain	75	10	15
Switzerland	78	9	13
(*d*) *Blasting Powders :*			
Austria-Hungary	60·2	18·4	21·4
France	72	13	15
Germany	70	14	16
Great Britain	75	10	15
Italy	70	18	12
Russia	66·6	16·7	16·7

Blasting powders, however, vary in composition far more than this Table indicates, powders with different rates of burning being used for rocks of different degrees of hardness. Thus the French Government factories make three sorts of mining powder :

	Saltpetre	Sulphur	Charcoal
Ordinary Powder	62	20	18
Slow Powder	40	30	30
Strong Powder	72	13	15

---

[1] *Vennin et Chesneau*, p. 322, give the proportions 75 : 12·5 : 12·5.

The powders manufactured in Belgium have the following compositions :

	Saltpetre	Sulphur	Charcoal
Rifle Powder	75	12·5	12·5
Cannon Powder	75	12·5	12·5
Sporting Powder	78	10	12
Blasting Powder	75	12	13
Slow Powder or Pulvérin . .	70	13	14 & 3% wood meal
Slow Powder in cartridges . .	70	13	14 & 3% dextrine
Export Powder	68	18	22

In France "pulvérin" is also prepared for the manufacture of fireworks, etc. According to Chalon it has the composition 75 : 12·5 : 12·5,[1] but Vennin gives the proportions as 62 : 20 : 18.[2]

Grinding the ingredients.

Before they are mixed together the three ingredients are powdered. As they are not explosive when separate, they can be ground up in any suitable mill. In this respect, however, some reserve must be made as regards the sulphur : this has a great tendency to become electrified, and as it is also very inflammable an electric spark may easily set it alight or cause the explosion of a mixture of sulphur-dust and air. Rapid-moving machinery is therefore to be avoided ; the parts should all be made of metal and "earthed." According to Voigt the drum for pulverizing sulphur should not make more than ten revolutions per minute.[3] In some works the sulphur is mixed with a small proportion of the saltpetre before grinding to prevent this electrification, which has the further disadvantage that it causes the sulphur to cake together and so escape proper grinding. At Waltham Abbey the sulphur is ground under steel edge-runners similar to those used for incorporating the powder.

The charcoal is generally ground in a machine resembling a large coffee mill (*see* Fig. 6), but in some factories ball-mills are used, the charcoal being placed in a drum with bronze balls. The drum is then rotated until the constant falling of the balls on to the charcoal has reduced it to a sufficiently fine state of division.

Sulphur and saltpetre may also be ground in the Excelsior mill, but if the saltpetre is already in fine crystals it need not be ground, but only sifted. In France the saltpetre is mixed with 6 per cent. of charcoal and pulverized in an iron drum with bronze balls. The charcoal makes the saltpetre easier to grind, and this small proportion does not make it explosive. The remainder of the charcoal is mixed with the sulphur and pulverized in a similar drum. After grinding these binary mixtures are passed through a sieve with holes

---

[1] *Explosifs Modernes*, pp. 228, 263.

[2] *Vennin et Chesneau*, p. 322.

[3] *Herstellung der Sprengstoffe*, vol. i., p. 52.

0·65 mm. in diameter to separate foreign matters. The two binary mixtures are then mixed together by hand before being milled.[1]

Weighing and mixing. The three ingredients are carefully weighed out, preferably each in separate scales. An extra amount of saltpetre is often taken to allow for the moisture in it, the actual proportions weighed out being sometimes 76·0 : 15·0 : 10·0 instead of 75·0 : 15·0 : 10·0. But the charcoal usually contains quite as high a percentage of moisture as the saltpetre. It is not surprising therefore that analysis sometimes shows a percentage of charcoal which is below the theoretical.

The ingredients are then given a preliminary mixing. In Germany this is done in a rotating drum with lignum vitæ balls. The drum is made of wood and may be lined with leather; iron must be avoided in its construction; the axle must be covered with leather. At Waltham Abbey the mixing is done in a cylindrical drum of copper or gun-metal about 18 inches long and 2 feet 9 inches in diameter. Through the centre passes an axle carrying eight rows of fork-shaped arms, called "flyers." The drum rotates in one direction making 40 revolutions per minute. The axle moves in the other direction and makes 120 revolutions per minute. The ingredients are mixed for five minutes, and then sifted through a fine-mesh sieve of copper or brass wire. The sifting at this stage is very important, as any hard particles left in the charge are likely to cause an explosion in the incorporating mill. For this reason the sifting is sometimes done by hand. The "green" charge is now placed in a waterproof bag ready to be taken to the incorporating mill.

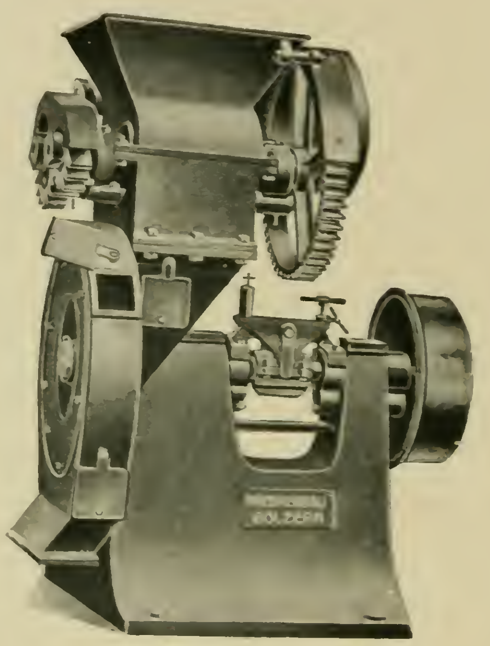


Fig. 6. Excelsior Mill, made by Maschinenbau A.-G. Golzern-Grimma.

ncorporating r milling. On the Continent stamp-mills are still used to a small extent for incorporating as well as mixing gunpowder. In Germany the stamp-heads may be made of copper, zinc, bronze or other suitable alloy.[2] The charge is placed in a spherical hole in a block of wood, with a piece of specially hard wood inserted

---

[1] *Vennin et Chesneau*, p. 327.

[2] *Unfallverhuttungsvorschriften*, 1912, p. 182.

at the bottom for the stamp to play upon. The stamping is carried on for about fourteen hours. If continued longer the density of the powder diminishes and the ballistics deteriorate.

In France the use of stamp-mills was definitely abandoned in 1884,[1] the powders there being incorporated in drums and mills. The cheaper sorts of powder are incorporated entirely in drums containing wooden balls. In England also stamp-mills are not used, and the standard method is to grind the ingredients together in incorporating mills. Formerly these consisted of two heavy stone edge-runners working on a stone bedplate. Now it is more usual to have iron runners working on an iron bed-plate: of course iron must not work upon stone, or vice versa, on account of the danger of generating sparks. In the most usual type of mill the runners are 6 or 7 feet in diameter and about 15 inches wide, and weigh about 4 tons each. They rotate on the opposite ends of a horizontal shaft, which is carried by a cross-head, which again is attached to a vertical shaft making about eight revolutions a minute. Usually the two edge-runners are mounted at different distances from the central shaft so that one works the outer part of the charge and the other the inner, but their paths overlap. There are two ploughs of wood covered with leather, which are fixed to the shaft and travel round with it. These continually push the charge away from the centre and the curb respectively, and bring it under the edge-runners again. The mills make 7½ or 8 revolutions per minute.

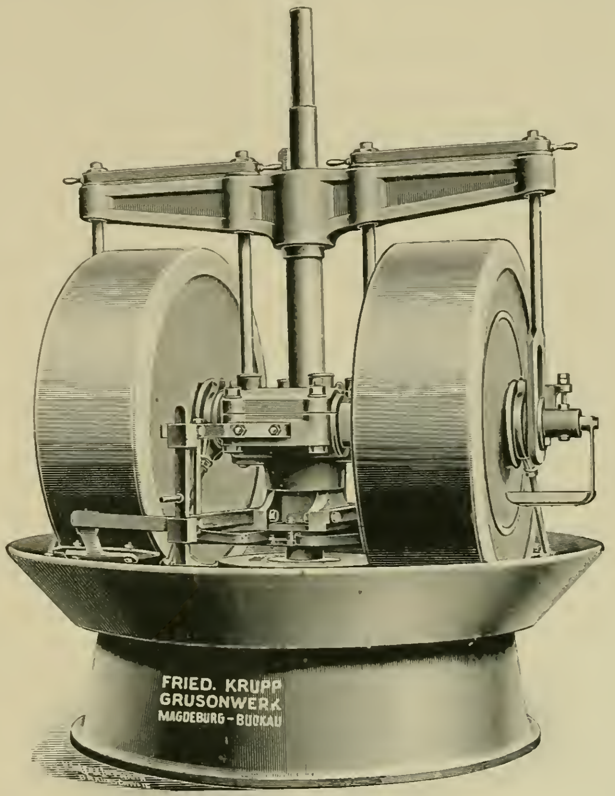


FIG. 7. Gruson Gunpowder Mill.

---

[1] *P. et S.*, vol. iii., p. 18.

In the Gruson mill (Fig. 7) the iron runners do not rest on the bed but are suspended a short distance above it, so that there is no danger of a very thin layer of powder being subjected to great friction. The bearings are so suspended that either runner can travel upwards independently of the other when an extra thick portion of charge comes underneath it. The runners weigh about 5½ tons each and rotate equidistantly round the main vertical shaft. The ploughs are made of phosphor bronze, and each runner is also provided with a scraper to prevent the charge being thrown off the bed. The drive is by means of a large bevelled gear-wheel, which may be arranged either above the machine or below it.

In Germany iron runners are not allowed to work on an iron bed-plate unless they are suspended, as in the Gruson mill. If they actually rest upon the bed, it must be made of wood fastened down with brass screws.

By the action of the runners the ingredients are crushed and ground together very intimately without subjecting the mixture to any violent action.

Usually about six incorporating mills are arranged in a row and driven from a common shaft actuated by a single water-wheel or steam-engine. Each mill is separated from the next by a strong masonry wall. Explosions in these mills are fairly frequent in spite of every precaution, but as a rule no very serious damage is done. In 1907 there were nine such explosions in England, but only one man was injured; in 1908 there were five explosions and two men were injured; in 1909 there were seven explosions and no men were injured. The reason why there are so few men killed or injured in these accidents is that as a rule there is no one in the mill house: after the charge has been started the man in attendance goes on to see to other mills and only comes occasionally to see that all is right and to add a little water to the charge if necessary. In France there is less than one explosion in 100,000 milling operations.[1] In Germany no workman is allowed to remain in the building whilst the mill is working at full speed.

A charge consists of 60 to 80 lbs., the time of incorporation varies with the description of the powder: the longer the incorporation the faster the powder burns. Cannon powders were usually milled for three or four hours, rifle powders eight, and sporting powders as much or more. The charge when placed in the mill contains 2 to 3 per cent. of moisture. It must be kept moist the whole time; for this purpose the mill-man adds water from time to time, preferably condensed water from a steam trap. Formerly urine was frequently used instead of water. For fine grain powders 1½ to 3 per cent. of moisture should be present in the finished mill-cake, for larger sizes 3 to 6 per cent.

In France mills similar to the Gruson mill are used, but the charge is only 20 kg. or 25 kg. in the case of mining powder. It contains 8 per cent. moisture when introduced and 2 to 4 per cent. at the finish. The mill makes 10 revo-

---

[1] *Vennin et Chesneau*, p. 333.

lutions per minute and requires 7 horse-power. The following table gives the times of milling and the densities of the mill cake :

	Time	Density
Military rifle powder, F_3	2 –2½ hours	1·740
Sporting powder, ordinary	1½ ,,	1·725
,, ,, strong	5 ,,	1·80
Dust reworked	½	—
Mining powder	½	1·57

The density is of importance because in France the powder is not pressed. The density can be increased by milling slowly, half a turn per minute, with the outer plough removed.[1]

In Germany the charge is generally about 75 kg. and the mill makes about nine revolutions per minute. The time of milling is :

Military powder	2½–3 hours.
Sporting ,,	4 ,,
Mining ,,	1½ ,,

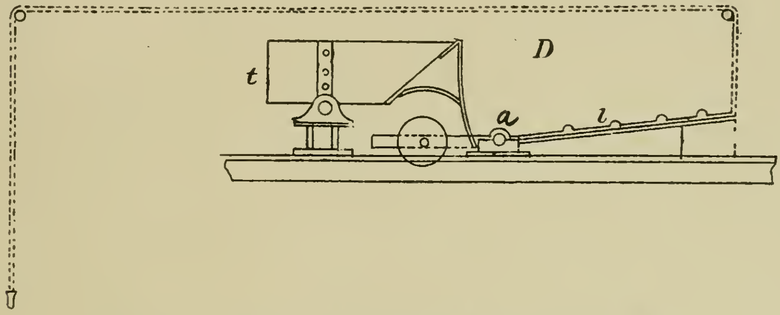


FIG. 8. Drenching Arrangements for Powder Mills.

Before the charge is removed the mill is run slowly for a time to increase the density, but the powder undergoes a pressing operation also, except in the case of mining powder.[2]

Automatic drenchers.

In order to prevent the explosion in one mill being communicated to the other mills of the group, each one is provided in England with an automatic drenching arrangement (*see* Fig. 8). This consists of a lifting board *l*, provided with a counterpoise weight. There is also a tank *t* full of water, supported on a hinge and a leg at one end that rests on a projection from the lifting board. When the latter is lifted, the leg is released, the tank tips forward and the water is poured over the charge in the mill. The axle *a* is common

---

[1] *Vennin et Chesneau*, p. 332.

[2] Voigt, *Herstellung der Sprengstoffe*, i., pp. 55, 56.

to all the lifting boards of the group of mills, so that if there be an explosion in one of the mills the corresponding board *l* is raised, taking with it all the other similar boards, and all the charges in the group are drenched and so rendered unexplosive. In order to make the mechanism sufficiently sensitive it is important that the boards be not too small and not too near the roof, and that they be directly over the mills. The second point is essential, because if the board be very near the roof a reflected wave of pressure reaches it almost immediately after the direct wave and before the mechanism has had time to act.

Removing the mill-cake. The mill-cake often becomes caked on to the bed very firmly. Many accidents having been caused by removing this with metal tools, H.M. Inspector of Explosives issued a letter on December 27, 1883, proposing the adoption of the following special rule in all black powder works:

"Whenever it may become necessary in mills or other buildings to remove any powder incrustations (whether from the machinery or elsewhere), which cannot be easily brushed off, such removal is to be effected without the use of any metal tool whatever: the hard powder is to be removed by means of water, supplemented, if need be, when the whole incrustation has been thoroughly saturated, by a suitable wooden instrument gently applied."

Breaking down. The mill-cake is next reduced to a rough powder by hand or by passing it through gun-metal rolls in a machine somewhat resembling the granulating machine, but simpler.

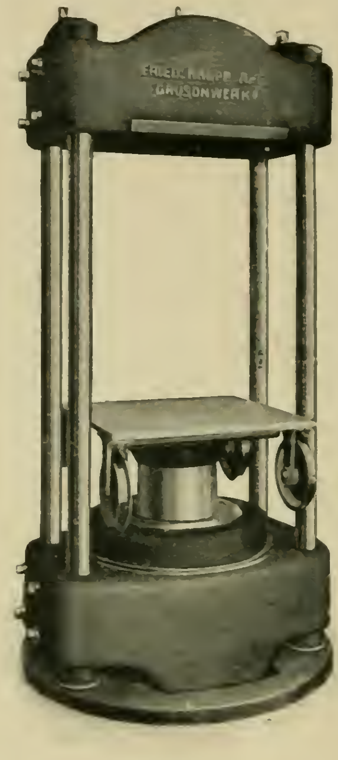


Fig. 9. Gunpowder Press.

Pressing. Then the mixture is subjected to high pressure in a press. This converts it into a hard mass, the constituents of which have no tendency to separate again from one another, and also increases the density of the powder. Formerly the powder was compressed in a very strong box, but this is no longer done on account of the dangerous friction against the sides.

For moulded powders and blasting cartridges special presses are used, which will be described later. Granulated powders are pressed in presses of the type shown in Fig. 9. The mill-cake is built up on a small trolley: first a plate of copper, bronze, or ebonite is put down, and a temporary frame put round it, then a layer of the mill-cake about ¾-inch thick is carefully spread, then another plate and another layer of powder, until about 10 cwt. of mill-cake has been built up with about twenty plates. The temporary frames are then removed and the trolley is wheeled on to the press, and the pressure is gradually applied. The amount of compression required varies with the amount of moisture in the mill-cake and the density to be attained in the finished powder. For a mixture containing about 3 per cent. of moisture it is necessary to apply a pressure of about 400 lb. per square inch of plate surface for 1½ to 2 hours to obtain a density of 1·7. The amount of compression is measured by the motion of the press rather than by the hydraulic pressure ; this motion may be 24 or 30 inches according to the dimensions of the press, etc. The pressure is usually released and reapplied several times to obtain a satisfactory result.

Ebonite plates are sometimes preferred to metal because they keep their shape better and yet give sufficiently to transmit the pressure evenly. If the cake be very dry the ebonite may become electrified, however, and so produce very dangerous sparks. In Germany the use of ebonite plates is forbidden, and cloths are laid between the plates and the powder. The four columns of the press should be made of mild steel with an ample margin of strength even if the whole pressure is borne by only two of them. They may with advantage be covered with leather. It was recommended by H.M. Inspector of Explosives [1] that the press should not be worked directly off the hydraulic pump, but from an accumulator, and that the drive of the pump should not be positive, but by friction.

The explosion of a press-house is more destructive than that of any other building in a black powder works, as might be expected, considering that there is about half a ton of powder in one mass strongly compressed. The house should therefore be specially well isolated from other buildings by mounds, etc. In some works the workmen are not allowed to be in the press-house whilst the pressure is on the powder ; the pressure can be applied and controlled from another compartment, where there is also an indicator showing the position of the platform of the press.

When sufficiently pressed the pressure is released and the trolley is wheeled away, and the press-cake removed from it by hand or with wooden tools. The outer portion of each slab is rejected as it is not sufficiently compressed ; it is added to a later pressing.

Blasting powder is sometimes compressed between rollers.

Granulating or corning.

The broken-up press-cake is put in barrels and taken to the granulating or corning house. Here there is a machine having three or four pairs of gun-metal rolls, through which the press-cake is passed, and a number of automatic sieves, which sort out the grains of the required size (*see* Fig. 10). The top pair of rollers usually has pyramidal teeth : from this the material passes

---

[1] Special Report No. 138.

over a sieve to the next pair of rolls, which has smaller teeth. The lowest pair are plain. The pieces that are not fine enough are passed through the machine again: the dust and fine powder are milled for a short time and pressed again. The bearings of one or both rolls of each pair are provided with springs or weights to keep them in position, and are not rigidly fixed. Consequently if an extra hard piece of cake passes through the rolls it is not subjected to great violence: the rolls give way and the piece passes through.

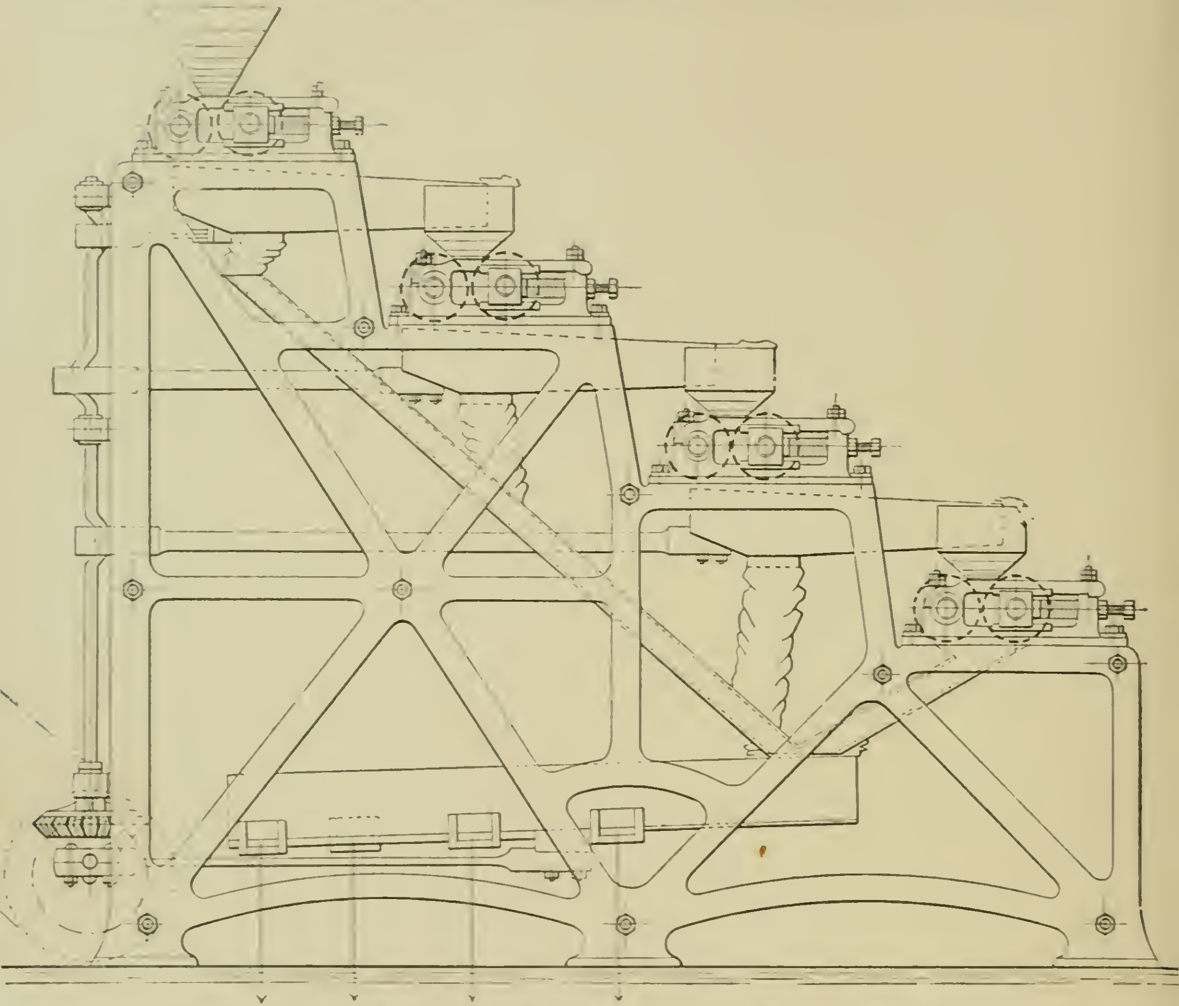


Fig. 10. Corning Machine, made by Maschinenbau A.-G. Golzern-Grimma

This type of granulating machine was invented in 1819 by Colonel Congreve.

and is the one in most general use. Various other types have been tried, but none produces such a good angular grain.

In France the granulation is carried out in a horizontal drum covered with metal sheet perforated with fine holes of a size suited to the sort of powder that is to be produced. The broken down mill-cake is placed inside this drum together with pieces of hard wood, which are caused by longitudinal strips to fall continually on to the powder and break it up. A charge of 20 kg. is granulated in ten to twelve minutes and yields 35 to 55 per cent. of grains of the size required.

Dusting. Powders made with dog-wood charcoal produce a lot of dust in the corning process, and it is best to remove this by passing the powder through a dusting reel. This is simply a cylindrical reel set at an angle of about 4° to the horizontal and covered with fine woven wire of copper or brass. It is open at both ends and rotates on its axis, making about forty revolutions per minute. The powder is simply passed through this and caught again in a barrel.

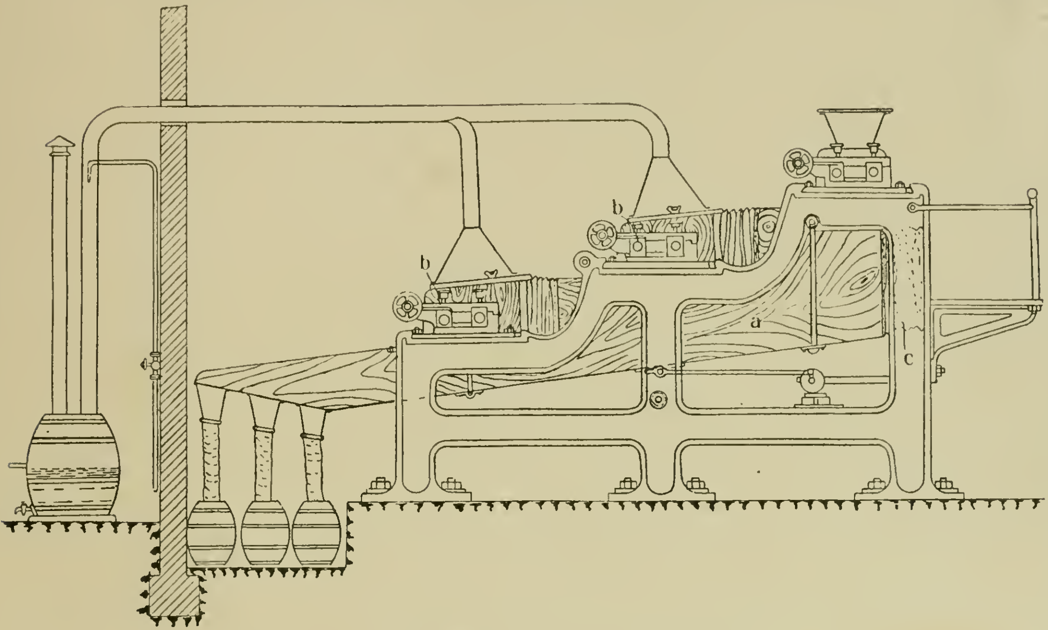


FIG. 11. Corning Machine with Dust-Remover

Glazing. The glazing operation is carried out in wooden drums, which rotate on their axis about thirty times a minute. Cannon powders receive an addition of a small proportion of graphite and are glazed for two or three hours. Rifle and sporting powders, and others that are required to burn quickly, do not receive any graphite, but are glazed longer.

Stoving or drying. The stove may be heated either by forcing hot air through it, or by arranging hot water or steam pipes in it. The easiest and most economical method is to dry with steam, and as black powder is not very sensitive and is not liable to spontaneous decomposition, this method is usually adopted. Only low-pressure steam should be used, the exhaust being open to the air. The powder is placed on canvas trays supported on wooden racks. Inlets and outlets are provided for the air, and the temperature is kept at about 40° C. (104° F.). The time required to dry the powder varies from one to four hours according to the size of grain.

nishing and ending. To remove the last traces of dust and give the powder a good "colour" it is now treated for some two hours in the finishing reel, which is covered with fine canvas, and finally thoroughly blended into large uniform batches. The last operation is performed at Waltham Abbey by pouring it into a hopper, which is provided with four delivery shutes, so that the contents of the hopper are divided into four equal portions. By repeating this operation in a systematic manner the desired object is attained very effectually.

t powders. Powder for cannon of large size, 6 to 12-inch bore, was made by cutting the press-cake into cubes. The slabs from the press were passed under a roll armed with longitudinal knives, whereby the cake was cut into strips, and these were then passed under another similar roll in the other direction and so cut into cubes. The glazing, stoving, finishing and blending were very much as for granulated powder, except that the stoving had to be continued for about thirty hours at 55° C. These cut powders are but little made now, as they have been displaced by smokeless powders.

The following Table gives particulars of some of the powders made formerly at Waltham Abbey [1]:

Powder	Size of grains Meshes to 1 in.	Charcoal		Incorporation		Glazing hrs.	Stoving		Finished Powder	
		Wood	Time of burning	Time hrs.	Moisture in mill-cake		hrs.	Temp.	Density	Moisture
RFG	12–20	Dogwood	4 hrs.	4	1·7 %	5½	1	100° F.	1·58–1·62	0·9–1·2
RFG^2	12–20	,,	8 ,,	8	2·5	10	2	100	1·72–1·75	0·9–1·2
RLG^2	3–6	Alder and willow	3½ ,,	3	2·5	1½	2	110	1·65	1·0–1·3
RLG^4	2–3	,,	4 ,,	3	4	3	6	115	1·65	1·0–1·3
P	⅝″ cubes	,,	4 ,,	3	4–5	4	36	130	1·75	1·0–1·3

oulded owders. Moulded powders also are but little used for the same reason, but much the same process is used for making moulded cartridges of mining powder, and also

---

[1] *Treatise on Service Explosives*, 1907 ed., pp. 123, 124.

pellets for time and percussion fuses and for other ammunition. The general form of all these articles is practically the same : a hexagonal or round cylinder with a central perforation. The powder is pressed, granulated, dusted and blended as already described, and then taken to the moulding house. Two different types of press are used, worked by hydraulic and mechanical pressure

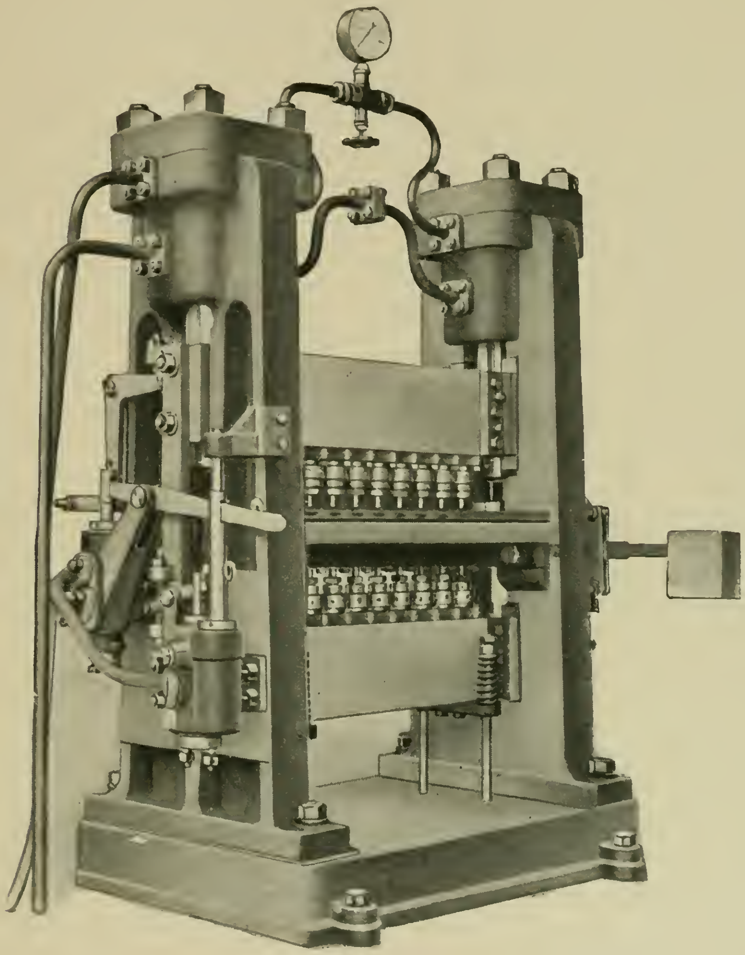


FIG. 12. Hydraulic Automatic Press for Moulded Powders and Blasting Cartridges (Maschinenbau A.-G. Golzern-Grimma)

respectively (*see* Figs. 12 and 13). The general principle is, however, the same. The granular powder is put into a hopper and flows from there into a measure that automatically measures off the right quantity, which then passes into the die. The dies are arranged in rows in a plate, so that whilst one row is being filled another is being pressed. The pressure is usually applied simultaneously from above and below by two different plungers. The central hole is formed by means of a pin which passes through the lower plunger and into the other. Hydraulic presses are safer, but mechanical ones more rapid in their action. For blasting cartridges, machines are also made with rotating tables containing a number of dies: each operation, filling, pressing, removing, is performed at a different position of the table. Such machines are quite automatic and require very little attention.

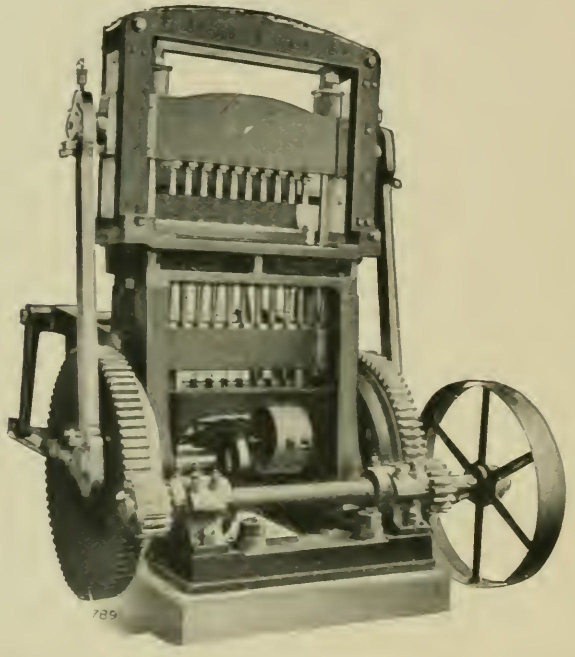


Fig. 13. Mechanical Press for Moulded Powders, etc. (F. Krupp A.-G. Grusonwerk)

Both black and brown powders have been moulded into prisms which are usually 25 mm. high and 40 mm. wide, measured across the corners of the hexagons. The following Table gives the details of the English and German powders:

Country	Name	Charcoal	Proportions	Density
England .	Prism[1] Black . .	Black .	75 : 10 : 15	1·76
,, .	Prism[1] Brown . .	Brown .	79 : 3 : 18	1·80
,, .	E.X.E. . . .	,, .	77·4 : 5 : 17·6	1·80
,, .	S.B.C. . . .	,, .	79 : 3 : 18	1·85
Germany .	P.P.C./68 . . .	Black .	74 : 10 : 16	1·66
,, .	P.P.C./75 . . .	,, .	74 : 10 : 16	1·76
,, .	P.P.C./82 . . .	Brown .	78 : 3 : 19	1·86
,, .	P.P.C./85 . . .	,, .	80 : 0 : 20	1·88
France[1] .	P.B.	,, .	78 : 3 : 19	1·85–1·87

[1] *Vennin et Chesneau*, pp. 322, 341.

P.P.C./68 has seven holes, all the others, English and German, only one. The value of the brown straw charcoal is that under the high pressures it flows and holds the mixture together, making it into an impervious mass, which can only burn at the surface, whereas black powders have slight pores through which the flame can penetrate. This may be seen by examining the powders under the microscope.[1]

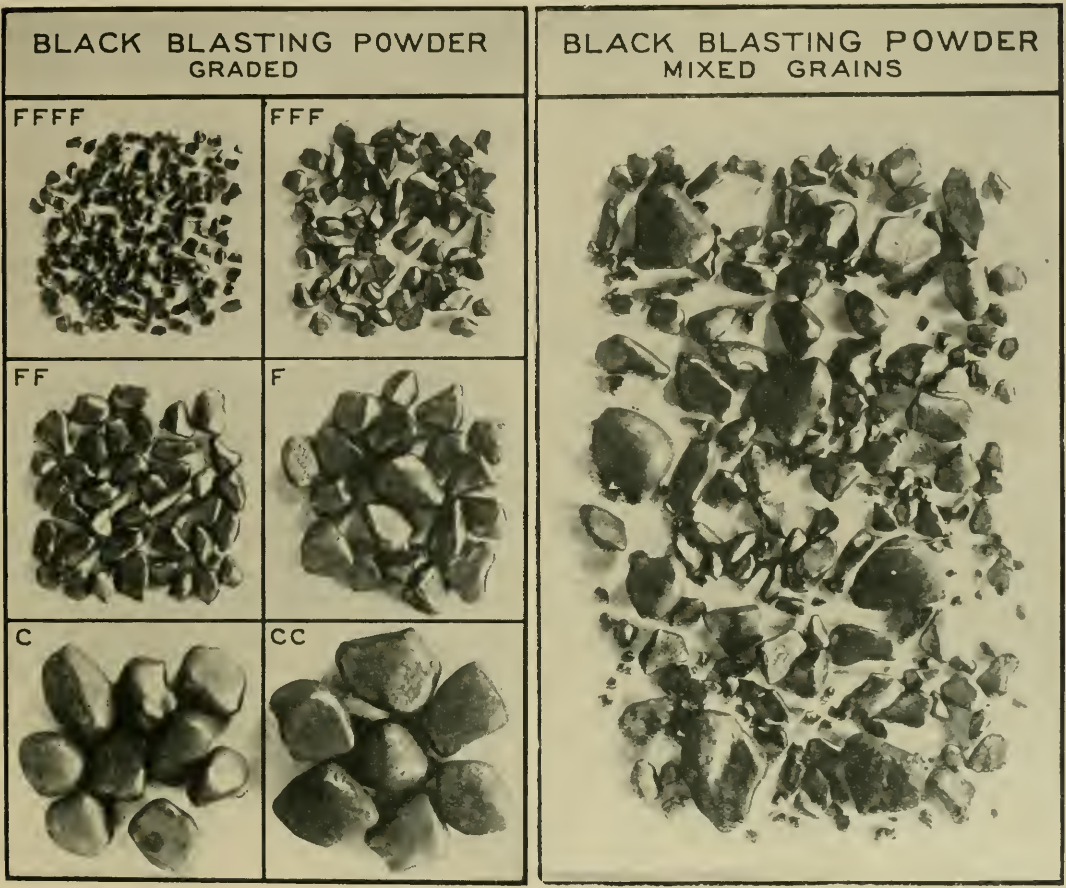


FIG. 14. American Black Blasting Powders (Munroe and Hall)

Blasting powders. The usual composition of black blasting powders has already been stated (p. 74). The violence of the powder can be varied by altering the composition, the density or the size of the grains: the powder is made slower by diminishing the percentage of saltpetre, compressing to a higher density or making

[1] *See* Cronquist, *S.S.*, 1906, p. 53.

the grains coarser. In France the mining powders manufactured in the State mills are incorporated, not under edge-runners, but in copper drums with wooden and bronze balls, and the granulation is also effected in drums with the aid of a spray of water.

In America enormous quantities of blasting powder are used containing sodium nitrate (Chili saltpetre) instead of the potassium salt. This burns more slowly than ordinary gunpowder, but is more powerful, as it evolves a greater volume of gas and more heat, but its principal advantage is its low price, for it is used for many purposes where in Europe hand labour would be employed. According to Chalon,[1] the composition varies between the following limits :

		Mean
Sodium nitrate	67·3 to 77·1	74
Sulphur	9·4 to 14·3	10
Charcoal	22·9 to 8·6	16

The usual proportions in this "black blasting powder" are given by Munroe and Hall [2] as 73 : 11 : 16. The incorporation is not so thorough as in the case of ordinary black powder, and the charcoal is generally obtained from coarser-grained woods. As the sodium nitrate is hygroscopic, care must be taken not to expose the powder to damp air more than can be helped. The following are the sizes of American black blasting powders :

	Diameters of round holes in screens in $\frac{1}{64}$th inches	
	Through which grains pass	On which grains collect
CCC	40	32
CC	36	24
C	27	18
F	20	12
FF	14	7
FFF	9	3
FFFF	5	2

The following blasting explosives resembling black powder in composition are made in Germany, and are allowed to be sent as goods in unlimited quantities, as they are considered safer to handle than ordinary black powder :

Sprengsalpeter "Sprengsalpeter" (blasting saltpetre) is a mixture of sodium nitrate, sulphur and brown coal in about the proportions 75 : 10 : 15, and is very largely used in the Stassfurt salt-mines where the soft and brittle nature of the salts, such as carnallite, require an explosive that is milder than ordinary blasting powder. It possesses the advantage of being cheap and not giving rise to poisonous fumes. Harder materials, such as sylvinite and rock-salt,

---

[1] *Les Explosifs Modernes*, 3rd ed., 1911, p. 264.

[2] *Primer on Explosives for Coal Miners*, Washington, 1911, p. 16.

are blasted with a combined charge of nitro-glycerine explosive and Sprengsalpeter.

Cahuecit.

"Cahuecit" was invented by R. Cahuc some forty years ago and was manufactured at one time at Dartford under the name of Safety Blasting Powder or Carboazotine. It had the composition :

Saltpetre	64
Sulphur	12
Lampblack	7
Bark or wood-pulp	17

to which was added 1 to 5 per cent. of sulphate of iron. After mixing the ingredients roughly in a drum they were introduced together with a considerable bulk of water into a steam-jacketed pan where the mixture was heated with constant stirring until almost dry. The mixture was imperfect in consequence of the tendency of the soluble salts to crystallize out.[1] It is still manufactured in Germany, and has been found good for blasting basalt.[2] The official German definition is : a compressed mixture of not more than 70 per cent. saltpetre, 8 per cent. lampblack, about 12 per cent. flowers of sulphur, at least 10 per cent. cellulose, and a small quantity of iron sulphate.

Petroklastit

"Petroklastit" (Haloklastit) has approximately the following composition :

Sodium nitrate	69
Potassium nitrate	5
Sulphur	10
Coal tar pitch	15
Potassium bichromate	1

Its strength and sensitiveness as compared with black blasting powder[3] are :

	Tranzl test	Falling weight
Petroklastit	157	100
Black powder	108	65

Its official definition is : a compressed mixture of sodium nitrate, sulphur, coal-tar pitch, saltpetre, and not more than 1 per cent. potassium bichromate, also with an addition of not more than 10 per cent. charcoal. It has been used in stone quarries and potash mines.

Bobbinite.

In English coal-mines the most largely used explosive has been Bobbinite, which is a black powder mixture with an addition of the sulphates of copper and ammonium, or of starch and paraffin-wax. It is the only explosive of this class that was able to pass the Woolwich test for "Permitted Explosives" ; it does not pass the Continental and Rotherham tests. In 1906 a

---

[1] Guttmann, *Manufacture*, vol. i., p. 273 ; *see also* Cundill and Thomson, p. 142.

[2] *S.S.*, 1908, p. 97.

[3] Zschokke, pp. 42, 57.

Departmental Committee was held at the Home Office to inquire whether this explosive should be removed from the list. This has not been done, but by the Explosives in Coal-Mines Order of September 1, 1913, its use has been restricted to mines that are not gassy or dusty. In these its use is permitted for a period of five years from January 1, 1914. The following is its composition according to the official definitions, and an analysis made by Hall and Howell :[1]

	Official definitions		Hall and Howell
	First	Second	
Nitrate of potassium	62·0–65·0	63·0–66·0	65·31
Charcoal	17·0–19·5	18·5–20·5	19·52
Sulphur	1·5–2·5	1·5– 2·5	2·63
Sulphate of ammonium Sulphate of copper . .	13·0–17·0	—	—
Rice or Maize starch . . .	—	7·0– 9·0	8·73
Paraffin wax	—	2·5 –3·5	3·35
Moisture	0·0– 2·5	0·0– 3·0	0·46

In 1914 more than a million lbs. of Bobbinite were used in British mines and quarries.

Vater-soluble owder.

Raschig proposes to make a cheap blasting powder consisting of 65 per cent. sodium nitrate and 35 per cent. sodium cresol-sulphonate. These are dissolved in water and the solution is evaporated very rapidly on a rotating drum heated by high-pressure steam. It is claimed that the expensive and dangerous operation ot incorporation is thus done away with. It is necessary to select a combustible constituent like the cresol-sulphonate, that has a high solubility of the same order as the nitrate, otherwise there would be a tendency for the substances to separate during the evaporation. Safety explosives containing ammonium nitrate instead of the sodium salt have been registered under the name of "Raschit."[2]

roducts of xplosion.

The products formed on the explosion of gunpowder were investigated by Bunsen and Schischkoff,[3] Linck,[4] and Karolyi,[5] but the most complete series of experiments was carried out by Noble and Abel.[6] Debus[7] showed

[1] U.S. Bureau of Mines. *Bull.* 15, 1912, p. 179.

[2] *See Ang.* 1912, p. 1194 ; Ger. Pat. App. R. 54,360 of 3/2/12 ; *S.S.*, 1912, p. 292.

[3] *Pogg. Annalen*, 102, 1857, p. 321.

[4] *Annalen der Chemie*, 109, 1858, p. 53.

[5] *Pogg. Annalen*, April, 1863 ; *Phil. Mag.*, Ser. 4, No. 26, 1863, p. 266.

[6] *Phil. Trans.*, 1875, 49.

[7] *Proc. Roy. Soc.*, 30, 1880, p. 198 ; *Phil. Trans.*, 1882, p. 523.

that they had made an error in giving potassium hyposulphite as a primary product of the explosion. Noble and Abel [1] accordingly corrected their results. The mean percentages from R.L.G. Powder were :

Gases	42·98%
Solids	55·91
Water	1·11

Gases, per cent. by volume		Solids, per cent. by weight	
Carbon dioxide	49·3	Potassium carbonate	61·0
Carbon monoxide	12·5	Potassium sulphate	15·1
Hydrogen	2·2	Potassium sulphide	14·5
Methane	0·4	Potassium sulphocyanide	0·2
Nitrogen	32·9	Potassium nitrate	0·3
Sulphuretted Hydrogen	2·6	Sulphur	8·7

From 1 g. of the powder 271·3 c.c. of gas were produced, measured at 760 mm. and 0° C., and the quantity of heat liberated was 700·7 calories.

The products obtained from mining powder have been given by J. Harger,[2] and the analysis of the gases from American blasting powder has been published by C. M. Young.[3] Hall and Howell [4] have investigated the products from Bobbinite.

---

[1] *Phil. Trans.*, 1880, p. 203.

[2] *J. Soc. Chem. Ind.*, 1912, p. 415.

[3] *Bull. Am. Min. Eng.*, 1910, pp. 637–662 ; *Ang.*, 1911, p. 1886.

[4] *U.S. Bureau of Mines Bull.* 15, 1912, p. 179.

PART III

ACIDS

CHAPTER VII

SULPHURIC ACID

Manufacture : Purification : Concentration : Melting-points : Specific gravities : Calculations : Supplies in war-time

Manufacture.

THE manufacture of sulphuric acid is treated fully in special works such as Lunge's *Sulphuric Acid and Alkali*. Here only the general principles can be dealt with and those special features which are of importance to the manufacturer of explosives.

Until the end of the last century, or the beginning of this, practically all the sulphuric acid was made by the "chamber process." Now very large quantities are produced by the "contact process." In both processes the first stage is to burn sulphur, or a sulphur ore such as zinc-blende or pyrites, in an excess of air, thus producing a gaseous mixture consisting mostly of oxygen, nitrogen, and sulphur-dioxide. It is necessary now to make the sulphur-dioxide combine with a further quantity of oxygen. In the chamber process this is done by mixing a small proportion of oxides of nitrogen with the gases and water in the form of spray or steam. Various intermediate products are formed, but the final product is "chamber acid," containing about 70 per cent. sulphuric acid and 30 per cent. water, or "Glover tower acid," containing about 80 per cent. acid.

In the contact process the sulphur-dioxide is made to combine with oxygen to form the trioxide, SO^3, by passing the gases over a heated contact substance, such as platinum or iron oxide. The burner gases are purified by washing with water and sulphuric acid, but afterwards no steam or spray of water is introduced, and consequently it is not necessary afterwards to concentrate the acid to bring it up to a high strength, as is the case with the chamber process. On the contrary the sulphur-trioxide has to be absorbed in weak sulphuric acid so as to obtain an acid of convenient strength. Very great difficulties were experienced at first because after a short time it was found that the spongy platinum used as the contact material ceased to be active. It was discovered, however, that this was due to the presence in the gases of traces of impurity, such as arsenic, which "poisoned" the platinum. When these are entirely removed the contact material retains its activity for a long time. The principal motive of the inventors in working out the contact process was to produce at a reasonable cost a fuming acid for use in the manufacture of artificial indigo, but large quantities of strong acid are also required in the explosives industry, and some explosives works have in fact erected contact plants of their own.

In the burners pyrites is generally burnt, but sometimes blende. The burnt pyrites or blende is afterwards sent to smelting works, where the metal is extracted. Sulphur (brimstone) is used only in localities where there are no smelting works available.

Purification. For the manufacture of explosives a high degree of purity is generally required of the sulphuric acid, especially freedom from arsenic. Acid made by the contact process always has sufficient purity, as arsenic and other foreign substances are necessarily removed in the course of manufacture. Sulphuric acid made from pyrites by the chamber process generally contains a considerable amount of arsenic and other impurities. These can be removed by treating the acid with sulphuretted hydrogen and allowing it to settle before concentrating it.

Concentration. Acid of 70 per cent. strength can often be concentrated up to 80 per cent. by passing it down a Glover tower. Where this is not available the concentration is generally carried out in lead pans heated either by a fire underneath or by steam coils laid in the bottom of the pan. Above this strength lead pans cannot be used as they are attacked too much by the hot acid. For the production of pure water-white concentrated sulphuric acid the further concentration may be carried out in glass or platinum stills heated from below. The greater part of the water is thus distilled off together with a little acid. The glass stills, however, are liable to break and the consumption of fuel is considerable. Platinum is very expensive and has risen in price considerably of late years. The platinum is sometimes coated with gold to diminish the loss. In neither glass nor platinum can sulphuric acid of the highest strength be produced; to obtain this a further concentration in cast-iron pans is necessary. Those works that have a contact sulphuric acid plant can use their recovered acid to absorb the sulphur-trioxide, and so bring it up to any required strength. In factories where the acid is purchased the same object can be accomplished by mixing the weak recovered acid with fuming acid (N.O.V.)[1] containing 20 or 60 per cent. anhydride. But in some processes of manufacture as, for instance, the displacement process for gun-cotton, such large quantities of weak acid are produced that reconcentration is necessary. Such reconcentration is nearly always carried out in the explosives works themselves, as it does not pay to transport such a material backwards and forwards by road or rail.

---

[1] The commercial term for sulphuric acid of 92 to 96 per cent. strength (s.g. 1·83–1·84) is C.O.V. (concentrated oil of vitriol), that of the fuming acid containing anhydride is N.O.V. (Nordhausen oil of vitriol) or oleum.

Cascade pl

The concentration is carried out either in a "cascade" plant or by direct contact with hot gases. In the cascade plant the acid is made to flow in turn through a large number of beakers or basins, each one of which is at a slightly lower level than the last. These are all heated from below by means of a suitable furnace. Formerly the vessels were made of glass or porcelain, but much trouble was caused by the continual breakages. Now basins of fused silica ware or special iron are used and breakages are comparatively rare.

Kessler's plant.

A type of plant used very extensively in the explosives industry is that of Kessler, the principle of which is to bring a current of hot gas from a gas producer in contact with the acid in a plant constructed of volvic stone, which is only very slightly attacked by the hot concentrated acid. Fig. 15 shows an early form of the plant, which has since been modified in some details. The hot gas from the producer enters by the tube *O* into the "saturex" *S*, where it passes down the channels *q*, and is caused by baffles to rush over the surface of the acid into the channels q^1. From here it passes up through the "plateaux" *A*, *B*, *C*, *D*, where the inverted cups cause it to bubble through the acid which passes down from one plateau to the other by means of the overflow pipes *n*. The acid thus receives a preliminary concentration, and the gas is partially cooled down before it goes through the dome *Z* and the pipe *P* to the condenser. The weak acid is introduced on the top plateau, and the concentrated acid flows out of the saturex through the pipe *m* into a lead tank, where it is cooled by means of a coil through which water flows. The arrangement of the baffles in the saturex has now been altered; they run transversely to the direction of flow of the gas and acid, and the hot gas passes under each of them in turn.

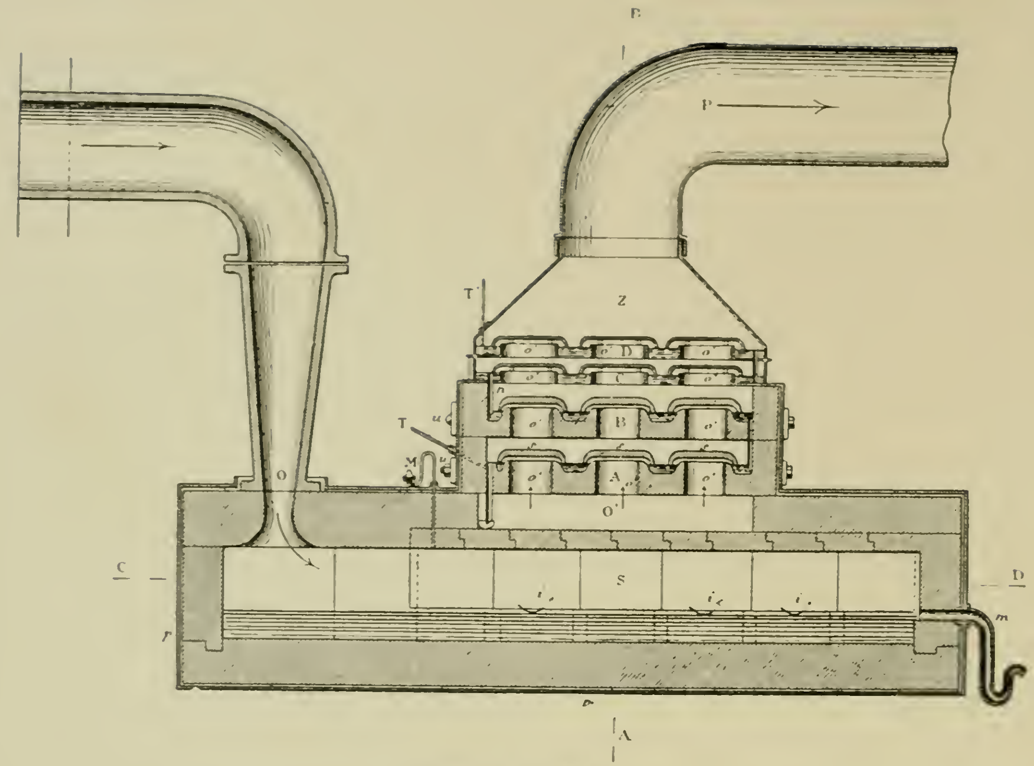
The gas passing away through *P* carries with it a considerable amount of sulphuric acid, mostly in the form of very fine mist, which is very difficult to remove and is very injurious to the surroundings. The gas is therefore passed through a condenser consisting of a large lead tank packed with carefully graded coke. Formerly the gas was drawn off by means of a steam injector in the pipe *P*, but this was very extravagant in steam and caused the condensed acid to be very dilute. Now a fan is used instead. Water is sprayed into *P* to assist the condensation of the acid. The general arrangement of the plant is shown in Fig. 16. Careful regulation of temperatures and draughts is necessary to ensure the best results.

Melting-points.

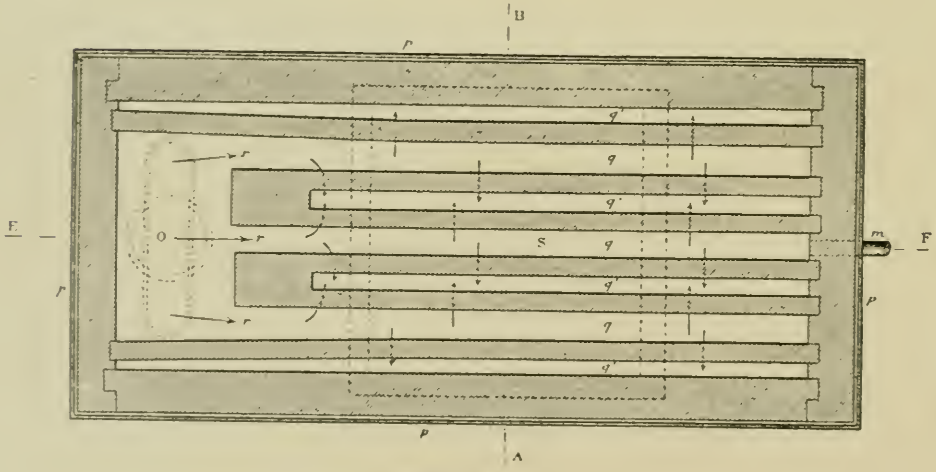
In deciding what strength of oleum it is best to use one of the properties that must be carefully considered is that of the melting-points of the acids. In Fig. 17 (pp. 104-5) are given the values as determined by Knietsch and published by him in the important paper on the contact process, which he read before the German Chemical Society in October 1901.[1] It will be seen that there are

---

[1] Ber., 1901, 4093; *Chem. Ind.*, 1902, p. 6.



Sectional Elevation



Sectional Plan

FIG. 15. Kessler Concentrator

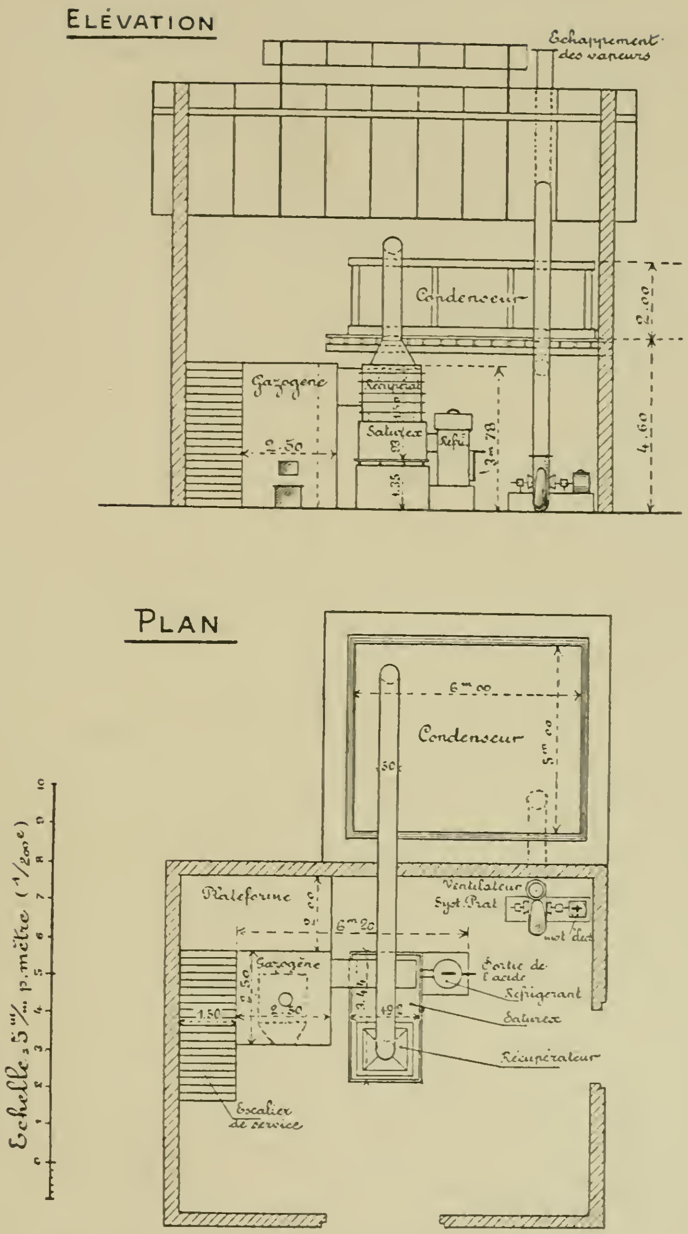


FIG. 16. Arrangement of Kessler's Plant for the Concentration of Sulphuric Acid

maxima at the points corresponding to (H_2SO_4, H_2O), (H_2SO_4), (H_2SO_4. SO_3) and (SO_3), and minima at intermediate points. A strength that is much used is one containing 18 to 20 per cent. anhydride : it has the advantage that it is liquid at all ordinary temperatures. With an increase of strength the melting-point rises rapidly until with 45 per cent. anhydride it reaches 36°, a temperature at which it is very inconvenient to deal with an acid that gives off dense fumes even at the ordinary temperature and boils below 90°. From here the melting-point falls again until with a strength of 60 to 65 per cent. anhydride an acid is obtained which is liquid in summer and can be easily melted at any time of the year. The choice of acid to be used therefore rests between C.O.V. and N.O.V. containing 18 to 20 per cent. and 60 to 65 per cent. anhydride. The decision must depend on the price at which the acids can be obtained and the facilities for reconcentrating or using the weak acids produced in manufacture. Where such facilities are deficient it is better to use the stronger oleum. Very little waste acid will then be produced. Otherwise most works prefer to use the 20 per cent. oleum. C.O.V. is now little used in explosives works for revivifying waste acids.

One of the disadvantages of the 20 per cent. oleum is that it attacks iron much more strongly than either C.O.V. or the 60 per cent. oleum.[1] On the other hand, the vapour tension of the weaker oleum is considerably smaller than that of the stronger. Whereas C.O.V. containing 98·5 per cent. H_2SO_4 boils at 317°, and 100 per cent. acid at about 270°, 20 per cent. oleum boils at about 140° and 60 per cent. at 60° C.

pecific ravities.

Tables of the specific gravities of mixtures of sulphuric acid and water have been published by various investigators. There are slight differences between the best of them, due principally to the difficulty of determining the strength of the acid with a very high degree of accuracy, and perhaps partly to the presence of traces of impurity in the material. The Tables of Lunge and his co-workers Naef and Isler are much used, but upon the whole the figures of Pickering seem to be the best. Many of the Tables are not directly comparable because the specific gravities have been taken at different temperatures or are referred to water at different temperatures ; in some cases the gravities are corrected for air displacement and in others not. For general work it is best to weigh both the acid and water at the ordinary temperature and not to correct for air displacement, for the introduction of small corrections is not only troublesome but is liable to lead to error. Pickering's figures were therefore calculated by me to this basis,[2] and are given in the following Table :

---

[1] *See* Knietsch, *loc. cit.*

[2] *J. Soc. Chem. Ind.*, 1903.

SPECIFIC GRAVITIES OF SULPHURIC ACID AT 15°/15° C. IN AIR.

Specific gravity	0	1	2	3	4	5	6	7	8	9
1·00	0·00	0·14	0·28	0·43	0·57	0·71	0·86	1·01	1·15	1·30
1·01	1·45	1·60	1·75	1·89	2·04	2·19	2·34	2·49	2·64	2·79
1·02	2·93	3·08	3·23	3·38	3·53	3·67	3·82	3·97	4·12	4·26
1·03	4·41	4·56	4·70	4·85	5·00	5·14	5·29	5·44	5·58	5·73
1·04	5·88	6·03	6·17	6·32	6·46	6·60	6·75	6·89	7·04	7·18
1·05	7·32	7·47	7·61	7·76	7·90	8·04	8·19	8·33	8·47	8·62
1·06	8·76	8·90	9·04	9·18	9·33	9·47	9·61	9·75	9·89	10·03
1·07	10·17	10·31	10·45	10·59	10·73	10·87	11·00	11·14	11·28	11·42
1·08	11·56	11·69	11·83	11·97	12·11	12·24	12·38	12·52	12·66	12·79
1·09	12·93	13·07	13·20	13·34	13·48	13·61	13·75	13·89	14·02	14·16
1·10	14·29	14·43	14·56	14·70	14·83	14·97	15·10	15·24	15·37	15·51
1·11	15·64	15·78	15·91	16·05	16·18	16·31	16·45	16·58	16·71	16·84
1·12	16·98	17·11	17·24	17·37	17·51	17·64	17·77	17·90	18·03	18·16
1·13	18·30	18·43	18·56	18·69	18·82	18·95	19·08	19·22	19·34	19·47
1·14	19·60	19·73	19·86	19·99	20·12	20·25	20·38	20·51	20·64	20·77
1·15	20·90	21·03	21·16	21·28	21·41	21·54	21·67	21·80	21·93	22·05
1·16	22·18	22·31	22·44	22·56	22·69	22·82	22·94	23·07	23·20	23·32
1·17	23·45	23·57	23·71	23·83	23·96	24·08	24·21	24·34	24·46	24·59
1·18	24·71	24·84	24·97	25·09	25·22	25·34	25·47	25·59	25·72	25·84
1·19	25·97	26·09	26·22	26·34	26·47	26·59	26·71	26·84	26·96	27·09
1·20	27·21	27·33	27·46	27·58	27·71	27·83	27·95	28·08	28·20	28·32
1·21	28·45	28·57	28·69	28·82	28·94	29·06	29·18	29·31	29·43	29·55
1·22	29·68	29·80	29·92	30·04	30·17	30·29	30·41	30·53	30·65	30·78
1·23	30·90	31·02	31·14	31·26	31·38	31·50	31·62	31·75	31·87	31·99
1·24	32·11	32·23	32·35	32·47	32·59	32·71	32·83	32·95	33·07	33·19
1·25	33·31	33·43	33·55	33·67	33·79	33·91	34·02	34·14	34·26	34·38
1·26	34·50	34·62	34·74	34·86	34·98	35·09	35·21	35·33	35·45	35·57
1·27	35·68	35·80	35·92	36·04	36·15	36·27	36·39	36·51	36·62	36·70
1·28	36·86	36·97	37·09	37·21	37·32	37·44	37·56	37·68	37·79	37·91
1·29	38·03	38·14	38·26	38·37	38·49	38·60	38·72	38·83	38·95	39·06
1·30	39·18	39·29	39·41	39·52	39·64	39·75	39·86	39·98	40·09	40·20
1·31	40·32	40·43	40·54	40·66	40·77	40·88	40·99	41·11	41·22	41·33
1·32	41·45	41·56	41·67	41·79	41·90	42·01	42·12	42·23	42·35	42·46
1·33	42·57	42·68	72·79	42·90	43·01	43·12	43·23	43·35	43·46	43·57
1·34	43·68	43·79	43·90	44·01	44·12	44·23	44·34	44·45	44·56	44·67
1·35	44·77	44·88	44·99	45·10	45·21	45·32	45·43	45·53	45·64	45·75
1·36	45·86	45·97	46·07	46·18	46·29	46·39	46·50	46·61	46·71	46·82
1·37	46·92	47·03	47·14	47·24	47·35	47·45	47·56	47·67	47·77	47·88
1·38	47·98	48·09	48·19	48·30	48·40	48·50	48·61	48·71	48·82	48·92
1·39	49·02	49·13	49·23	49·34	49·44	49·54	49·65	49·75	49·86	49·96
1·40	50·06	50·16	50·26	50·37	50·47	50·57	50·67	50·77	50·88	50·98
1·41	51·08	51·18	51·28	51·38	51·48	51·58	51·68	51·78	51·89	51·99
1·42	52·09	52·19	52·29	52·39	52·49	52·59	52·69	52·79	52·89	52·98
1·43	53·08	53·18	53·28	53·38	53·48	53·58	53·68	53·78	53·88	53·97
1·44	54·07	54·17	54·27	54·36	54·46	54·56	54·65	54·75	54·85	54·94

Specific Gravities of Sulphuric Acid at 15°/15° C. in Air—*continued*

Specific gravity	0	1	2	3	4	5	6	7	8	9
1·45	55·04	55·14	55·24	55·33	55·43	55·53	55·62	55·72	55·82	55·91
1·46	56·01	56·11	56·20	56·30	56·39	56·49	56·59	56·68	56·78	56·87
1·47	56·97	57·06	57·16	57·25	57·35	57·44	57·54	57·63	57·73	57·82
1·48	57·92	58·01	58·10	58·20	58·29	58·38	58·48	58·57	58·66	58·75
1·49	58·85	59·94	59·03	59·12	59·22	59·31	59·41	59·50	59·59	59·68
1·50	59·78	59·87	59·96	60·05	60·14	60·23	60·33	60·42	60·51	60·60
1·51	60·69	60·78	60·87	60·96	61·05	61·14	61·24	61·33	61·42	61·51
1·52	61·60	61·69	61·78	61·87	61·96	62·05	62·14	62·23	62·32	62·41
1·53	62·50	62·59	62·68	62·77	62·86	62·95	63·04	63·13	63·22	63·31
1·54	63·40	63·49	63·58	63·67	63·76	63·85	63·94	64·03	64·12	64·20
1·55	64·29	64·38	64·47	64·55	64·64	64·73	64·82	64·91	65·00	65·08
1·56	65·17	65·26	65·35	65·44	65·52	65·61	65·70	65·79	65·88	65·96
1·57	66·05	66·14	66·23	66·31	66·40	66·49	66·57	66·66	66·75	66·83
1·58	66·92	67·01	67·10	67·18	67·27	67·36	67·44	67·53	67·62	67·70
1·59	67·79	67·88	67·97	68·05	68·14	68·23	68·31	68·40	68·49	68·57
1·60	68·66	68·74	68·83	68·92	69·00	69·09	69·17	69·26	69·35	69·43
1·61	69·52	69·60	69·69	69·78	69·86	69·95	70·03	70·12	70·20	70·29
1·62	70·38	70·46	70·55	70·63	70·72	70·80	70·89	70·97	71·06	71·14
1·63	71·23	71·31	71·40	71·48	71·57	71·65	71·74	71·82	71·91	71·99
1·64	72·07	72·16	72·25	72·33	72·42	72·50	72·59	72·67	72·76	72·84
1·65	72·93	73·01	73·10	73·18	73·27	73·35	73·43	73·52	73·60	73·69
1·66	73·77	73·86	73·94	74·02	74·11	74·19	74·27	74·36	74·44	74·53
1·67	74·61	74·69	74·78	74·86	74·95	75·03	75·12	75·20	75·29	75·37
1·68	75·46	75·54	75·63	75·71	75·80	75·88	75·97	76·05	76·14	76·22
1·69	76·31	76·39	76·48	76·56	76·65	76·74	76·82	76·91	76·99	77·08
1·70	77·17	77·25	77·34	77·42	77·51	77·60	77·68	77·77	77·85	77·94
1·71	78·03	78·11	78·20	78·28	78·37	78·46	78·54	78·63	78·72	78·80
1·72	78·89	78·97	79·06	79·15	79·23	79·32	79·41	79·49	79·58	79·67
1·73	79·75	79·84	79·93	80·02	80·11	80·20	80·29	80·38	80·47	80·56
1·74	80·65	80·74	80·83	80·92	81·01	81·10	81·19	81·28	81·37	81·46
1·75	81·55	81·64	81·73	81·82	81·92	82·01	82·11	82·21	82·31	82·41
1·76	82·51	82·61	82·71	82·80	82·90	83·00	83·10	83·20	83·29	83·39
1·77	83·49	83·59	83·69	83·78	83·88	83·98	84·08	84·18	84·29	84·39
1·78	84·50	84·60	84·71	84·81	84·92	85·03	85·14	85·25	85·36	85·47
1·79	85·60	85·72	85·84	85·96	86·08	86·20	86·32	86·45	86·58	86·71
1·80	86·84	86·97	87·10	87·23	87·36	87·50	87·64	87·78	87·92	88·06
1·81	88·20	88·34	88·49	88·64	88·79	88·95	89·11	89·27	89·44	89·61
1·82	89·79	89·97	90·15	90·33	90·51	90·70	90·90	91·10	91·30	91·52
1·83	91·74	91·98	92·22	92·46	92·71	92·98	93·26	93·56	93·87	94·20
1·84	94·57	94·96	95·40	96·02	96·93					
1·84	99·88	99·61	99·29	98·84	98·08					
1·8442	97·50									
1·8394	100·00									

For concentrated acid the determination of the specific gravity is not of much value as an indication of its strength, because the density reaches a maximum at about 97·5 per cent.

The following Table gives the corrections to be applied to the specific gravities if the temperature varies from 15°.[1]

Sp. Gr.	Correction for 1°
Up to 1·170	0·0006
1·170 ,, 1·450	0·0007
1·450 ,, 1·580	0·0008
1·580 ,, 1·750	0·0009
1·750 ,, 1·820	0·0010

For the effect of impurities on the specific gravity of sulphuric acid *see* Marshall, *J. Soc. Chem. Ind.*, 1902, p. 1508. Fig. 18 (p. 106) gives the specific gravities of a number of trade samples of C.O.V., some of which had become contaminated with traces of nitric acid, also some acids that had been used and reconcentrated several times in a Kessler plant. The curves corresponding to the Tables of Pickering and Lunge are also given for comparison.

Knietsch has determined the specific gravities of fuming acids (*loc. cit.*). His figures are to be found in the following Table :

Free SO_3 per cent.	Total SO_3	Corresponding H_2SO_4	Sp. gr. 15°/15° in air	Sp. gr. 45°
10	83·46	102·2	1·888	1·858
20	85·30	104·5	1·920	1·887
30	87·14	106·7	1·957	1·920
40	88·97	109·0	1·979	1·945
50	90·81	111·2	2·009	1·964 (max.)
60	92·65	113·5	2·020 (max.)	1·959
70	94·48	115·7	2·018	1·942
80	96·32	118·0	2·008	1·890
90	98·16	120·2	1·990	1·864
100	100·00	122·5	1·984	1·814

Calculations

The strength of the fuming acid is generally expressed as per cent. free SO_3, but sometimes as total SO_3. When determining the strength by analysis it is most convenient to express it first as per cent. H_2SO_4, and there are other advantages in expressing it thus. A figure is, of course, obtained which is greater than 100, but it gives at once the quantity of sulphuric acid that will be formed if 100 parts of it be added to a mixture, and if 100 be deducted from it, the remainder is the amount of water that will disappear from the mixture to form this sulphuric acid. This remainder multiplied by SO_3/H_2O (=

---

[1] Lunge and Hurter, *Alkali-Maker's Pocket-book.*

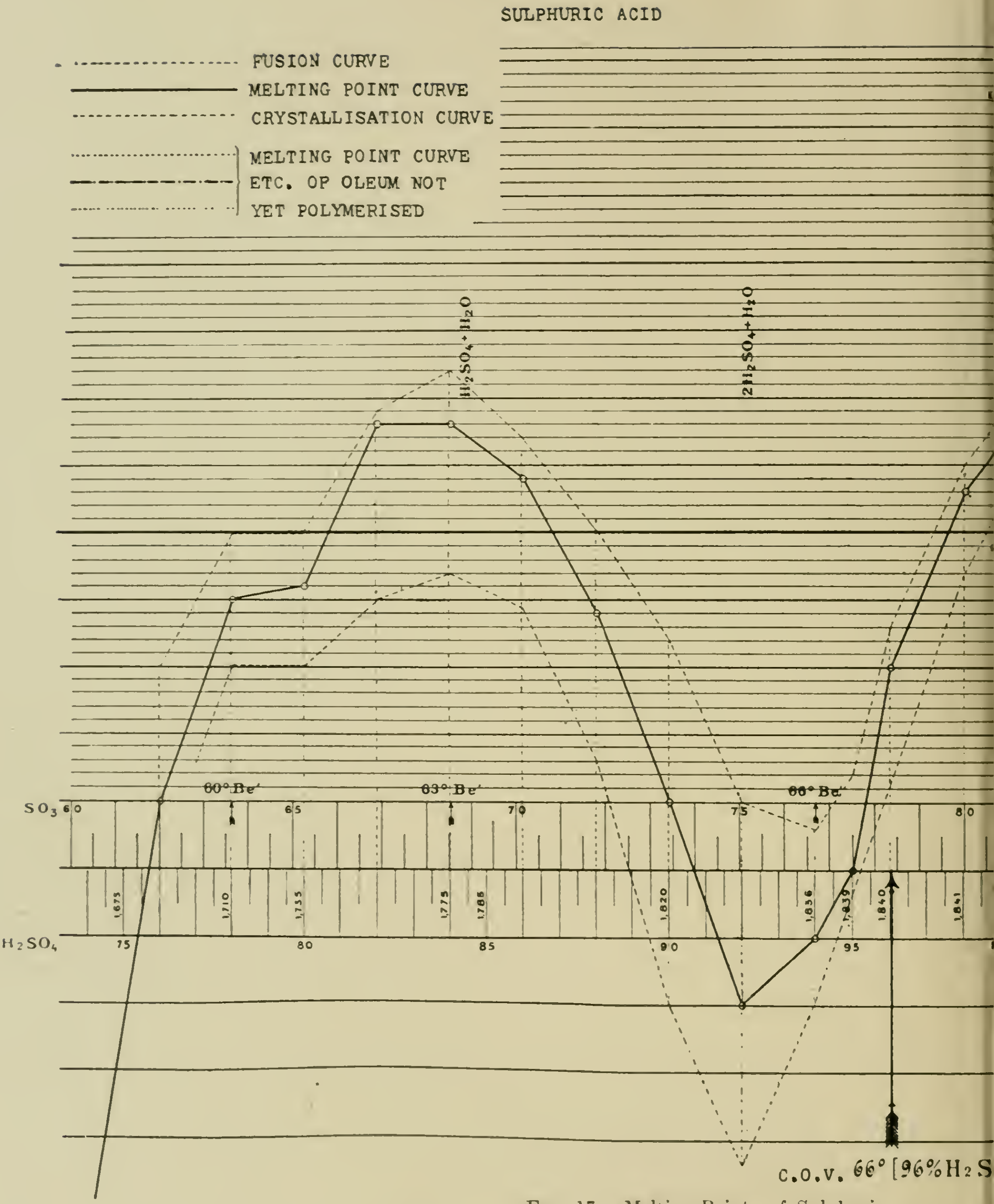
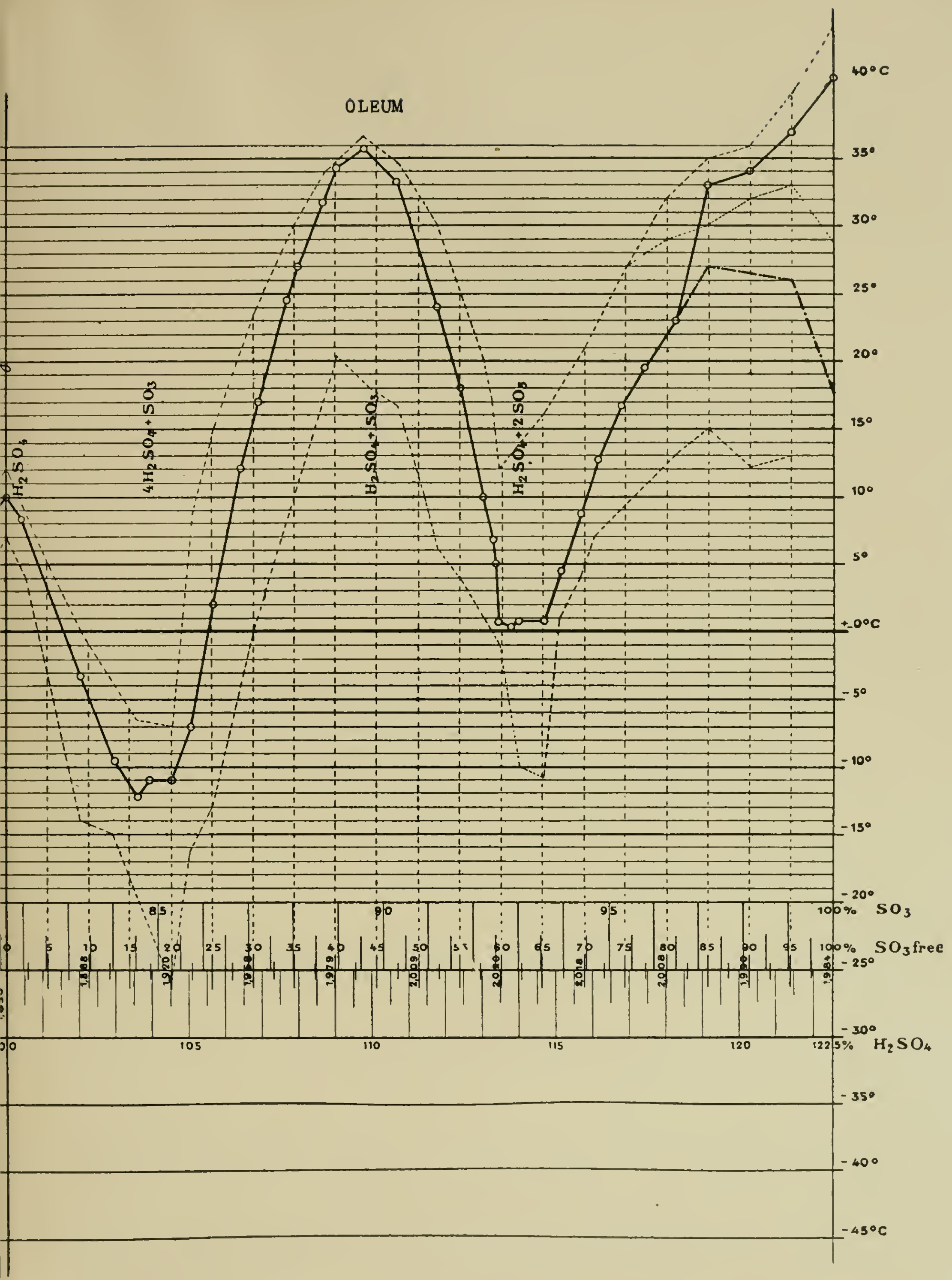


FIG. 17. Melting-Points of Sulphuric



Acid and Oleum (Knietsch)

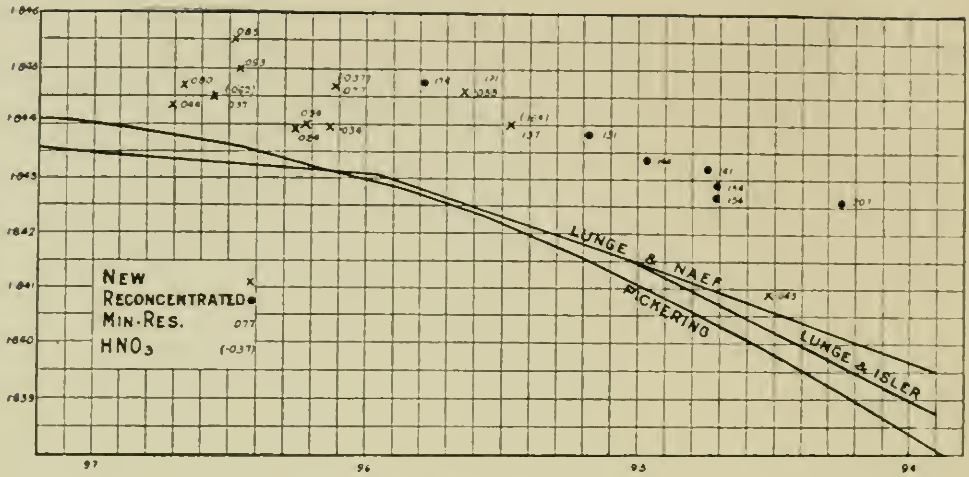


Fig. 18. Specific Gravities of Sulphuric Acid

80/18 = 4·44) gives the percentage of free SO_3. The percentage of H_2SO_4 multiplied by 80/98 (= 0·8163) gives the total SO_3. Similar rules may be made for converting any of these three expressions into any other :

if F be the percentage of free SO_3
and T ,, total SO_3
and H ,, H_2SO_4
then $F = 4{\cdot}444\ (H - 100)$
$= 5{\cdot}444\ T - 444$
and $T = 0{\cdot}8163\ H$
$= 0{\cdot}1837\ F + 81{\cdot}63$
and $H = 0{\cdot}225\ F + 100$
$= 1{\cdot}225\ T$

The conversion can also be effected by means of the scales at the base of Fig. 17.

upplies in
ar-time.

All countries during the war are suffering more or less from a shortage of sulphuric acid due to the enormous demands and the disturbances in the supply of the raw materials. In Germany the cessation of the imports of pyrites from over-seas appears to have caused considerable trouble in spite of the fact that they have the Belgian acid works at their disposal as well as their own, and that ores can be obtained from Norway, Hungary and Styria.[1] They are said to be making sulphuric acid from calcium sulphate (gypsum) and magnesium sulphate (Kieserite).[2]

---

[1] *See* F. G. Donnan, *Nature*, March 23, 1916, p. 82.

[2] *Chem. Trade Jour.*, Nov. 27, 1915.

CHAPTER VIII

NITRIC ACID

Manufacture : Recovery of nitrous fumes : Storage : The distillation : Nitre cake : Nitric acid from the atmosphere : Direct oxidation : Cyanamide process : Serpek's process : Haber's process : Ostwald's process : Properties : Specific gravities : Freezing-points : Boiling-points : Vapour pressures

Manufacture.

NITRIC acid is usually made by distilling Chili saltpetre with sulphuric acid in large iron retorts. Formerly these were made of such a size as to take a charge of about half a ton of sulphuric acid and the same quantity of nitrate : now they are generally made to take twice as much or more. Fig. 19 shows a retort somewhat similar to those used for the Valentiner system. To take a ton of nitrate the retort should be about 6 feet in diameter and 6 feet high : it must not be too small on account of the danger of frothing over or "priming." Horizontal cylindrical stills are also used.

At one time nitric acid was only made of about 60 per cent. strength, but when a large demand for stronger acid arose for the manufacture of explosives it was found that there was no real difficulty in obtaining nearly the whole of the acid of 92 to 94 per cent. strength. By the recovery of nitrous fumes acid of 60 per cent. strength is still produced : formerly it was sometimes concentrated by distillation with sulphuric acid, but now it can be utilized directly mixed with C.O.V. or oleum.

Condensers.

The nitric-acid vapours were formerly condensed by air cooling, by leading them through a large number of stone-ware jars connected by stone-ware pipes, but this system was inefficient and required much plant and space. The reason for its adoption was that metal condensers could not be used because they were attacked by the acid, and stone-ware condensers cooled with water would have cracked with the changes of temperature. But with the improvements that were made in the manufacture of earthen and stone-ware this has been altered. The Guttmann condensing battery has been much used (Fig. 20.) It consists of a number of vertical stone-ware pipes immersed in a tank through which water circulates ; at the bottom these pipes are connected by cross-pieces in such a way that whilst the fumes have to pass up and down the pipes one after the other, the condensed acid flows along from one cross-piece to another through inverted siphons and finally to the storage tank.

In the Valentiner plant (Fig. 21) stone-ware coils are used, and these are also adopted now by many who do not work by Valentiner's system. When first introduced there were frequent breakages, especially at the upper extremity where the coil entered the water. The coils could be repaired by the addition of a piece of lead pipe joined on. for the strong acid has but little action upon it. Such breakages are not so frequent now: they can be avoided to a large extent by not immersing the first coil in water, but cooling it by running water over cloths laid on the coil. Coils can now be obtained made of fused silica or "vitreosil" as much as 2 inches in diameter and 60 feet long. These are much more resistant than stone-ware and can be repaired when broken.

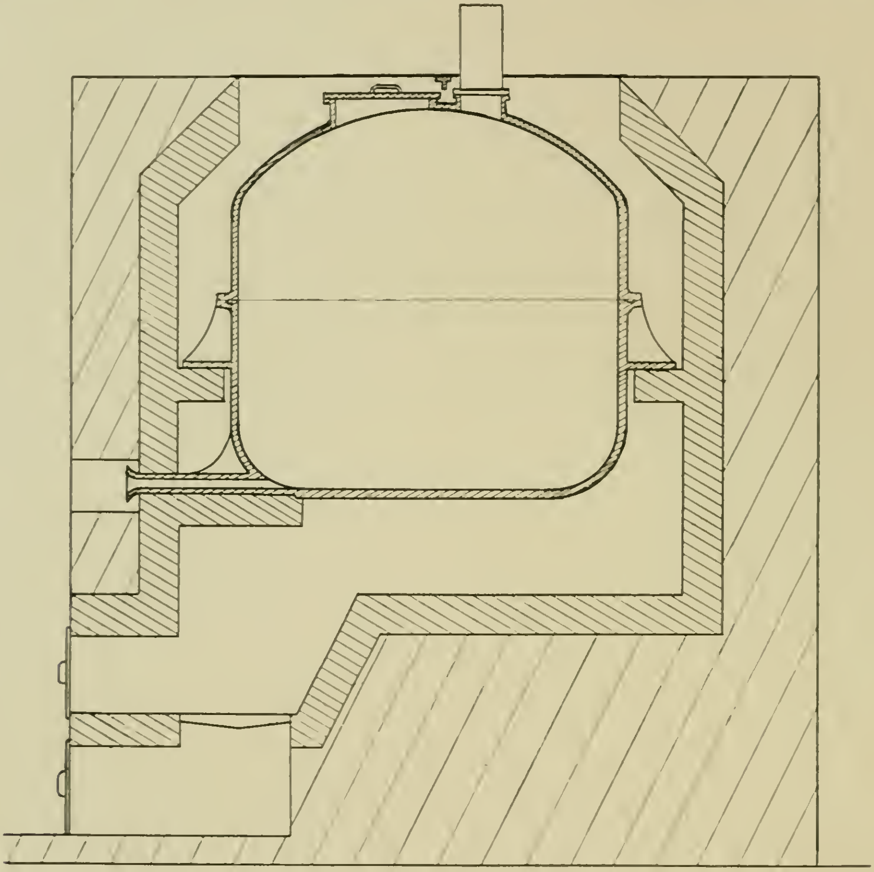


FIG. 19. Nitric Acid Still

Valentiner system.

The principal peculiarity of Dr. Valentiner's system is that the distillation is carried out *in vacuo*. At the end of the series of condensers and jars shown in Fig. 21 there is a vacuum pump, which with every stroke draws in some caustic soda solution to prevent the acid fumes attacking the metal of the pump too much. The large number of small washing jars is also to absorb the acid fumes as far as possible before they reach the pump. The advantages claimed for the system are that the time of working a charge is much shortened by the use of a vacuum, that the process is under better control, and that

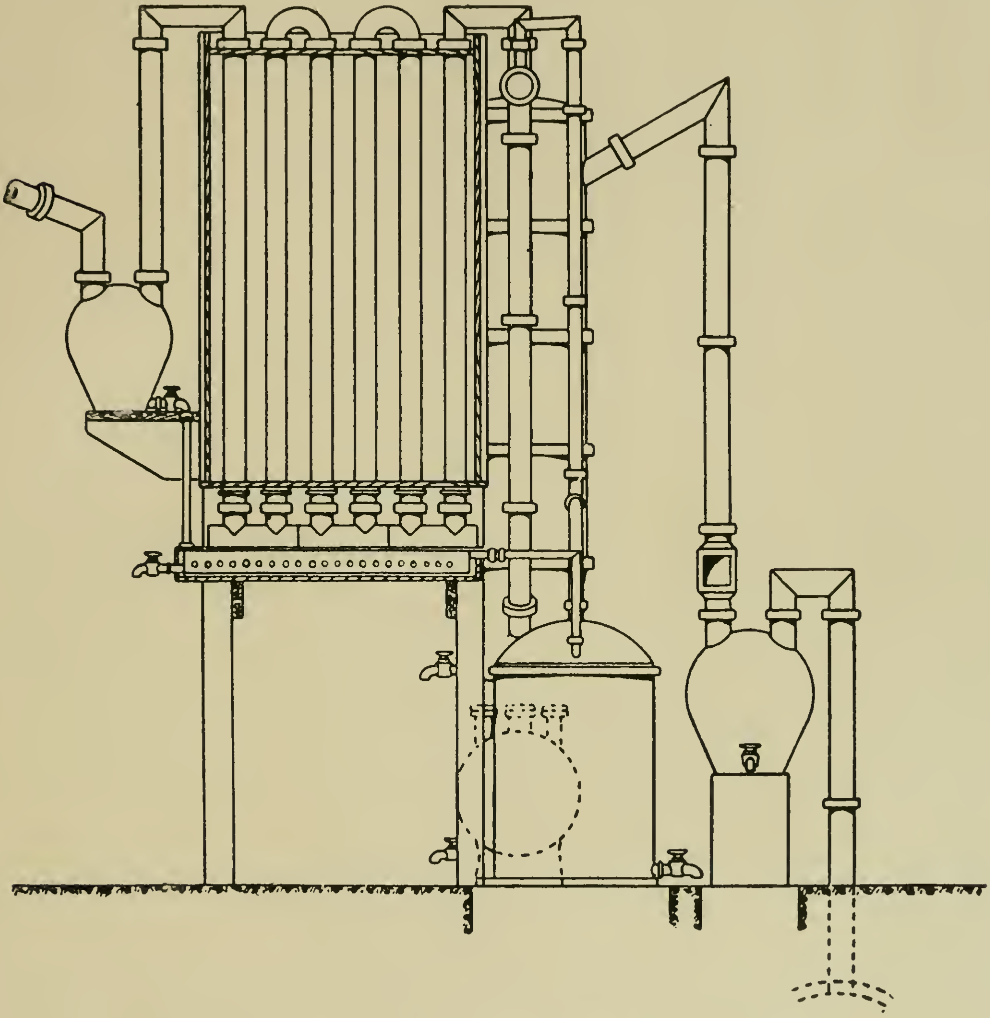


FIG. 20. Guttmann's Condensing Battery for Nitric Acid.

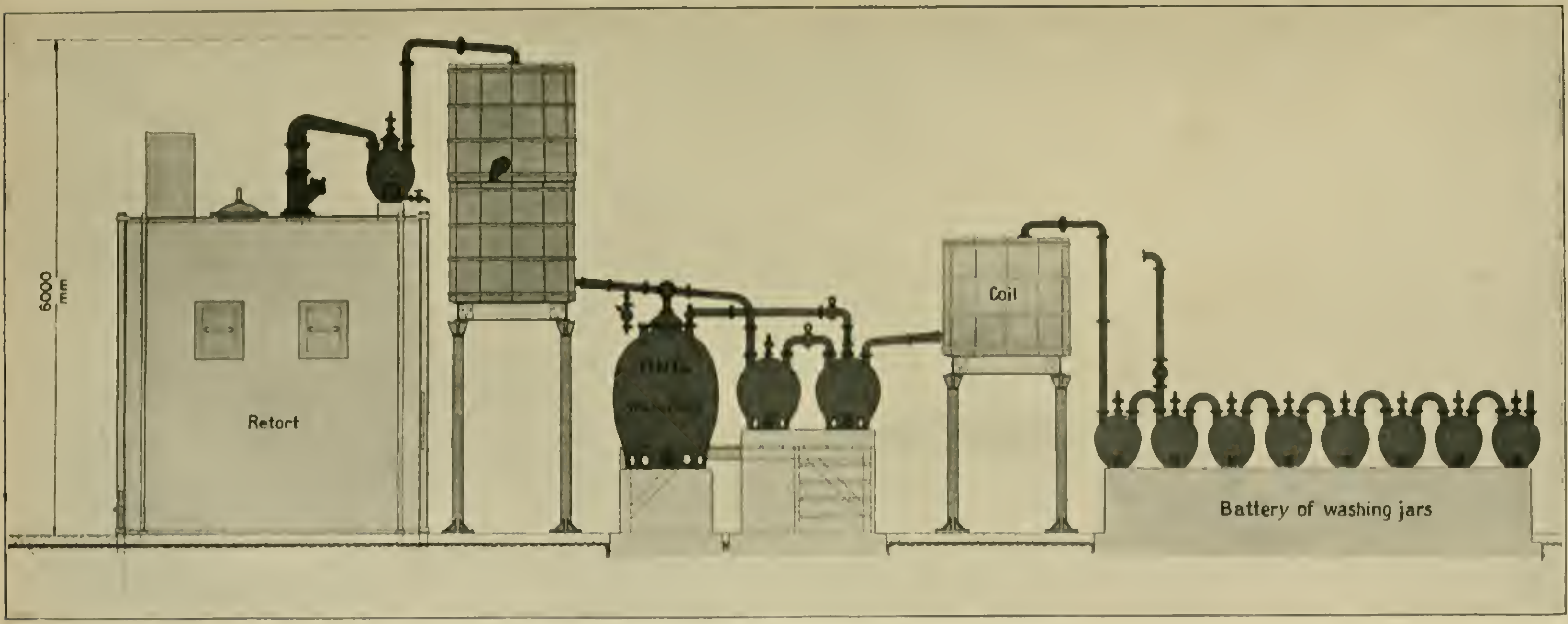
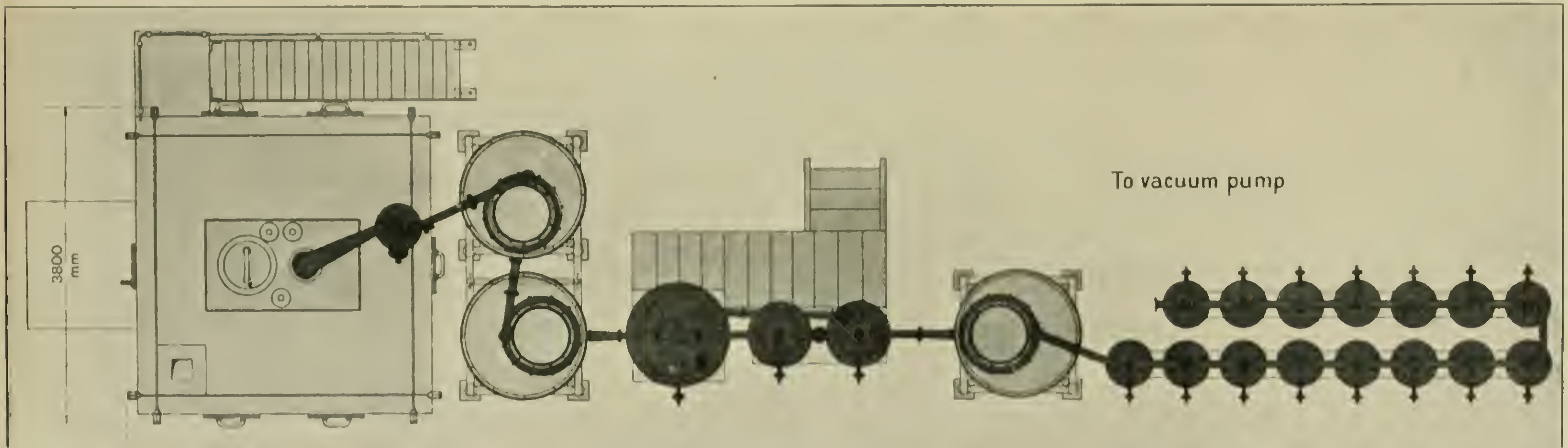


FIG. 21*a*. Valentiner's Nitric Acid Plant. Elevation.



there is less breakage of coils because the temperature is lower, also that the acids are purer. The plant is well designed and made, and consequently the users have generally found it satisfactory, but some who have tried working both with and without vacuum state that they can achieve equally good results at the ordinary pressure, and with less complicated appliances.

In the Skoglund process the gases and vapours from the still are made to pass up a reaction tower and then up a condenser instead of down. The result of this is that the oxides of nitrogen are removed almost completely from the condensed nitric acid. The plant is used in many explosives factories in North America and in several French dynamite works.[1]

Processes for the continuous or semi-continuous manufacture of nitric acid have also been tried.[2]

Recovery of nitrous fumes

In the retort a certain proportion of the nitric acid is always reduced through various causes to lower oxides of nitrogen. Some of this is dissolved by the strong acid in the condensers and is an objectionable impurity. In order to prevent this solution taking place air is sometimes drawn over the acid whilst it is still warm, and this carries away the greater part of the lower oxides. Whether this is done or not, there is always some nitrous gas that is not condensed in the coils, and this must be recovered not only because it is valuable, but also because it would cause a nuisance. After passing through the condensing coils, therefore, the residual gases are made to pass up a series of towers filled with Lunge-Rohrmann plates or Guttmann-Rohrmann balls. A jet of air is also introduced partly to draw the gases along better and partly to oxidize the nitrous gases. These consist principally of nitric oxide and nitric peroxide, NO and NO_2; the former is rapidly converted by free oxygen into the latter, so that then there is only NO_2, which when it comes in contact with water forms a mixture of nitric and nitrous acids:

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

But nitrous acid is only sparingly soluble in water or weak nitric acid, and consequently it is given off again as a mixture of nitric oxide and peroxide:

$$2HNO_2 = NO + NO_2 + H_2O.$$

In the presence of oxygen and water the cycle of changes then recommences. Although the combination of the nitric oxide with oxygen is rapid, the reaction with water is rather slow, and consequently a considerable amount of tower space is necessary for the almost complete absorption of the fumes.

Storage of nitric acid.

Nitric acid of 90 to 95 per cent. strength can be stored either in large stone-

---

[1] *See* A. F. Otto, *S.S.*, 1906, p. 325; E. Wolff, ibid., p. 373; O. Guttmann, ibid., p. 376; also G. Lunge, *Sulphuric Acid and Alkali*, 4th ed., vol. i., p. 178.

[2] *See* Lunge, *loc. cit.*, p. 154.

ware vessels or in iron tanks lined with chemical lead. The action of the acid on the lead is very slight, and such tanks last for years before they require to be relined. For weaker acid, stone-ware and glass are practically the only materials that are available. The maximum theoretical strength of acids running from a tower of this kind is that of the constant boiling mixture of nitric acid and water, which contains 68 per cent. of the former and has a specific gravity of 1·41 (42° B.), but generally it is considerably weaker than this and has a specific gravity of about 1·38, corresponding to 61 per cent. HNO_3. If a series of towers is installed, the weak acid from one should be raised continuously and made to flow down the next in the opposite direction to that of the gases.

The distillation. The nitrate is dried by being spread on iron plates on the top of a retort, whilst a previous charge is being worked. It is passed in through the manhole in the top of the retort, sulphuric acid is run in, and the lid of the manhole is closed and luted down with clay or a mixture of asbestos powder and water-glass. Theoretically, 1·153 parts of H_2SO_4 are required to convert 1 part of $NaNO_3$ into $NaHSO_4$: in practice it is usual to add rather less, 1·04 to 1·08 parts, so that the nitre cake contains about 20 per cent. of the neutral sulphate Na_2SO_4. To use too much acid would not only involve a waste of this substance, but would make the bisulphate too soft and acid, and therefore difficult to handle. It is always well to add a little weak nitric acid to the charge or some weaker sulphuric acid, or waste acid from the manufacture of nitro cotton. In this way not only is some of the weak acid worked up, but the yield of good nitric acid is increased. If the charge is practically free from water, some of the nitric acid in the retort is converted into nitric anhydride, which breaks down very readily into nitric peroxide and oxygen, and produces a dark acid. The charge having been introduced, the fire is lit and the retort is gradually heated. If working *in vacuo* under a pressure of 7 inches of mercury, acid begins to come over at about 100° C.; if at atmospheric pressure, somewhat higher. As the distillation becomes more active, the heat must be moderated to prevent priming. The first runnings are liable to contain a considerable proportion of hydrochloric acid and other impurities as well as much nitrous acid. Therefore, if acid of good quality be required the first portion should be collected separately and not added to the main bulk, or a current of air should be drawn over the still warm acid as mentioned above. The last runnings are liable to be rather weak, so that if acid of the highest strength be required they also should be collected separately.

To work off a charge of nitric acid takes about ten hours, but it is claimed that in the latest Valentiner plant it can be done in four and a half hours.

Nitre cake. When the charge is finished, and whilst the contents of the retort are still hot, the plug in the opening at the bottom is removed, and the residue in the retort is allowed to run out through a removable gutter into a trolley or a shallow cast-iron trough. The latter is preferable, as the "nitre-cake" is easier to break up if it is in a thin layer. This is done by means of a crowbar or sledge-hammer, and the broken cake is removed to a convenient place of storage until it can be disposed of. Nitre-cake consists mostly of sodium bisulphate with some neutral sulphate, a fair amount of moisture (especially if it has been exposed to the atmosphere long or has been rained on), a little nitric acid, and other impurities.

It is generally used either for making superphosphate manure or hydrochloric acid and sodium sulphate; in out-of-the-way districts its disposal is often a matter of difficulty, as its value is small, and it is troublesome to transport on account of its corrosive qualities. At the present time (1916) these difficulties are much accentuated by the enormous increase in the manufacture of nitric acid for the production of military explosives, and fresh outlets are being sought for this by-product.[1] J. Grossmann [2] has worked out a process for treating the nitre-cake with calcium sulphite and lime and so converting it into caustic soda and sodium sulphate. As there is a great demand for sulphuric acid, nitre-cake solution is being used for many purposes where formerly oil of vitriol was employed. Apparently it is being used successfully in the wire making industry and for various purposes in connexion with textiles.[3] Proposals to use it for the manufacture of ammonium sulphate have been adversely criticised.[4] Other uses are: acidifying the phenolates obtained in the working up of coal tar, acidifying soap stock, preparing sulphates, treating rubber scrap and pickling iron and steel.

Nitric acid from the atmosphere

During the last ten years great advances have been made in the manufacture of nitrogen compounds from the nitrogen of the atmosphere. Until recently the materials thus made were used almost entirely as fertilizers: for the manufacture of explosives Chile saltpetre remained almost the sole source of nitrogen. After the outbreak of war in August 1914 the Central European Powers were cut off from Chile, and in Germany energetic steps were taken to develop the manufacture of nitrates and nitric acid from the atmosphere. Rapid development of this industry was possible as the pioneer work had already been done.

Many different processes have been proposed and several are in actual operation on a large scale. They may be divided into two classes: those in which the oxygen and nitrogen are made to combine together directly, and those in which ammonia is first formed and then oxidized to nitric acid by Ostwald's method. The advantage of the latter process lies in the fact

---

[1] *J. Soc. Chem. Ind.* 1915, p. 1121, 1916, p. 77.

[2] Ibid., 1916, p. 155.

[3] *Chem. Trade Jour.*, Jan. 8, 1916, *J. Soc. Chem. Ind.*, 1916, p. 109.

[4] *Chem. Trade Jour.*, Mar. 4, 1916, Mar. 11, 1916, pp. 233, 235.

that ammonia is more easily produced than nitric oxide, as it is formed with evolution of heat, whereas nitric oxide is an endothermic compound :

$$\begin{aligned} N_2 + 3H_2 &= 2NH_3 + 24 \text{ Calories} \\ N_2 + O_2 &= 2NO \quad - 43{\cdot}2 \quad ,, \end{aligned}$$

And the oxidation of the ammonia is also an exothermic reaction, as the conversion of the hydrogen into water supplies the necessary heat.

Direct oxidation.

Processes for the direct oxidation of nitrogen were those first worked out commercially. These require temperatures of several thousand degrees, which can only be obtained by means of an electric arc. Air is passed through the arc and then rapidly cooled to prevent the nitric oxide decomposing again into oxygen and nitrogen. About 2 per cent. of nitric oxide is obtained, and this is converted into dilute nitric acid by passing it up towers down which water is flowing. The various processes differ in the means taken to pass a sufficiently large volume of air through the arc and then cool them. In the Birkeland-Eyde furnace an alternating arc is made to spread out fan-wise by means of electro-magnets. In the Pauling furnace the arc is V-shaped, due to the use of long electrodes inclined to one another at an angle. And in the Schönherr furnace a spiral flame is obtained by blowing air through inclined holes in a tube forming one of the electrodes.

The consumption of energy in these processes is about 60 kilowatt-hours per kilogramme of nitrogen fixed. Consequently they can only be worked at a profit where there is a very large supply of cheap water power, and Norway is the principal seat of the industry. The emerging air contains about 2 per cent. of nitric oxide, and this is mostly converted into weak nitric acid by passing it up towers down which water is flowing.

The 40 per cent. nitric acid thus obtained could be concentrated by distillation with sulphuric acid, but as nitric acid is difficult to transport it is usually converted into calcium nitrate by neutralizing it with limestone and milk of lime and evaporating down. The product thus obtained is known as Norwegian saltpetre and is used as a fertilizer. Ammonium nitrate is also made by neutralizing with ammonia liquor. And sodium nitrite is obtained in the last scrubbing towers by running sodium carbonate solution down them. It is said that at a Swiss works controlled by the Elektrochemische Werke in Bitterfeld the nitric oxide is allowed to oxidize to peroxide, which is recovered in the form of snow by strongly cooling the air.[1] This is then to be allowed to melt and sent into Germany in tank wagons, and there made into nitric acid by treatment with air and water. Nitric peroxide freezes at about 10° C. and boils at about 26° C. ; it is far less corrosive than nitric acid.

Cyanamide process.

The manufacture of calcium cyanamide was worked out by Frank and Caro, and is now the basis of a whole series of important chemical industries.

---

[1] Badermann, *S. S.*, 1914, p. 327.

It is made from calcium carbide, which is manufactured by heating lime and anthracite coal together in an electric furnace at about 3000° C. The carbide is powdered and placed in a retort which can be heated externally by means of a gas or electric furnace, and nitrogen is passed in. The nitrogen is now generally obtained by liquefying air and fractionally distilling it.

$$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Nitrogen}}{N_2} = \underset{\text{Calcium cyanamide}}{CaN_2C} + \underset{\text{Graphite}}{C}$$

The reaction starts at about 800° C. and proceeds with the evolution of heat. The temperature must not be allowed to rise above 1400° C., or some of the cyanamide will be reconverted into carbide. The cyanamide is used on a large scale directly as a manure, and also as a source of ammonium sulphate which is applied for the same purpose. It is also converted into cyanides, guanidine, dicyandiamine and other compounds. For the conversion of cyanamide into ammonia it is treated in a closed tank with steam under pressure in the presence of water and alkali. The reaction is exothermic and proceeds for a time after the steam has been shut off. When the steam has been applied three times the yield is almost theoretical.[1] The cyanamide process is apparently the one which the German Government is developing most largely for the production of nitric acid for the manufacture of explosives. The consumption of power is considerably less than in the direct oxidation methods: about 24 kilowatt-hours per kg. of fixed nitrogen as compared with 60, and the raw materials required, coal, lime, nitrogen and steam are all cheap. Consequently the process can be worked wherever power can be produced at a moderate cost.

Serpek's process.

In this process bauxite, a natural crude alumina, is converted into aluminium nitride by heating it with coal in an atmosphere of nitrogen in an electric furnace at 1700° to 1800° C.

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO \quad -243 \text{ Calories}$$

Producer gas, a mixture of nitrogen and carbon monoxide, is used as the source of nitrogen.

The nitride is then treated with a solution of caustic soda, which converts it into ammonia and sodium aluminate

$$AlN + 3NaOH = NH_3 + Na_3AlO_3.$$

Many of the impurities of the bauxite are eliminated during these operations and consequently the aluminate can be used for the manufacture of aluminium. The power required is only about 12 kilowatt-hours per kg. of fixed nitrogen, but bauxite being a comparatively expensive material the process can only be used in combination with aluminium works.

---

[1] *See* W. S. Landis, *J. Ind. Eng. Chem.*, 1916, p. 156.

aber's
ocess.

Professor Haber worked out his method for the direct production of ammonia from nitrogen and hydrogen by a thorough study of the physical chemistry of the reaction. The process has been taken over and developed commercially by the powerful Badische Anilin und Soda Fabrik. The mixture of gases is passed at high temperature and pressure over a solid contact substance, which promotes the reaction. Osmium and uranium are some of the materials that have been used for this purpose, but apparently iron is more satisfactory in some respects. The temperature is maintained at 500° to 700° C. and the pressure at about 200 atmospheres. The gases are circulated round a closed circuit with heat and cold regenerating appliances, first over the heated contact substance and then through a cooler, where the temperature is reduced to — 60° or — 70° C., which causes the ammonia to separate as a liquid. In each circuit about 6 per cent. of ammonia is formed and liquefied. This process is said to require power only to the extent of 2 kilowatt-hours per kg. of fixed nitrogen, but very great difficulties had to be overcome before plant could be made to work satisfactorily at the enormous pressure required. The low cost for power is also compensated to some extent by the comparatively high cost of hydrogen. It is obtained either by the electrolysis of water or from producer gas by liquefying out the carbon monoxide and purifying it. Haber's process is apparently being developed by the German Government in addition to the cyanamide process.

twald's
ocess.

If ammonia, together with oxygen or air, be passed over a suitable contact substance it is converted into oxides of nitrogen, from which nitric acid can be obtained. This has long been known, but about 1900 Professor Ostwald commenced to investigate the most favourable conditions for the reaction. He found that platinum was a suitable catalyzer, but it should not be in too fine a condition, and the gases should be passed over it very rapidly, otherwise the oxides of nitrogen formed are further decomposed into nitrogen and oxygen. So long as the ammonia was practically only a by-product in the destructive distillation of coal, the amount available was too small, and the other demands for it too great, to make this process very successful or remunerative. But with the introduction of synthetic ammonia, made by the cyanamide and Haber's processes, the conditions were altered entirely.

The ammonia mixed with 10 volumes of air is passed through a plug of platinum sponge 2 cm. thick at a temperature of 300° C. at such a velocity that it remains in contact with the platinum only 0·002 seconds. About 85 per cent. of the ammonia is oxidized, not to nitric acid, which cannot exist at this temperature, but to nitric oxide, which promptly combines with further oxygen to form nitric peroxide. The gases pass up a tower where they meet nitric acid: here the water formed in the reaction

$$2NH_3 + 2\tfrac{1}{2}O_2 = 2NO + 3H_2O + 106{\cdot}8 \text{ Calories}$$

is condensed and with the nitric peroxide and further oxygen yields nitric acid, which is obtained from the tower with a strength of about 58 per cent. Instead of platinum other catalyzers have been proposed, a mixture of ceria and thoria by Frank and Caro, burnt pyrites by F. Bayer & Co., etc.

The development of these processes for the synthetic production of nitric acid has been of great value to Germany in the war, in fact, she probably could not have continued the struggle without them, for the stocks of Chile saltpetre must have been exhausted after about a year.

Properties nitric aci

The concentrated acid has very little action upon metals. The more dilute acid acts energetically on all the common metals; if the acid be quite free from nitrous acid there is no action, but as commercial acid always contains some nitrous this is not a matter of great practical importance. The concentrated acid is not very stable and tends to decompose into NO_2, oxygen and water. The nitric peroxide dissolves readily in the strong acid, which consequently always has a more or less reddish colour. In weaker acid the solubility is less, and nitric acid of 1·4 specific gravity dissolves very little of the peroxide.

Specific gravities.

The Tables of Lunge and Rey superseded the earlier inaccurate ones, but the more recent determinations of Veley and Manley[1] are more numerous. The figures have been interpolated graphically, those above 63 per cent. by Veley and Manley, those below by myself, and are given in the Table on p. 118.

The influence of nitric peroxide on the specific gravity is considerable and has been ascertained by Lunge and Marchlewski[2] for an acid having the specific gravity 1·496.

Per cent. N_2O_4	Alteration of sp. gr.	Per cent. N_2O_4	Alteration of sp. gr.
0·25	·0005	5·0	·0323
0·50	·0008	6·0	·0395
0·75	·0015	7·0	·0465
1·00	·0030	8·0	·0533
1·25	·0048	9·0	·0600
1·50	·0068	10·0	·0660
1·75	·0078	11·0	·0730
2·00	·0105	12·0	·0785
3·0	·0180	12·75	·0835
4·0	·0253		

---

[1] *Phil. Trans. A.*, vol. 191, p. 365 (1898), and *Proc. Roy. Soc.*, 1901, p. 86, and *J. Soc. Chem. Ind.*, 1903, p. 1227.

[2] *Ang.*, 1892, p. 10.

The figure in the second column is to be subtracted from the specific gravity before ascertaining the strength of the nitric acid by means of the specific gravity Table. The amount of lower oxide is, however, often calculated as nitrous acid. The figures in the first column of the above Table must be multiplied by ·519 to give the corresponding amounts of nitrous acid in accordance with the equation:

$$N_2O_4 + H_2O = HNO_2 + HNO_3.$$

reezing
oints.

The freezing-points of mixtures of nitric acid and water are shown in Fig. 22, which is based on the determinations of Küster and Kremann.[1] It will be seen that all mixtures solidify at temperatures considerably below the freezing-point

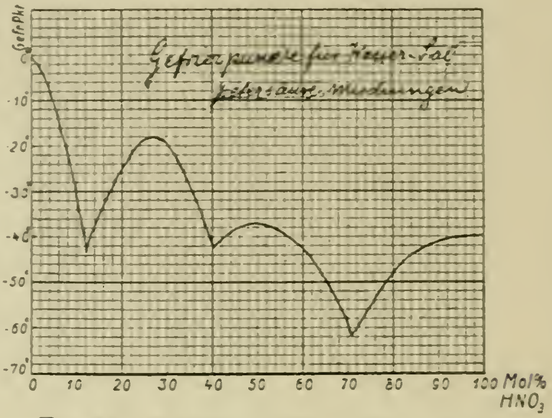


FIG. 22. Freezing-points of Nitric Acid.

SPECIFIC GRAVITIES OF NITRIC ACID AT 15°/4° IN VACUO
(Veley and Manley)

Specific gravity	Per cent. HNO_3	Difference for 1° C.	Specific gravity	Per cent. HNO_3	Difference for 1° C.
1·000	0·02	·0001	1·270	42·7	·0010
1·010	1·90	·0002	1·280	44·3	·0011
1·020	3·8	·0002	1·290	45·8	·0011
1·030	5·6	·0002	1·300	47·4	·0011
1·040	7·3	·0003	1·310	49·0	·0011
1·050	9·0	·0003	1·320	50·5	·0012
1·060	10·7	·0004	1·330	52·1	·0012
1·070	12·4	·0004	1·340	53·8	·0012
1·080	14·0	·0005	1·350	55·6	·0013
1·090	15·6	·0005	1·360	57·6	·0013
1·100	17·2	·0005	1·370	59·5	·0013
1·110	18·9	·0005	1·380	61·4	·0014
1·120	20·5	·0006	1·390	63·1	·0014
1·130	22·0	·0006	1·400	65·1	·0014
1·140	23·5	·0006	1·410	67·4	·0016
1·150	25·0	·0007	1·420	69·6	·0015
1·160	26·5	·0007	1·430	72·0	·0015
1·170	28·0	·0007	1·440	74·5	·0015
1·180	29·5	·0007	1·450	77·0	·0016
1·190	31·0	·0008	1·460	80·3	·0016
1·200	32·4	·0009	1·470	83·3	·0016
1·210	33·8	·0009	1·480	86·3	·0017
1·220	35·3	·0010	1·490	89·6	·0017
1·230	36·8	·0010	1·500	94·0	·0017
1·240	38·2	·0010	1·510	97·8	·0018
1·250	39·6	·0010	1·520	99·8	·0020
1·260	41·1	·0010			

---

[1] *Z. f. anorg. C.*, 1904, p. 21.

of water. In the first portion of the curve ice separates out, in the second crystals of $HNO_3,3H_2O$, in the third HNO_3,H_2O, and in the last solid nitric acid.

Boiling po

Pure nitric acid boils at about 86° C. under atmospheric pressure, and at 21·5° under a pressure of 24 mm. When water is added to the acid the boiling-point increases until it reaches a maximum at about 68 per cent. HNO_3, and then falls again. If acid either stronger or weaker than this be evaporated or fractionally distilled, the composition tends to approach this percentage, and when it is reached the mixture distils unchanged. The composition of the constant boiling mixture depends upon the pressure, however; *in vacuo* a mixture containing 66·3 molecular per cent. HNO_3 boils at 13°, giving a distillate of the same composition; under 735 mm. pressure the constant boiling mixture contains 68·0 per cent. and boils at 120·5°; under 1220 mm. the composition is 68·6 per cent.[1]

Saposhnikoff has made a few determinations of the vapour pressures of nitric acid at 15° C.[2]

Per cent. HNO_3	Vap. pres. 15° C. mm.	Per cent. N in vapour	Molecular per cent. HNO_3
98·0	46·2	23·7	93·5
92·9	42·6	23·5	79·0
88·6	29·7	23·0	68·7
82·1	16·6	22·6	56·5
78·1	9·4	22·5	50·0
65·3	1·9	19·3	34·7

Vapour pressures

With reference to the third column of the above Table it is to be borne in mind that HNO_3 contains 22·2 per cent. N. It is therefore evident that the vapours from the nitric acid contain nitric peroxide or nitric anhydride, which have 30·6 and 25·9 per cent. N respectively.

---

[1] Roscoe, *Lieb. An.*, 1860, pp. 116, 203. *See also* H. J. M. Creighton and J. H. Githens. *J. Franklin Inst.*, 1915, p. 161.

[2] *Z. phys*, C., 1905, pp. 53, 225.

CHAPTER IX

MIXED AND WASTE ACIDS. MANIPULATION

Mixed acid : Mixing the acids : Properties of mixed acids : Specific Gravities : Vapour pressures : Waste acid : Gun-cotton waste acid : Nitro-glycerine waste acid : Nitro-compound waste acid : Denitration plant : Manipulation of acids : Materials : Raising acid : Oleum

Nitration, whether of glycerine or cotton or an aromatic compound, such as toluene, is always carried out with a mixture of sulphuric and nitric acids, and not with nitric acid alone, for even the strongest nitric acid does not act well by itself. One of the main functions of the sulphuric acid is to combine with the water that is formed during the reaction and prevent it diluting the nitric acid, but it appears probable that it also takes an active part in the reaction, and that to some extent at any rate it combines first with the substance to be nitrated to form a sulphuric ester or sulphonic acid, and that it is this which is afterwards acted upon by the nitric acid. In the presence of sulphuric acid the nitration is not only more complete but also more rapid.

ixing the cids.

The two acids are mixed together in iron tanks. For work on a moderately large scale old steam-boilers can be used for this purpose, the fire tubes being removed and the openings closed by riveting on plates. For work on a large scale it is better to have special tanks built, large enough to hold several days' supply of mixed acid. The best form is a cylinder with its axis vertical, the height being somewhat less than the diameter. Passing through the cover there should be a shaft to which arms are attached, so that by rotating the shaft the contents of the tank can be stirred. When the mixing is carried out in small boilers the agitation of the liquid usually has to be effected by blowing air through it, which causes a slight loss of nitric acid.

roperties of ixed acids.

When nitric acid is added in small quantities to sulphuric acid, the specific gravity at first rises sharply in spite of the fact that nitric acid has a lower density than sulphuric. The specific gravity attains a maximum and then falls again, as is shown in Fig. 23 and in the Table [1] on p. 21. Saposhnikoff [2]

---

[1] Marshall, *J. Soc. Chem. Ind.*, 1902, p. 1508.

[2] *Zeitsch. Physikal. Chem.*, 1904, pp. 49, 697 ; 1905, pp. 53, 225.

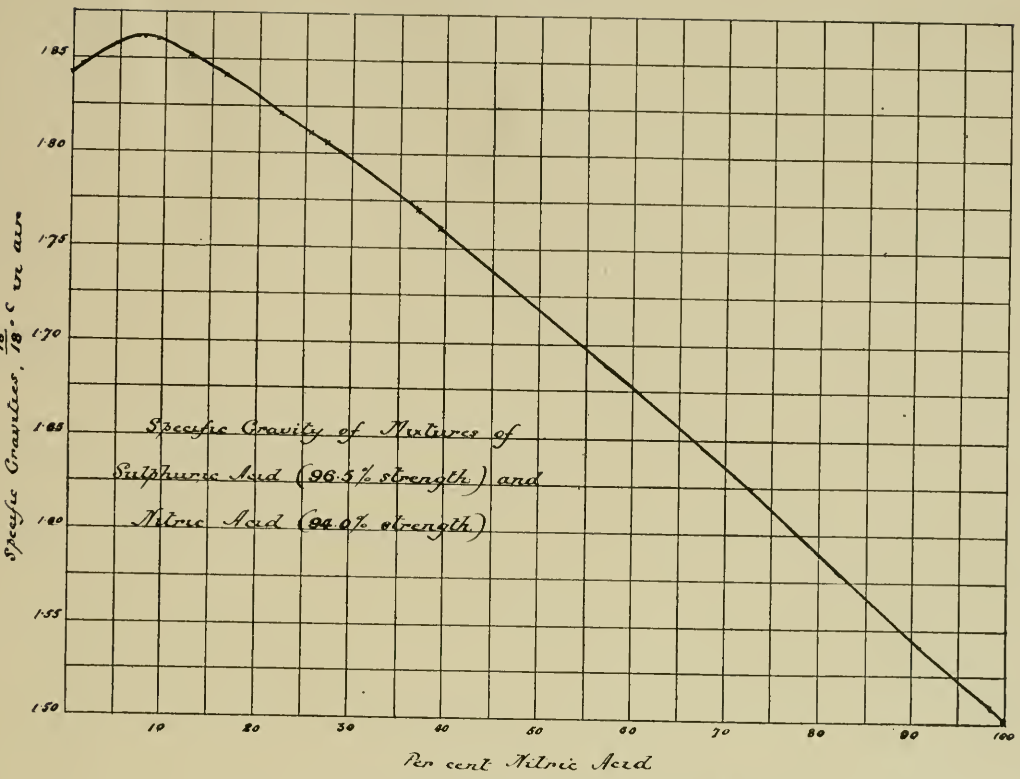


Fig. 23. Specific Gravities of Mixed Acids (Marshall)

HNO_3 Per cent.	Sp. gr. 18°/18° in air
0·00	1·8437
0·57	1·8456
1·05	1·8476
4·67	1·8586
7·17	1·8618
7·37	1·8620
7·75	1·8619
9·10	1·8605
11·33	1·8557
12·71	1·8520
16·52	1·8414
22·51	1·8215
25·56	1·8112
27·29	1·8053
32·53	1·7863
37·03	1·7700
39·49	1·7601
57·78	1·6879
72·89	1·6227
90·76	1·5408
98·19	1·5080
100·00	1·5009

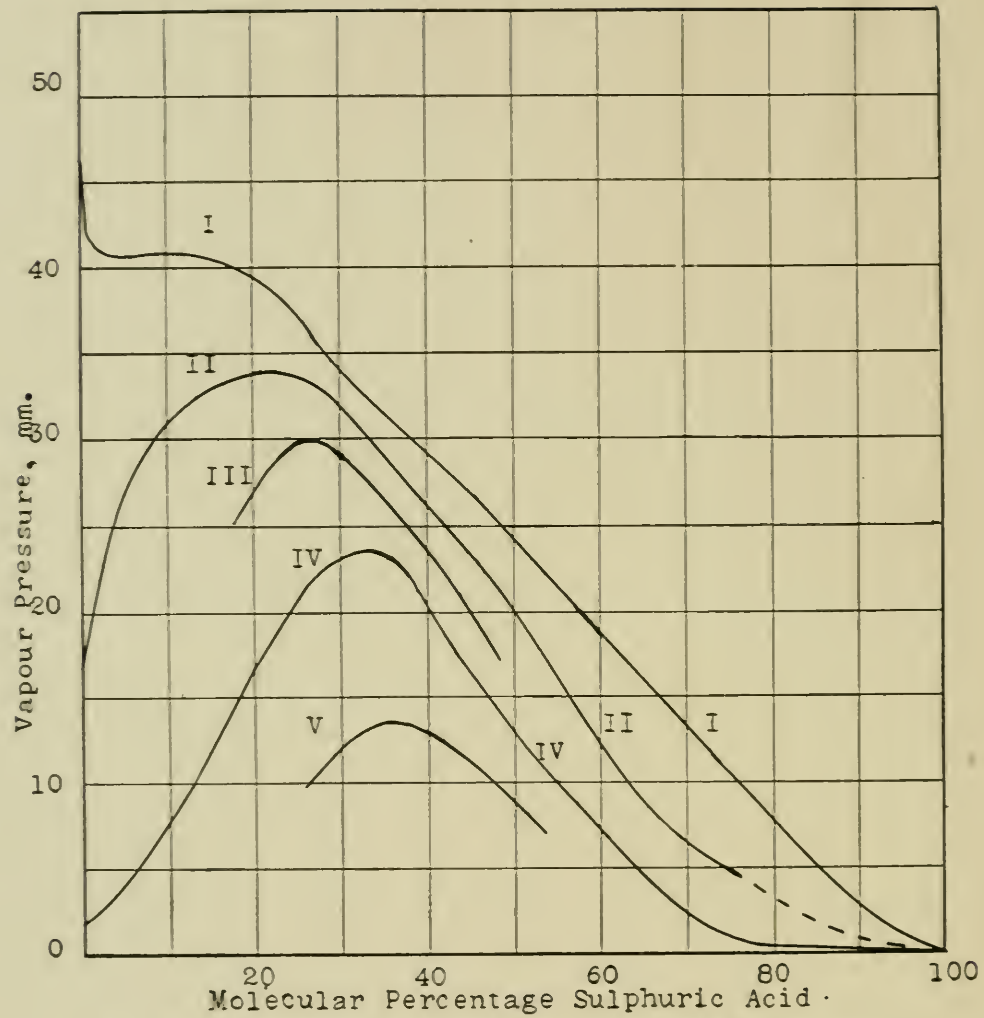


FIG. 24. Vapour Pressures of Mixtures of Sulphuric Acid with Nitric Acids of Various Strengths

Curve	Strength of nitric acid, per cent. By weight	Molecular
I.	98·0	93·5
II.	85·2	62·3
III.	77·8	50·0
IV.	65·5	35·4
V.	50·0	22·2

has obtained similar results. The following are two maximum specific gravities observed by him with mixtures containing different amounts of water :

Sp. gr. 25°/25°	1·8810	1·865
Sulphuric acid	89·32 per cent.	89·94 per cent.
Nitric acid	10·13 ,,	6·57 ,,
Water	·28 ,,	3·49 ,,
Oxide of nitrogen	·27 ,,	— ,,

The second of the above is almost identical both in composition and density with the maximum observed by Marshall. From the results of his measurements of the vapour pressures Saposhnikoff came to the conclusion that there is little or no combination of the two acids to form complex molecules, and he ascribed these high specific gravities to the formation of nitric anhydride, N_2O_5. But as this substance has a specific gravity of only 1·64, the explanation does not appear sufficient. It seems possible that the high densities are due to some reversible reaction taking place between the sulphuric and nitric acids.

Vapour pressures.

Saposhnikoff's determinations of the vapour pressures of mixed acids are shown in the curves in Fig. 24, in which mm. of pressure are plotted against the molecular percentage of sulphuric acid in the mixtures. The sudden fall at the left end of curve *I* is due to the fact that the nitric acid used contained about 0·9 per cent. of nitric oxide, which is very volatile as compared with nitric acid. When a little sulphuric acid was added it combined with this to form nitro-sulphuric acid, which is not volatile. Through the greater part of its course this curve is practically straight : if the acids had been quite anhydrous and free from impurities it would probably have been straighter. With acids containing water the addition of sulphuric acid increases the vapour pressure, because it combines with the water and decomposes the compound of nitric acid and water. The pressure is at a maximum when there is nearly a molecule of sulphuric acid for each one of water : then it falls again. These vapour-pressure curves are also given in another form in Fig. 28, which shows the connexion between the vapour pressure and the degree of nitration of cotton. That there should be such a connexion might have been anticipated, as the activity of a substance in solution generally increases when the vapour tension increases, but mixtures with equal vapour pressures do not by any means always produce nitro-cottons with equal amounts of nitrogen, as a careful examination of the diagram will show.

WASTE ACID

Gun-cotton waste acid.

The waste acid from the manufacture of nitro-cotton is usually revivified by the addition of strong sulphuric and nitric acid, and used again, but if the whole quantity were strengthened up in this way each time the quantity would steadily increase. It is therefore necessary to discard some of the waste acid. The quantity of waste acid produced in the displacement process for the manufacture of gun-cotton is more than in the older methods, for the recovery of the waste acid is much more complete and some of it becomes diluted with the water used for the displacement. When nitrated by the Abel process or in centrifugals a considerable amount of acid remains in the gun-cotton after the bulk has been removed in the centrifugals. If oleum of 60 to 70 per cent. be used together with nitric acid of about 93 per cent. strength, the fresh acid does not bring the volume of acid much above its original bulk, for it does not much exceed what is lost in the manner just mentioned, together with the nitric acid actually consumed in the nitration. In small factories, which do not possess the plant for working up the waste acids again, this is a great advantage because only a very inadequate price can be obtained for the waste acid if it has to be sold. Where the nitric acid can be recovered on the spot it is more usual to use oleum of 20 to 25 per cent. strength.

These revivified acids are little, if at all, less efficient than new acid, at any rate for the manufacture of the more insoluble varieties of nitro-cellulose. The organic impurities formed in the nitration process apparently either pass away in the nitrated product and so eventually into the waters used for the purification, or else are oxidized completely away by the acid if they have passed into solution. The quantity of organic impurity in the acids remains small therefore; but Will found nitro-sugars in the acids.

The portion of the waste acid that is not revivified can generally be utilized to some extent for the manufacture of nitric acid. The remainder, if any, must be reconverted into the separate acids, nitric and sulphuric. The greater part of the nitric acid can be distilled off in a retort, and is thus obtained as concentrated acid again. Some weak nitric acid can be added to the charge in the retort at the same time, and so be worked up again. It is not practicable to distil off the last traces of nitric acid in this way, and consequently it is necessary to pass the residual sulphuric acid down the denitrating tower before reconcentrating it in a Kessler plant. In many works no attempt is made, however, to recover any of the nitric acid in concentrated form, and all the waste acid to be treated is passed at once down the denitrating tower.

Nitro-glycerine waste acid.

The waste acid from the manufacture of nitro-glycerine always contains some of this substance, or mono- or di-nitro-glycerine in solution. When the waste acid is heated this decomposes with the production of considerable quantities of the lower oxides of nitrogen. For this reason it is difficult to obtain strong nitric acid of good quality directly from it. It cannot be revivified either, because the organic matter in solution would be liable to decompose when the acid was heated by the addition of strong sulphuric acid. Moreover, there would be some nitro-glycerine formed, which would separate out in the storage tanks and other places and give rise to accidents. The whole of the nitro-glycerine waste acid has therefore to be denitrated.

Nitro-compound waste acid.

The waste acid from the manufacture of nitro-aromatic compounds can often be utilized after revivification for the nitration of a further charge. In some cases it is used in a lower stage of the nitration. Some further information about this is given in Chapters XIX and XX.

Denitration plant.

The denitration of the waste acid is carried out in a tower, down which the acid runs: at the bottom steam or hot air, or both, are blown in. The nitric and nitrous acids are thus removed from the liquid and pass up the tower as vapour and gas respectively. These towers are frequently made of volvic stone cemented together with water-glass and asbestos powder, and filled with pieces of broken stone-ware and glass. They are often as much as 10 feet high and 18 inches in diameter to deal with some 1500 lb. of acid per hour, but a much smaller plant would deal with this quantity equally effectively. A short denitration tower has the advantage that the gases are not heated so long, and consequently there is less loss of nitric acid by formation of nitrogen and nitrous oxide. It is, of course, important that the liquid and gases be well distributed and brought into intimate and repeated contact with one another. In England it is usual to denitrate with steam only: it is thus easy to drive the nitric acid completely out of the weak sulphuric. This is facilitated by the dilution which the sulphuric acid undergoes from the condensation of the steam, for weak sulphuric acid does not retain nitric and nitrous acids so obstinately as when it is concentrated. In Germany the steam is often made to inject heated air with it into the base of the denitrating tower:[1] a somewhat stronger sulphuric acid is thus obtained, containing 78 instead of 70 per cent., but as it has to be reconcentrated in any case, this is not a matter of great practical importance. Moreover the stronger acid retains nitrous acid very obstinately in the form of nitrososulphuric acid, $HSNO_5$. In Evers's patent plant, steam and hot air are injected at four different places in the tower (*see* Fig. 25); the heat of the sulphuric acid flowing from the base of the tower is utilized to heat the air. Superheated steam is also used sometimes.[2]

Recovery of nitric acid.

The gases escaping from the top of the tower consist of nitric acid, water vapour and oxides of nitrogen, and if air has been injected nitrogen and oxygen, also some carbon monoxide and dioxide from the decomposition of the organic matter in the waste acid. In order to condense the nitric acid it is necessary to cool the gases. Formerly this was done by air cooling, the gases being led through a number of earthenware jars or "tourils"; in the

---

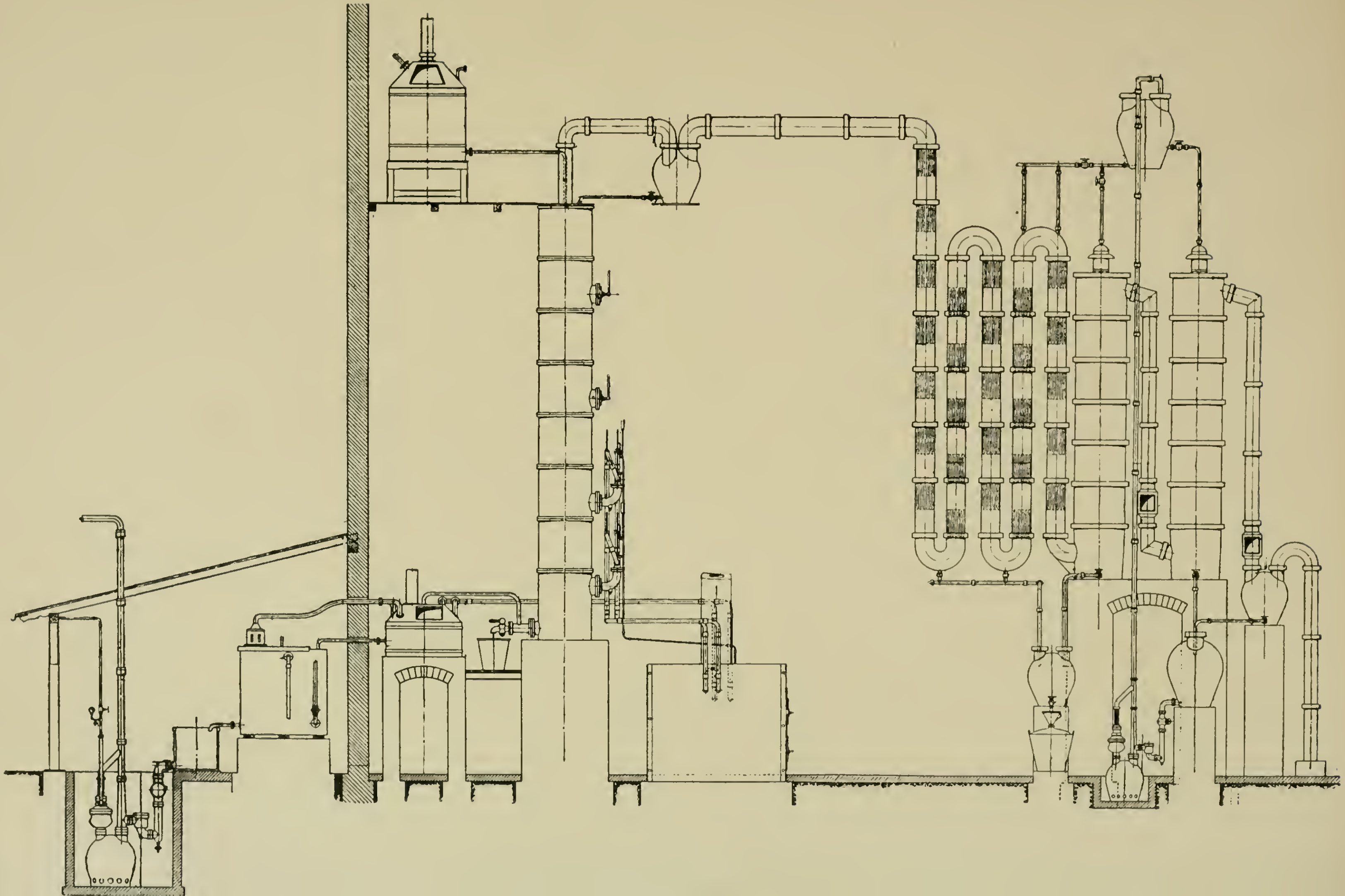
[1] *See* Rudeloff, *S.S.*, 1907, p. 247.

[2] *See* H. Lemaitre, *Moniteur scientifique Quesneville*, 1913, pp. 217–231: *S.S.*, 1914, pp. 30 and 48.

Evers plant (Fig. 25) air-cooled earthenware pipes are used, the surface being increased by subdividing the pipes at intervals into a large number of small pipes. The best method of cooling is, however, to take the gases through pipes immersed in a trough of water so arranged that the condensate can flow away into receivers. Before cooling the gases they should be mixed with air, if it has not already been injected in sufficient quantity. This oxidizes any nitric oxide to peroxide, and if water be present it converts part of it into nitric acid.

From the condenser the gases pass to absorption towers, where they meet a stream of water and the remaining nitric oxide is converted into nitric acid. It is essential that an excess of oxygen be present in the gas to effect the conversion in accordance with the equation : $4NO_2 + O_2 + 2H_2O = 4HNO_3$. Whether the condensation is complete can be seen by the appearance of the gas escaping from the last tower : it should not be red nor give much fume with the air. Whether there is an excess of oxygen in the gases can be ascertained by analysis : a sample of the gas is first shaken with distilled water until there is no further absorption, then with caustic alkali to absorb any carbon dioxide, and finally with alkaline pyrogallol, when there should be a distinct further diminution of volume.

The absorption towers are of stone-ware and should be filled with some acid-resisting material so as thoroughly to distribute both the ascending gas and the descending liquid, and bring them repeatedly into intimate contact with one another and cause them to mix. The Lunge plates do all this very efficiently if they are in perfect working order, but if the plates are not quite true, or if they get slightly out of the level, the liquid all runs down one side of the tower and the gas ascends on the other, and very little absorption takes place. If one lays one's hand on a Lunge tower that is working, one will often find that at one part of the circumference the shell is quite hot whilst the rest is cold, showing that action is only taking place in a portion of the tower. Guttmann's hollow stone-ware balls give a very good result and have the merit that no special care is required in filling them into the tower. There are many other forms of stone-ware filling for towers procurable. In order to effect complete absorption of the oxides of nitrogen two or three towers are necessary. A slow stream of water is run into the last one and distributed uniformly over the cross-section of the tower. A weak nitric acid runs out at the bottom of the tower and is raised from there by means of a continuously acting appliance to the top of the next one. As weak nitric acid attacks all the common metals, glass and stone-ware are the only materials that can be used for the construction of the pipes and vessels. For raising the liquid to the tops of the towers small Kestner automatic eggs made of stone-ware can be used, but as the quantity is very small it is better to use a small appliance, which causes the acid to raise itself and works on



the well-known principle of making the ascending column of liquid lighter than a descending one by mixing it with air.[1] From the base of a tower a glass tube descends a distance equal to about half the height of the tower. It then turns through 180°, and a small distance beyond the bend compressed air is injected in through a number of small holes. When once the rate of admission of the air has been adjusted the appliance works continuously and requires very little attention. The mixture of acid and air should be delivered into the top of the tower below the cover, so that the air cannot carry away part of the acid fumes. This air also serves a useful purpose.in that it renews the supply of oxygen, which has been partially exhausted by the oxidation of the nitrous gases. The greater part of the absorption of the gases takes place in the middle tower or towers: in the first tower the acid is strengthened up slightly to near the limit theoretically possible. namely. 68 per cent. HNO_3. In the last tower the last traces of fume are absorbed.

The acid from the condenser generally has a specific gravity of 1·41 to 1·42 and contains 67 to 69 per cent. HNO_3: that from the towers is somewhat weaker.

MANIPULATION OF ACID

So far as possible acids of all sorts should be conveyed about the works in pipes and not in tanks. carboys or bottles. In a factory which makes its own acids and reconcentrates them there is no reason why these vessels should ever be used at all except in case of emergency. Wherever it is feasible the acids should run from one place to another by gravity. but of course this is only possible to a limited extent. and when the acid has come down to the ground level it is necessary to raise it again.

Materials. For strong sulphuric. mixed and waste acids, tanks. pipes and other appliances of either iron or lead can be used and last for a very long time. Iron is cheaper in first cost. but lead can be sold for a good price after it has been used ; iron has the further advantage that it can be fitted up by any skilled workman, whereas lead can only be joined by a lead burner. Special sorts of iron are made. such as tantiron. duriron and corrosiron. which resist acids particularly well. so that they can even be used for concentrating sulphuric acid and condensing nitric acid. These metals are very rich in silicon and are consequently more brittle than ordinary cast iron. Ordinary 2-inch wrought-iron steam piping fulfils most of the purposes of an acid factory. Storage tanks can also be made of iron or steel boiler-plates. Strong nitric acid has little action upon iron. but the dilute acid dissolves it rapidly. The vapour that rises from the surface of the acid is much more dilute than the

---

[1] *See P. et S.*, vol. vii., 1894, p. 91.

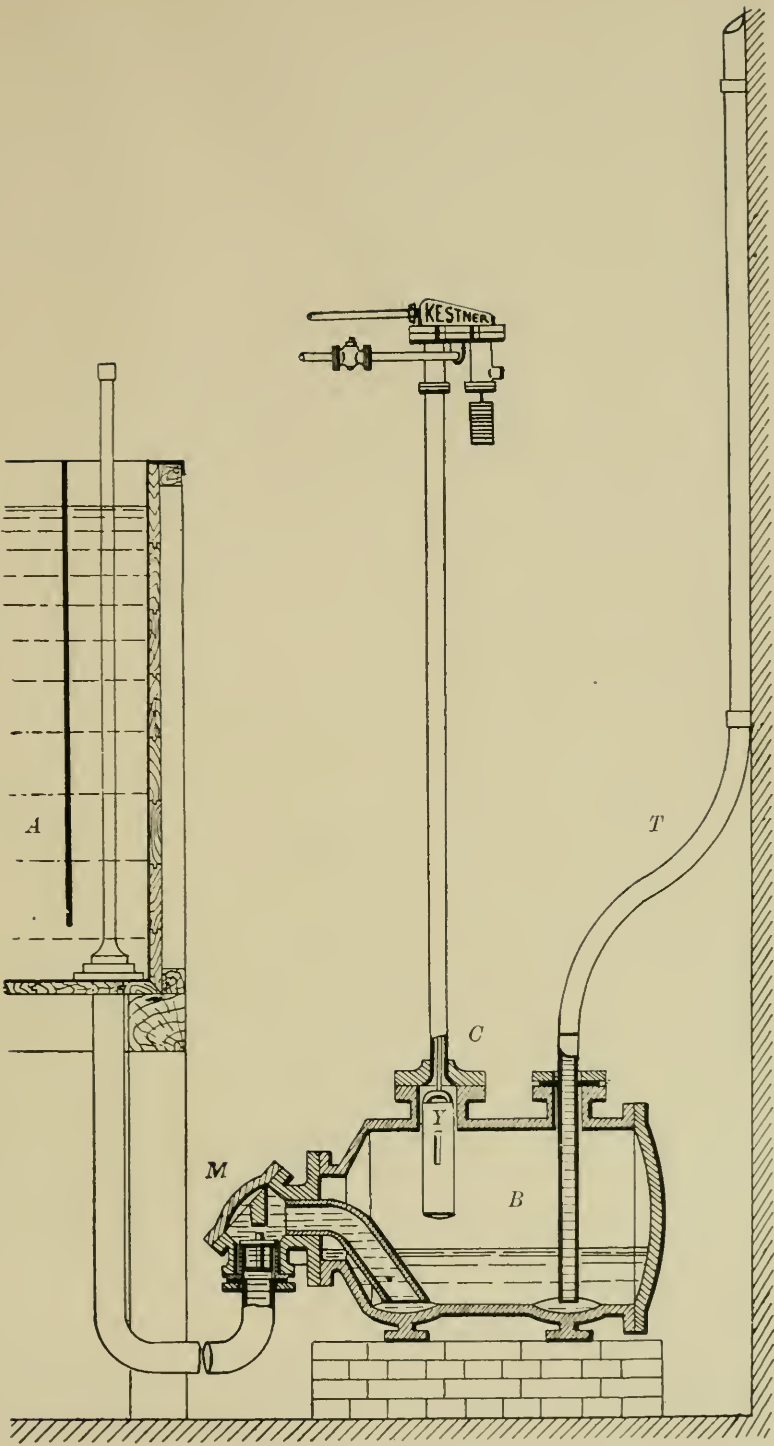


Fig. 26. Kestner Automatic Elevator or "Egg"

acid itself, and where this condenses it is liable to attack iron strongly. Consequently it is better to use vessels and pipes of lead for this acid. Stone-ware is also used very largely with nitric acid. Fused silica ware, such as vitreosil, is however better, especially where hot acids are dealt with, as its coefficient of expansion is very small and consequently there is very little tendency to crack. For use at high temperatures a proportion of zirconium or titanium oxide is added to prevent devitrification of the silica. Condensers for nitric acid, basins of cascade plants for the concentration of sulphuric acid, caps for Kessler plants and many other articles are made of this material. Aluminium is also sometimes used as a material of construction for acid plant, but in most cases possesses no advantage over iron or lead.

Raising acid. Where acid is running in a continuous stream one of the best appliances to use for raising it is an automatic egg such as that of Kestner, the construction of which is shown in Fig. 26. The liquid in the feed-tank, *A*, runs by gravity into the body, *B*, of the elevator or egg. As soon as the body is full the liquid raises the float, *Y*, which by means of the rod, *C*, closes the air exhaust valve and opens another valve which admits compressed air. The pressure closes the valve, *M*, and forces the liquid up the pipe, *T*, into a high-level tank. The air after delivering the liquid exhausts through the same pipe causing the pressure

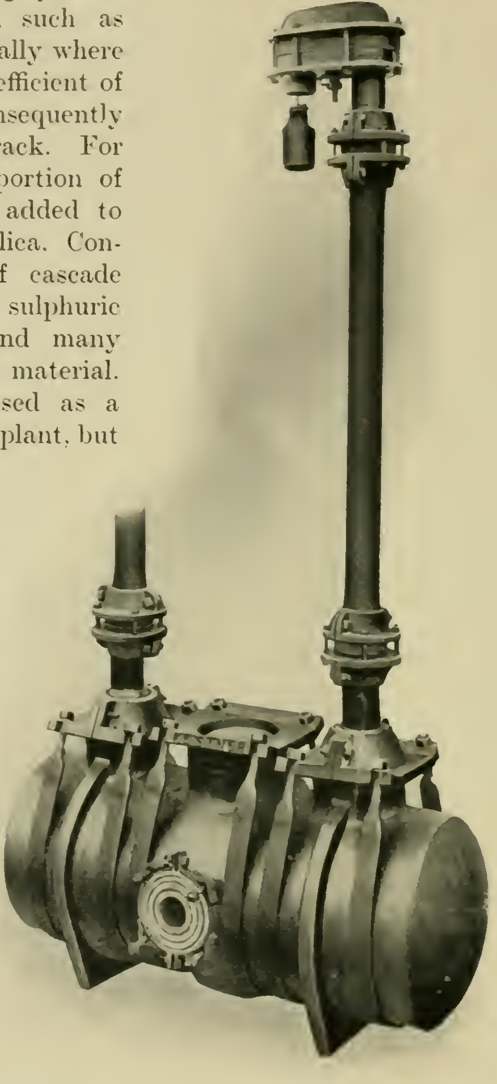


FIG. 27. Kestner Automatic Elevator for Nitric Acid.

to fall and the valves to resume their former positions : the cycle of operations then repeats itself automatically in the same manner. These eggs can be obtained made of iron, with or without a lead lining, or of earthenware. Fig. 27 shows one type of the appliance specially devised for nitric acid. It can be fitted with a meter, which automatically registers the quantity of liquid that has been raised. A type of elevator is also made with a double body so connected up as to give a continuous stream of acid. Acid can also be raised by means of a centrifugal pump driven either electrically or by a belt.

Where the acid has to be raised only occasionally, a non-automatic egg can be used. This is simply a strong vessel made of one of the materials just mentioned and fitted with three pipes, one for the admission of the liquid, one for delivery, and one for air. The inlet and the air pipes are provided with valves which are operated by the attendant.

Oleum.

When acids have to be transferred from bottles, carboys or drums to a storage or mixing tank, they can be tipped in through a funnel placed higher than the top of the tank and connected with it by a pipe. In the case of oleum containing 60 to 70 per cent. anhydride there is some difficulty in consequence of the great volumes of most objectionable fumes that it gives off, especially as the acid has to be warmed to keep it liquid. The production of fumes can be almost entirely avoided by the following device : The drum of acid is raised to a platform above the level of the tank to which it is to be transferred, and a pipe is inserted through the bung-hole, the other end of the pipe going to the bottom of the tank. A vacuum is then produced in the tank by means of a steam-jet working through an ejector : as soon as there is sufficient vacuum the oleum starts to flow over, and will then siphon over by itself without any further assistance from the ejector. These ejectors can be obtained made of special acid-resisting alloys, but those made of ordinary iron withstand the mixture of steam and acid fumes quite well.

Oleum is kept and transported in wrought-iron drums ; cast-iron is liable to burst in consequence of the oxidizing action of the acid on the carbon. Metals are attacked by 60 per cent. oleum considerably less than by 20 per cent. oleum.

PART IV

NITRIC ESTERS OF CARBOHYDRATES

CHAPTER X

THEORY OF NITRATION OF CELLULOSE

Stages of nitration of cellulose : Highest attainable nitration : Solubility : Soluble nitro-cellulose : Quantity of acid : Consumption of acid : Effect of nitrous acid : Temperature and time of nitration : Nature of the cotton : Nitro-cottons of low nitration : Pyroxylin : Collodion

Stages of nitration o cellulose.

Highest attainable nitration.

CELLULOSE being a non-volatile colloid, all the ordinary methods of determining its molecular weight are inapplicable, and it is only possible to deduce it from a study of the compounds that it forms. At first the simplest possible formula was assumed for cellulose, $C_6H_{10}O_5$, and gun-cotton of high nitrogen percentage and low solubility in ether-alcohol was supposed to be formed by the substitution of three NO_2 groups for hydrogen atoms, $C_6H_7O_5(NO_2)_3$, and was consequently called trinitro-cellulose. The less nitrated product soluble in ether-alcohol was similarly supposed to be the dinitro-cellulose $C_6H_8O_5(NO_2)_2$. Later workers obtaining evidence of intermediate stages of nitration proposed to increase the formula of cellulose : Eder [1] doubled it, Vieille [2] quadrupled it, and Mendeléeff [3] octupled it, giving 48 atoms of carbon to each molecule, and hydrogen and oxygen in proportion. A nitro-cellulose having the composition of the above-mentioned trinitro-compound would contain 14·14 per cent. nitrogen. Quite as much as this has never been found by the analysis of any product that has ever been obtained, but various investigators by nitrating with mixtures of nitric acid and phosphorus pentoxide, or with concentrated sulphuric and nitric acids and extracting the product with ether-alcohol have obtained percentages between 13·9 and 14.[4] Lunge and Bebie [5] found that with mixtures of sulphuric and nitric acids the highest percentage of nitrogen was attained, not with anhydrous acids, but with mixed acids containing 11 or 12 per cent. of water : with a mixture in which the proportions $H_2SO_4 : HNO_3 : H_2O$ were 63·35 : 25·31 : 11·34 they produced a nitro-cotton containing 13·92 per cent. N, but this

---

[1] *Ber.*, 13, p. 169.

[2] *P. et S.*, p. 2 ; *C.R.*, 95, p. 132.

[3] *Moniteur scientifique*, 1897, p. 510.

[4] *See* Eder, Vieille, *loc. cit.* ; Hoitsema, *Ang.*, 1898, p. 173 ; Lunge and Weintraub, *Ang.*, 1899, p. 144.

[5] *Ang.*, 1901, p. 514.

was not stable.[1] After keeping in the wet state it was re-analyzed and found to contain then only 13·5 per cent. N, and other nitro-cottons nitrated almost as highly were found to decompose rapidly until the same composition was reached, even though the material was kept under water. This corresponds very closely with the formula $C_{24}H_{29}O_{20}(NO_2)_{11}$, endeka-nitro-cellulose. Hence the authors conclude that the molecule with 24 atoms of carbon fits the facts sufficiently well, but point out that this is only the lower limit of the possible size of the cellulose molecule, as to the real magnitude of which there is little or no evidence.

Hake and Bell, by nitrating filter-paper with a mixture of concentrated sulphuric and nitric acids in the proportion 3 : 1 for several days, obtained a percentage of nitrogen as high as 13·96, but their product was washed only with cold water, whereas Lunge and Bebie washed theirs for several days with hot water.[2]

With the possible exception of this endeka-nitro-cellulose no definite stages of nitration can be recognized : nitro-celluloses with every percentage of nitrogen from 7 to 13·5 and more can be produced, and those of the same degree of nitration may be soluble to very different extents in ether-alcohol. To characterize a nitro-cotton it is better to specify the percentage of nitrogen and the solubility rather than to state the number of NO_2 groups that it is supposed to contain in each molecule. The following Table shows the percentages of nitrogen and the volumes of gas evolved in the nitrometer by the different nitro-celluloses of the C_{24} series. The figures have been calculated using the latest atomic weights.

	Formula	C.c. NO per 1 g.	Per cent. N
Dodeka-nitro-cellulose	$C_{24}H_{28}O_{20}(NO_2)_{12}$	225·6	14·14
Endeka-nitro-cellulose	$C_{24}H_{29}O_{20}(NO_2)_{11}$	215·0	13·48
Deka-nitro-cellulose	$C_{24}H_{30}O_{20}(NO_2)_{10}$	203·5	12·76
Ennea-nitro-cellulose	$C_{24}H_{31}O_{20}(NO_2)_9$	190·9	11·97
Okto-nitro-cellulose	$C_{24}H_{32}O_{20}(NO_2)_8$	177·3	11·12
Hepto-nitro-cellulose	$C_{24}H_{33}O_{20}(NO_2)_7$	162·4	10·18
Hexa-nitro-cellulose	$C_{24}H_{34}O_{20}(NO_2)_6$	146·0	9·15
Penta-nitro-cellulose	$C_{24}H_{35}O_{20}(NO_2)_5$	127·9	8·02
Tetra-nitro-cellulose	$C_{24}H_{36}O_{20}(NO_2)_4$	107·9	6·77

Nitro-cellulose containing up to 12·7 per cent. N can be obtained by

---

[1] It is of interest to note that the velocity of nitration of aromatic compounds dissolved in sulphuric acid is at a maximum when the molecular proportion of sulphuric acid to water is 1 : 0·7 or about 11·4 per cent. H_2O by weight. (Martinsen, *Z. f. physik. C.*, 1904, 50, p. 385.)

[2] *See J. Soc. Chem. Ind.*, 1909, p. 457.

nitrating with nitric acid alone, but only with difficulty, and the structure of the fibres is much damaged. In practice mixtures of sulphuric and nitric acid are always used. Various investigators have made numerous experiments to ascertain the effect upon the product of altering the composition of the acid mixture. The results published by Bruley,[1] Lunge and Bebie (*loc. cit.*), and Saposhnikoff have been collected together by the last-named and plotted on triangular co-ordinates, the best method of representing the composition of ternary mixtures.[2] The numbers on the central line running from each corner (Fig. 28) represent not the percentages by weight but the molecular percentages, obtained by dividing the percentage by weight of each of the three constituents by its molecular weight, adding together the figures thus obtained and working out the percentages afresh. On the same figure Saposhnikoff has also given the vapour tensions, which have already been presented in another form in Fig. 24. It will be seen that for equal percentages of nitric acid the vapour tension is a maximum on the line joining the points marked HNO_3 and H_2O, H_2SO_4, or slightly to the left of it. This shows that when water is present in excess it combines with the nitric acid to form a less volatile compound, but on the addition of sulphuric acid this removes the water from the combination and combines with it instead. There is no evidence of any combination of the sulphuric with the nitric acid. The three curves, I, II, and III, indicate the degree of nitration of the cotton : the space inside curve I is the region of the endeka-nitro-cottons (about 13·5 per cent. N), that between I and II the region of the deka-nitro-cottons (12·8 per cent. N), and between II and III that of the lower nitrates with nine to six nitro groups (12 to 9 per cent. N) ; beyond curve III nitration is incomplete. It will be seen that the nitration curves follow a course similar to that of the vapour pressure curves : it seems that the compound HNO_3,H_2O has little action on cellulose and that the presence of sulphuric acid is required to set free the nitric acid from this combination before it can act.

Solubilities. The percentage of nitrogen in a nitro-cellulose is the principal factor in determining the amount of energy that will become available when it explodes ; hence the importance of attaining a high degree of nitration. A very large proportion of the nitro-cellulose manufactured is afterwards converted into a dense colloid by treatment with a solvent, whereby the original fibrous structure of the cellulose is destroyed. The properties of this colloid and the nature of the solvent to be employed depend upon the solubility of the nitro-cellulose : hence the importance of determining this property. The solvent used for the determination is almost invariably a mixture of two parts of ether and one part of alcohol. The series of experiments by Bruley and Lunge and Bebie included determinations of the solubilities of the

---

[1] *P. et S.*, vol. viii., 1895–1896.

[2] Report of 7th Inter. Congress Applied Chem., Section IIIB., p. 41 ; *S.S.*, 1909, p. 442.

nitro-cottons. Their results are shown in Fig. 29 together with Saposhnikoff's nitration curves : inside the inner U-shaped dotted curve is the region of the collodion cottons completely or almost completely soluble in ether-alcohol. The nitro-cottons between the two curves have an intermediate degree of solubility, 10 to 90 per cent. : those outside the outer one are almost insoluble.

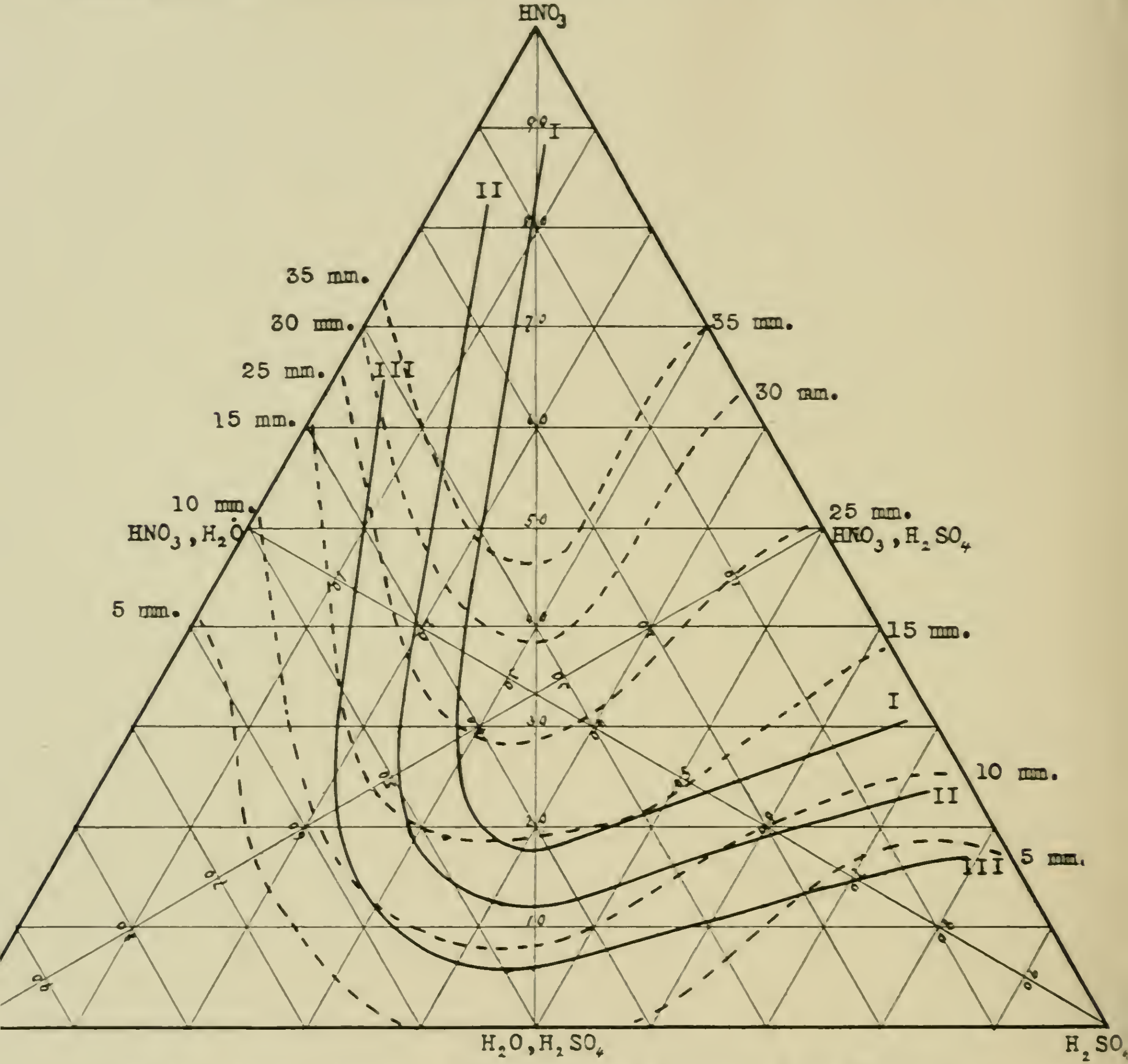


FIG. 28. Degree of Nitration of Nitro-cotton as a Function of the Molecular Composition of Mixed Acid and the Vapour Tension of the Nitric Acid

It will be seen that the molecular percentage of water in the mixed acid is the principal factor in determining the solubility. This diagram will be of assistance in determining what composition of acid is required to produce a nitro-cotton with any specified degree of nitration and solubility, but it must be remembered that it is based on laboratory experiments, which were

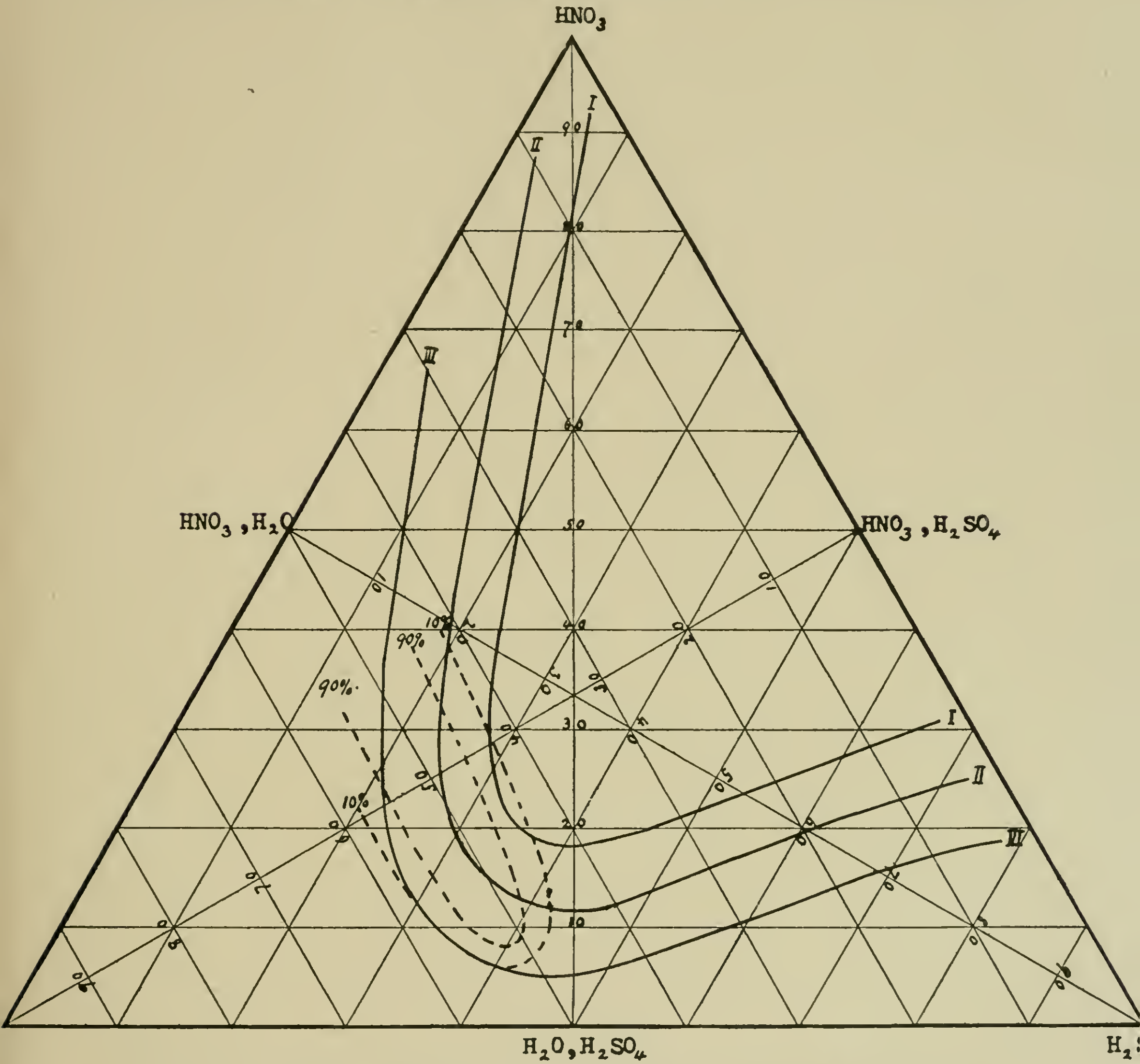


FIG. 29. Degree of Nitration and Solubility of Nitro-cotton as a Function of the Composition of the Acid

carried out under very different conditions from those that prevail in the works.

The cotton used for these experiments was generally cotton-wool, which is different in many respects to the cotton waste mostly used on the large scale: it is of much more open texture, each fibre being separated from the others, so that the acid can soak in very readily, thus facilitating the nitration. But as a result the material is very bulky, and for this reason inconvenient to use on a manufacturing scale, as it requires a very large proportion of mixed acid. Cotton-wool has often been subjected to a very drastic bleaching and scouring process, whereby the properties of the cellulose and of the resulting nitro-cellulose are injuriously affected.[1]

Soluble nitro-cellulose.

With acids containing a very large proportion of water or sulphuric acid nitration proceeds very slowly and is never complete. By raising the temperature of nitration this can be overcome to some extent, but then other reactions also take place: oxycellulose and nitro-oxycellulose are formed, and a considerable proportion of the cellulose is broken down altogether and passes into solution. Thus Lunge and Bebie obtained the results shown below with an acid of the composition:

	HNO_3	H_2SO_4	H_2O
Per cent. by weight . . .	42·15	38·95	18·90
Molecular per cent. . . .	31·7	18·8	49·5

Time of nitration	Temperature	Per cent. N	Solubility in ether-alcohol	Yield per cent.
4 Hours	17°	11·50	95·6	155
24 ,,	17°	11·58	99·8	156
4 ,,	40°	11·49	99·6	148
4 ,,	60°	10·81	99·8	52
¼ Hour	60°	11·46	99·7	147

The nitration was practically complete in four hours at the ordinary temperature; there was only a slight increase in the nitration, solubility and yield, when the time was extended to twenty-four hours. Increase of the temperature to 40° diminished the yield somewhat, showing that the cellulose molecule itself was being attacked. At 60° in four hours this action was so strong that the fibres were entirely destroyed and the nitro-cellulose could

---

[1] *See* Kilner, *J. Soc. Chem. Ind.*, 1904, p. 967.

only be recovered by pouring the acid mixture into water. When the time was cut down to a quarter of an hour this destruction of the fibre was much reduced. Lunge and Bebie found that with increase in the proportion of water there was an increase in the effect on the structure of the fibre. Up to 15 per cent. of water by weight in the acid mixture the structure appeared to be unaltered; but from 18 per cent. upwards the fibres were somewhat drawn together and the characteristic twisting of the cotton fibre disappeared. With a further increase in the percentage of water the structure was destroyed almost completely, the lumen was torn open, and the fibres disintegrated into small particles which were felted together forming little lumps. With 23 to 25 per cent. of water this destructive action attained a maximum; with still more dilute acids the fibres remained intact again, but on prolonged action they were broken down into smaller portions. By nitrating cotton with a mixture of H_2SO_4 35–46 per cent., HNO_3 35–45 per cent., H_2O 18–20 per cent. in the proportion of 30 of acid to 1 of cotton at a temperature of 40–50°, Claessen obtains a nitro-cotton entirely soluble in alcohol (96 per cent. by vol.) suitable for the manufacture of celluloid. (Germ. Pat. 163,688 of 1904.)

Mendeléeff and other Russian investigators have adopted a formula of the following form to express the effect of nitrating with acids of any particular composition: if the composition be written $2HNO_3 + aH_2SO_4 + cH_2O$, then the "characteristic" is m, which is equal to $(1 + a - c)$. Acid mixtures with $m > 0$ were supposed to give products of high nitration and low solubility, those with $m < 0$ soluble ones. Those in which the value of m exceeded -1 by only a little give soluble nitro-cottons with a maximum of nitrogen. If m lies between $-0{\cdot}3$ and $+0{\cdot}3$ the solubility is uncertain. If Fig. 29 be examined with reference to this formula, it will be seen that acids with equal values of m lie on a series of straight lines all passing through the point marked H_2O,H_2SO_4 in the centre of the base line. If $m = -1$ the locus of the points is the line running from the centre of the base line to the point HNO_3,H_2O. These acids contain the same number of molecules of water as of sulphuric and nitric acids together. It will be seen that this is indeed the locus of maximum solubility, but that the degree of nitration may vary considerably on this line. Apparently in order to get a product perfectly soluble in ether-alcohol it is necessary to have enough water not only to convert all the sulphuric acid into H_4SO_5, but also all the nitric acid into H_3NO_4. For $m = +1$ the locus of the points lies on the straight line going vertically upwards from the centre of the base to the apex.

Quantity of acid.

Nitration is affected to some extent by the proportions of acid to cotton, because during nitration nitric acid is used up and water is formed, so that the composition no longer remains the same. If the proportion of acid to cotton be very great the composition only alters slightly, of course. In the experiments on which Figs. 28 and 29 were based the proportions were generally 50 or 100 : 1, and the consequent alteration in position on the diagrams would only correspond to 0·5 to 1·5 molecular per cent. As a molecule of water is formed for every molecule of nitric acid used up, the molecular percentage of the sulphuric acid remains unaltered, and the point representing the molecular composition descends at an angle of 60° parallel to the lines marking the percentage of sulphuric acid.

Consumption of acid.

To produce a nitro-cellulose with 12·96 per cent. N, exactly one part by weight of nitric acid is used up for each part of cellulose, and 1·71 parts of the nitro-cellulose should theoretically be obtained. In practice the yield is as a rule very nearly equal to the theoretical. More generally the connexion between percentage of nitrogen and consumption of acid is given by the equations :

$$y = \frac{1400x}{63 + 45x}$$

$$x = \frac{63y}{1400 - 45y}$$

$$z = \frac{1400}{1400 - 45y} = \frac{280}{280 - 9y}$$

where x is the nitric acid used up in the nitration of one part of cellulose, and y the percentage of nitrogen in the nitro-cellulose formed, and z is the maximum theoretical yield from 100 parts of cotton. These equations apply equally well to all nitration processes, whether of hydrocarbons such as toluene, or alcohols such as glycerine.

Effect of nitrous acid.

Lunge with his co-workers, Weintraub and Bebie, investigated the effect of using nitric acid containing a considerable proportion of nitrous acid. They found that nitric acid containing as much as 6 per cent. HNO_2 gave as good yields, as high nitrogens and as low solubilities as acid free from this impurity. Even when the proportion of nitrous acid was higher than this, the effect was only slight. Lunge and Bebie also examined the stability of the products by determining the explosion points and the Abel heat tests. They came to the conclusion that the nitro-cotton made with acids containing nitrous acid is as stable as that made with acids free from it, but their results hardly bear this out. The tests were in all cases rather unsatisfactory, showing that the products had not been stabilized sufficiently : the Abel tests were no worse for the "nitrous" products than for the others, but with the explosion test the former gave slightly worse results in every instance. The true stability of a nitro-cellulose is very difficult to determine with certainty, unless it is very bad indeed ; it can only be ascertained by storage trials under various conditions extending over months or years. The evidence, such as it is, indicates that nitrous acid has a slightly bad effect on the stability. If the products had been thoroughly stabilized perhaps the evil effect would have been eliminated.

Temperature and time of nitration.

Lunge and Weintraub studied the influence of temperature and time of nitration of cotton wool with a mixture of concentrated sulphuric and nitric acids in the proportion 3 : 1, and found that with a rise of temperature the velocity of the action increases considerably.[1]

Temperature	Time hours	Per cent. N	Yield per cent.	Yield (calc.)	Per cent. loss of cellulose
0°	½	10·71	152·3	153	Trace
0°	7	13·19	173·3	174	Trace
10°	7	13·37	175·8	176	—
15°	7	13·38	175·6	176	—
19°	½	12·72	166·1	170	—
19°	7	13·39	175·6	176	—
40°	½	13·07	172·3	173	Trace
40°	7	13·06	169·6	173	1·61
60°	½	13·08	169·2	173	1·95
60°	4½	13·07	162·1	173	5·67
80°	¼	13·07	161·2	173	6.52
80°	½	13·12	125·2	173	27·4
80°	3	13·12	81·5	173	52·8

It will be seen that at high temperatures the nitration proceeds rapidly to a maximum and then the yield falls again ; the cellulose is first converted quantitatively into nitro-cellulose, and if the action of the acids be prolonged the product dissolves partly, and the yield is consequently diminished. The part which is not dissolved is also attacked, with the consequence that the percentage of nitrogen is reduced. In the case of acids containing a considerable proportion of water, this is demonstrated by the Table on p. 120, and is confirmed by the following figures, which were obtained by nitrating with concentrated acids at 32° :

Time of nitration		Per cent. nitrogen
5 Minutes	. .	13·27
15 ,,	. .	13·44
30 ,,	. .	13·47
60 ,,	. .	13·50
120 ,,	. .	13·40

---

[1] *See also* Lunge, *J. Amer. Chem. Soc.*, 1901, 23, p. 527.

Further Tables show the influence of time with mixtures of concentrated nitric and sulphuric acids in different proportions :

HNO_3	H_2SO_4	One-half hour		Twenty-four hours		Three days	
		Per cent. N	Yield	Per cent. N	Yield	Per cent. N	Yield
1	0	12·58	162·7	12·62	163·3	—	—
1	$\frac{1}{10}$	—	—	12·66	165·0	—	—
1	$\frac{1}{4}$	13·45	175·7	13·44	175·8	—	—
1	$\frac{1}{2}$	—	—	13·42	175·2	—	—
1	1	13·36	174·6	13·39	174·8	—	—
1	2	13·23	174·1	13·32	176·0	—	—
1	3	12·72	166·1	13·40	176·4	13·38	175·6
1	4	—	—	13·20	175·1	—	—
1	5	8·14	130·9[1]	13·10	166·6	—	—

HNO_3	H_2SO_4	Three days			Fifteen days		
		Per cent. N	Yield	Unnitrated cellulose per cent.	Per cent. N	Yield	Unnitrated cellulose per cent.[2]
1	6	12·63	162·4	0·85	12·74	169·8	None.
1	7	10·86	151·6	10·46	—	—	—
1	9	7·74	120·1	Much.	—	—	—
		Eight days			Thirty days		
1	8	10·88	144·6	10·7	11·70	152·0	4·48
1	10	5·43	65·0	41·1	—	—	—

These results indicate that when the proportion of sulphuric acid is increased the velocity of action is diminished. This applies not only to the nitration process itself, but also to the subsidiary actions. They show that it is not only cheaper but also better to nitrate with a mixture containing a considerable proportion of sulphuric acid, provided that the acid can be allowed to act on the cotton for some hours, but that if it be desired to obtain a high degree of

---

[1] 25·4 unnitrated cellulose.

[2] The "unnitrated cellulose" was determined by treating the product with sodium ethylate solution. The authors use the term "unaltered cellulose," but the word "unnitrated" is preferable, because the cellulose is not unaltered, although it has not been nitrated to an appreciable extent.

nitration in a short time, as when nitrating in centrifugals, for instance, the proportion of nitric acid must not be too small.

Hake and Bell [1] found that the course of the nitration is greatly affected by the physical form of the cellulose. If this be very dense, the acid cannot readily penetrate it, and the partly exhausted acid can only diffuse away and be replaced very slowly. Thus filter-paper is much slower in attaining its maximum degree of nitration than cotton-wool, and the thicker and denser the paper is the more is the nitration delayed. A larger proportion of sulphuric acid also combines with the more dense material.

Time of nitration	Cotton wool	Swedish filter paper Density 1	"Heat test" paper Density 1·22	Thick filter paper Density 1·52
	Per cent. N	Per cent. N	Per cent. N	Per cent. N
5 minutes	11·71	10·69	—	6·1
15 ,,	13·18	12·84	11·73	10·18
30 ,,	13·41	13·20	13·17	11·23
1 hour	—	13·35	13·38	12·52
2 hours	—	13·31	—	13·17
3 ,,	—	13·69	13·84	13·24
6 ,,	—	—	13·74	13·43
1 day	—	13·67	13·86	13·57
3 days	—	13·93	13·87	13·60
6 ,,	—	13·96	13·84	13·51
10 ,,	—	13·82	13·64	13·65
16 ,,	—	13·90	13·82	13·76

The acid used was a mixture of concentrated sulphuric and nitric acids in the proportion 3 : 1 ; the products were not stabilized but merely washed in cold water.

Nature of cotton.

In order to make sure that the cotton wool which they used for their experiments did not give different results from other sorts of cotton, Lunge and Bebie carried out comparative nitrations with these different materials. The acid used had the following composition by weight : H_2SO_4 63·84 per cent., HNO_3 16·96 per cent., H_2O 19·20 per cent. ; the results were :

	Per cent. N	Yield
Cotton wool, chemically pure	11·76	159
American cotton (middling fair)	11·56	157
American cotton (Florida)	11·67	153
Egyptian cotton, white (Abassi)	11·69	155
Egyptian cotton, natural yellow quality	11·61	154

There is very little difference between the results with the different cottons ;

---

[1] *J. Soc. Chem. Ind.*, 1909, p. 460.

the difference in the percentage of ash will account for a large proportion of what difference there is. The cotton wool contained only 0·05 per cent. ash, the other cottons about 0·5 per cent. The nitro-cottons were all completely soluble in ether-alcohol. The viscosity of the solutions was not determined; in this respect there would no doubt have been differences.

The above were all normal celluloses of good quality; it is when abnormal celluloses are nitrated that differences are found in the yields and nitrogen percentages.

Nitro-cottons of low nitration.

Lunge and Bebie (*loc. cit.*) by nitrating with acid of the composition: HNO_3 37·17 per cent., H_2SO_4 34·41 per cent., H_2O 28·42 per cent. by weight obtained a nitro-cotton containing only 6·50 per cent. N, but the large amount of basic dye-stuff that it absorbed indicated that it was to a large extent nitro-oxycellulose. With nitric acid alone of specific gravity 1·4 (34·8 mol. per cent. HNO_3) a product was obtained, of which 62·9 per cent. was unnitrated fibre as determined by treatment with sodium ethylate: allowing for this the nitrated portion contained 4·00 per cent. N. It contained little or no oxycellulose or nitro-oxycellulose. When 5 per cent. of sulphuric acid was added to the nitric, a product was again obtained which contained a large proportion of oxycellulose or nitro-oxycellulose; there was about 58 per cent. unnitrated fibre, and the nitrated portion contained 5·12 per cent. N. Crane and Joyce[1] have nitrated cotton with acids containing little nitric acid and much sulphuric and water. With an acid of the composition:

	By weight	Molecular
HNO_3	9·0	6·4
H_2SO_4	65·5	30·0
H_2O	25·5	63·6

they obtained a product containing 3·51 per cent. N. It was insoluble in acetone, ether-alcohol, and all the other usual solvents for nitro-cellulose, but soluble in strong acids, caustic alkalis, and phenol. Ultimate analysis gave results agreeing with the formula, $C_{24}H_{38}O_{20}, NO_2 + 2H_2O$. It contained 0·34 per cent. sulphur and must therefore have been unstable. The composition indicates that it was a nitro-hydro-cellulose.

Pyroxylin.

Soluble nitro-cellulose or "pyroxylin" is used very largely outside the explosives industry for the manufacture of varnishes, photographic films, artificial silk, celluloid, etc. For practically all these purposes ready solubility is essential, and high viscosity generally a disadvantage. Therefore the nitration is usually carried out at a fairly high temperature, but it should not be too high, else the cohesion of the material is injuriously affected, and this is one of its most important properties. According to figures given by

---

[1] *J. Soc. Chem. Ind.*, 1910, p. 540.

Worden,[1] Hyatt prepares the material for high-class celluloid by nitrating tissue paper with acid of the composition :

	By weight	Molecular
HNO_3	35·4	26·5
H_2SO_4	44·7	21·5
H_2O	19·9	52·0

The nitration is carried out at a temperature of 55° and lasts a half to one hour ; there are 22 lb. of acid per lb. paper. The product contains 11·0 to 11·2 per cent. N and about 0·1 per cent. ash ; the yield is 140 per cent.

For commoner qualities a smaller proportion of nitric acid is used.

Collodion is much used to seal surgical wounds, for application to cuts and abrasions, and as a vehicle for the application of drugs to the skin when prolonged local action is required. The pharmacopœias of the various countries contain directions for the preparation of the pyroxylin for these collodions, but satisfactory or uniform products are not likely to be obtained by following them.

Collodio

If the collodion cotton be of a suitable quality and it be dissolved in ether-alcohol together with camphor and castor-oil, the solution on drying will leave a film, which does not contract. In this way incandescent mantles are coated with material which enables them to bear transit. If the film were to contract on drying the mantle would be crushed, and when the collodion was burnt off the mantle would fall to pieces.

---

[1] *Nitrocellulose Industry*, p. 113.

CHAPTER XI

CELLULOSE

Nature of cellulose : Ligno-cellulose : Compound celluloses : Reactions of cellulose : With sulphuric acid : With nitric acid : Mercerized cotton : Viscose : Cellulose benzoates : Acetates : Schweitzer's reagent : Hydrate cellulose : Oxy-cellulose : Nitro-oxycellulose, etc. : Viscosity : Overbleached cotton : Nitrated mercerized cotton : Effect of dilute alkali : Cotton used in manufacture : Wood cellulose : Action of bacteria : Structure of cotton fibre : Dead cotton

Nature of cellulose.

COMPLETE knowledge of the nature of the process of nitration and the stability of nitro-cellulose would require a thorough acquaintance with the structure of the cellulose molecule, but in spite of numerous investigations there is still much that is unknown about the chemistry of this substance. There are few substances which are more complex, or about which it is more difficult to arrive at a definite conclusion. This is partly due to the fact that cellulose comprises whole series of allied substances, which are known by this name, and these are not all distinct from one another, but are liable to modifications, which cause one variety to merge gradually into another. Cellulose may be converted by reagents into products, such as oxy-cellulose and hydro-cellulose, which are very similar to the original substance in appearance and properties, and only differ from it very slightly in elementary composition. They are, however, somewhat more reactive, more liable to be attacked by chemical reagents. But true cellulose obtained from different sources also shows considerable variations, although no difference can be detected in the composition. Even the best cotton contains a proportion of material, which can be removed from it by treatment with bleaching powder and alkali, but the separation can never be carried to completion, because the treatment also attacks the true cellulose although to a less extent. The chemical behaviour of cellulose cannot be represented by a formula containing 24 or any other number of carbon atoms : in the nitration no definite stages or well-characterized nitrate can be distinguished ; on the contrary the nitration appears to be a continuous process from 6 up to 13·5 per cent. N. Cross and Bevan explain all this by the theory that cellulose consists of a "solution aggregate," that it is a solid solution in which substances of similar but not identical constitution are dissolved in one another. Others consider that the union of these different constituents is more intimate, and is chemical rather than physical; that the cellulose molecule consists of a large number of smaller groups combined together, and that these groups may differ slightly from one another in configuration and even in composition. The whole subject of the chemistry of the colloids, of which class cellulose is such an important member, abounds with difficulties, and it is only recently that any considerable effort has been made to solve its problems.

Cellulose is the principal constituent of the framework or cellular tissue of plants; cotton and linen are almost pure cellulose, but can be further purified by judicious treatment, and are then characterized by their resistance to chemical action, as compared not only with most other organic materials but also with the allied cellulosic substances, such as ligno-cellulose, pecto-cellulose, and the products obtained by the action of reagents on cellulose, such as oxy-cellulose and hydro-cellulose. Cellulose has the empirical formula $C_6H_{10}O_5$.

Ligno-cellulose

Of the ligno-celluloses jute fibre may be taken as a representative. It differs from cellulose by having a higher ratio of carbon to oxygen:

	C	H	O
Cellulose	44·37	6·36	49·27
Jute fibre	46–47	6·1–5·8	47·9–47·2

By treatment with chlorine the "non-cellulose" can be removed, but even then the residual cellulose is more reactive than normal cotton cellulose and contains a considerable proportion of $-O.CH_3$ groups. It is supposed that cellulose is first formed in the plant, and is afterwards converted into ligno-cellulose. With the exception of a few materials, such as cotton, hemp, and to lesser extent ramie, practically all the vegetable fibres contain a considerable proportion of the non-cellulosic substance "pectose." In wood fibre the lignification has proceeded further than in jute. By treatment with alkaline sulphites a fairly resistant cellulose can be prepared, and this is now manufactured on a very large scale for paper-making, but the material thus obtained is more reactive than cotton cellulose. It has been used to a considerable extent for the manufacture of sporting smokeless powder, for which purpose a high degree of nitration is not so important as a thorough control of the rate of burning. Nitration experiments with jute, were carried out by Mühlhaeuser,[1] using various mixtures of the concentrated acid. The fibre was purified first by boiling with 1 per cent. caustic soda solution.

---

[1] *Dingler's Pol. Jour.*, 1892, 283, p. 88.

$H_2SO_4 : HNO_3$	Acids : fibre	Time of nitration (hours)	Yield per cent.	Nitrogen per cent.	
1 : 1	10 : 1	1	130	12·10	11·80
2 : 1	15 : 1	2½	132	12·26	12·04
2 : 1	15 : 1	3–4	145	12·03	11·96
3 : 1	15 : 1	3	136	12·03	11·80

Ligno-celluloses give a number of characteristic reactions.[1] Salts of aniline colour the fibre a deep golden-yellow. Phloro-glucinol, dissolved in hydrochloric acid, gives a deep magenta coloration. Iodine is absorbed in large quantity, colouring the fibre a deep brown. The fibre readily combines with chlorine, as shown by the characteristic magenta coloration developed on the subsequent addition of sodium sulphite. Very characteristic is the reaction with ferric ferricyanide, obtained by mixing equivalent proportions of potassium ferricyanide and ferric chloride: the fibre is stained a deep blue and takes up a considerable quantity of pigment.

ompound elluloses.

Matthews[2] classifies the compound celluloses as follows:

(*a*) Pecto-celluloses, related to the pectin compounds of vegetable tissues; represented among the fibres by raw flax; resolved by hydrolysis into pectic acid and cellulose.

(*b*) Ligno-celluloses, forming the main constituent of woody tissue and represented among the fibres by jute; resolved by chlorination into cellulose and chlorinated derivatives of aromatic compounds soluble in alkalis.

(*c*) Adipo-celluloses, forming the epidermis or cuticular tissue of fibres, leaves, etc.: resolved by oxidation with nitric acid into derivatives similar to those of the oxidation of fats and cellulose.

The fibres of cork and other barks belong to the last class, but all such materials contain also large proportions of oils and waxes, tannins, ligno-cellulose and nitrogenous substances. Adipo-cellulose (or cuto-cellulose) contains a larger percentage of carbon than pure cellulose; pecto-cellulose, on the other hand, has a high proportion of oxygen.

Reactions of ellulose. With sul- huric acid.

Besides the nitro-celluloses produced by the action of mixtures of sulphuric and nitric acids, each of these acids alone yields products. Concentrated sulphuric acids chars cellulose and dissolves it, forming dextrine and, finally, glucose and other products of a comparatively simple nature. If the acid be diluted first with a third of its weight of water, the cellulose dissolves without charring with the formation of hydro-cellulose $C_{12}H_{22}O_{11}$, sometimes called amyloid, and cellulose-sulphuric acid $C_{12}H_{20}O_{10}(SO_3)_2$ (?); if the

---

[1] Allen's *Com. Org. Anal.*, 4th ed., vol i., p. 434. [2] *Textile Fibres*, 1907, p. 221.

action be only allowed to proceed for a short time and the cellulose be then washed, the surface is converted into a gelatinous non-fibrous film. In this way vegetable parchment is made. Cellulose combines very readily with sulphuric acid of moderate strength, but the compound formed undergoes further changes very rapidly. There is reason to believe that in the ordinary nitration process the cellulose first combines with the sulphuric acid, and that the product then reacts with the nitric acid to form nitro-cellulose.

Mixed est with nitr and sulp acids,

Hake and Bell found, however, that a proportion of sulphuric acid always remains combined with the nitro-cellulose, and that the amount does not diminish below a certain amount when the time of nitration is increased. From this they concluded that in normal nitration the nitric acid reacts directly with the cellulose, and that the formation of the mixed esters is due to the absence of a sufficient amount of nitric acid, and the consequent intervention of some of the sulphuric.[1] But the evidence is inconclusive, as the compound first formed when cellulose is immersed in sulphuric acid is probably quite different from the mixed esters. (For further discussion of these mixed esters *see* p. 188.)

With nit acid.

With concentrated nitric acid nitro-cellulose is obtained. Vieille [2] found the following percentages of nitrogen in the products yielded by acids of different strengths :

Molecular per cent. HNO_3	Per cent. N
80	12·7
75	11·5
67	10·2
57	9·0 dissolves in acid, reprecipitated with water.
40–42	7·0 friable mass.

With acid weaker than this very little nitration takes place ; Saposhnikoff, with an acid containing 34·7 molecular per cent. HNO_3, obtained a product containing only 1·46 per cent. N. Hake and Bell, with concentrated nitric acid, obtained nitro-cellulose with as much as 13·5 per cent. N.[3]

Labile n

Knecht [4] found that when cotton is immersed in weak nitric acid it swells up and forms a " labile " nitrate, from which the nitric acid can be removed again by washing with water ; if the cotton be in the form of yarn, a contraction of length takes place. To estimate the amount of acid retained by the cotton Knecht squeezed it out and then let it stand for several days in a vacuum desiccator over quicklime, then immersed it in water and titrated the acid removed. The following are some of the results that he obtained with acids of different strengths :

---

[1] *J. Soc. Chem. Ind.*, 1909, p. 457.

[2] *Compt. Rend.*, 1862, 95, p. 132.

[3] *J. Soc. Chem. Ind.*, 1909, p. 458.

[4] *Ber.*, 1904, p. 549.

Nitric acid		HNO_3 retained by cellulose Per cent.	Contraction of yarn Per cent.
Molecular per cent.	Sp. gr.		
38·4	1·415	35·8	13·0
34·8	1·400	27·3	10·0
31·2	1·380	10·8	2·5
30·4	1·375	7·5	1·0
23·0	1·325	7·1	1·0

If cellulose be heated with acids of these strengths it is converted into oxycelluloses, which contain a higher proportion of oxygen than cellulose does, and perhaps a lower proportion of hydrogen.[1]

Xyloidine. As mentioned above, Vieille found that cellulose was dissolved by acid containing about 57 molecular per cent. nitric acid. This matter has been more fully investigated by Jentgen,[2] who found that the most suitable strength for the preparation of these "xyloidines" at a temperature of 18° is 58·2 to 63·7 molecular per cent. (1·469 – 1·479 sp. gr.). When solution is complete it should be poured into a large volume of cold water. Products were thus obtained containing 6·2 and 7·2 per cent. N; they were insoluble in ether-alcohol, amyl acetate and acetone; ethyl acetate, cold acetic acid and acetic anhydride only caused them to swell up, but hot glacial acetic acid dissolved them. With slightly stronger acid a somewhat higher degree of nitration is attained, and the products are more soluble. A similar product may be obtained by dissolving cellulose in sulphuric acid and pouring into nitric acid, or by dissolving in nitric acid and pouring into sulphuric.[3]

Mercerized cotton. The formation of the labile nitrate of cellulose is very similar to that of the compound with caustic soda. If cotton be immersed in a solution of this alkali, it absorbs some of it, forming a combination in the proportion $C_6H_{10}O_5$, NaOH; the cotton swells up, and if it be under tension it acquires a lustre resembling that of silk. The soda is removed again on washing with water, but the cotton is found to have changed in its properties, its tensile strength has become greater and it can be dyed more easily. This process is known as "mercerization," and is much used industrially; for an investigation of it *see* Hübner and Pope, *J.S.C.I.*, 1904, p. 404. Many other reagents besides caustic soda and nitric acid produce much the same results, although not to the same extent as soda, *e.g.* solutions of sodium sulphide, potassium mercuric iodide, barium mercuric iodide and strong hydrochloric acid. Sulphuric

---

[1] *See also* E. Knecht and A. Lipschitz, *J. Soc. Chem. Ind.*, 1914, p. 116.

[2] *Ang.*, 1912, p. 944.

[3] Haeussermann, *S.S.*, 1908, p. 305.

and phosphoric acids of certain strengths also react in the same way, but at the same time gradually dissolve the cellulose.

Viscose. Cellulose treated in this way is much more reactive than untreated cotton. If to the mixture of cellulose and caustic soda solution carbon bisulphide be added, the material gradually swells up and eventually goes into solution, forming sodium cellulose xanthate. This solution can be made into fine threads by passing it through narrow jets, and if these threads are treated with alcohol and other reagents, the soda and carbon bisulphide are removed and a cellulosic material is regenerated. This is the basis of the Viscose artificial silk process.

Cellulose benzoates. If the alkali cellulose be treated with benzoyl chloride, cellulose benzoates are obtained. Of these two are known: the monobenzoate (C_6) retains the form of the original cellulose; the dibenzoate is a structureless amorphous powder soluble in acetic acid and chloroform.

Acetates. Cellulose acetates are formed by the action of acetic acid and acetic anhydride on cellulose that has been converted into hydro-cellulose by the action of strong acids or alkali. With unchanged cellulose there is little or no action. In this respect the formation of all other cellulose esters is essentially different from that of nitro-cellulose, for which the most resistant cellulose is best. The triacetate (C_6) has recently come into use on a large scale for making films for cinematographs, etc. It is soluble in chloroform, acetone and phenol. A tetracetate and other still higher derivatives were formerly supposed to exist, but the supposition was apparently founded on erroneous analysis.

Schweitzer's reagent. Cellulose dissolves in a solution of copper hydroxide in aqueous ammonia known as Schweitzer's reagent. If the ammonia be neutralized, a cellulosic substance is regenerated. Pauly's artificial silk process is founded on this solubility. Cellulose also dissolves in a solution of zinc chloride and hydrochloric acid, and in various other salt solutions.[1]

Hydrate cellulose. The cellulose regenerated from any of these solutions differs from the untreated material in being more reactive, and in containing a larger proportion of hydrogen and oxygen: the elementary composition agrees with the formula $C_{12}H_{20}O_{10}$, H_2O, or some mixture of this with normal cellulose. The treatment of cellulose with acids and alkalis yields very similar products, and those obtained by the hydrolysis of nitro-celluloses and other esters have the same characteristics. There are considerable differences, however, between celluloses which have been treated by the different processes. Cellulose, which has been mercerized and washed out, or has been converted into viscose and regenerated, is not so reactive, with Fehling's solution for instance, as cellulose that has been treated with acid. Cross and Bevan have proposed the name "hydrate cellulose" for the former; whereas the latter is called "hydro-cellulose." Hydrate cellulose gives off its extra water at a tempera-

---

[1] *See* Denning, *J. Amer. Chem. Soc.*, 1911, p. 1515.

ture of 120°–125°, whereas hydro-cellulose retains its water obstinately, and at this temperature gives off less than untreated cellulose.[1]

Oxy-cellulose.

By treatment with weak nitric acid, potassium permanganate, bromine, and other oxidizing agents a certain amount of oxygen is caused to combine with the cellulose, producing "oxy-cellulose," which also is more reactive than normal cellulose.

Nitro-oxy-cellulose, etc.

The effect upon the nitration of the presence of these various abnormal celluloses has formed the subject of a number of investigations of recent years. Wichelhaus and Vieweg[2] found that mercerization does not affect the percentage of nitrogen, but considerably increases the solubility in ether-alcohol.

Berl and Klaye have treated cellulose with various reagents, nitrated them, and examined the products before and after nitration.[3] The following are the materials they experimented with:

I. Cotton wool treated with 2 per cent. soda solution to remove fat, and washed with hot distilled water until there was no alkaline reaction. By combustion analysis it was found to contain 44·38 per cent. C and 6·35 per cent. H calculated on the ash-free material: calculated for $C_6H_{10}O_5$ 44·42 per cent. C and 6·23 per cent. H.

II. Hydro-cellulose made by dipping the above in 3 per cent. solution of sulphuric acid, drying and heating for three hours at 70° in a closed vessel. Found 42·75 per cent. C, 6·43 per cent. H: calculated for $3C_6H_{10}O_5 + H_2O$ 42·86 per cent. C, 6·35 per cent. H.

III. Hydral-cellulose: 15 g. cellulose digested with 30 c.c. of a 30 per cent. solution of hydrogen peroxide for thirty days. Found 43·24 per cent. C, 6·25 per cent. H: calculated for $4C_6H_{10}O_5 + H_2O$ 43·24 per cent. C, 6·30 per cent. H.

IV. $KMnO_4$-Oxy-cellulose: 32 g. cellulose treated with a solution of 30 g. permanganate in 300 c.c. water for thirty-six hours with frequent shaking. Then decolorized with sulphurous acid and digested with dilute sulphuric acid. Dissolved in 10 per cent. caustic soda solution and reprecipitated with acid. Found 43·61 per cent. C, 6·30 per cent. H; calculated for $4C_6H_{10}O_5 + C_6H_{10}O_6$ 43·58 per cent. C, 6·05 per cent. H.

V. Br-Oxy-cellulose: 25 g. cellulose allowed to stand for a day with a mixture of 5 g. bromine, 75 g. calcium carbonate and 400 c.c. water. The bromine was then driven off on the water-bath, 50g. bromine and 75 g. calcium carbonate again added and the mixture shaken in a machine. Found 43·83 per cent. C, 6·31 per cent. H: calculated for $8C_6H_{10}O_5 + C_6H_{10}O_6$ 43·96 per cent. C, 6·11 per cent. H.

VI. $Ca(MnO_4)_2$-Oxy-cellulose: 5 g. cellulose allowed to stand for a week with 22 g. calcium permanganate and 1000 c.c. water, decolorized with

---

[1] *See* Ost and Westhoff, *C.Z.*, 1909, p. 197; *J. Soc. Chem. Ind.*, 1909, p. 325.

[2] *Ber.*, 1907, p. 441.

[3] *S.S.*, 1907, p. 381.

sulphurous acid and washed. The permanganate was added gradually. Found 43·52 per cent. C, 5·20 per cent. H; calculated for $3C_6H_{10}O_5 + C_6H_8O_6$ 43·51 per cent. C, 5·74 per cent. H.

VII. HNO_3-Oxy-cellulose: 50 g. cellulose heated on a water-bath for two and a half hours with 350 c.c. nitric acid of sp. gr. 1·3. Found 43·17 per cent. C, 5·95 per cent. H; calculated for $2C_6H_{10}O_5 + C_6H_8O_6$ 43·03 per cent. C, 5·98 per cent. H.

VIII. $KClO_3$-Oxy-cellulose: 30 g. cellulose heated to 100° with a solution of 150 g. chlorate in 3000 c.c. water and 135 c.c. hydrochloric acid (20° B.) gradually added. Found 43·34 per cent. C, 6·39 per cent. H; calculated for $3C_6H_{10}O_5 + C_6H_{10}O_6$ 43·37 per cent. C, 6·02 per cent. H.

IX. Bleaching Powder-Oxy-cellulose: cellulose allowed to stand in the air with a solution of bleaching powder of 10° B., washed with slightly acidified water, dissolved in 10 per cent. caustic soda solution and precipitated with acid. Found 43·62 per cent. C, 6·36 per cent. H; calculated for $4C_6H_{10}O_5 + C_6H_{10}O_5$ 43·58 per cent. C, 6·05 per cent. H.

These products were examined also as to the colorations they gave with various reagents, but these were affected to a considerable extent by the different physical structures of the materials.

	Ash per cent.	Methylene blue, mg. absorbed by 1 g.	Coloration with			Microscopic examination
			$I + H_2SO_4$	$I + ZnCl_2$	Fehling solution	
I. Cellulose . .	0·10	3·7	blue	blue-violet	7	Normal.
II. Hydro-cellulose	0·18	4·1	blue	blue	6	Fibres partly attacked, twisted.
III. Hydral-cellulose	0·16	6·5	blue	blue	4	Structure retained, interference colours.
IV. $KMnO_4$–O/c. .	0·96	4·4	blue	blue	7	Granular powder.
V. Br–O/c. . .	1·20	6·0	pale blue	blue	1	Structure almost destroyed, interference colours.
VI. $Ca(MnO_4)_2$–O/c.	0·77	6·7	pale brown	blue	5	Structure little changed. strength small.
VII. HNO_3-O/c. .	0·27	6·8	yellowish	blue	2	Structureless, hard grains.
VIII. $KClO_3$-O/c. .	0·32	9·5	yellow-brown	blue	1	Broken down, interference colours.
IX. Bleach. Pow. O/c.	0·55	8·1	pale blue	blue	3	Granular powder.

These products were nitrated with acid having the composition:

	Per cent. by weight	Molecular per cent.
H_2SO_4	46·22	26·5
HNO_3	42·03	37·8
N_2O_4	·25	
H_2O	11·50	35·7

for twenty-four hours at a temperature of about 20°, after which they were washed for three days, first with cold and then with hot water. Ultimate analyses, etc., were made of the nitro-celluloses :

	Nitrogen by		Atomic ratios from analyses	Solubility in Et. Al.	Methylene blue test	Viscosity
	Nitrometer	Dumas	C : H : N : O			
I. Cellulose . .	13·50	13·32	24·0 : 34·0 : 11·0 : 41·8	1·8	0·6	10,000·0
II. Hydro-cellulose	13·23	13·36	24·0 : 36·6 : 10·9 : 42·1	12·15	2·4	65·7
III. Hydral-cellulose	13·07	—	24·0 : 36·3 : 10·6 : 41·2	22·5	2·4	8·1
IV. $KMnO_4$–O c. .	13·31	—	24·0 : 32·8 : 10·8 : 41·5	18·0	1·6	5·2
V. Br–O c. . .	12·92	13·29	—	15·5	3·5	9·1
VI. $Ca(MNO_4)_2$–O c.	13·25	—	24·0 : 35·5 : 10·8 : 41·4	20·5	3·3	11·1
VII. HNO_3–O c. .	12·87	13·28	24·0 : 34·0 : 10·4 : 40·0	34·0	5·0	7·9
VIII. $KClO_3$–O c. .	13·04	—	24·0 : 33·9 : 10·2 : 40·5	18·0	3·0	7.2

The following were the results of the microscopic examination :

I. Fibres intact, in polarized light steel blue.
II. In polarized light grey fibres as well as steel blue.
III. Structure retained, in polarized light steel blue.
IV. In polarized light blue.
V. In polarized light blue together with many grey fibres.
VI. Fibres nearly intact, in polarized light blue.
VII. Grains, resolved by high magnification into separate fibres, in polarized light blue and translucent at the edges.
VIII. In polarized light blue with violet tinge.

Viscosity.

In the case of No. VII the atomic ratio is calculated from the nitrogen determination by the Dumas method. The authors do not consider that any conclusions can be drawn from the differences in the nitrogen determinations by the two methods, because the quantities taken for analysis were in some cases very small. The increase in the solubility in ether-alcohol is no more than might have been expected from the lower percentage of nitrogen. The higher ratio of oxygen to carbon, which was to be observed in the unnitrated products after treatment, disappears in the nitrated products. The absorption of basic dye is higher, the viscosity much lower in the nitro-oxy-celluloses, etc., than in the nitro-cellulose. The viscosities were determined with 2 per cent. solutions in acetone by the method of Cochius. For comparison a number of nitro-celluloses were prepared by nitrating cotton with mixtures of equal weights of sulphuric and nitric acids, to which different proportions of water were added :[1]

Per cent. water in mixed acid	Per cent. N in product	Methylene blue absorbed	Viscosity
11·50	13·50	0·63	10,000·0
13·20	13·02	1·74	578·0
15·49	12·48	2·43	503·0
20·53	10·41	3·19	56·0
25·31	9·09	3·66	15·0
Xyloidine	12·40	—	1·15
		Acetone	1·09

The xyloidine was made by dissolving in sulphuric acid and pouring into nitric acid.

The great fall in the viscosity of the solutions of nitro-oxy-cellulose as compared with nitro-cotton indicates that the size of the molecules has been much reduced.

In a later communication[2] Berl returns to the question of the effect of various treatment on the viscosity. Cotton which had been mercerized was nitrated with mixed acid of practically the same composition as that used by himself and Klaye ; the product contained 13·5 per cent. N. This was dissolved in acetone, and the viscosities were compared with similar solutions from unmercerized cotton :

	Nitro-cotton from Mercerized cotton	 Unmercerized cotton
1 per cent. solution . .	14 . .	1,378 secs.
2 per cent. solution . .	122 . .	22,080 ,,

Merely heating the nitro-cotton reduces the viscosity :

Gun-cotton, unheated	4·26 secs.
,, heated for 3 hours at 130° . . .	1·47 ,,

Heating the cotton before nitration has a similar effect, especially if oxygen be present. The following were the viscosities of 1 per cent. solutions of the nitro-cottons in acetone :

Cotton dried but not heated	2330 secs.
,, heated 60 hours at 100° in atmosphere of oxygen . .	463 ,,
,, ,, ,, ,, hydrogen. .	1063 ,,
,, ,, ,, ,, carbon dioxide	1110 ,,

---

[1] *See also* T. Chandelon, *Bull. Soc. Chim. Belg.*, 1914, 28, p. 24.

[2] *S.S.*, 1909, p. 81.

These matters are of some practical importance as different degrees of viscosity are required for different purposes.

The effect produced by heating in a current of dry oxygen indicates that oxidation takes place. Cunningham and Dorée [1] found that ozonized oxygen has a very powerful effect on moist cotton at the ordinary temperature, forming a peroxide of cellulose, which when boiled with water gave an oxy-cellulose with a copper value of 15 to 17.

Over-bleached cotton.

The nitration of cotton that has been over-bleached has been studied by Piest,[2] as also that of cotton that has been mercerized and heated to a high temperature. The experiments were done on a manufacturing scale and the nitro-celluloses were tested for stability. The results of the bleaching were as follows :

Experiment	Treatment	Fat	Ash	Wood-gum	Copper value	Consumption of N/2 NaOH
Standard	Normally prepared cotton . .	·24	·37	0·92	1·85	1·6
Ia.	24 hours with bleaching powder solution of 3½° B.	·15	·44	2·86	2·17	—
Ib.	48 hours with bleaching powder solution of 3½° B.	·10	·64	4·54	3·40	2·8
IIa.	8 days with solution of 2½ kg. bleaching powder in 50 l.	·11	·60	8·13	10·73	5·2
IIb.	8 days with solution of 5 kg. bleaching powder in 50 l.	·19	·85	10·4	16·3	6·4

Of these materials Ia and Ib were white : IIa was yellowish-white and the fibres were short : IIb was yellowish and consisted of particles adhering tightly to one another. They were nitrated with acid of the composition :

	By weight Per cent.		Molecular Per cent.
HNO_3	20·5	. .	20·2
H_2SO_4	69·0	. .	43·6
H_2O	10·5	. .	36·2

The time of nitration had to be varied in order to ensure that the acid had penetrated to the interior of the fibres in all cases. After nitration the material was washed first with cold and then with successive lots of hot water in a hollander.

---

[1] *Trans. Chem. Soc.*, 1912, pp. 497–512.

[2] *Ang.*, 1909, p. 1215.

Experiment	Time of nitration	N	Solubility in			No. of hot washes	Stability	
			Ether-alcohol after		Absolute alcohol		B.J. method	Obermüller method
			First cold wash	Last hot wash				
	Hours	Per cent.					c.c.	mm.
Standard	½	13·07	—	6·0	2·40	7	3·4	119
Ib.	4½	12·84	18·8	26·8	4·75	27	8·3	148
IIa.	1	12·91	21·8	24·0	3·34	36	5·7	167
IIb.	2½	12·72	33·4	40·9	9·00	25	1·6	117

The number of hot washings required to obtain a satisfactory stability was much higher in the case of the bleached cottons, but as judged by the Bergmann-Junk test none of the nitro-celluloses was really stable except the last, for the official limit in Germany is 3 c.c., and a good gun-cotton does not give more than 2.

Nitrated mer cerized cotto

Similar experiments were carried out with mercerized cotton and cotton that had been heated at 150° in a current of CO_2:

Experiment	Treatment	Fat	Ash	Wood-gum	Copper value
Standard	Normally prepared cotton . .	·23	·28	1·44	1·77
IV.	Mercerized 20 minutes with 18·5 per cent. soda lye	·16	·25	0·21	1·59
VIa.	Heated 10 hours in CO_2 at 150° .	·23	·23	1·52	1·69
VIb.	Heated 100 hours in CO_2 at 150° .	·42	·25	2·44	2·29

The heated cottons were yellowish-white and yellow respectively. The following were the results of nitration :

Experiment	Time of nitration	N	Solubility in		No. of hot washes	Stability	
			Ether-alcohol	Absolute alcohol		B.J. method	Obermüller method
	Hour	Per cent.				c.c.	mm.
Standard	½	13·07	6·0	2·40	7	3·4	119
IV.	½	12·96	21·8	3·82	17	4·4	131
VIa.	¾	13·32	4·9	1·72	9	3·8	—

Mercerization reduced the percentage of nitrogen only to a slight extent, but greatly increased the solubility in ether-alcohol and impaired the stability; it also increased the quantity of unnitrated material as determined by treating the nitro-cellulose with sodium sulphide solution. In the nitrated mercerized cotton this amounted to 1·8 per cent., whereas in all the other of the above products it varied between 0·6 and 0·8 per cent. Heating the cotton in carbon dioxide made very little difference to the nitro-cotton, but it was somewhat more difficult to stabilize.

The general conclusion from this investigation is that both over-bleaching and mercerization have a very bad effect on cotton intended for the manufacture of nitro-cotton.

Piest has also investigated the action of alkalis and ammonium sulphide solution on nitro-celluloses prepared from normal, over-bleached and mercerized cotton.[1] He found that the material from over-bleached cotton withstood these reagents less well than ordinary gun-cotton, but that the material from mercerized cotton withstood them somewhat better. The regenerated cellulose had a much higher copper value than the original cottons, whence Piest concludes that it has been converted into oxy-cellulose, but does not consider whether it may not rather be hydro-cellulose. Vignon[2] similarly found that nitrated hydro-cellulose was more attacked by caustic potash solution than normal nitro-cellulose, and nitrated oxy-cellulose still more.

Vignon[3] considers that ordinary gun-cotton is really nitro-oxy-cellulose. He prepared the product of maximum nitration according to Lunge's directions and made an elementary analysis of it. The results were in accord with the formula $3C_6H_7(NO_2)_3O_5 + C_6H_7(NO_2)_3O_6$. But this view is not generally accepted. The cellulose could only be oxidized by the nitric acid, some of which would be reduced to nitrous acid, whereas there is practically no formation of nitrous acid in the nitration process. Moreover, there are distinct differences between the nitration products of normal and oxy-cellulose.

Effect of dilute alkali.

As regards the effect upon cotton of treating it with dilute caustic soda lyes of different strengths and at different temperatures, some curious observations have been made by Schwalbe and Robinoff.[4] They tried the effect upon pure cotton cellulose which had been prepared by Tamin's method[5] by boiling with a solution of resin soap and alkali without pressure, washing hot and bleaching very carefully; in this way they obtained a material which had a copper value of only 0·042.

---

[1] *Ang.*, 1910, p. 1009.

[2] *C.R.*, 1898, p. 1658.

[3] *Compt. Rend.*, 138, 1904, p. 898.

[4] *Ang.*, 1911, p. 256.

[5] *Rev. mat. col.*, 1908, p. 313.

Soda per cent.	Cotton dissolved	Copper values					
	Temp. 20°	Temp. 20°	Temp. 100°	Temp. 135°	Temp. 150°	Temp. 179°	Temp. 213°
0	—	·042	·109	·153	·190	·30	—
1	·74	·150	·180	·142	·10	—	—
2	·53	·166	·20	·17	·15	·11	—
3	·49	·195	·262	·395	·28	·128	—
4	·42	·257	·528	·89	·70	·445	—
5	·34	·135	·168	·285	·12	·05	0
7	·14	·154	—	—	—	—	—

When an over-bleached cotton is heated with water under pressure to a temperature above 150° there is a great increase in the copper value :

Temperature		Copper value
20°	..	·368
100°	..	·312
120°	..	·331
135°	..	·40
150°	..	·479
165°	..	1·43
179°	..	1·78
213°	..	3·43

The authors conclude that the strength of the soda used for the purification of cotton should never be allowed to fall below 5 per cent. and should be made up from time to time to this strength if necessary, also that temperatures above 150° should not be employed. They also found that the acid for subsequently acidifying need not be of greater strength than 0·1 per cent. ; with weaker acid the cotton is even whiter but the copper value is higher.

It has been found by Trotman [1] that the addition of neutral salts to soda lye considerably reduces the loss of weight of cotton boiled in it, and hence he concludes that the purification of the cotton is interfered with by the presence of these salts.

Cotton use
manufactu

Cotton wa

Von Lenk for his gun-cotton used cotton in the form of hanks of yarn. When Abel had discovered the very beneficial effect of pulping the gun-cotton there was no longer any object in using such an expensive variety of raw material, and he used instead cotton waste, the residual cotton from the spinning-mills. In the early days of the industry there was little demand for this material and the cotton waste supplied to the explosives industry was generally of good quality, but in course of time the demand for cotton

---

[1] *J. Soc. Chem. Ind.*, 1910, p. 249.

waste not only for the manufacture of nitro-cotton but also for other purposes grew, and it is now difficult to obtain a really satisfactory cotton waste. Moreover, a special industry has sprung up—the cotton-waste industry—which collects the waste from all the mills and prepares it for various purposes. The object of the suppliers of cotton waste is to produce a material that will pass a specification, rather than to supply a really good cotton which can be made into stable gun-cotton, a matter about which of course they know little or nothing. Cotton waste for nitrating is made largely from the sweepings of the cotton-mills; it contains some spun thread, but it is liable to consist largely of "fly," the fluffy material which escapes into the air during the various mechanical operations. This fly is the least resistant portion of the cotton as it is supplied to the mills. The presence of a very large proportion of dirt and oil and all manner of foreign matter makes it necessary to submit the cotton waste to a very drastic scouring and bleaching process, and this, as may be seen from the preceding pages, must inevitably produce a considerable proportion of oxy-cellulose and other modifications of the normal resistant cotton cellulose. At the same time more and more demands are being made upon the stability of the nitro-cottons, especially those used for the manufacture of smokeless powders for military and naval purposes. Consequently the explosives works have been obliged to give more attention to the question of their supplies of cotton. A few of the largest obtain their cotton waste unpurified and uncleansed from the mills and purify it themselves, and undoubtedly this is the best method where it is practicable.

Waste from weaving mills might also be used for making nitro-cotton, but it is liable to be contaminated with starch, which is applied to the warps to increase their strength. Starch on nitration gives an unstable nitration product, and consequently must be removed from the cotton by suitable treatment. New cotton can also be used, the only objection to it being its high price; its employment for the manufacture of smokeless powder would only involve slight alterations to the dies, etc.

Purification of cotton.

The cotton is subjected to various purification processes before it can be used. To remove the greater part of the oil and fatty matter it is extracted with a volatile solvent in an extraction vessel. The solvent after it has soaked through the cotton flows into a chamber where it is boiled by means of steam pipes; the vapour is condensed and again flows through the cotton. When the extraction is finished the solvent is distilled off into a receiver and the last portions of it are removed from the cotton by blowing steam through it. As a solvent benzine or benzol can be used: both are very inflammable and somewhat poisonous and precautions should be taken accordingly. Carbon bisulphide is still more inflammable. Carbon tetrachloride and other chlorinated carbon compounds are not imflammable, bvt are more poisonous than benzine or benzol. The choice of the solvent will depend on the price and the local conditions. After extraction the cotton is boiled in a kier with a weak solution of caustic soda or sodium carbonate, and well washed with water either in the kier or in a poacher. After this it is generally bleached with a weak solution of bleaching powder or sodium hypochlorite. This operation is often carried out in stone cisterns, but if the bleaching solution be very weak iron vessels can be used. Next it is treated again with dilute alkali to destroy the bleach and then washed again thoroughly. The bulk of the water is then removed in a centrifugal machine and the cotton is finally dried and made into bales. It is important that cotton whilst alkaline be not exposed to air at a high temperature.

For the removal of the fatty matters, soaps, especially resin soaps, can be used. The whole purification process can be varied in many different ways, and must be adapted to the sort of cotton that is to be treated. It is required to remove all matters except normal resistant cellulose, without injuriously affecting the character of the latter. Although the methods of treating ordinary cotton goods have formed the subject of numerous investigations, the preparation of cotton for nitration has not received the attention which its importance calls for.

B. S. Levine recommends treating the cotton with bacteria instead of bleaching. He claims that the impurities are thus removed more completely.[1]

Cop-botton

For the manufacture of collodion cotton for blasting gelatine cop-bottoms are generally used. This is spun thread in a tangled condition, the last portion left on the spindle. This undoubtedly is a very good class of material, but is usually considered too expensive for the manufacture of smokeless powder.

Linters.

After the long staple fibres or "lint" have been removed by the first ginning, there is on American upland cotton seed still about 10 per cent. of short fibre cotton, which is recovered by a second process, and is known as "linters." From "sea-island" cotton, which is grown near the coast, and Egyptian cotton long staple fibres only are obtained, and consequently these varieties yield no linters. This would form quite good material for the manufacture of nitro-cotton, if it could be freed mechanically from the adherent resin and all particles of seed-husk, but this does not appear to be possible, and consequently the linters have to be submitted to a very drastic chemical treatment, which damages the cellulose. Moreover the seeds often remain for a long time before the linters are removed and during this time they undergo a certain amount of fermentation and the fibre is attacked.[2] When nitrated linters consequently give somewhat low nitrogens and high solubilities in ether-alcohol. They are, however, used on a considerable scale in America and Germany, but not so much in England.

Tissue pape

For the manufacture of collodion for high-class lacquers and celluloid, cellulose is used in the form of tissue paper. Although this is somewhat

---

[1] *J. Ind. Eng. Chem.*, 1916, p. 298.

[2] Piest, *Ang.*, 1912, p. 396.

expensive, it has great advantages for this class of work: by inspection of the sheets it is possible to detect and then to remove every particle of foreign matter. Moreover, these thin sheets are nitrated completely in a very short time. The paper must, of course, consist of pure cellulose and should not be calendered.

Wood cellulose. Schultze sporting powder has always been made from purified wood fibre, and the makers claim that this gives a powder with the right rate of burning more readily than cotton. Other makers of "bulk" shot-gun powders have also used nitrated wood cellulose.

Wood-cellulose, or chemical wood-pulp, is made by three different methods called the sulphite, soda and sulphate processes. In all of these finely ground wood pulp is boiled with a solution which destroys the non-cellulose. In the sulphite process a solution of calcium or sodium bisulphite is used, in the soda process caustic soda, and in the sulphate process a solution of caustic soda and sodium sulphide.

A number of wood and straw celluloses, and nitro-celluloses prepared from them, have been examined by Nitzelnadel.[1] The wood celluloses were prepared by the sulphite process, the straw celluloses by the sulphate process. None of the latter proved satisfactory, but one of the sulphite celluloses gave a good yield of nitro-cellulose, which could be rendered stable. C. B. Schwalbe and A. Schrimpf [2] have also prepared nitro-celluloses in the laboratory from wood celluloses made by different processes from various woods. They obtained nitro-celluloses of a high degree of nitration and satisfactory stability so far as the tests could show. For the preparation of high-class smokeless powder for rifled fire-arms it would be necessary to purify the wood cellulose very carefully and to make it into thinner sheets than is usual. Under normal conditions this must make the wood cellulose almost, if not quite, as expensive as the cotton waste generally employed, and as the true stability of the smokeless powder can only be ascertained by keeping trials extending over many years, it is easy to understand that most of the Powers have not used it for their powders. The Japanese, however, are said to be using wood cellulose from Sakhalin,[3] and it is probable that the Germans are using it, since they can no longer import cotton.

Action of bacteria. Cellulose is attacked by various bacteria, especially if it be mixed with substances which provide food that favours their development. The methane which rises from marshes is apparently derived principally from the fermentation of cellulose; the intestines of animals also contain bacteria and ferments, which attack cellulose. Even pure cotton cellulose can be thus entirely destroyed; Hoppe-Seyler [4] found that Swedish filter-paper was completely

---

[1] *S.S.*, 1912, pp. 257, 301, 339, 384 and 409.

[2] *Ang.*, 1914, p. 662.

[3] A. Buisson, *Le Problème des Poudres*, Paris, 1913, pp. 175, 177.

[4] *Z. physiol. Ch.*, 10, p. 401.

resolved into gaseous products in the presence of river mud. He considered that cellulose was first hydrated $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$, and was then converted into methane and carbon dioxide, $C_6H_{12}O_6 = 3CO_2 + 3CH_4$. Omelianski [1] found two different ferments in river mud, one of which produced hydrogen, and the other methane.[2] The bacteria were anaerobic, but aerobic organisms capable of destroying cotton and linen have been found by Herson.

If cotton be stored for a long time under unfavourable conditions as regards heat and moisture, it is liable to be affected injuriously. In extreme cases it may become quite friable and dusty, but even before this stage is reached it is unsuitable for the production of stable nitro-cotton, probably on account of the formation of hydrated cellulose. If such a material be nitrated and stored for some time in a warm place it undergoes decomposition with the formation of a considerable amount of water and other decomposition products.

Structure
cotton fibr

The micro-photographs (Fig. 30) reproduced from a paper by de Mosenthal [3] show very clearly the structure of the cotton fibre. In No. 1 the characteristic twisting of the fibre is seen ; Nos. 2, 3, 5 reveal the pores through the outer cuticle. No. 4, a longitudinal section of the fibre, is almost unique on account of the extreme difficulty of obtaining such a view ; it clearly shows the inner and outer cuticles and the matter in the centre of the tube. The material forming the greater part of the walls of the tubes consists of true cellulose. It is granular in structure and is held in position by the inner and outer cuticles, which exert so much pressure on it that the fibre is seen to be doubly refracting when examined in polarized light. If one of the cuticles be removed so as to relieve the pressure, colours are no longer seen under the polarizing microscope. When treated with dilute soda and bleaching solution, the compound cellulose of the outer cuticle is no doubt attacked to a considerable extent, but the inner cuticle and the matter in the interior of the tube cannot be reached so well by the solutions, and consequently must escape treatment. De Mosenthal observed that a single fibre has no capillary action, but when several are bundled together liquids are drawn up between them. This indicates that there is no free passage up the centre of the fibre ; that the tube is obstructed at intervals. The material in the centre of the fibre probably gives rise to unstable products on nitration, and it is perhaps the function of the pulping process to render it possible to remove these partly from the nitro-cotton.

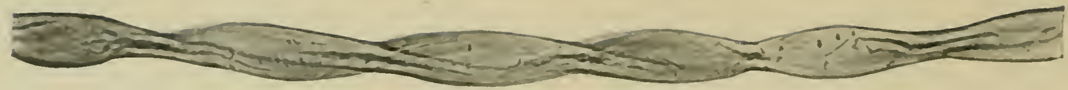
When treated with cuprammonium solution (Schweitzer's reagent), the cuticle dissolves much less readily than the bulk of the fibre (*see* No. 5, Fig. 30), and the same thing occurs when nitro-cotton is dissolved in acetone or other solvents. When passed through a Pasteur filter these particles of cuticle

---

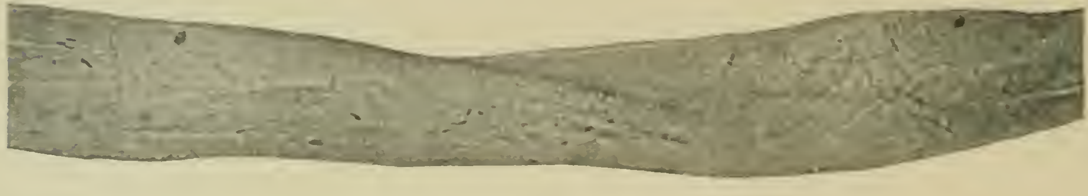
[1] *Compt. Rend.*, 121, 1905, p. 653.

[2] *See also* Lafars *Handbuch der technischen Mykologie*, Bd. 3, Kap. 9.

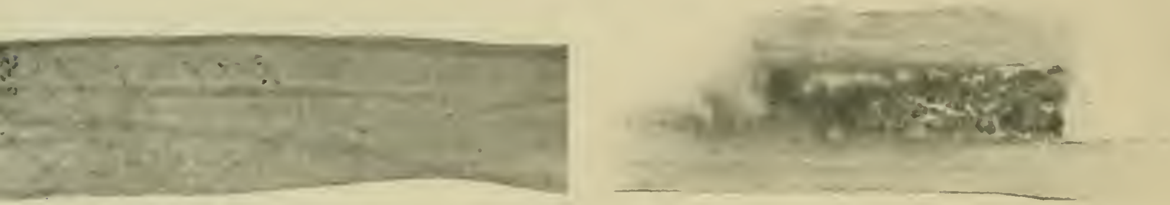
[3] *J. Soc. Chem. Ind.*, 1904, p. 292.



1. Natural Cotton Fibre × 300

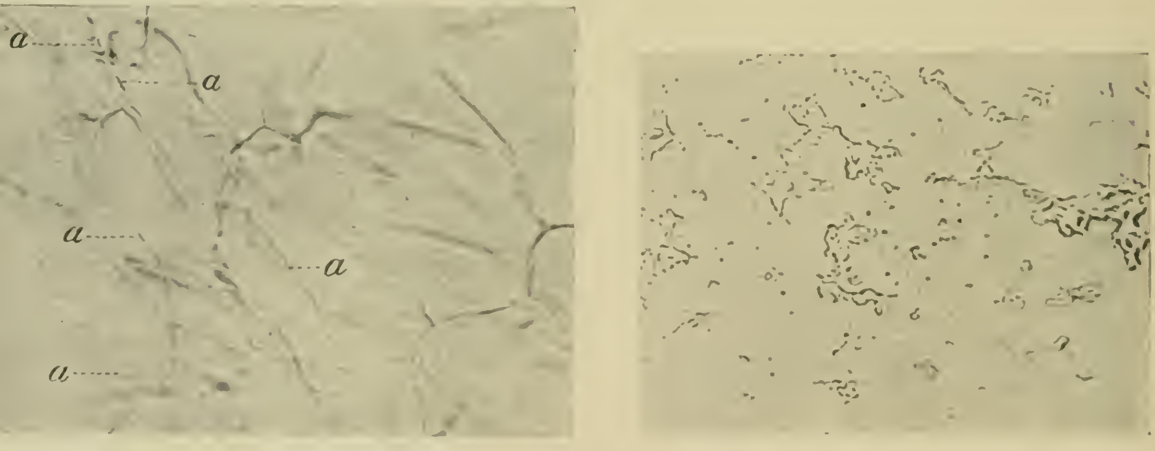


2. Portion of same Fibre × 1000



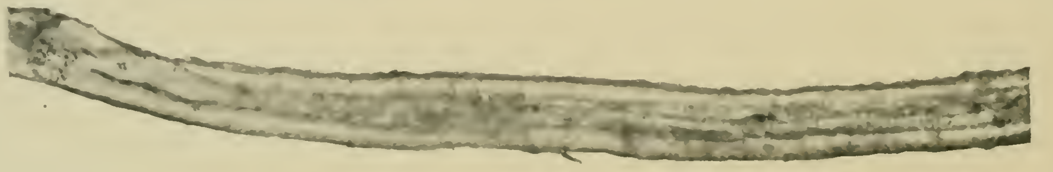
Portion of (2) Focussed to Show Stomata × 1000

4. Longitudinal Section of Cotton Fibre × 1000



5. Portion of a Fragment of Cotton Cuticle from a Solution in Cuprammonium × 1100
a . . . . indicates the Stomata

6. Granules from a 6½ per cent. Solution of Nitrated Cotton × 1500



7. Portion of a Nitrated Cotton Fibre × 300

Fig. 30. Microphotographs of Cotton (de Mosenthal).

are removed from the solutions to a great extent. For the manufacture of artificial silk such filtration is necessary, because otherwise the orifices of the "silk-worms" get stopped up. It is somewhat remarkable that the molecules of nitro-cellulose, which must be very large, can pass through the minute pores of a Pasteur filter, which stop the molecules of many organic dye-stuffs. It can only be explained on the assumption that the cellulose molecule is in the form of a long string. The molecules of nitro-cellulose will not pass through a dialyzer.[1]

When cotton is nitrated the pressure exerted by the cuticle is released, with the consequence that the twists of the fibres disappear (*see* No. 7), and the interference colours become much less brilliant. Similar changes in appearance occur when cotton is mercerized or submitted to other actions of a like nature.

Dead cott

All cotton contains a proportion of immature fibres, called dead or unripe cotton. These have very thin walls and either no central channel or a very flat one. They are weak and consequently liable to break during the spinning operations. Therefore they constitute a large proportion of the "fly" which passes into the cotton waste. It is less easily nitrated or acetated than ripe cotton. It generally has a smaller twist, but the fibres retain this twist on treatment with an 18 per cent. solution of caustic soda. It behaves differently with dye-stuffs also.

If the cotton bolls be allowed to remain on the plant for some time after they are ripe the cotton acquires characters very similar to these. Cotton is liable to form in portions of the length of the fibre solid parts, which do not take up dye properly. This is usually at the tip, which is consequently brittle and breaks off during the spinning processes. In the body of the fibre this structure is seldom found except in the coarser varieties, such as Surat and Peruvian.[2]

---

[1] De Mosenthal, *J. Soc. Chem. Ind.*, 1907, p. 447.

[2] F. H. Bowman. *Structure of the Cotton Fibre*, p. 113. *See also Chem Zeit.*, Sept., 1915.

CHAPTER XII

MANUFACTURE OF NITRO-CELLULOSE

Picking the cotton : Teasing : Drying : Nitrating : Abel's process : Centrifugal process : Direct dipping : Displacement process : Hyatt nitrator : High nitrogen gun-cotton : Partially soluble nitro-cottons : Soluble nitro-cottons : Pyro-collodion : Collodion for blasting gelatine : Collodion for other purposes

Picking the cotton. WHEN the raw material used is purified cotton waste, it is necessary to pick it over first by hand in order to remove all string, pieces of wood and metal, hard knots of cotton and all other matter which would not nitrate satisfactorily. This work is generally done by women.

Teasing. Next the material must be opened out by means of a teasing machine. The simplest form of this consists of a rapidly rotating drum armed with numerous iron teeth and a pair of feed-rollers that grip the unteased cotton firmly and gradually feed it up to the drum, which tears it off in small portions and throws it out at the other side of the machine. The whole should be enclosed to prevent the fine cotton dust flying about.

Drying. The cotton as supplied generally contains about 8 per cent. of moisture, and it is desirable to reduce this to about 0·5 per cent. This may be effected in any ordinary form of stove. The simplest type is a cupboard with a number of perforated shelves on which the cotton is placed, and steam-pipes underneath. Suitable openings allow hot air to circulate through the cotton and escape at the top of the cupboard. The disadvantage of this form is that the cotton in the lower trays gets much hotter and dryer than that in the top ones. Instead of having the steam-pipes underneath they may be in a separate heater through which air is forced by means of a fan and then through the stove, but the utilization of the heat is not very good, as the air is cooled down before it can take up more than a small proportion of water. In the most economical stoves these two methods of heating are combined, that is to say the air is blown through a heater into the stove, which is provided with a number of steam-pipes, which maintain the temperature at about 90° C. The cotton should be made to pass continuously through the stove by means of travelling bands. The drying takes about three-quarters of an hour Overheating or too prolonged drying should be avoided.

Nitrating.

The method of nitration worked out by Baron von Lenk was described at length in the paper published by Abel in the *Proc. Roy. Soc.*, 1866, p. 269.[1] This was only slightly modified by Abel, and was followed at Waltham Abbey and in other factories until recently, the principal difference made being the use of cotton waste instead of the skeins of yarn used by von Lenk. The method as carried out at Waltham Abbey until 1905 was described thus by Sir F. L. Nathan : [2]

Abel's pro

The nitrating acid was composed of three parts of sulphuric acid of 96 per cent. mono-hydrate to one part of nitric acid of 91 per cent. mono-hydrate, thoroughly mixed and cooled. This acid was run from the store tanks into cast-iron dipping pans, holding about 220 lb. each, the pans being supported in an iron tank through which cold water circulated to keep the temperature below 70° F. The dipping pans were provided at the back with gratings, on which to press out some of the acid from the charge. The charge of cotton waste weighed 1 lb. 4 oz., and on removal from the cooling box was passed from the back through an earthenware pipe in the partition running along the back of the pans, and raked by a dipper, as rapidly as possible, into the acid. After remaining in the acid bath for about eight minutes the cotton was removed to the grating, and a portion of the acid squeezed out by means of an iron lever having an iron plate attached to one end. After a charge had been removed from the dipping pan about 13¾ lb. of the mixed acid was run into it to replace the amount removed with the charge. The charge, now weighing with the adhering acid about 15 lb., was placed in an earthenware pot provided with a cover and transferred to the cooling pits, through which a stream of cold water flowed, and where it remained for twelve hours. During this period of digestion the conversion of the cotton into gun-cotton was completed. The contents of the pots were now emptied into a centrifugal wringing-machine, and the bulk of the waste acid extracted. The gun-cotton was then removed from the centrifugal machine and placed in galvanized iron pans with long handles. These pans when filled were carried quickly across to the immersing tank, and the gun-cotton thrown into a large bulk of water, the workmen standing by the tank and pushing the gun-cotton at once under the water with a stout wooden paddle. The immersing had to be done as quickly as possible, as, if the gun-cotton were allowed to come gradually in contact with water, it was liable to fume off. The immersing tank was fitted with a perforated copper plate to allow the water to overflow, so that fresh water was constantly passing through the tank. The gun-cotton was kept well stirred by means of a wooden paddle. When 2 cwt. had been

---

[1] This paper and Abel's later one on the Stability of Gun-cotton (*Trans. Roy. Soc.*, 1867, p. 181) are out of print and not always accessible, but they have been translated into German by Dr. B. Pleuss and published by Friedländer, Berlin, 1907.

[2] *J. Soc. Chem. Ind.*, 1909, p. 180.

immersed, the inflow of water was stopped and the tank drained down. When all the water had been run off the tank was filled up again with fresh water. This was repeated six times, or until the gun-cotton no longer tasted acid. When this stage had been reached the gun-cotton was wrung in a centrifugal machine, water from a hose-pipe being turned on the gun-cotton for one minute during the wringing, and it was then ready for boiling.

"This process, although it undoubtedly produced a good gun-cotton, had certain disadvantages, and the amount of labour required was very great. The plant, although individual items were not expensive, very rapidly deteriorated. and the cost of renewals and replacements was heavy. Power was required to drive the centrifugal machines, large quantities of water were used both for cooling and immersing, and decompositions, in the pans, pots, and acid centrifugals, were by no means infrequent."

In order to save the laborious and unpleasant operations of transporting the nitrating pots from the dipping pans to the cooling pits and from there to the acid centrifugals, and the transfer of the acid and cotton from one vessel to another a method has been adopted, especially in Germany, of nitrating in the centrifugal itself. A centrifugal machine used in this way lasts much longer than might be expected, for several years in fact with only occasional repairs. The firm which has had the widest experience in building this plant, Selwig and Lange, of Brunswick, has introduced several improvements in it. The basket of the centrifugal is fitted with a secondary driving gear, which can cause it to rotate slowly during the period of nitration, thus making the acids circulate, and their temperature can be kept at any desired point by means of a water jacket.

Centrifugal process.

The nitrating centrifugal is not very suitable for making gun-cotton of low solubility in ether-alcohol, because unless the cotton used is of good quality, parts of it will not be completely nitrated in the short time that it remains in contact with the acid.

The method of working is as follows: First, the acid is run into the centrifugal by turning on the cock on the pipe communicating with the supply tank. Then the cotton is immersed in the acid a little at a time until there is about 1 part of cotton to 50 of acid. The lid is then shut down and the nitration is allowed to proceed, usually for a quarter to three-quarters of an hour, according to the sort of nitro-cotton that is being made. Then the acid is allowed to drain away by a cock communicating with the waste-acid tank. The centrifugal is then rotated, slowly at first and gradually more rapidly until the proportion of free acid in the cotton has been sufficiently reduced. When making insoluble gun-cotton by this process it is generally desirable to leave not less than 1½ parts of free acid to every part of gun-cotton, because if the wringing be carried further there is danger of the charge fuming off, or even exploding.[1] With nitro-cotton of lower nitration the wringing can be carried somewhat further.

When the centrifugal has been stopped the nitro-cotton is taken out by means of tongs made of iron or aluminium, and removed to tanks where it is immersed in running water. Selwig and Lange have introduced an automatic hydraulic conveyor, the entrance to which is just by the centrifugal and may be seen at the back of Fig. 31. A ring of water jets directed downwards just below the opening immediately immerses the nitro-cotton as it is introduced, and the stream of water carries it along to a tank where the washing with cold water is completed. The somewhat dangerous operation of carrying the acid cotton in wooden boxes or other receptacles is thus avoided, and there is also a saving of labour.

During the operations of introducing the cotton into the acid and of removing the acid cotton after nitration, a considerable amount of acid fume is given off, and it is therefore necessary to provide the machine with a draught to draw the fumes away. Provision for doing this is shown on the left side of Fig. 31, where an upright earthenware pipe may be seen communicating with the interior of the centrifugal. This is intended to be connected by means of earthenware pipes with a stone-ware fan. I have found, however, that the draught produced in this way was very inadequate, and that the men who did the nitrating suffered much from the fumes which were not drawn away. A better arrangement was to make the lid of the centrifugal open to one side, and run a wooden shaft about 18 inches square along the back of the row of centrifugal machines with an opening just by each machine that could be closed with an aluminium door. At the other end of the wooden shaft there was an ordinary propeller fan with aluminium blades driven from a shaft. This created a much better draught with a smaller expenditure of power, and the cost of the arrangement was much less than that of the stone-ware fan, etc. The woodwork had to be renewed from time to time, but this was far less expensive than the repairs to the stone-ware fan had been.

Information about the various types of nitrating centrifugals will be found in a paper by Gründlich.[2]

Direct dipp

At Nobel's factory at Ardeer a method was adopted known as "direct dipping." According to a communication by Mr. Lundholm to Sir F. L. Nathan the process was as follows:

"The installation consists of parallel double rows of long iron tanks known as 'coolers.' Iron pots, termed 'dippers,' in which nitration is carried out

---

[1] At the K. B. Pulverfabrik at Ingolstadt the contents of a nitrating centrifugal exploded on July 1, 1911, killing one man and injuring another. The machine was being emptied at the time. It is supposed that it had been spun too long. As a rule the contents merely fume off. (*S.S.*, 1912, p. 60.)

[2] *S.S.*, 1910, Nos. 18, 21, 22, 23, 24.

stand in the coolers, sixty-two to each cooler. Sliding wooden covers rest on the coolers to guide the fumes from the dippers into earthenware pipes with openings at intervals, through which they are drawn by exhaust fans.

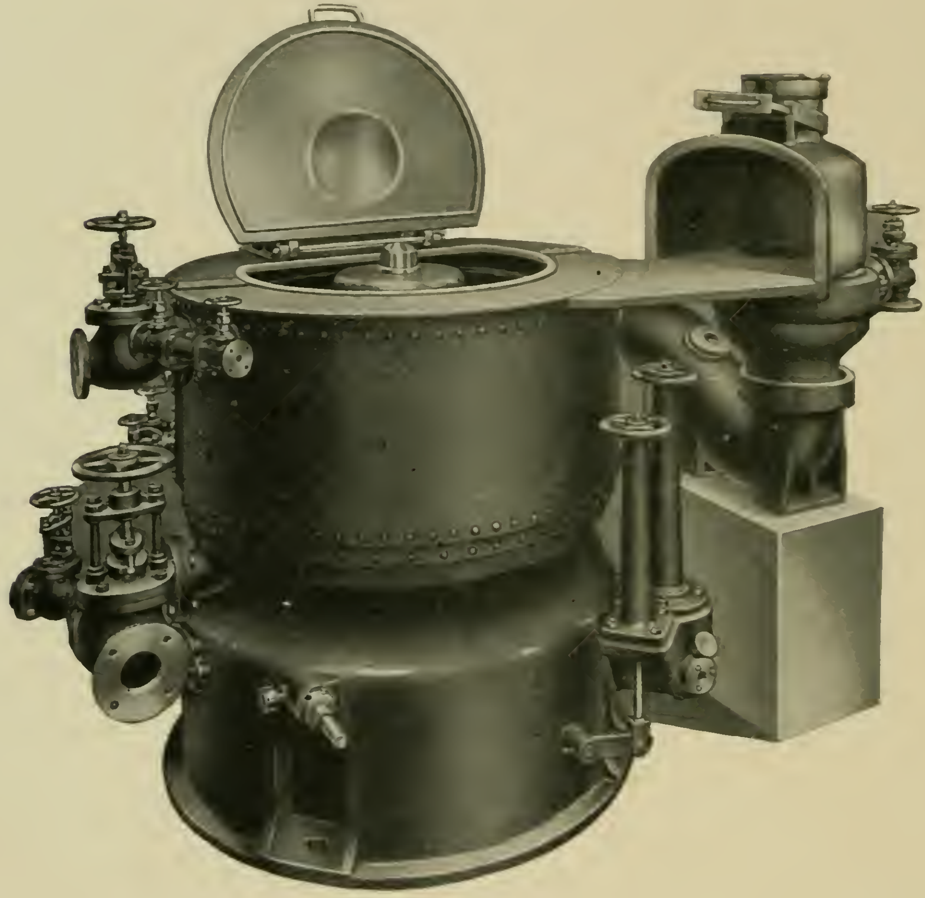


FIG. 31. Nitrating Centrifugal with Hydraulic Conveyor for the Nitro-cotton (Selwig and Lange).

The mixed acid, either cooled or warmed as necessary, is carried by lead pipes placed between each row of coolers, and is supplied to the dippers through earthenware cocks at intervals.

"*Nitration*. The water in the coolers is kept at 15° C. The dippers, having been placed in position in the coolers, are each filled with 127 lb. of mixed acid by measurement from the acid taps; 4½ lb. of cotton waste are steeped in each dipper. To minimize decompositions each charge of cotton waste is added in about ten instalments. The wooden covers are only removed to allow steeping to be done, and are then at once replaced. The temperatures of nitration are: Initial temperature of mixed acid, 15° C.; maximum after steeping, 25° C.; temperature at end of nitration, 20° C. The duration of the nitration varies according to the output required from the plant. One, two, or three shifts may be worked per twenty-four hours, and the time of nitration may therefore be twenty-four, twelve, or eight hours respectively.

"The average composition of the mixed acid for a twelve hours' immersion is as follows: Sulphuric acid, 75·0 per cent.; nitric acid, 15·75 per cent.; nitrous acid, 1·30 per cent.; water, 7·95 per cent. For an eight hours' immersion a higher percentage of nitric acid and less water is used; for a twenty-four hours' immersion less nitric and more water. The average composition of the waste acid for a twelve hours' immersion is: Sulphuric acid, 77·8 per cent.; nitric acid, 11·0 per cent.; nitrous acid, 1·5 per cent.; water, 9·7 per cent.

"*Recovering the waste acid.* When the nitration is complete, the 'dippers,' covered with light aluminium lids, are placed on barrows, wheeled to the centrifugals situated at the end of the 'coolers,' and the whole contents tilted out into the centrifugals. Four dippers are loaded into each centrifugal, and the gun-cotton having been uniformly spread round the basket, the centrifugal is run for six minutes to remove waste acid. At the end of that time about 1 lb. of waste acid is still adhering to each pound of gun-cotton. The centrifugal cover, made of light aluminium, is not fixed to the centrifugal in any way, so that as little resistance as possible may be offered when there is a decomposition. This is the usual arrangement in the case of acid centrifugals. The cone of the centrifugal projects through a circular opening in the centre of the lid and is covered by a small loose aluminium box. Small holes are cut in the sides of this box, and are of service in warning the workmen when there is a decomposition, as fumes are generally seen to issue there first.

"*Drowning the gun-cotton.* When the waste acid has been removed, the gun-cotton is quickly lifted out of the centrifugals and thrown under the revolving paddles of the drowning tanks, which immediately immerse it. The men who do the discharging are provided with rubber gloves and wear thick flannel hoods, which completely cover the head, arms, and breast. The hoods are fitted with strong glass windows, and are connected by light rubber tubing to a supply of pure compressed air.

"*Pre-washing.* After a given quantity of gun-cotton has been drowned, the water in the tanks is run off and the gun-cotton thrown on to draining tables forming part of the drowning tank. It is then loaded into the pre-washing centrifugals, the acid water wrung out, and washed for a few minutes with cold water from a hose to remove adhering acid. No special precautions, however, are taken to remove all acid at this stage. The bulk of the water having been removed, the gun-cotton is loaded from the centrifugals into bogies and conveyed to the boiling-house.

"The sixty-two dippers in each cooler form a 'charge.' Eight charges are worked by each shift. The yield is 159 per cent. of dry gun-cotton on the dry-carded cotton. The output per shift consisting of seventeen men is therefore : 4·5 × 159 × 62 × 8 ÷ 100 = 3549 lb.

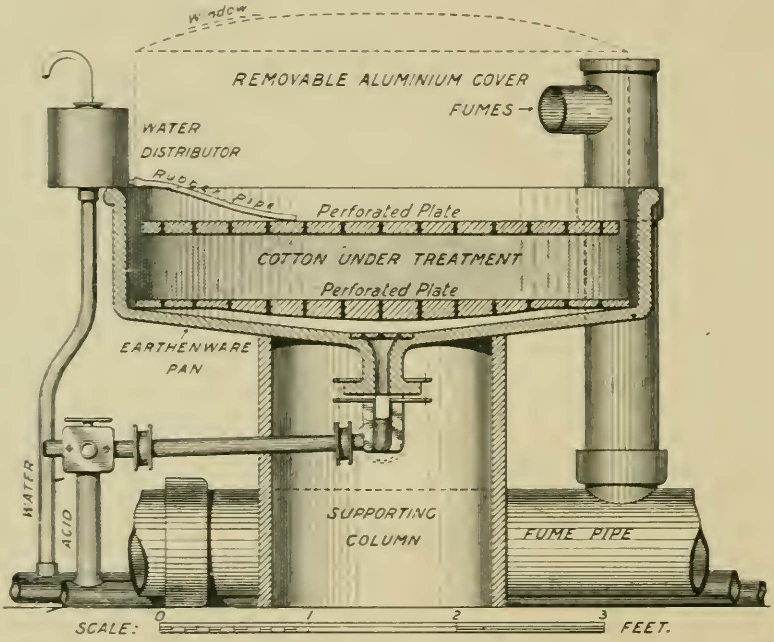


FIG. 32. Section of Displacement Apparatus (from *Arms and Explosives*).

Displacement process.

"Gun-cotton has been made at Waltham Abbey by Nathan and Thomson's displacement process since August 1905. The installation consists of a number of units of four pans worked together. The pans are of earthenware [1] and circular, 3 feet 6 inches in diameter, and 10 inches deep at the side of the pan ; the bottom has a fall of 2 inches to the outlet, which is ¾-inch in diameter. They are supported on earthenware pedestals about 1 foot 10 inches above the floor level. The four pans are connected together by lead pipes, and these are again connected to the nitrating acid supply pipe, to the strong and weak waste acid pipes, and to a waste water pipe, through a gauge-box, where the

---

[1] Pans of acid-resisting iron are also being tried. A.M., 1916.

rate of flow is determined whilst the waste acids are being run off. Gravities of the acids are also taken in this box. The process proceeds as follows :

"A small perforated plate is placed over the outlet of each pan, and four perforated segment plates making a complete disc about 1 inch less than the inside diameter of the pan, are placed on the bottom. Aluminium fume hoods, which are connected to an exhaust fan, having been placed on the four pans, the stone-ware cock on the acid supply pipe is opened, and the acid allowed to rise in the pans to the proper level. The nitrating acid is cooled in summer and warmed in winter, so as to maintain the same temperature of final nitration all the year round. The composition of the nitrating acid is 70·5 per cent. sulphuric acid, 21 per cent. nitric acid, 0·6 per cent. nitrous

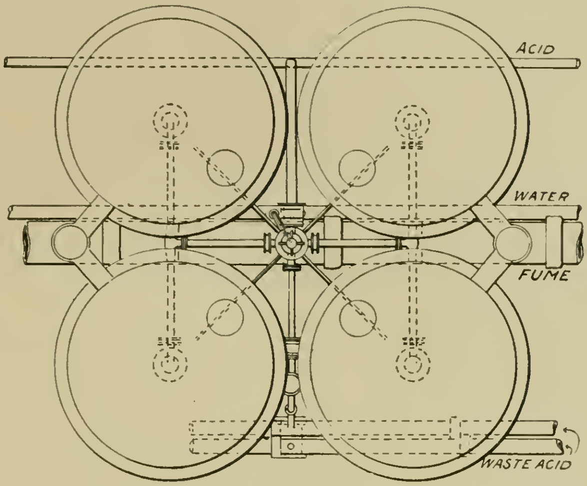


FIG. 33. A Unit of Four Pans (from *Arms and Explosives*).

FIG. 34. View showing Arrangement of Units in Rows (from *Arms and Explosives*).

acid, and 7·9 per cent. water; the quantity in each pan above the bottom plates is 600 lb., and below the plates is an additional 50 lb. A charge of 20 lb. of cotton waste is then immersed in the acid, handful by handful, aluminium dipping-forks being used for the purpose. When all the cotton waste has been pushed under the surface of the acid, perforated plates in segments are placed on the top of it, care being taken that all cotton waste is below the surface of the acid, and a film of water at a temperature from 5° C. to 8° C. is run very gradually on the surface of the plates through a distributor. The film of water prevents the escape of acid fumes, and the fume hoods are then removed. The time required for dipping a charge is a quarter of an hour.

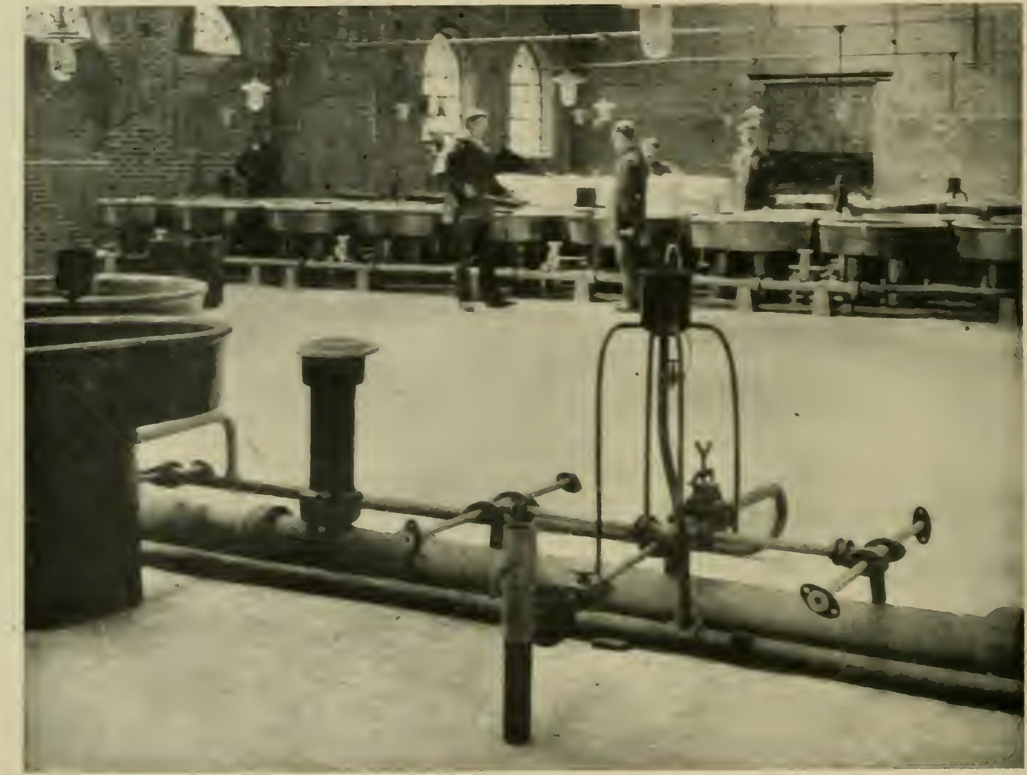


Fig. 35. Plumbing Installation for Displacement Plant (from *Arms and Explosives*).

"The nitration is allowed to proceed for two and a half hours. At the expiration of this period the cock leading to the gauge-box is opened, and the waste acid allowed to run off at the rate of about 17 lb. a minute. Water, cooled, if necessary, is run on the top of the perforated plates, through the distributor, at an equivalent rate. The major portion, amounting to about 80 per cent. of the total waste acid, is returned to the acid store tanks to be revivified with Nordhausen sulphuric and new nitric acids. The composition of this waste acid is 72·70 per cent. sulphuric acid, 17·30 per cent. nitric acid, 0·65 per cent. nitrous acid, and 9·35 per cent. water. The remaining 20 per cent. of the waste acid is sent to the acid concentration factory for denitration and concentration. The quantity of acid thus dealt with amounts to about 4 lb. for every pound of gun-cotton. Its composition is 61·0 per cent. sulphuric acid, 17·35 per cent. nitric acid, 0·55 per cent. nitrous acid, and 21·10 per cent. water. A small proportion of the water which follows the recoverable waste acid is slightly acid to the extent of 0·1 lb. for every pound of gun-cotton made. This is the total quantity of acid that is lost during the process. In the direct dipping and nitrating centrifugal processes the quantity of waste acid left in the gun-cotton is at least equal to the weight of the gun-cotton.

"The whole of the acid is displaced in three hours, and the water, which should fill the pan, is run through the gun-cotton, the gun-cotton drained down and sent over to be boiled. These operations occupy about an hour."

The following Table gives the principal figures in connexion with the four nitration processes described :

Process	Waltham Abbey Abel	Ardeer direct dipping	Dartford nitrating centrifugal	Waltham Abbey displacement
Acids, Analysis :				
H_2SO_4 . . .	74·0	75·0	69·35	70·5
HNO_3 . . .	18·0	15·75	23·15	21·0
HNO_2 . . .	0·6	1·3	—	0·6
H_2O	7·4	7·95	7·5	7·9
Quantity, lbs. . .	13·75	127	800–1100	650
Cotton waste, lbs. . . .	1¼	4½	16–24	20
Acid per lb. cotton . . .	11·0	28·2	50·0	32·5
Time of nitration, hours . .	12	12	1	2½
Yield on dry cotton, % . .	164	159	160	170
Output per man per week, lb. .	458	1112	(3000)	1742

NOTE.—The output with nitrating centrifugals is not given in the original paper. It is approximately as stated.

The following are the principal advantages which the displacement process possesses over the Abel process, and over the direct dipping and nitrating centrifugal processes where they are similar to the Abel process :

(1) The displacement process takes the place of the processes of dipping, squeezing out excess acid, digesting in pots, acid centrifugaling, immersing, and water centrifugaling.

(2) The actual dipping of the cotton waste is a very much less laborious operation—the heavy labour of squeezing out the excess acid is done away with; the absence of fumes makes the work much healthier, and injuries to workmen from acid splashes are almost unknown.

(3) Loss of gun-cotton due to decomposition in the digesting pots and acid centrifugals, and consequent inconvenience and danger to workmen from nitrous fumes, are done away with, and the heavy loss from breakages of pots and lids is saved. Three and a half years' experience has proved that the earthenware pans are very lasting.

(4) Fumes during dipping, loading, and unloading acid centrifugals and immersing, are avoided.

(5) The quantity of acid lost is very much reduced. This reduction means also very much less pollution of the escaping washing water.

(6) The recovered waste acid is very much cleaner, a matter of the greatest importance from the point of view of revivification and concentration.

(7) The mechanical loss of gun-cotton in the acid and water centrifugaling processes, and in the immersing process, is saved.

(8) A more thorough preliminary washing of the gun-cotton is obtained with an expenditure of about one-fifth of the quantity of water, and less boiling, and consequently less steam, is required in order to reach a given standard of purity.

(9) Great saving in power is gained by the abolition of the acid and water centrifugals, and by the reduction in the quantity of water which has to be pumped.

(10) Renewals of plant, and repairs to plant and buildings are exceedingly low.

(11) The number of hands employed for any given output is much less—the total cost of labour being reduced by two-thirds.

(12) The yield is improved; it averages 170 per cent.

(13) Finally, a more stable gun-cotton, of more uniform composition, is produced. It is also far cleaner and contains notably less mineral matter.

The last claim especially has proved to be amply justified. Cordite made from gun-cotton manufactured by the displacement process shows promise of lasting about twice as long under adverse climatic conditions, as that in which the Abel process was used, in spite of the fact that the latter would compare favourably with any other gun-cotton made except by the displacement process.

This improved stability is probably connected with a curious fact which has been observed by MacDonald.[1] He found that as the displacement proceeds, the percentage of nitric acid in the waste acid after falling slightly has a distinct rise and then falls again (*see* Fig. 36). The ratio of nitric to

[1] *J. Soc. Chem. Ind.*, 1911, p. 251.

sulphuric acid also, after a very slight fall, rises steadily until the end of the displacement and washing. This can only be due to a partial denitration of the gun-cotton, and evidently the more unstable products are decomposed to a greater extent than the normal stable gun-cotton.

The recovery of the waste acid is far more complete than by any other process, but, on the other hand, it is diluted somewhat with the water used for the displacement. Consequently a considerable plant is required for working up the acids again and reconcentrating them. According to MacDonald the loss of acid is only 0·08 lb. per pound of gun-cotton produced, but his own figures, as has been pointed out by Delpy,[1] indicate a very much higher loss.

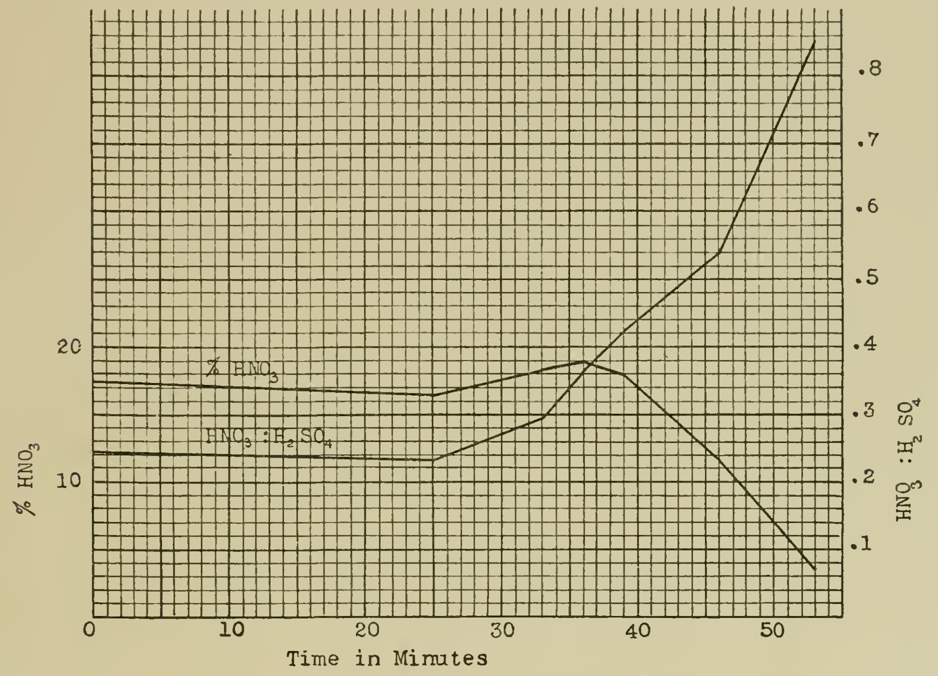


FIG. 36. Composition of Displaced Acids.

In all the processes except that of displacement there is liability of the charge fuming off either in the pots or centrifugals. This is especially the case in hot weather or if the cotton has not been sufficiently purified from grease, etc., or has hard lumps in it which the acids can only penetrate slowly.

Hyatt nitr

According to Worden,[2] tissue paper for lacquers is nitrated in America in pots, which are placed on a rotating table, about which are arranged inlets

---

[1] *S.S.*, 1912, p. 237.

[2] *Nitro-cellulose Industry*, p. 110.

for acid, a stirring apparatus, and a mechanism for tipping the pots into a centrifugal. The plant must be somewhat cumbersome and expensive, and is not likely to be adopted for the manufacture of explosives.

High nitrogen gun-cotton. The details given by Sir F. L. Nathan refer to the manufacture of gun-cotton containing about 13 per cent. N. If it be desired to obtain a product with a higher percentage of nitrogen, it is necessary to increase the proportion of nitric acid in the mixed acid (*see* Figs. 28, 29), but it is not very often that it is required to obtain a percentage much higher than 13, because such products are less stable and are more expensive to manufacture. It has been shown by Lunge and Bebie that beyond 13·5 per cent. the products are quite unstable (*see* p. 136).

Partially soluble nitro-cottons. For the manufacture of various smokeless powders nitro-cottons partially soluble in ether-alcohol are used. The acid mixture to be employed depends upon the sort of cellulose and the method of nitration.

Soluble nitro-cottons. For a nitro-cotton totally soluble in ether-alcohol there should, according to Fig. 29, be a molecule of water for every molecule of acid, whether nitric or sulphuric, but in practical manufacture a smaller proportion of water is generally used, especially if a high percentage of nitrogen is required. At one time it was thought to be impossible to prepare a totally soluble product containing more than 12 per cent. N. Mendeléeff, however, who worked at this subject from 1891 to about 1895, produced a soluble nitro-cotton with about 12·5 per cent. N, and he pointed out that a product with 12·44 per cent. contains just enough oxygen to convert all the carbon into CO and all the

Pyro-collodion. hydrogen into water. This material, which has been called pyro-collodion, was adopted as the basis of the Russian military smokeless powder, and later the United States adopted a powder made from a pyro-collodion containing about 12·5 to 12·7 per cent. N. This is produced by nitrating at a comparatively high temperature. According to Worden,[1] in Picatinny Arsenal the nitration is now carried out in Thomson's displacement plant. The acid has the composition :

	By weight		Molecular
HNO_3	21–22	..	18·7
H_2SO_4	63–64	..	36·3
H_2O	15	..	45·2

The temperature is 30°–32°, and the charge in each pan consists of 20 lb. cotton and 700 lb. acid.

Collodion for blasting gelatine. A high degree of nitration is also desirable for the collodion used for the manufacture of blasting gelatine and other similar high explosives, but the nitro-glycerine contains an excess of oxygen, and the proportion of collodion cotton is small, so that high power is not of the same importance as in the case of a military powder. The great essential is that the collodion cotton shall

---

[1] *Nitro-cellulose Industry*, p. 97.

give a good stiff colloid with the nitro-glycerine. Other things being equal a cotton of high nitrogen will give a stiffer gelatine than one of low, but it will dissolve more slowly, with the result that the material will become stiffer on prolonged storage and less sensitive, and this may cause missfires. The percentage of nitrogen in collodion cotton for blasting explosives is usually between 11·5 and 12 per cent. The official definition of H.M. Inspectors of Explosives gives an upper limit of 12·3 per cent. It is of great importance that the cotton before nitration shall not be submitted to drastic treatment either with chemicals or heat, for this breaks down the molecules of cellulose and makes the blasting gelatine soft. For the same reason the nitrated product is not boiled, as is done in the case of gun-cotton, but it is treated for some days with water at a temperature of about 90°. The pulping also is not carried so far.

Collodic for othe purpose

For the manufacture of artificial silk and lacquers, etc., a collodion is required that shall be as little viscous as possible, so that only a comparatively small proportion of solvent is required. A high degree of nitration is objectionable. Consequently the process of manufacture differs in many respects from that of collodion for blasting gelatine. The nitration may be carried out at a high temperature, 40° say, for several hours with a mixed acid containing about 18 per cent. water and about 20 per cent. nitric acid.[1] For other purposes, such as the preparation of collodion solution for dipping incandescent mantles, a collodion of intermediate viscosity is required.

---

[1] *See* T. Chandelon, *Bul. Soc. Chim. Belg.*, 1914, **28**, pp. 13, 24.

CHAPTER XIII

THE STABILIZATION OF NITRO-CELLULOSE

Early methods : Boiling : Pulping : Removal of foreign bodies : Poaching : Blending : Addition of calcium carbonate : Moulding, etc. : The beater : Alkaline method of stabilization : Sulphuric esters : Velocity of hydrolysis of nitro-cellulose : U.S. Ordnance method : Cellulose nitrites : Products of decomposition : Washing collodion cotton

Early methods. THE gun-cotton that was manufactured in the early days was purified by washing in cold water only, and it is principally to this very inadequate treatment that the numerous catastrophes of those times are to be ascribed. One of von Lenk's most important improvements was the introduction of a boiling of fifteen minutes with a potash solution of specific gravity 1·02. Sir F. Abel tried pulping the gun-cotton with the object of obtaining it in a more compact and convenient form. In his patent specification, No. 1102 of 1865, he says :

" Now my invention has for its object to assimilate the physical condition of gun-cotton as nearly as possible to that of gunpowder by mechanically converting it into a solid conglomerate state, and imparting to it either a granular or other suitable form that will present the exact amount of surface and compactness required for obtaining a certain rapidity or intensity of combustion.

" I first convert cotton wool by the processes now well known into gun-cotton. For this purpose I prefer to use the cotton in the form of a loose roving. When the gun-cotton has been purified from acid by washing in running water and in very dilute alkali, I transfer it to a beating engine of the description commonly used in the manufacture of paper, where it is reduced to a pulp, which is then converted into solid masses. . . ."

Boiling. Prolonged boiling with water, which is an essential feature of the modern process of stabilization, was not introduced until considerably later. Sir F. L. Nathan remarks [1] that : " Boiling as now understood did not form part of the process of gun-cotton manufacture when manufacture was started at Waltham Abbey early in 1872. About the middle of 1873, however, boiling

---

[1] *J. Soc. Chem. Ind.*, 1909, p. 180.

vats were put up at Waltham Abbey, but no records exist, unfortunately, about the details of the early boiling processes. In the official *Notes on Gunpowder and Gun-cotton*, published by the War Office in 1878, it is stated that gun-cotton manufactured at Waltham Abbey underwent two boilings by steam in wooden vats for eight hours each, the water being extracted after each boiling by wringing for three minutes in clean water centrifugal machines. The same boiling process was in use in 1888, according to a later edition of the same book. Five years later each boiling was extended to twelve hours, and the boiling lasted for five days and nights—that is, the gun-cotton received ten boilings of twelve hours each. In April 1894, this system of boiling was replaced by a system characterized by short boilings at the commencement of the process, the time of successive boilings being gradually increased. The scheme of boiling was as follows:

No. of boiling	Duration in hours	No. of boiling	Duration in hours
1	2	7	6
2	2	8	6
3	4	9	9
4	4	10	9
5	6	11	12
6	6	12	12

"This system of boiling was continued with but slight modifications until August 1905. On the introduction of the displacement dipping process it was found, as already stated, that gun-cotton made in this way was brought to a condition of stability by the boiling process then in use, and just referred to, at an earlier stage than gun-cotton made by the Abel process. A probable explanation of this fact is that during the displacement process a zone of acid liquid at a comparatively high temperature—somewhere about 40° C.—passes through the whole of the gun-cotton in the dipping pan. The action of this hot acid liquid may be to oxidize certain organic impurities which are certainly present, and to cause the breaking down of unstable nitrogen compounds into soluble or non-reactive bodies. Systematic experiments were therefore carried out, in 1905, to determine the most suitable and most economical method of purification by boiling for displacement process gun-cotton. In the principal experiments two types of boiling were employed—one in which long boilings were used at first, followed by short boilings; the other in which short boilings were used at first, followed by long boilings. The following deductions were made from the results obtained in these experiments:

"(1) Purification of gun-cotton obtained by means of long boilings at the beginning followed by shorter boilings later, is superior to that obtained when the reverse condition holds. This is substantiated by the following considerations: Examination of the waters showed that neutrality is obtained earlier; that less decomposition of the gun-cotton takes place; that the stability, as shown by the various stability tests, is greater; and that a stable condition is attained earlier.

"(2) A displacement washing after a long acid boiling at an early stage is a beneficial treatment.[1] This treatment is probably responsible for the early attainment of neutrality.

"The system of boiling determined on as a result of these experiments was as follows:

No. of boiling	Duration in hours	No. of boiling	Duration in hours
1	12	6	4
2	12	7	4
3	4	8	2
4	4	9	2
5	4	10	2

with a cold water displacement wash after the first two boilings. A full account of these investigations was given by Dr. Robertson in a paper on the purification and stabilization of gun-cotton.[2] This system of boiling is still in use at the Royal Gunpowder Factory.

"The question of how the purification of gun-cotton can best be effected cannot, however, be considered as settled, nor can the system which has just been described, although it undoubtedly gives an excellent gun-cotton at the Royal Gunpowder Factory, be applied to gun-cotton made by other processes at other factories, without full investigations as to its suitability. Another matter which must be taken into account in connexion with the purification of gun-cotton by boiling, is the nature of the water available. The water at Waltham Abbey is very hard, and its alkalinity may be an important factor in the success of the boiling treatment in use there. This question is perhaps connected with another one, and that is, that the boiling of gun-cotton can be carried too far. The effect of boiling, whilst it no doubt breaks down impurities, also, no doubt, breaks down the stable ester itself. It is well known that if gun-cotton is boiled for a sufficiently prolonged period, the percentage of soluble matter will rise and the nitrogen-content will fall. The breaking down of ester will be accompanied by the formation of acid

---

[1] A good method is to run in cold water at the bottom of the vat, which remains full of water the whole time. The contents then do not settle down to a compact mass.

[2] *J. Soc. Chem. Ind.*, 1906, p. 624.

bodies, and the presence of alkali in the water will neutralize them and prevent them from reacting on the gun-cotton."

Since the above was written it has been found possible to reduce the time of boiling still further without affecting injuriously gun-cotton made by the displacement process.

Pulping.

" On completion of the boiling process the gun-cotton is transferred to a beating engine somewhat similar to that employed for pulping the raw material used in the manufacture of paper. It consists essentially of a large iron roller armed with steel knives, and a bed-plate also provided with knives. The roller revolves, and as the gun-cotton passes between the two sets of knives, it is reduced to pulp of any desired fineness. As the pulping process proceeds, the roller is gradually lowered nearer to the bed-plate.

" Since the introduction of a thorough system of purification by boiling, Abel's original idea that the pulping and washing the gun-cotton received in the pulping process had a very material effect on its purification, no longer holds good to the same extent. At the same time there is no doubt that the very long staple gun-cotton before pulping retains in its tubes unstable bodies which no reasonable amount of boiling will remove. The effect of pulping is to reduce materially the length of the fibres and, at the same time, to produce a certain amount of crushing in them. This allows of impurities of an acid character in the tubes being removed, either mechanically or by diffusion.

Removal
foreign bo

" After pulping, it is now customary to treat the gun-cotton in some mechanical way, in order to remove from it particles of metal, grit, and foreign bodies of a similar character. At the Royal Gunpowder Factory this is effected by running the gun-cotton pulp, suspended in a large volume of water, through grit traps, placed at intervals in a long shallow trough, the bottom of which is covered with blanket. The foreign bodies, being almost entirely heavier than the gun-cotton pulp, are retained in the grit traps, and the fine sand, also present in some quantity, is caught by the woolly blanket. An electro magnet in the last grit trap removes any magnetic particles passing the ordinary grit traps. It is surprising what a large quantity of foreign bodies are removed by these arrangements. In addition to grit traps and troughs, some factories use what is known as a knotter, the function of which is to remove small knots and any large pieces of gun-cotton which may have escaped complete pulping.

Poaching.

" Washing the gun-cotton during the pulping is effected in some factories by the use of drum washers fixed to the beating engine ; in the Royal Gunpowder Factory and other factories this washing is done in separate vessels termed 'poachers.' The poachers in use at Waltham Abbey hold about 10 cwt. of gun-cotton and 1100 gallons of water, and are fitted with power-driven paddles for agitation purposes. The gun-cotton receives at least three washings ; it is allowed to settle down after each washing, and the washing water is removed by a skimmer. The washing water contains in suspension foreign bodies of a lower specific gravity than gun-cotton, and in the case of the earlier washing waters, there is always present a scum containing nitro-bodies of low stability

Blending.

"A further purpose served by poaching is the thorough blending of a number of different batches. This is a final blending, but at the Royal Gunpowder Factory there exists a regular system of blending right through the whole of the manufacturing processes. This system is briefly as follows: The cotton waste reaches the factory in consignments from different contractors. The waste is drawn from the store in proportion to the quantities on the contracts, and is mixed and passed through the teasing machine in these proportions.

"The next process where blending is possible is in charging the boiling vats. Two vats are filled simultaneously from a number of sets of pans—two pans of each set of four going into one vat; the other two of the set into the other vat. On completion of the boiling, four vats are emptied simultaneously into thirty-two beaters. This ensures the gun-cotton from the four vats being blended together in the beating process.

"On the completion of the pulping the beaters are run alternately into the poachers in such a manner that the contents of the thirty-two beaters are blended into eight poachers. The gun-cotton in the eight poachers is therefore uniform throughout.

"The system produces gun-cotton of very uniform nitrogen-content. In 1907–1908, 291 tests, representing 600 tons of gun-cotton, gave the following nitrogen result":

Maximum	Minimum	Mean
Per cent. 13·05	Per cent. 12·93	Per cent. 13·0195

Addition of Calcium Carbonate.

From the poacher the pulp passes to a "stuff-chest" or large tank provided with stirring arms. About this stage, if the gun-cotton is to be made into compressed blocks for blasting, stabilizing matters are added, usually calcium carbonate. If the water used be hard a considerable amount may be precipitated on the fibres by the addition of lime water. If the water be soft, or the quantity of calcium carbonate to be added be large, it may be added in the form of whiting.

Moulding, etc.

To remove the great bulk of the water the pulp may now be passed into a centrifugal machine, lined with fine canvas. The damp mass thus obtained still contains 40 or 50 per cent. of water. It may be sent away from the gun-cotton factory in this form, or it may be moulded first into blocks. This is done by loading it into a hydraulic press, where it is subjected to a pressure of 30 or 40 lb. per square inch. Presses are also made which dispense with the preliminary wringing in the centrifugal machine. These have hollow plungers covered with fine wire gauze, and the bulk of the water is drawn off through these by the application of a vacuum. The hydraulic pressure is then applied whereby the gun-cotton is moulded into a block or cylinder, which can be handled conveniently.

The beater.

An important point concerning the beating engine is to secure a very good circulation of the water. In the machines used in the paper industry the rotation of the drum causes the water to move round so fast that the fibrous cellulose material cannot settle, but is carried round and round, so that it comes repeatedly under the knives, until it has been reduced to the required degree of fineness, and the machine requires very little attention. But if the same machine be used to pulp nitro-cotton, it is found that the solid material tends to settle down at the bottom, and it is necessary for a man to attend the machine and help the material round with a wooden paddle. This is not due entirely to the increase of the specific gravity, for that of nitro-cotton is only 1·67, whilst that of cotton is about 1·61, but in the nitration the weight of each fibre has increased about 70 per cent. The length has not become greater, probably it has diminished somewhat, consequently each fibre has become much stouter, as may be seen clearly on comparing micro-photos 1 and 7, Fig. 30. There is therefore much more weight for the

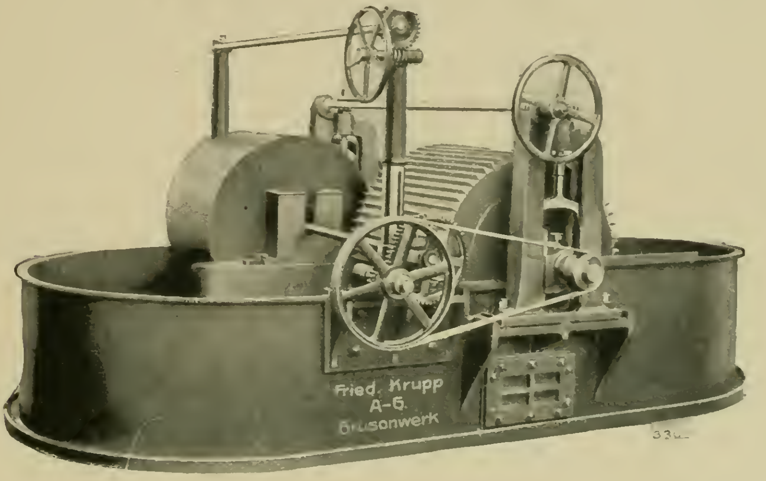


Fig. 37. Beater for Pulping Gun-cotton.

same amount of surface, and consequently the material is borne along by the water with greater difficulty.

A good form of beater is that of Hoyt, in which the material is made to circulate vertically instead of horizontally. The drum carries the water and pulp right over, after which they descend a steep incline, then another under this sloping in the opposite direction to the lowest point of the knife drum.

The fixed knives under the rotating drum require to be sharpened frequently, and it is usual to have a duplicate set. The knife-blades on the drum also require sharpening from time to time. They thus become gradually shorter, and this causes the circulation of the pulp to become worse.

The knives are sometimes made of phosphor bronze, as it has been found that particles of iron have a deleterious effect on the stability of the nitrocellulose, but they have the disadvantage that they wear faster than steel knives.

Alkaline method of stabilization.

The development of the method of stabilization took a somewhat different course in some factories; a boiling process has been introduced, after the pulping, and was carried out in large iron tanks fitted with stirring gear and valves for running off the water at different levels. The water had to be kept alkaline throughout the operations, else the acid developed by the nitrocotton would attack the iron of the vessels. At first sight it appears as though the boiling in the pulped state must purify the material much more effectually than when the material is compact, but experience has proved that this is not so. Robertson has shown that the most important part of the purification is the boiling with dilute acid, and in the alkaline method this is omitted altogether. Actual tests and trials have shown that the gun-cotton stabilized by this process is distinctly inferior to that prepared by the Waltham Abbey process.

Sulphuric esters.

The reason for this, or at least one reason, was revealed by the observation of Cross, Bevan, and Jenks, that mixed esters containing both sulphuric and nitric acid residues are liable to be formed when cellulose is immersed in the mixed acids.[1] The observation was confirmed by Hake and Lewis,[2] and was further investigated by Hake and Bell.[3] When these products are allowed to stand they gradually become acid in consequence of the formation of free sulphuric acid, which may ultimately lead to the spontaneous explosion of the gun-cotton. Hake and Lewis suggested that the disastrous explosion at Stowmarket in 1871 was probably caused by the presence of sulphuric esters.

It was shown by Robertson [4] that the sulphuric esters are decomposed hydrolytically by boiling with acid water much more rapidly than with alkaline

---

[1] *Ber.*, 1901, p. 2496; *Researches on Cellulose*, vol. ii., p. 51.

[2] *J. Soc. Chem. Ind.*, 1905, pp. 374 and 914.

[3] *J. Soc. Chem. Ind.*, 1909, p. 457.

[4] *J. Soc. Chem. Ind.*, 1906, p. 624.

water ; in fact treatment with alkalis seems to fix the sulphuric group firmly into the product. This behaviour is very similar to that of the cellulose aceto-sulphates, which have been investigated by Cross, Bevan, and Briggs.[1] They found that even under the action of cold distilled water the sulphuric acid residue of these mixed esters was gradually split off, but much more rapidly in boiling water, whereas on treatment with alkaline solutions the whole of the acetic acid residue could be eliminated by saponification, whilst the combination between the cellulose and the sulphuric acid remained intact in the form of a cellulose sulphate. This behaviour was explained by the fact that the sulphuric acid residue in these esters exists in the form of — SO_4H, which is readily hydrolysed by the action of water or acids, but becomes — SO_4M in the presence of alkalis, towards which it is remarkably stable.[2] It has been possible to study the aceto-sulphates more thoroughly than the nitro-sulphates because a larger proportion of sulphuric acid can be made to combine in the former case.

It was shown by Robertson[3] that the sulphuric esters are eliminated more rapidly from the gun-cotton if the first boilings are long, that is not less than twelve hours each, than if they are short. The reason is that under these conditions the material is in contact with hot dilute acid for a considerable time, whereas if the water be renewed constantly, the alkalinity is restored each time, and this impedes the saponification of the sulphuric esters.

Velocity of hydrolysis o nitro-cellu-lose.

Although the sulphuric esters are hydrolysed so much more rapidly by acid than alkali the reverse is the case with the nitric esters. The velocity with which a nitro-cellulose containing 12·84 per cent. N is hydrolysed by solutions of barium hydrate at a temperature of 39° was measured by Silberrad and Farmer.[4] They found that the velocity is given by the equation: $q(s - v) = kv$, in which q is the quantity of nitro-cellulose in grammes per 400 c.c. of the solution, v is the observed velocity with which the alkalinity of the solution diminishes measured in gramme-equivalents per litre per hour, s is the limiting velocity for a solution saturated with nitro-cellulose, and k is a constant. Further, as the velocity is proportional to the concentration of the baryta, the equation may be written :

$$v = \frac{cqs}{k + q},$$

c being the concentration of the baryta in gramme-equivalents per litre ; $s = 0·168$ and $k = 26·5$.

For hydrolysis by means of nitric acid the values found for these constants were $s = 0·000347$ and $k = 3·21$. Hence when the proportion of nitro-cellulose to liquid is high, as it is in the boiling vats, hydrolysis is about 480 times

---

[1] *Ber.*, 1905, pp. 38 and 1859.

[2] Briggs, *J. Soc. Chem. Ind.*, 1906, p. 626.

[3] *J. Soc. Chem. Ind.*, 1906, p. 624.

[4] *Trans. Chem. Soc.*, 1906, p. 1759.

as rapid in an alkaline solution as in an acid solution of equal strength. For this reason it is unadvisable to use strong alkalis for the stabilization; caustic alkalis should be avoided and sodium carbonate should only be used when the water otherwise contains no alkali. Hard water possesses sufficient alkali in the form of calcium bicarbonate without any addition, and this is the most suitable for stabilizing nitro-cellulose. Moreover, treatment with strong alkali is liable to convert the nitro-cellulose into unstable decomposition products.

The two methods of stabilization are often combined, that is to say, after the nitro-cotton has been boiled and pulped it is again boiled. The instructions of the U.S. Army Ordnance Department as revised up to April 18, 1908, are, for instance:

.S. Ordnance ethod.

"*Nitrating.*—Cellulose of standard quality shall be dried at a temperature not exceeding 110°. When cold this cotton shall be nitrated in mixed nitric and sulphuric acids. After nitrating, the nitro-cellulose shall be washed in water before boiling.

"*Preliminary boiling.*—The nitro-cellulose shall be boiled at least forty hours, and with not less than four changes of water, in tubs so constructed that the nitro-cellulose shall not come in contact with the steam at a temperature greater than 100°. There shall be complete ebullition or boiling over the entire surface of the tubs. No alkali shall be used in this preliminary purification.

"Pulping.—The nitro-cellulose shall then be pulped in fresh water, to which shall be added just enough sodium carbonate to preserve a slight alkaline reaction to phenol-phthalein solution: the process is continued until the material is thoroughly and evenly pulped to a satisfactory degree of fineness, and shows a clean break when a handful is squeezed and broken into parts. During this process the water shall be changed to such an extent as may be necessary to remove the impurities.

"*Poaching.*—After pulping, the nitro-cellulose pulp shall be run to the poachers, settled, and the water decanted. The nitro-cellulose shall then be boiled six hours in fresh water, and during this time not more than 10 gallons of carbonate of soda solution for each 2000 lb. dry nitro-cellulose may be added at intervals. This solution shall contain 1 lb. carbonate of soda per gallon. During this and all other boiling in the poachers the pulp shall be thoroughly agitated by mechanical stirrers. After boiling the nitro-cellulose shall be allowed to settle, and the clear water decanted as completely as possible. The tubs shall then be filled with fresh water, boiled two hours, settled, decanted and refilled with fresh water. The boiling shall then be continued for one hour, and this process repeated three times."

This makes a total of twelve hours' boiling with five changes of water, viz. 6, 2, 1, 1, 1, 1. With only the first of these is an addition of soda allowed.

"After boiling the nitro-cellulose shall have ten cold water washes, each washing to consist of agitation by mechanical means for half an hour in a sufficient amount of fresh water, thorough settling and decanting the clear water; at least 40 per cent. of the total contents of the poacher shall be drawn off. A sample shall then be taken for subjection to the various tests prescribed for nitro-cellulose. Should the nitro-cellulose fail to meet the required heat test, it must be boiled again with two changes of water, the time of actual boiling being five hours without the use of alkali, and then it must be given ten cold water washes in the manner prescribed for the regular treatment."

One of the disadvantages of boiling the pulp in iron hollanders is that it may be necessary to add alkali to neutralize the acid formed. It is better to add it in the form of finely divided calcium carbonate (whitening) than sodium carbonate. Another disadvantage is that the water cannot be removed nearly as completely as when the unpulped nitro-cotton is boiled in wooden vats, from which the water can be allowed to drain very thoroughly. If the pulp be allowed to settle in the hollander too long, it forms a dense mass at the bottom, which prevents the rotation of the stirring arms, and it may be necessary to dig it out.

Cellulose nitrites.

Another class of unstable products that may be present in nitro-cellulose is that of the nitrous esters. These are apparently formed in the hydrolysis of nitro-cellulose; on treatment with dilute alkali or acid the cellulose residue becomes oxidized whilst the acid residue is reduced. The nitrites of cellulose are so unstable, however, that they are never present in a normal product to any considerable extent. Nicolardot and Chertier [1] succeeded in preparing them by the action of nitrous acid on viscose cellulose suspended in dilute nitric acid. A certain amount of nitrate is formed at the same time, but this can be separated from the nitrite by dissolving it in acetone. It can also be made by passing nitrous gases through a mixture of acetic acid and acetic anhydride in which viscose cellulose or ramie fibre is suspended. The products thus prepared are of a grey colour, gelatinous when moist, brittle when dry, insoluble in water, alcohol, ether, acetone, chloroform and ethyl-acetate. The percentage of nitrogen, as determined by Schloesing's method, could not be obtained higher than 2·5 per cent., that is to say, the higher nitrites decomposed before they could be analysed. In the Lunge nitrometer they gave no evolution. Even those with 2·5 per cent. gradually evolve nitrous fumes at the ordinary temperature, and water and strong acids split the nitrous acid off rapidly, but acetic acid has little effect. It is possibly the presence of these nitrites which causes unstabilized gun-cotton to give low results when tested in the nitrometer. It is found that on boiling, the nitrogen as determined by the nitrometer goes up, whilst that as determined by the Schloesing (Schultze-Tiemann) method goes down. Although nitrites of

---

[1] *Compt. Rend.*, 1910, 151, p. 719.

cellulose are probably formed to some extent in the nitration process, their presence is to be ascribed more to the decomposition of the nitric esters. Their presence must be a cause of instability.

Products of decomposition.

The intermediate products formed in the decomposition of nitro-cellulose have engaged the attention of various investigators, who have hoped to obtain evidence as to the constitution of the cellulose molecule. Thus Kerkhoff [1] detected tartaric and citric acids among the products of saponification, and Hadow [2] found oxalic acid and ammonia and an acid similar to saccharic. Divers [3] found in the decomposition products acids which from their reactions he identified as pectic, and para- and meta-pectic acids. Abel [4] confirmed the presence of these in gun-cottons that were badly decomposed; he also found formic and oxalic acids and cyanogen, and when the material was heated with potash, ammonia was given off. Fermentable carbohydrates were only formed in a few instances. Silberrad and Farmer [5] extracted with water 100 kg. of gelatinized nitro-cellulose powder, which had been heated for twenty-three weeks at 54·4°. In the extract they detected ethyl nitrite, ethyl nitrate, ethyl-alcohol (these evidently derived from the alcohol used for the gelatinization), nitric and nitrous acids, ammonia, formic, acetic, butyric, dihydroxy-butyric, oxalic, tartaric, isosaccharic and hydroxy-pyruvic acids. Carbohydrates were found to be present by the fermentation test, and some other compounds were obtained, but could not be identified by reason of the complexity of the mixture and their minute quantity. Hydroxy-pyruvic acid, $C_3H_4O_4$, has also been found by Will [6] and Vignon [7] among the products of the alkaline saponification of nitro-cellulose and nitro-oxy-cellulose respectively. Berl and Smith [8] obtained it (called by them oxy-pyruvic acid) by the alkaline hydrolysis not only of nitro-cellulose but also of the nitrates of glucose and levulose, showing the intimate relationship of cellulose with these other carbohydrates. From starch nitrate a similar but not identical acid was obtained. They also found that hydroxy-pyruvic acid is very susceptible to oxidation and fermentation, and consequently may be the substance which others have described as "fermentable carbohydrates." Berl and Fodor [9] found that the relative proportions of the different acids formed vary according to the concentration of the alkali used, a dilute solution yielding compounds containing 4 to 5 carbon atoms, whilst with concentrated alkali acids with 1 to 3 carbon atoms predominated. In addition to hydroxy-pyruvic acid they detected malic, trihydroxy-glutaric, malonic, tartronic, oxalic, glycollic and dihydroxy-butyric acids.

---

[1] *J. f. prakt. C.*, 1847, p. 284.

[2] *J. Chem. Soc.*, 1854, p. 201.

[3] *J. Chem. Soc.*, 1863, p. 91.

[4] *Phil. Trans.*, 1867, p. 181.

[5] *J. Chem. Soc.*, 1906, p. 1182.

[6] *Ber.*, 1891, pp. 400, 3831.

[7] *Compt. Rend.*, 1907, p. 872.

[8] *J. Soc. Chem. Ind.*, 1908, p. 534.

[9] *S.S.*, 1910, pp. 296, 313.

Berl and Fodor[1] have also examined the nitrogenous residues left on treatment with alkali. A solution of collodion cotton was shaken for several weeks with a dilute solution of sodium carbonate. At the surface between the two liquids a flocculent substance separated out, which was found to contain 8·4 per cent. nitrate nitrogen as determined by the nitrometer, and 9·0 per cent. total N by the Dumas method. The same substance was separated from the ether-alcohol solution after the unchanged nitro-cellulose had been removed by precipitation with water. When the aqueous liquid thus obtained was acidified a precipitate was obtained (also a slight smell of prussic acid), and this was purified by dissolving in 96 per cent. alcohol and reprecipitating with water. The action of caustic potash on collodion cotton in solution also yielded the same substance. It was soluble in alcohol but insoluble in ether; on analysis it gave results agreeing with the formula $C_{24}H_{33}O_{21}(NO_2)_5$, and may therefore be considered as a penta-nitro-oxy-cellulose. It differed from normal penta-nitro-cellulose in having two hydrogen atoms replaced by one oxygen. Its solutions showed little viscosity, and molecular weight determinations gave results agreeing fairly well with the formula. The authors gave the substance the name "cellonic acid nitrate." Besides this another substance was obtained, which was soluble in ether. This was considered to be cellonic acid nitrite. The cellonic acid nitrate was not very stable; it exploded at 163°.

Will and Lenze[2] considered that the instability of some samples of nitro-cellulose may be due to the formation of sugars from the cellulose, and the conversion of these into nitrates. They accordingly prepared and examined various nitrates of the carbohydrates (*see* next chapter), which they found to be all more or less unstable. Sugar nitrate cannot be formed in the nitration of cellulose, however, unless the sugar be present beforehand, as the nitration is a much more rapid reaction than the formation of sugar from cellulose, and although sugars are apparently formed sometimes in the decomposition of nitro-cellulose, they are among the products of the ultimate breaking down of the material, and they are no longer nitrated. The presence of these foreign carbo-hydrates should be excluded from the cellulose used for nitration; starch is the one that is most likely to occur.

Washing collodion cotton.

Collodion cotton for the manufacture of blasting gelatine is not boiled, because the power of forming a stiff colloid would thereby be much reduced. It is washed repeatedly with hot water slightly below the boiling-point.

---

[1] *S.S.*, 1910, pp. 254, 269.

[2] *Ber.*, 1898, p. 68.

CHAPTER XIV

NITRIC ESTERS OF OTHER CARBOHYDRATES

Nitro-starch : Nitro-sugars

Nitro-starch. NITRO-STARCH has been known even longer than nitro-cotton, for it was first prepared by Braconnot in 1833[1] by dissolving starch in strong nitric acid and pouring the viscous translucent liquid into water. The resulting cheesy white substance was called by him "xyloidine," a name which is now applied generally to any product that is made by dissolving a carbo-hydrate in nitric acid and pouring into water or sulphuric acid, or by dissolving in sulphuric acid and pouring into nitric. Nitro-starch was afterwards investigated by Pélouse,[2] Liebig, Buijs-Ballot, Gerhard, Béchamp,[3] and Reichardt. In spite of the cheapness of the raw material, starch, it has never been able to displace nitro-cotton ; this is partly due to the instability of nitro-starch, and partly to the mechanical difficulties in nitrating and purifying it. If the starch be introduced into the mixed acids in the same way that cotton is, it forms clots, which are not thoroughly acted upon, and are difficult to purify subsequently. Hence in all the early attempts to manufacture the substance the starch was dissolved in nitric acid and poured into sulphuric acid. Such, for instance, was the method of the Austrian engineer officer Uchatius.[4] The process of the Viennese Nobel Company[5] consisted in dissolving ground starch in nitric acid (specific gravity 1·501), and then injecting it as a spray into the waste acids from nitro-glycerine (HNO_3 10 per cent., H_2SO_4 70 per cent., H_2O 20 per cent.), the temperature being kept down to 20° to 25°. The nitro-starch was then filtered off on a filter of gun-cotton, washed with water and treated for twenty-four hours with 5 per cent. soda. It was then ground to a paste and washed in a centrifugal or filter-press and impregnated with aniline with the object of making it stable. Until it was required for further use it was kept wet, containing about 33 per cent. water and 1 per cent. aniline.

---

[1] *Ann. chim. phys.*, 52, p. 290.

[2] *Ann. pharm.*, 1839, (29), p. 38 ; *Compt. Rend.*, 23, p. 893.

[3] *Ann. chim. phys.*, 1862, p. 311.

[4] *Dingler's Poly. Journ.*, 1861, p. 146.

[5] Germ. Pat. 57,711.

Hough's process[1] differs from previous ones in that he injects powdered starch by means of a jet of air into mixed acid containing an excess of sulphuric anhydride, which excess is maintained during nitration by the addition of more oleum. The nitrated product is filtered off and treated with hot ammonia. He claimed thus to obtain a stable product containing about 16·5 per cent. N. These claims have been investigated by Berl and Bütler,[2] only they did not treat the product with alkali, as this could only have an injurious effect on the stability: they treated it with water only. They found that the products were very unstable, the heat tests low, as also the ignition points, and they contained 0·50 per cent. combined sulphuric acid. The percentage of nitrogen also was very much lower than as stated by Hough; in no case was it more than about 13·4 per cent., which was the same as nitro-cotton contained when it was nitrated in the same manner.

The Nobel and other methods were similarly investigated by Mühlhäuser.[3] The principal results are collected together in the following Table:

Method of Preparation	Per cent. N.	Solubility in		Ignition Point	Remarks
		Alcohol	Ether-Alcohol		
Pptd. with N/G waste acid	11·02	sol.	sol.	175°	M, Nobel process
,, water . .	10·54	,,	,,	170°	M
,, 3·5 pts. H_2SO_4 .	12·50	insol.	,,	121°	M
,, 3 ,, .	12·87	,,	,,	152°	M
,, 3 ,, .	13·32	,,	,,	155°	M
Injection. Wheat starch .	13·23	,,	dif. sol.	121°	B, Hough process
,, Potato ,, .	13·44	,,	,,	120°	B, ,, ,,
,, Rice ,, .	12·86	,,	sol.	135°	B, ,, ,,
,, Soluble ,, .	13·35	,,	,,	120°	B, ,, ,,

M means investigated by Mühlhäusen; B by Berl and Bütler.

None of these were stable except the first two, which contained only 11 and 10·5 per cent. N respectively, but, on the other hand, Will and Lenze,[4] by treatment with solvents, obtained a stable product with 14·04 per cent. N. To prepare this they dissolved the dried starch in concentrated nitric acid (specific gravity 1·52), which was kept cool, and after twenty-four hours sulphuric acid was gradually added. The product was washed with water, then extracted first with cold alcohol and afterwards twice with hot alcohol.

---

[1] U.S. Pats. 751,076 of February 2, 1904, and 790,840 of May 23, 1905.

[2] *S.S.*, 1910, p. 82. [3] *Dingler's Polyt. Jour.*, 1892 (284), p. 37. [4] *Ber.*, 1898, p. 68.

It was dissolved in a mixture of acetone and alcohol and the acetone evaporated off, thereby precipitating the nitrate as a white powder. This was then boiled with alcohol, washed with water and dried. The product purified in this way ignited only at 194°, and after keeping at 50° for six months was still quite stable. Such a process is, of course, quite unsuitable for use on a commercial scale, but it seems to indicate that nitro-starch itself is fairly stable if it can be separated from impurities.

Nitro-starch dissolves readily in acetone and ethyl-acetate. The solubilities in alcohol and ether-alcohol are given in the above Table. That made by the Nobel process dissolves very readily in nitro-glycerine, but does not gelatinize it as collodion cotton does. This is in accordance with the low viscosity of the solutions in acetone. Berl and Bütler obtained the following viscosities for solutions of potato starch nitrated by Hough's method and for nitro-cellulose nitrated in the same way, both containing 13·4 per cent. N.

	1 per cent. solution	2 per cent. solution	5 per cent. solution
Potato starch nitrate	1·74	2·66	9·47
Cellulose nitrate	95·1	1,005	85,640

Acetone = 1

Other varieties of starch gave even lower viscosities. The molecular complexity is in fact small; Saposhnikoff[1] determined the molecular weight in a Beckmann apparatus with boiling acetone for two different products each containing 13·4 per cent. N, and obtained results agreeing with a C_{36} formula.

One of the disadvantages of nitro-starch as compared with nitro-cotton lies in the fact that it absorbs a much larger amount of moisture from the air, just as starch is more hygroscopic than its homologue, cellulose. Thus Will[2] found that the materials after being dried in an oven at 40° took up the following amounts in an atmosphere nearly saturated with moisture at 25°:

	Hygroscopicity (per cent)
Cotton	7 to 8
Wheat starch	11·4
Maize ,,	10·6
Potato ,,	14·1
Rice ,,	11·4
Soluble ,,	11·3

and the corresponding figures for the nitrated products were found by Will and Berl and Bütler to be:

---

[1] *J. Russ. Phys. Chem. Soc.*, 1903, p. 126; *J. Chem. Soc.* Abs., 1903, p. 402.

[2] *Mitt. a. d. Centralstelle*, No. 4.

	Per cent. N	Hygroscopicity	Hygroscopicity of nitro-cotton with same percentage N°
Rice starch nitrate (W) . .	8·51	7·37	6·1
Soluble ,, ,, (W) . .	12·95	8·40	1·6
Potato ,, ,, (B) . .	13·44	6·57	1·2

Nitro-starch has never come into general use in Europe, principally because of its unsatisfactory stability, in spite of the efforts of Uchatius and the Austrian Nobel Company to make smokeless powders with it. It is not authorized for manufacture or importation into England. In America, however, it is used as a component of high explosives.

Nitro-suga

By the action of nitric acid on various sugars products can be obtained containing 16 to 17 per cent. N. They can be exploded by friction and go off with great violence. Attempts have therefore been made to use them for percussion-caps, but they have hitherto proved too sensitive, too hygroscopic, and too liable to spontaneous decomposition. A number of these substances were prepared and examined by Will and Lenze.[1] The general method of preparation was to dissolve the sugar in nitric acid, add sulphuric acid, separate, wash with ice water, and purify by recrystallization from alcohol. The following Table gives the principal results :

	Melting-point	Per cent. N	Loss at 50°	Decomposes at
MONOSACCHARIDES—				
Pentoses, $C_5H_{10}O_5$:				
Rhamnose tetranitrate .	135°	16·08	1·2% in 30 days	—
Arabinose ,, .	85°	16·75	1·5% in 1 day 40% in 40 days	120°
Xylose ,, .	141°	14·57	—	—
Hexoses, $C_6H_{12}O_6$ Aldoses :				
Glucose pentanitrate .	10°	16·96	38% in 1 day	135°
Galactose ,, . α	115°–116°	17·18	42% in 10 days	126°
,, ,, . β	72°–73°	17·08	42% in 1 day	125°
Mannose ,, . .	81°–82°	17	46% in 1 day	124°
Ketoses :				
Levulose trinitrate . α	137°–139°	14·12	0 in 180 days	145°
,, ,, . β	48°–52°	13·83	1–3% in 8 days	135°
Sorbinose ,, . .	40°–45°	14·04	—	—

---

[1] *Ber.*, 1898, pp. 68–90.

	Melting-point	Per cent. N	Loss at 50°	Decomposes at
MONOSACCHARIDES—(*continued*)				
Heptoses. $C_7H_{14}O_7$:				
Glucoheptose hexanitrate .	100°	17·39	—	—
Glucosides :				
α-Methylglucoside tetranitrate	49°–50°	15·14	0·7% in 5 days	135°
α-Methyl-d-mannoside tetranitrate	36°	15	—	—
DISACCHARIDES. $C_{12}H_{22}O_{11}$:				
Cane sugar octonitrate .	28°–29°	15·79	11% in 3 days	135°
Lactose .. .	145°–146°	15·48	0·7% in 8 days	135°
		16·40	40% in 40 days	
Maltose .. .	163°–164°	15·83	1·3% in 11 days	163°–4°
			23% in 43 days	
Trehalose .. .	124°	16·11	—	136°
TRISACCHARIDES. $C_{18}H_{22}O_{11}$:				
Raffinose endekanitrate .	55°–65°	15·39	—	136°

The product from levulose appears to be the most stable : those from maltose and lactose also did not decompose very readily.

PART V

NITRIC ESTERS OF GLYCERINE

CHAPTER XV

GLYCERINE

Source of glycerine : Soap boiling : Purification of spent lye : Concentration : Autoclave process : Combined process : Twitchell process : Ferment process : Distillation

Source of Glycerine.

Glycerine, $C_3H_8O_3$, is a by-product in the manufacture of soap and stearine candles from oils and fats, which consist almost entirely of the glycerides of the fatty acids, compounds formed by combining three molecules of a fatty acid, stearic acid for instance, $C_{17}H_{35}CO_2H$, with one of glycerine and eliminating three molecules of water. When the oils or fats are heated with solutions of caustic alkalis or acids, or even with water alone the glyceride is split up :

$$\underset{\text{Water}}{3H_2O} + \underset{\text{Tristearine}}{C_3H_5(C_{17}H_{35}CO_2)_3} = \underset{\text{Glycerine}}{C_3H_5(OH)_3} + \underset{\text{Stearic acid}}{3C_{17}H_{35}CO_2H}$$

If caustic soda has been used, it combines with the acid to form a soap such as sodium stearate, $C_{17}H_{35}CO_2Na$. Stearine candles, on the other hand, are made from the free fatty acid and principally from stearic and palmitic acids.

The soap industry is, of course, a very old one, but it is only in modern times that the recognition of the advantages of cleanliness has caused it to assume really large dimensions. Formerly the glycerine was either left in the finished soap, or was allowed to run to waste. It is only since the development of the industry of nitro-glycerine explosives that there has been a large demand for the product. The demand for glycerine for the manufacture of explosives is now so great that it often absorbs all the available supplies. The European production is estimated at 80,000 or 90,000 tons per annum. It now pays the soap-maker to recover a much larger proportion of the glycerine than formerly.

Soap-boil

The simplest method of making soap is to boil the oil with caustic soda solution in open tanks (" kettles "), which usually hold 40 to 50 tons. The saponification is started with a weak lye of specific gravity 1·05 (4·6 per cent. NaOH), and when the action is well started stronger lyes are added. When the action is almost complete, salt is added to render the soap insoluble in the water. Two layers are thus obtained : an upper one of soap, and a lower one of brine containing the glycerine dissolved in it. The soap is separated, the saponification is completed by the addition of a little more soda, and it is submitted to such further processes as are necessary to produce the class of soap required.

There are a number of other processes of splitting up the fats with separation of the fatty acids as such, and these acids can subsequently be combined with soda to form soaps. These methods have been used largely in Germany for soap-making, but the manufacture of soap is thus rendered much more difficult: the soap is often dark in colour, and is apt to "grain" on keeping, and in many cases becomes rancid. These disadvantages more than compensate for the fact that the recovery of the glycerine is easier. In England saponification with soda is practically universal, and it is the process most used in America. The tendency in Germany is also to return to this method for the manufacture of soap.

urification of
pent lye.

The spent lye contains, besides glycerine and much water, a large amount of sodium chloride, and various impurities, organic and inorganic. It is first necessary to remove some of the impurities. The free alkali is first neutralized with sulphuric or hydrochloric acid, and if impure soda has been used, ferric or aluminium chloride is added as long as a precipitate is formed to free the liquid from hypo-sulphites, sulphides, cyanides, sulpho-cyanides, etc. The precipitate, which is allowed to settle, contains Prussian blue and fatty matters, which are recovered. Other methods of purification are also adopted according to the composition of the lye.

oncentration.

The next step is to concentrate the lye. During this operation considerable quantities of salt separate and cause trouble by coating the solid surfaces and preventing the transmission of heat. Various types of plant have been devised for carrying out this operation, such as that of L. Droux, of Paris, consisting of a steam-heated drum revolving in a shallow tank filled with the liquid; the removal of the salt is easy with a plant of this kind. At the present time the concentration is usually carried out in single or multiple effect vacuum evaporators, in which the liquid is kept circulating rapidly, so that solid deposits may not be formed on the heating surfaces.

If the fatty acids are to be used for the manufacture of candles, other processes of treating the oil or fat can be used, as the acids have to be distilled *in vacuo* in any case, in order to remove the dark-coloured impurities. It is also necessary to remove from them oleic acid, which has a melting-point of only 14°, and would consequently make the material too soft; the melting-points of stearic and palmitic acids are 48° and 62° respectively. This is effected partly by filtration and partly by distillation.

The method which was first used for the manufacture of stearine was to saponify with an excess of milk of lime, separate the glycerine from the lime soap, and decompose the latter with sulphuric acid. The consumption of lime and sulphuric acid was considerable, however, and the process was troublesome. Then it was found that a much smaller proportion of lime would suffice, if the operation were carried out at a high temperature and pressure. The treatment is effected at a pressure of about 120 lb. per square inch in an autoclave, provided with a mechanism for stirring. A little zinc oxide is also added sometimes to hasten the reaction. According to Lewkowitsch[1] the yield of "saponification crude glycerine" of specific gravity 1·240 by this process is about 10 per cent.

Autoclave process.

It is possible to do away with the lime entirely, and resolve the fat into acids and glycerine by merely heating with water in an autoclave, but the temperature required is high and the time long, and consequently there is much decomposition, with the result that the yields are bad and the products impure. But instead of alkaline substances such as caustic soda and lime, many other materials may be used to accelerate the saponification. One of these is sulphuric acid, which is much used for the production of candle stearine. The fat is heated to about 120° and mixed intimately with 4 to 6 per cent. of C.O.V. The yield of glycerine by this process is only 8 or 9 per cent.; the acids are very dark in colour, but a large yield is obtained of material suitable for candle making, 61 to 63 per cent. as against 45 to 47 per cent. by the autoclave process. This is due to the action of the sulphuric acid upon the oleic acid, which is converted into iso-oleic and hydroxy-stearic acids, stearo-lactone and other bodies having comparatively high melting-points. Unfortunately some of these are broken down again in the subsequent distillation.

Combined process.

The advantages of both processes can be combined by first heating in an autoclave with a small proportion of lime, and subsequently treating the fatty acids with concentrated sulphuric acid. According to Lewkowitsch[2] the yields from 100 parts tallow are then:

Candle material	61–63	parts
Oleic acid	30–32	„
Crude glycerine (s.g. 1·240)	10	„
Pitch and loss	2–3	„

Twitchell process.

In the Twitchell process[3] the fat is treated with a reagent made by the action of sulphuric acid on oleic acid dissolved in an aromatic hydro-carbon, such as naphthalene. This reagent greatly accelerates the hydrolysis of the fat, but it is not known how it acts. The fat mixed with ½ to 1 per cent. of the reagent and some water is boiled for twelve to twenty-four hours with live steam in a tank closed to prevent access of air, which would make the acids dark. The fatty layer now contains 85 to 90 per cent. of free fatty acids. The contents of the tank are allowed to settle, and the aqueous layer containing the glycerine is drawn off. A small quantity of water is then added,

---

[1] *Oils, Fats and Waxes*, 4th ed., vol. iii., p. 178.

[2] *Loc. cit.*, p. 188.

[3] Amer. Pat., 601, 603, March 29, 1898.

and the boiling is continued for another twelve to twenty-four hours. The conversion is then 97 to 98 per cent. Barium carbonate is then added until the water is neutral to methyl orange, as the presence of strong acids causes the material to discolour. This process is much used in America for the manufacture of candle material.

Ferment process.

Another catalytic agent that is used to accelerate the saponification of fats is the enzyme contained in castor-oil seeds. The reagent is prepared by decorticating the seeds, grinding them up with water, and allowing them to ferment. A creamy emulsion rises to the surface containing some 4 per cent. of albumenoid substances, which constitute the active agent. The oil to be saponified is mixed with about 40 per cent. of water and stirred to an emulsion by means of air, 5 to 8 per cent. of "ferment" are added, and 0·2 per cent. of manganese sulphate, which greatly assists the action. The whole mass is kept at a suitable temperature, which should not be above 35°, but must, of course, be higher than the melting-point of the fat. In the case of fat of high melting-point it is necessary to mix it with oil. The fermentation is allowed to proceed for one or two days, and if the emulsion shows signs of settling out, it is stirred up again with air. It is not practicable to attain much more than 80 per cent. conversion by this process. When it is finished a little sulphuric acid is added to cause the emulsion to separate, and the temperature is raised to about 80° to destroy the enzymes. Some difficulty is caused by the slowness with which the emulsion separates out: the incompleteness of the conversion is also an objection. The advantages of this and the Twitchell process are that the plant required is very simple and inexpensive, and the colour of the acids is good. The losses by either may be heavy, however, if they are mishandled.

Distillation.

Glycerine that is to be used for the manufacture of nitro-glycerine has to be purified by distillation. At one time the distillation was carried out at atmospheric pressure with superheated steam in a still heated by a fire. Under these conditions much of the glycerine was decomposed and polyglycerines were formed. Distillation with saturated steam *in vacuo* did not give good results, because the temperature of the steam was reduced too much by the expansion. The distillation is now generally carried out with superheated steam *in vacuo*. There is no great difficulty in separating the glycerine from the water in the distillate, as the boiling-points are very far apart (290° and 100° respectively at atmospheric pressure), but the distillation must be carried out with proper care to obtain the glycerine in a satisfactory state of purity. The glycerine is generally condensed in a series of metal pipes cooled by exposure to the air. In the first tubes practically anhydrous glycerine condenses; in the later ones the condensate is somewhat dilute. The former only is used for the manufacture of nitro-glycerine, the latter for a variety of purposes, such as filling gas-meters, the manufacture of ink and sizes for textiles.

Fig. 38 shows a distillation plant of the type made by George Scott and Sons, London, and very largely used in England. Over the vertical still shown in the background is a catch-pot, in which high boiling impurities, such as polyglycerines are condensed, and material such as salt, that is carried along mechanically by the vapours, is held back. After passing through the air-cooled battery, shown in the foreground, in which the glycerine is condensed, the vapour passes to a condenser cooled with water, where the water is condensed, and then to a vacuum pump. The cost of distillation is stated to be about £1 per ton.

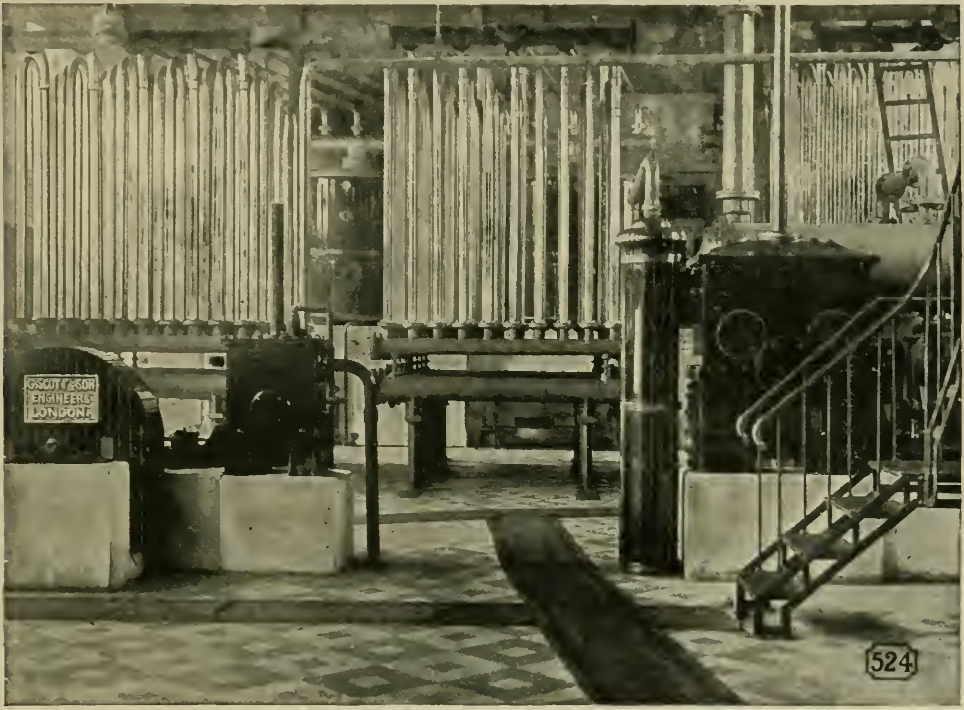


Fig. 38. Distillation Plant for Glycerine

CHAPTER XVI

MANUFACTURE OF NITRO-GLYCERINE

Early methods: Injector: Modern plant: Nitrator: Separator: Pre-wash tank: Washing: Filtering: Wash-waters: After-separation: Recent improvements: Abolition of cocks: Fume hoods: Plugs for air-holes: Softening the washing waters: Washing operations: Labyrinths: Nitrator-separator: Cooling coils: Prevention of after-separation: Drowning arrangements: Acids and yields: Time of separation: Conveyance of nitro-glycerine: Gutters: Location of factory: Air-supply: Limit boards: Thunder-storms: General precautions: Sensitiveness.

arly ethods.

IN the early days nitro-glycerine was made on quite a small scale by hand. The mixed acids were placed in a pot of iron, lead, or earthenware, surrounded by a trough containing cold water. The glycerine was then poured in slowly while the liquid was stirred by means of a rod of iron or glass. The yield obtained was sometimes as much as 2 lb. of nitro-glycerine from 1 lb. of glycerine, but was frequently considerably less. After all the glycerine had been added, the stirring was continued for a few minutes longer, then the liquid was allowed to stand and the nitro-glycerine was skimmed from the surface and poured into water, with which it was agitated. Finally it was separated from the water by means of a separating funnel. With the development of the dynamite industry the demand for nitro-glycerine grew enormously, and mechanical appliances were gradually introduced to enable larger quantities to be dealt with at a time, thus saving labour and improving the yield. Descriptions of these are to be found in the older text-books, such as those of Guttmann and Chalon.

A few years after the discovery of dynamite by Nobel in 1866 most of the essential features of the modern plant had been introduced. The nitrating vessel was a large cylindrical leaden tank with an outer wooden casing, forming a jacket through which cold water was circulated.[1] In the tank there were also coils through which cold water ran. Agitation was effected by means of compressed air led in through lead pipes, and in the earlier plants mechanical agitation was also employed. The glycerine was run in from a tank placed above the nitrator through a cock by means of which the inflow

---

[1] *See* Nathan and Rintoul, *J. Soc. Chem. Ind.*, 1908, p. 194.

was controlled. The fumes passed away through a glass pipe, which enabled the man in charge to observe their colour. He also watched the temperature by means of a long thermometer, the scale of which was above the cover, whilst the bulb was in the acid mixture. Below the nitrator a large tank was provided containing water into which the charge could be run if the temperature rose beyond control. On completion of the nitration the whole of the charge of waste acids and nitro-glycerine was run slowly into a large tank of water, which was kept in agitation by means of wooden paddles operated by hand or mechanically. The nitro-glycerine was allowed to separate out at the bottom of this tank, and was then drawn off into smaller vats and washed several times with soda solution and water until neutral.

This system involved the loss of the whole of the waste acids, and if the rate of flow into the water was not controlled very carefully, a dangerous amount of heating was liable to occur. In any case much nitrous fume was formed and there was some loss of nitro-glycerine through decomposition. For these reasons the separating tank was introduced towards the end of the 'seventies. The charge was run into this through a cock at the bottom of the nitrator, and the nitro-glycerine being lighter than the acids separated out at the top, and was transferred to the washing tank.

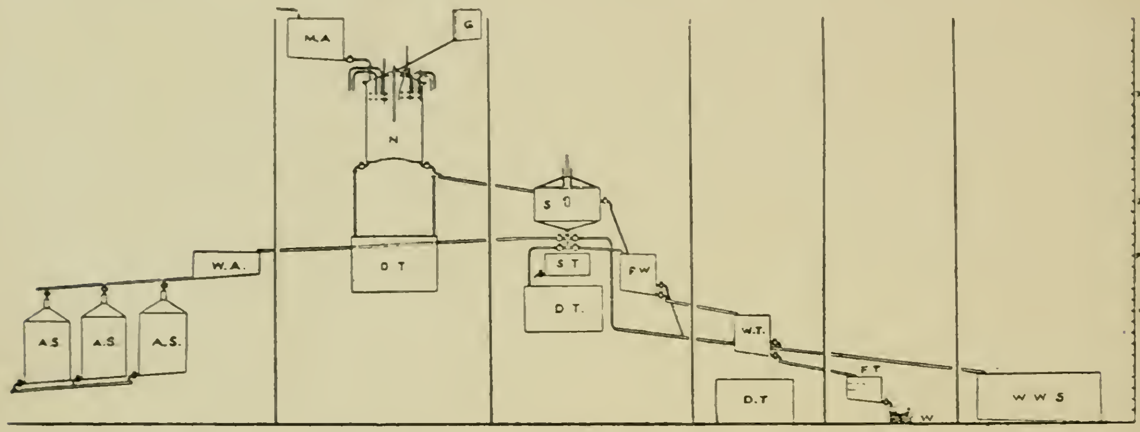
Modern plan

In America iron nitrators are still used. These have double walls, within which cold water circulates, and are provided with mechanical agitators instead of, or in addition to, compressed air. In Europe, however, such plant has long ago been superseded by leaden vessels in which the liquids are agitated by jets of air. The water before being passed through the coils is generally cooled by means of refrigerating plant to a temperature only a few degrees above its freezing-point. This enables the nitration to be carried out more rapidly and at a lower temperature. The outer water jacket has been done away with. The nitrator has frequently been made in the form of a wooden tank lined with lead, but the best modern practice is to construct it of lead only, sheet being used of sufficient thickness to stand without support.

Nitrator.

The form that the nitro-glycerine plant had generally assumed by the end of the nineteenth century may be seen from the diagram of the factory that was erected at Waltham Abbey in 1890 (Fig. 39). The nitrator was of the form that has just been described. The top consisted of a dome of lead, which was cemented on and provided with glass inspection windows. The air pipes, the pipe for the mixed acids, and the inlet and outlet pipes for the cold water coils all passed through holes in the cover; in the centre of the cover was a man-lid with an acid lute, and in the centre of that again was a hole for the insertion of the glycerine injector. This hole was closed by a loose lead plug when the injector was removed. The air used for the agitation was allowed to escape through a fume-pipe fitted with a glass cylinder to enable the man in charge to observe whether red fumes were being developed. The bottom of the tank was provided with two earthenware cocks, both of which were available if it should be necessary to drown the charge ; one of them was used for running the contents of the nitrator into the separating tank through a movable lead bend.

The mixed acids having been run into the nitrator the glycerine injector was introduced through the hole in the man-lid, and the glycerine was sprayed by means of air pressure under the surface of the acid. During nitration cold water was passed through the coils, and the contents of the nitrator were kept in a state of violent agitation by means of numerous jets of compressed air. The inflow of glycerine was regulated so as to keep the temperature of the charge at or below 22° C. When all the glycerine had been added, the injector was removed, the charge cooled down to about 15°, and then run off into the separator. In factories where refrigerated water is not available it is not always possible to nitrate at such a low temperature : the German official regulations lay down that the temperature shall never exceed 30°, and the charge must not be run into the separator until it has been reduced to 25°.



After separating house
W.A. Waste acid tank.
A.S. After separating bottles.

Nitrating house
M.A. Mixed acid tank.
G. Glycerine tank.
N. Nitrator.
D.T. Drowning tank.

Separating house
S. Separator.
S.T. Safety tank.
D.T. Drowning tank.
P.W. Pre-wash tank.

Washing house
W.T. Washing tank.
D.T. Drowning tank.

Weighing and mixing house
F.T. Filter tank.
W. Scales.

Wash water settling house
W.W.S. Wash water settling tank.

FIG. 39. Diagram of Old Nitro-glycerine Plant at Waltham Abbey.

Injector.

For introducing the glycerine into the acids an ingenious form of injector was used by Nobel, and was adopted in many factories. It consists of two metal tubes one within the other ; the outer one is for the glycerine, and the inner one for compressed air, and there are two flexible diaphragms so arranged that if the air pressure fail, or if it rise too high, the supply of glycerine is cut off. The air carries the glycerine in the form of a fine spray into the mixed acids. Formerly this appliance was made of iron, but it is now generally built of aluminium. Its one disadvantage is that it requires constant attention to keep it in good working order, and for this reason many prefer to use a simpler appliance consisting merely of a rose of lead or aluminium having a large number of holes. Through this the glycerine is forced from a closed tank. by means of air pressure, and falls as a fine rain on the surface of the acid, with which the globules are caused to mix at once by the violent agitation.

Separator.

At Waltham Abbey the separator was situated in the same building as the nitrator and the preliminary washing tank, but in many other factories the nitrator is in a building by itself, and the separator and preliminary washing tank in another. The separator at Waltham Abbey was a square lead tank, the bottom of which sloped down from all four sides to a central hole fitted with a vertical glass cylinder. A horizontal lead pipe with branches in four directions was connected to the lower end of the cylinder, and each branch was provided with an earthenware cock. Under the separator was a lead-lined tank for the purpose of catching the contents of the separator in case the glass cylinder should break. The separator was provided with a skeleton frame cover filled in with glass, the sides sloping up to a pipe which carried off the fumes; air pipes were led into the separator through the cover, so that if there should be any sign of spontaneous heating in the nitro-glycerine, it could be stirred up and mixed again with the waste acids, which would reduce the temperature once more. A thermometer passed through the lid of the vessel with its bulb in the nitro-glycerine and its scale above the lid, so that any rise of temperature could be seen at once. On the side of the separator there was a glass inspection window, also an earthenware cock situated about 4 inches below the surface of the nitro-glycerine. When the separation was complete, the bulk of the nitro-glycerine was run off through this cock into the preliminary washing tank. The waste acid was then run away through one of the branches of the bottom pipe to the "after-separating house." As soon as the rest of the nitro-glycerine was seen coming down into the glass cylinder, the cock leading to the after-separating house was closed, and the one leading to the "pre-wash" tank was opened, and the remainder of the nitro-glycerine run into this tank. Of the other two cocks at the bottom of the separator one was used for running to the "wash-water settling house" any thick sludge, that separated at the surface dividing the acid from the nitro-glycerine, and the other was connected to the drowning tank.

In some factories an open separator was used instead of a closed tank, and the nitro-glycerine as it separated was removed by hand with a metal skimmer, generally of aluminium, and transferred little by little to the pre-wash tank.

Pre-wash tank.

The old pattern of preliminary washing tank, usually called the "pre-wash tank," was fitted with two earthenware cocks, an upper one for running off the washing waters, and the lower one to run the nitro-glycerine to the washing house. The air pipe for agitating the charge was laid loosely on the bottom; another pipe was led into the bottom faucet down the inside of the tank; the tank was open at the top. The object of "pre-washing" is to remove the bulk of the acid from the nitro-glycerine as quickly as possible, and render it almost neutral before it is sent down to the washing house. To do this it is agitated for a few minutes with about four different lots of wash-water and then with a weak solution of sodium carbonate.

Washing. The washing tank was similar to this and was provided with cocks, one at the bottom for running off the nitro-glycerine, and one or more skimming cocks at different levels. An alternative arrangement for running off the wash-water was a skimmer, a saucer-shaped funnel attached to a rubber pipe, which led through the side of the tank to the wash-water gutter. The early form of skimmer was of lead supported by means of a rope and counter weight. Later patterns were made of lighter material, such as brass covered with rubber cloth.

Filtering. The filtration of the washed nitro-glycerine is generally carried out in the washing house in a leaden tank. Formerly it was filtered through dry, coarse-grained salt contained in a flannel bag supported on wire gauze. The greater part of the water in suspension in the nitro-glycerine was absorbed by the salt, whilst the nitro-glycerine flowed into the tank. This had an earthenware cock by means of which the nitro-glycerine was run into a rubber bucket standing on the pan of a pair of scales, so that the correct quantity could be weighed out for a charge of the explosive that was to be made. At the end of the day's work, or oftener if necessary, the salt bag was renewed, and the salt was dissolved in warm water to recover any nitro-glycerine it might contain.

The filtration is now carried out at Waltham Abbey not in the washing but in the mixing houses. The nitro-glycerine runs down a gutter to the mixing house, and from there into a plain lead tank with a false bottom of perforated lead, on which lies a layer of sponges sewn up in flannel. The nitro-glycerine filters through the sponges, which retain the moisture and flocculent matter. The nitro-glycerine is drawn off from the tank by means of a rubber tube, through which it flows to the measuring vessel (*see* p. 306) which is placed just below it.

Wash-waters. All the waters used for washing the nitro-glycerine and plant are run down lead gutters into a large tank in the "wash-water settling house," and the contents of the tank are kept agitated by means of compressed air. At the end of the day's work the air is shut off and any nitro-glycerine is allowed to settle out. This is drawn off from the bottom of the tank and returned to the pre-wash tank. The residual mud consists mostly of lead sulphate mixed with water and nitro-glycerine and some sand, wool, etc. It is rendered alkaline with soda solution, and filtered and washed with warm water in the "mud hut." This converts most of the lead sulphate into carbonate, and renders the material much less dangerous. The mud is subsequently wrung out in flannel to remove us much nitro-glycerine as possible, and finally it is mixed with kerosine and burnt. At Waltham Abbey the wash-waters are finally run into a small pond, in which a couple of dynamite cartridges are exploded every week so as to destroy any nitro-glycerine that may still be present.

After-separation.

The waste acid from the separator carries with it some nitro-glycerine, which is present in it in three forms: there are some minute globules, which have not had time to separate out completely, there is some in solution in the acids, and there is some, which may be called "potential nitro-glycerine," which has not actually been formed, but is present as mono- and di-nitro-glycerine, and may be converted into tri-nitro-glycerine on standing, so causing a further separation at the surface of the acids. In order to avoid the great danger that would be caused by the separation of nitro-glycerine in any part of the acid plant, the waste acid is generally allowed to stand first for several days in an "after-separator" (German: "Nachscheider"). This consists of a large cylindrical lead tank with a conical top surmounted by a glass cylinder. It is filled until the surface of the liquid is visible inside the glass. Any nitro-glycerine that separates is removed by the attendant with a small aluminium scoop, and washed with water in a small lead tank, and then carried over by hand in a rubber bucket to the washing house. The after-separating house contains a number of after-separators so that it can hold several days' supply of waste acid.

Recent improvements.

During the first years of the present century a number of important improvements were introduced at the Royal Gunpowder Factory, Waltham Abbey, into the methods of manufacturing nitro-glycerine, as also into the other processes carried out there. Those relating to the manufacture of gun-cotton have been mentioned in Chapters XII and XIII. Major (now Lt.-Col. Sir) F. L. Nathan was the Superintendent, and Mr. J. M. Thomson the Manager, and the nitro-glycerine plant was under the charge of Mr. W. Rintoul. The far-reaching alterations have been dealt with by the first two named of these in the *Journal of the Society of Chemical Industry*, 1908, p. 193.

Washing.

The operation of washing the nitro-glycerine would appear to be a comparatively safe one as the material is neutral or alkaline, and it is only subjected to agitation by means of compressed air; yet there have been a considerable number of fatal accidents in washing houses. H.M. Chief Inspector of Explosives in his Special Report No. 162 on the explosion at Faversham on November 9, 1903, gives a list of nine, which had occurred in Great Britain alone, and there was another one at Hayle on January 5, 1904 (Special Report No. 164), as well as a considerable number in other countries. One possible cause of some of these catastrophes was the presence of the loose air-pipe, which was simply laid on the bottom of the tank: it is quite conceivable that the jarring of this pipe on to the bottom of the tank might in exceptional circumstances cause an explosion. The air-pipe is now carried down the outside of the tank from above the level of the liquid and is burnt on to the under surface of the bottom of the tank. Holes are pierced through at intervals, and there is a hole in the end of each branch of the air-pipe so arranged that any nitro-glycerine, that has lodged in the pipe, will be blown out again into a shallow depression which slopes down to the outlet.

The wooden casing of the washing tanks has also been done away with. It was always possible that a small leak might be formed through which nitro-glycerine would pass and soak into the wood and there set up a dangerous decomposition, and nitro-glycerine was always liable to get spilt or splashed on to the wood.

Abolition of cocks.

Another possible source of danger was the presence of the numerous cocks through which the nitro-glycerine had to pass. Friction might be caused if the cock stuck, or if the nitro-glycerine froze in or around it: also if the hole through the key of the cock were not quite straight, there might be a pocket in which nitro-glycerine could lodge and set up decomposition. Soft rubber tubing has now been substituted for the cocks, arranged as is shown in Fig. 40, which, however, still shows a wooden casing to the tank. The soft rubber tube, *d*, is fixed over the outlet lead pipe, and is kept closed by slipping it over the hollow lead plug, *e*, through which a small current of air is passed whilst the nitro-glycerine is being washed. When the charge is ready to be run off, the air is shut down, and the rubber tube kinked in the hand and pulled off the plug. The flow of the nitro-glycerine can be controlled by pinching the tube with the hand. The skimming tube, *c*, is also of soft rubber: the hard and heavy skimmer has been done away with. This skimming tube has since been improved by widening it at the mouth funnel-wise and providing it with a rubber handle.

It has been suggested that the explosions in washing tanks may have been caused by the generation of electricity by the friction of the air when passing through the jets in the air-pipes. But air or other gas cannot produce electricity by friction, as was shown by Faraday.[1] It is only when the air carries with it particles of solid matter or liquid globules that any charge is formed, and then only if the solid or liquid matter be itself non-conducting. The nitro-glycerine is surrounded on all sides by conductors: on its upper surface by soda solution, and everywhere else by lead, so that any charge would be rapidly discharged, especially as the nitro-glycerine is kept in motion and is

---

[1] "Experimental Researches in Electricity." Series XVIII., *Phil. Trans.*, January 1843.

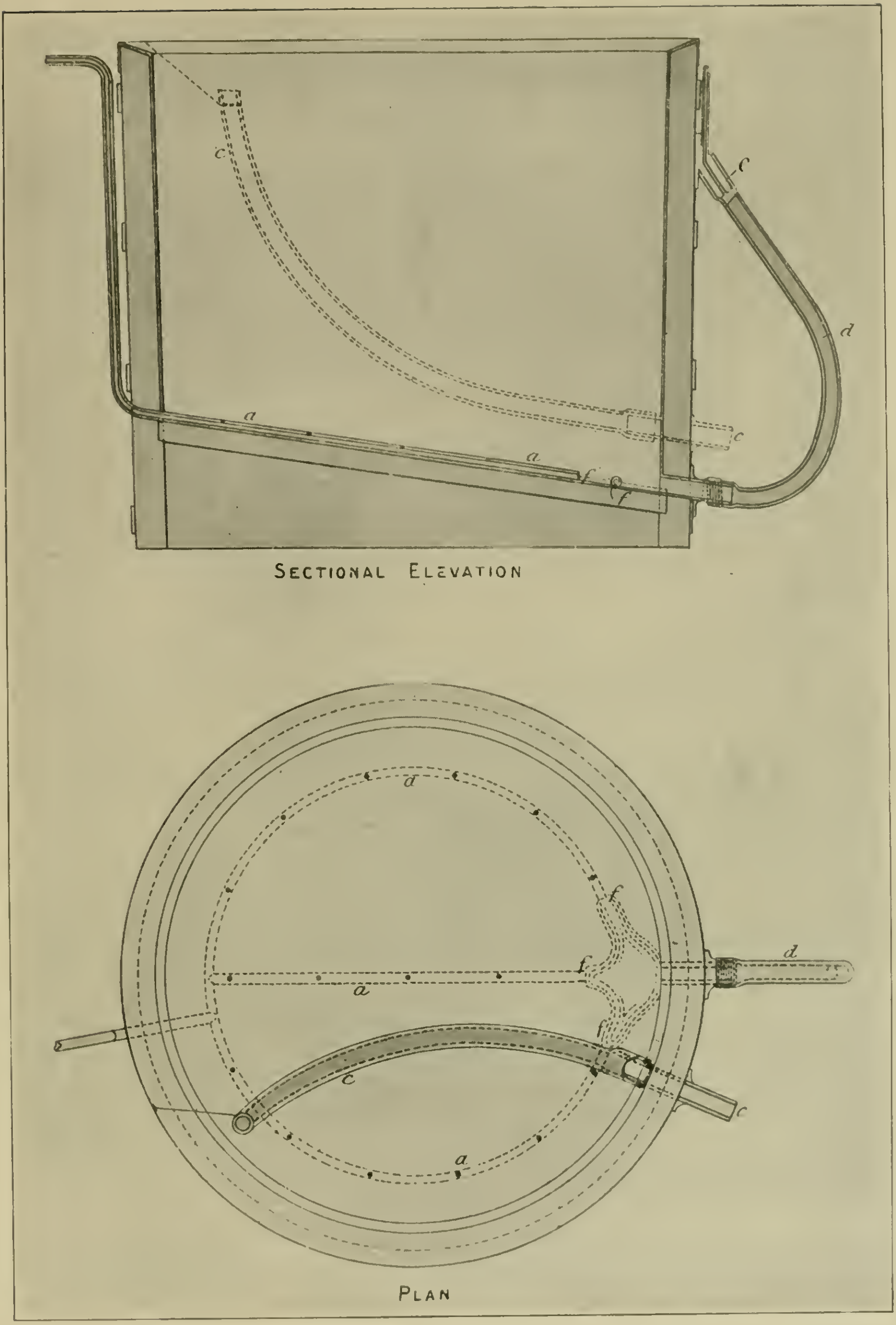


Fig. 40. Nitro-glycerine Washing Tank

a, Air-pipe

c, Skimming tube for wash-waters

d, Outlet pipe for nitro-glycerine

e, Hollow lead plug for end of *d*

ff, Holes in ends of branches of air-pipe mixed with drops of the soda solution. Experiments carried out at Ardeer failed to detect any charge of electricity.[1]

Fume hoods.

The pre-wash tank is constructed in the same way as the final washing tank: the principal difference lies in the arrangements made for conducting away the fumes. The air rising from the pre-wash tank carries some nitric acid with it as well as fumes of the nitric esters of glycerine: the tank has a fixed lead cover with an opening, which is kept covered with a small rubber flap, and there is a fume pipe through which the fumes are drawn by means of a jet of air or steam. From the washing tank the air carries away only vapour of water and nitro-glycerine, consequently the lead top is unnecessary: it is merely provided with a hood of rubber cloth shaped like a large inverted funnel, the stem of which passes out through the roof and is provided with an air jet to keep a current of air going in an upward direction during the whole of the time of the washing. The removal of the fumes of nitro-glycerine makes the work much less trying to the workmen. In the pre-wash tank the air-holes in the bottom are bushed with small perforated ebonite plugs to prevent the rapid enlargement of the holes, but in the final washing tanks these small plugs are unnecessary as the wear is very slow.

Plugs for air-holes.

Softening the washing water.

A very hard stony deposit consisting mostly of calcium carbonate used to be formed on the inside surface of the washing tank, due to the action of the soda solution on the hard water employed. This was another possible source of danger. The formation is now prevented by softening the water before use. There is a large tank in the charge house above the level of the nitrating house, and in this sufficient water is treated each day to suffice for all the washing operations of the next day. Enough lime and sodium carbonate is added to precipitate the bicarbonate and sulphate of calcium and the magnesia, and the water is well agitated and allowed to settle over night.

Washing tanks should be made wide and shallow, because a reduction in the depth of the liquid greatly diminishes the time required for the separation of the nitro-glycerine from the water. At the Royal Gunpowder Factory comparative trials were carried out with two different designs of tank, the proportion of water to nitro-glycerine and all other conditions being kept constant. The depth of liquid only was varied by having the tanks of different diameters. The results were:

Total depth of liquid	Mean time of separation
27¼ in.	34½, 28¼ secs.
18½ in.	10, 9½ „

Washing operations.

In the pre-wash tank the nitro-glycerine is usually washed about four times at a temperature of about 18° C. The first three washings are with water only, but the last with some soda, so as to remove all but a small quantity of the acid. The nitro-glycerine is then sent down a gutter to the washing house.

---

[1] *See S.R.*, 156, p. 8.

where the final washing is carried out. The number and duration of the washings vary considerably in different works, but the following scheme is a good one :

1st	washing	15	minutes	with dilute soda (3½ per cent. Na_1CO_3)
2nd	,,	30	,,	,, ,, ,, ,, ,
3rd	,,	45	,,	,, ,, ,, ,, ,,
4th	,,	15	,,	with softened water only
5th	,,	15	,,	,, ,, ,,

Temperature of washing 30° C., proportion of soda solution or water to nitro-glycerine 4 : 10 by weight.

Labyrinths

All the wash-waters from the pre-wash and final washing tanks are run through labyrinths before they pass to the wash-water settling tank, and from the latter they again pass through a labyrinth before they reach the pond. The labyrinth consists of a long lead tank open at the top and provided with a number of transverse partitions so arranged that the water has to flow alternately over one and under the next. The bottom is inclined gently to a central channel, which runs the whole length of the vessel ; there is also a fall towards the exit end. Most of the globules of nitro-glycerine collect in this central channel, and can be drawn off through a rubber tube arranged in the same way as the delivery tube of the washing tank. Since the introduction of these labyrinths at Waltham Abbey the amount of nitro-glycerine that is recoverable from the wash-water settling tank is only 1½ per cent., whereas formerly it was about 4½ per cent.

Nitrator-separator.

In those parts of the plant where the nitro-glycerine is mixed with strong acid, *i.e.* the nitrator and separator, it is not possible to make use of delivery tubes of rubber, such as have been substituted for cocks in all other parts of the nitro-glycerine plant. Yet cocks are specially dangerous here as the acid nitro-glycerine is more liable to spontaneous decomposition than when it is neutral or slightly alkaline. In January 1901, this danger was brought home at the Royal Gunpowder Factory in a very forcible manner : shortly after the charge had been run out of the nitrating apparatus an explosion occurred in one of the earthenware cocks leading to the drowning tank. If the apparatus had contained the charge, a serious accident must inevitably have occurred. This led to the idea of removing the nitro-glycerine at the top of the nitrator instead of at the bottom ; a method the accomplishment of which was rendered more easy by the fact that the nitro-glycerine separates out at the top of the charge. The simplest way to effect this was to raise the whole of the contents of the apparatus, so that the nitro-glycerine would flow over a suitable arrangement in the cover and run by gravity into the pre-wash tank, and the best method for raising the level was to introduce waste acid from a previous charge at the bottom of the vessel.

The form of plant adopted to carry out this principle is shown in Fig. 41, and is protected by English Patent No. 15,983, dated August 8, 1901, taken out in the joint names of Nathan, Thomson, and Rintoul. The separation of the nitro-glycerine from the acids takes place in the same vessel as the nitration, and for this reason the inventors call it a "nitrator-separator." It consists of a cylindrical lead vessel, *a*, with a bottom sloping in one direction, and containing cooling coils and air-pipes, the number of which depends on the size of the vessel. The cooling coils enter and leave through the sides just below the surface of the nitrating acid, as also do the air-pipes, *g*. The cooling water is led in and out again through one main pipe controlled by a single cock, and the coils, *h*, branch away from this main pipe inside the vessel. The supports for the coils are of lead, and are formed by loading up between the turns; this arrangement obviates the use of lead-covered iron supports, and entirely does away with interstices in which nitro-glycerine or sulphate can lodge. The cover is conical, and is burnt on to the cylindrical portion; it terminates in a cylinder, *e*, of small diameter open at the top and provided with glass inspection windows, *f*; the only other fitting in the cover is a gland, through which the thermometer, *s*, passes. A pipe, *k*, opens out of one side of the cylinder, and from this another pipe, *m*, branches for carrying away the fumes, suction being produced by means of an air-jet. At a little distance beyond this fume pipe *k* opens out to a gutter leading down at an incline to the pre-wash tank. The pipe, *d*, for introducing the mixed acid into the apparatus, as well as the waste acid for the displacement, enters the vessel at the bottom. In order to prevent any nitro-glycerine getting into the acid supply pipe it is carried vertically downwards below the bottom of the vessel and rises again into it. There are two branches, *b*, *c*, leading out of this pipe, each with an earthenware cock; *b* leads to the waste-acid egg, and *c* to the drowning tank.

Manipulation of nitrator-separator.

The waste acid from the previous charge having been run out of the vessel, the cock on the nitrating-acid tank is opened, and the acid is allowed to run into the nitrator-separator by opening the cock on the acid supply pipe, *d*. As soon as the acid has all run in, the cock on the nitrating-acid tank is closed as well as that on the acid supply pipe, and the acid having been brought to the desired temperature by means of the cooling coils the injector is inserted through the open top of the apparatus, and the nitration is commenced. The temperature of the cooling water, which flows through the coils is regulated so that the total time of nitration for any given charge is kept constant within fairly narrow limits both winter and summer. To enable this to be done the water is refrigerated when necessary. The advantages of using refrigerated water are that nitration is completed in a reasonable time, loss of nitric acid due to volatilization is reduced, and the time of nitration being constant the operations of the factory can be carried out in a systematic manner. The

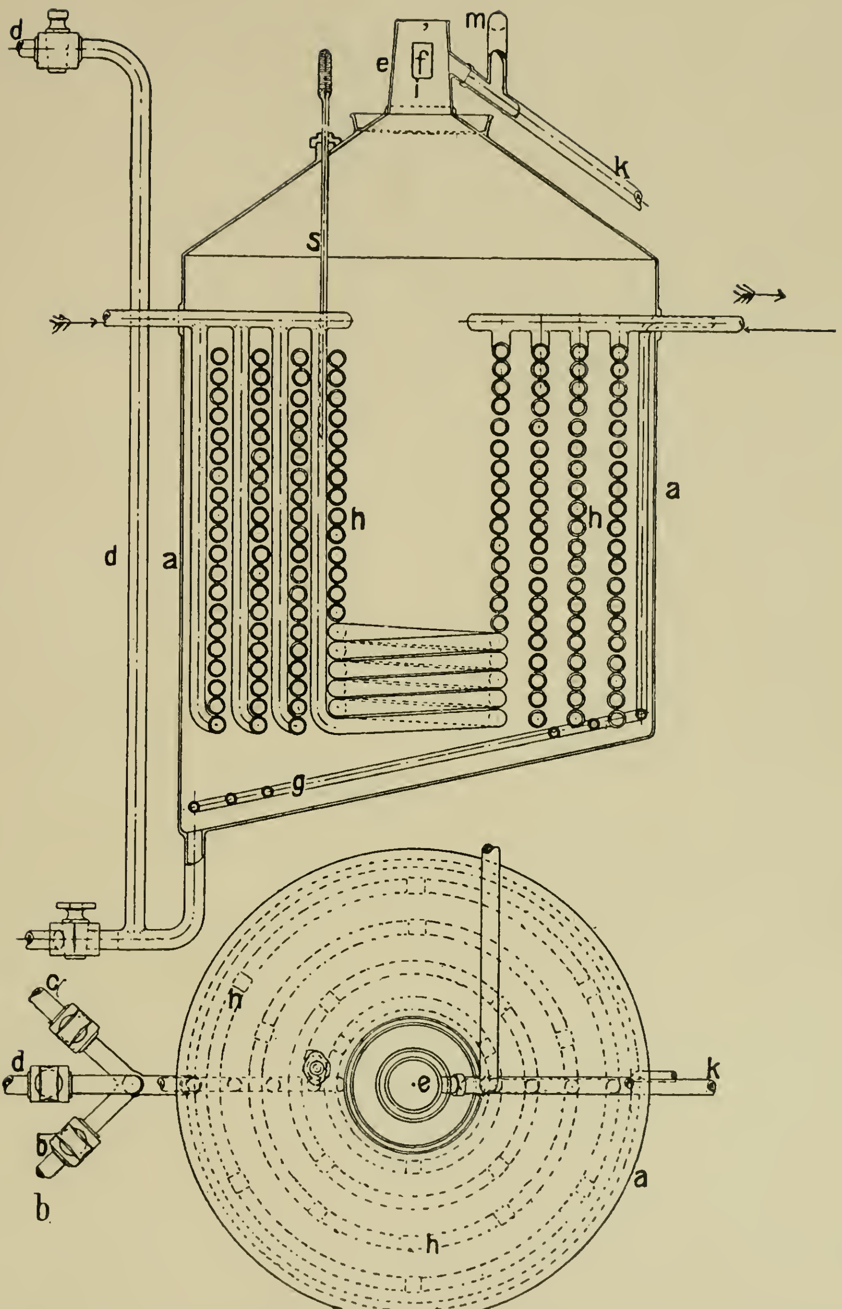


FIG. 41. Nitrator-Separator for the Manufacture of Nitro-glycerine (from *S S*)

volatilized nitric acid is carried away to a Guttmann condensing tower provided with a circulating arrangement for the liquid ; the fumes are thus condensed and about 18 lb. of nitric acid of specific gravity 1·32 are recovered per ton of nitro-glycerine produced. When nitration is completed, the injector is removed, and the nitro-glycerine is allowed to separate for a few minutes. The cock leading from the displacement waste-acid tank is then opened, and waste acid is allowed to enter the apparatus at the bottom by opening the acid supply pipe. The rate of inflow of the displacing acid can be regulated with the utmost nicety, so as to allow of the nitro-glycerine flowing over through the gutter to the pre-wash tank as it separates. The dividing line between the clear nitro-glycerine and the acid is watched through the inspection windows.

The nitrator-separator is left full of waste acid until it is required for the nitration of another charge. The result of this is that no part of the interior of the apparatus is exposed to acid fumes, and its life is greatly increased. In the old form of plant, in which this could not be done, and the coils entered through the cover, it was necessary to remove the cover and the coils as often as once in every three months to repair them. The new form of apparatus was in use for two and a quarter years without being opened up, and then the whole of the interior including the coils and air-pipes were found to be as good as new, and no repairs of any kind were required. As a precaution the cooling coils are tested every week by air pressure before commencing work ; any leak would be detected at once by the escape of air bubbles through the waste acid.

Cooling coils. It is well to arrange the exit pipe from the coils so that the water in them is under a slight vacuum. If a small leak does develop, the acid will then enter the coils where it will be drowned by the large volume of water, and the defect will be shown by a rise in the temperature of the water leaving the coils. In Germany several explosions have been ascribed to the bursting of the coils, but no such accidents appear to have occurred in England. It has been proposed by the Explosive Works, Dr. R. Nahnsen and Co. of Hamburg, to use chloroform, carbon tetrachloride, or other similar chlorine derivatives for circulating through the coils,[1] but this does not appear to be necessary provided that reasonable precautions are taken.

Prevention of after-separa- ion. The after-separating house has for some time ceased to exist at the Royal Gunpowder Factory. Its abolition was rendered possible by the fact that the addition of water to the waste acid not only prevents the formation of more nitro-glycerine, but also absorbs any that exists as minute globules in the waste acid.[2] Originally only 2 per cent. of water was added to the waste acid, as this quantity was found to be sufficient at the normal temperature of storage, 10° to 15° C., to prevent any further separation. But on

---

[1] Ger. Pat. Anm. 31,837, July 6, 1910 ; *S.S.*, 1912, p. 36.

[2] Nathan, Thomson and Rintoul, Eng. Pat. 3020, February 9, 1903.

January 15, 1906, a fatal accident occurred with a drum of nitro-glycerine waste acid, which was part of a consignment sent by the Explosives and Chemical Products Ltd., to Messrs. F. W. Berk and Co. In consequence of this, further experiments were carried out at Waltham Abbey, which are given in detail in Special Report No. 174 of H.M. Chief Inspector of Explosives. It was then found that in order to prevent further separation of nitro-glycerine, when the temperature of the waste acid is reduced to 0° C. it is necessary to add 5 per cent. of water. The fact that when the temperature is reduced the solubility of nitro-glycerine in waste acid is considerably diminished should be kept constantly in mind. In Germany, where large variations of temperature are more liable to occur than in England, there have been several accidents due to the further formation of nitro-glycerine on the surface of acid that had been subjected to after-separation for a considerable time. However the waste acids are treated, they should not afterwards be allowed to fall to a very low temperature, and the denitration should take place as

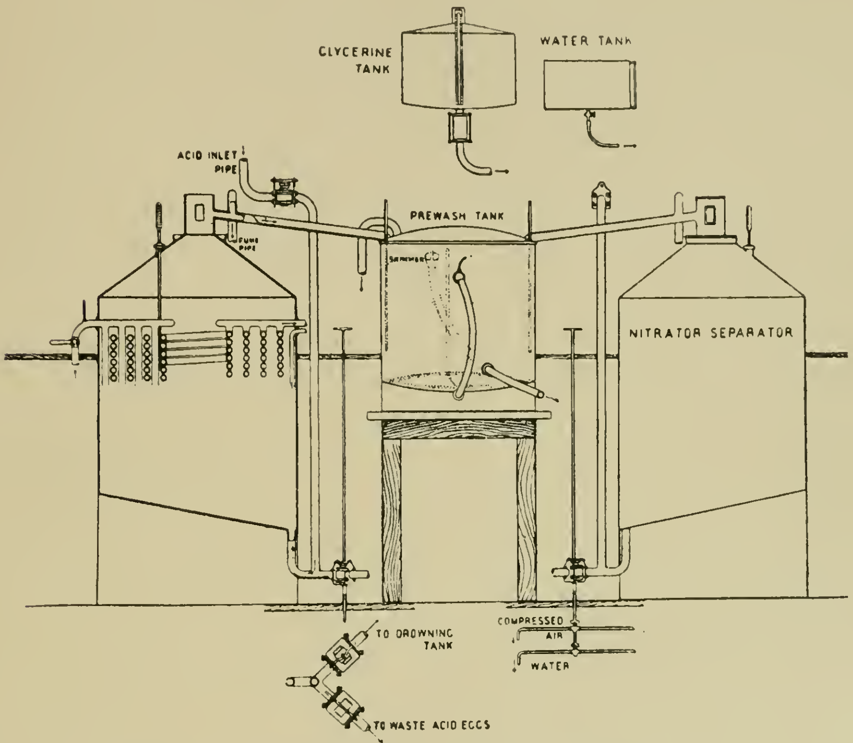
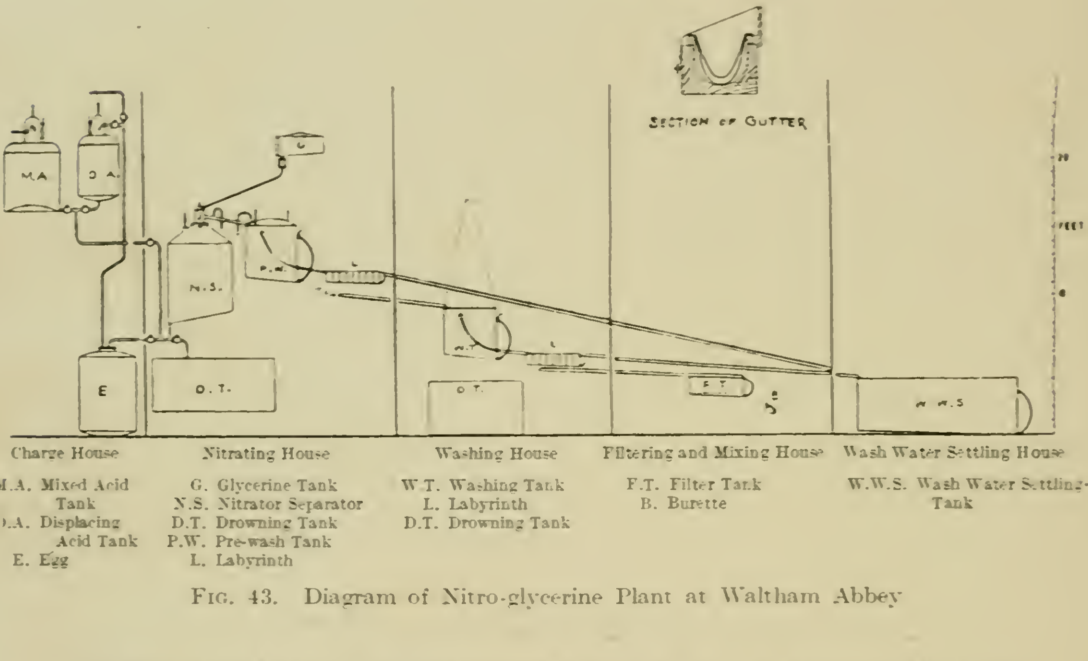


FIG. 42. Waltham Abbey Nitrating-House Plant

soon as possible. If after-separation has taken place without the addition of water, the acid should afterwards be kept at a higher temperature than that at which the after-separation was effected.

The method adopted for dealing with the waste acids in the nitrator-separator is as follows: The waste acid is allowed to remain in the vessel until this is required for another nitration, any nitro-glycerine separating in the interval being displaced in the usual way into the pre-wash tank. Further separation is promoted by cooling down the waste acid. When the nitrator is to be emptied, every trace of nitro-glycerine is removed from the surface of the acid, and the quantity of waste acid required for the displacement of a subsequent charge is then run out of the nitrator into an egg, and blown into the displacing acid tank in the charge house. To the remainder of the waste acid in the nitrator 2 per cent. of water is then added, the contents of the nitrator being strongly agitated meanwhile by means of air. The waste acid is then sent into an egg and blown up to a tank in the denitrating house. As a further precaution all waste acid is kept at a temperature of about 15° C.



Charge House

M.A. Mixed Acid Tank
D.A. Displacing Acid Tank
E. Egg

Nitrating House

G. Glycerine Tank
N.S. Nitrator Separator
D.T. Drowning Tank
P.W. Pre-wash Tank
L. Labyrinth

Washing House

W.T. Washing Tank
L. Labyrinth
D.T. Drowning Tank

Filtering and Mixing House

F.T. Filter Tank
B. Burette

Wash Water Settling House

W.W.S. Wash Water Settling-Tank

FIG. 43. Diagram of Nitro-glycerine Plant at Waltham Abbey

The new Waltham Abbey plant is shown diagrammatically in Figs. 42, 43. One great advantage of the plant is that the elevation of the nitrator above the wash-water settling tank is less than half what it was with the old style of plant, viz. 16 feet instead of $33\frac{1}{2}$ feet.[1] The separating and after-separating houses are dispensed with, with the result that the factory occupies less space, and there are fewer pieces of apparatus.

The safety of the manufacture is increased by the absence of cocks, and by the removal of the nitro-glycerine from contact with the acid as soon as it has separated from it. This is an especially great improvement over the procedure in the factories where the separator is in a different house to the nitrator, for there the acid nitro-glycerine has to flow down a long gutter from one house to the other. The presence of cooling coils during the separation is also an advantage. As fewer men are required to work the plant the risk to personnel is correspondingly reduced.

The diminution of danger during separation is a matter of considerable importance as there have been a number of disastrous explosions in nitro-glycerine separators. On February 18, 1904, the separator at the Cliffe Factory started to fume violently and then exploded, causing the death of four men and much structural damage.[2] At Avigliana, in Italy, a similar accident occurred in April 1912, and although the men in the house were able to escape before the explosion, it caused another house to blow up, and two men were thereby killed. In July 1912, a few days after the separating house had been rebuilt, it blew up again. This time the nitro-glycerine caught alight, but again the men in the house were able to escape before the remainder of the charge exploded ; no one was killed, but the material damage amounted to £8000. Similar cases of charges taking fire in the separator have occurred in Mexico. An explosion, due to violent decomposition of nitro-glycerine in a separator, took place on March 1, 1911, at the factory at Umbogintwini in South Africa ; it was ascribed to the use of defective glycerine made locally from whale oil. In 1907 a German nitro-glycerine factory was destroyed by an explosion originating in the separator.

Drowning arrangeme

The drowning cock is controlled by means of a long rod terminating in a handle situated on the operating platform. By turning this handle through a quarter of a circle not only are the contents of the nitrator-separator allowed to run into the drowning tank, but at the same time compressed air is turned on to agitate the contents of the tank, and water is also admitted. The drowning tank is always kept full of water, and is provided with an overflow. This drowning arrangement has the advantage of simplicity, and the continuous

---

[1] It has been proposed to reduce the necessary fall in the nitro-glycerine factory still further by causing the nitro-glycerine to rise from the bottom of the washing tanks through rubber tubes by the weight of a sufficiently high column of water introduced above (Wharton, Shacklady and Curtis's and Harvey, Ltd., Eng. Pat. 23,871, October 14, 1910). Messrs. Curtis's and Harvey have erected a plant with all the vessels for the different operations in the same building, so that the separating, washing, filtering, and measuring of the nitro-glycerine into boxes can be carried out without running it down long gutters to other buildings.

[2] *See S.R.*, No. 167.

supply of cold water keeps down the temperature due to the mixing of a large volume of acid with the water, and also allows of a smaller drowning tank being used than would otherwise be necessary.

The regulations of the German Trade Guild (§ 10) are somewhat similar. It is there laid down that the drowning tank must have a capacity equal to at least five times the volume of the acid, and is to be provided with stirring arrangements and a water inlet at the bottom of the tank of such a size that the acid will be rapidly displaced and no heating of the nitro-glycerine will take place. The drowning tanks must always be kept with the proper quantity of water in them. The water inlet and the air for stirring must be turned on simultaneously with the drowning cock, or must be so arranged that they can be operated from a place of safety outside the traverse. In some cases these cocks are so arranged that they are all operated simultaneously by compressed air, which can be turned on from several points,[1] but it is not advisable to make such arrangements too complex, as they are not only liable to fail, but through some combination of peculiar circumstances they may act wrongly in an emergency, and so whilst preventing an explosion in one house, cause one in another.

cids and
elds.

Before oleum could be obtained at a reasonable cost, it was usual to use an acid made by mixing about 5 parts of C.O.V. with 3 parts of concentrated nitric acid (sp. gr. 1·50). At Waltham Abbey 8 parts of the mixed acid were used to nitrate 1 of glycerine, but in some other works a smaller amount of acid was employed, often 7½ parts to 1 of glycerine.

Theoretically 100 parts of glycerine should give 246·7 parts of nitro-glycerine, but for several reasons this yield is never attained in practical manufacture. The average yield at the Royal Gunpowder Factory over a series of eight years was 214¼ per cent., but after the introduction of the nitrator-separator and other improvements it was 220·2 per cent. as an average of two years' working with the proportions just mentioned. There is practically no oxidation of the glycerine, consequently the reaction may be represented by the following Table :

Before nitrating			After nitrating		
		Per cent.			Per cent.
$C_3H_5(OH)_3$	100		$C_3H_5(NO_3)_3$	246·7	
H_2SO_4	480	60·0	H_2SO_4	480·0	73·5
HNO_3	273	34·1	HNO_3	67·6	10·3
H_2O	47	5·9	H_2O	105·7	16·2
	800	100·0		653·3	100·0)

---

[1] *See* Lesser, *S.S.*, 1907, p. 48.

The water present in the nitrating acids performs no useful function. It might be eliminated, and acid used as follows:

Before nitrating			After nitrating		
		Per cent.			Per cent.
$C_3H_5(OH)_3$	100		$C_3H_5(NO_3)_3$	246·7	
H_2SO_4	266·6	52·3	H_2SO_4	266·6	73·5
HNO_3	242·9	47·7	HNO_3	37·5	10·3
H_2O	0	0	H_2O	58·7	16·2
	509·5	100·0		362·8	100·0

But it is more usual to use an acid containing 1 to 2 per cent. water. The following results have, for instance, been recorded by:

	Soddy	Chalon	Hofwimmer
Acid:			
H_2SO_4	58·4	57·3	52·5
HNO_3	40·0	41·3	46·5
H_2O	1·6	1·4	1·0
Proportion Acid : Glycerine	6·12, 5·88	6·2	6·3, 5·3
Yield	232, 236	232	228, 221

The results given by Soddy were obtained with a nitrator-separator at a factory in Mexico;[1] those by Chalon in a similar plant in the dynamite works of Boceda, in Italy.[2] Hofwimmer's figures were obtained from laboratory experiments in which the proportion of acid to glycerine was varied through a wide range;[3] the maximum yield was obtained with the proportion 6·3 : 1, but the most remunerative proportion at the prices of materials assumed was 5·3 : 1. At Waltham Abbey, with a proportion 6·13 : 1, the yield for a period of nearly two years was 229 per cent.

The differences between the yields generally obtained and the theoretically possible yield of 246·7 per cent. is due to the influence of various factors. The practical yields are generally calculated upon the glycerine as nitrated, whereas this glycerine does not usually contain more than 97 per cent. of glycerol.

---

[1] *Arms and Exp.*, March 1911.

[2] *Explosifs modernes*, 1911, p. 222.

[3] *Chem. Zeit.*, 1911, 35, p. 1229. Hofwimmer has given the results of further laboratory experiments in *S.S.*, 1913, p. 36.

The waste acid produced on nitration absorbs a further quantity of the nitro-glycerine, the proportion absorbed depending upon the composition of the waste acid. A still further quantity of the nitro-glycerine disappears in solution in the wash waters from the pre-washing and washing operations.

The solubility of nitro-glycerine in acids of varying composition formed the subject of numerous experiments at the Royal Gunpowder Factory.[1] When nitro-glycerine is added to a mixed acid, it first dissolves unchanged, but part of it is at once decomposed with the formation of other esters, such as glycerol trisulphate, the production of which may be represented by the reversible reaction: $C_3H_5(ONO_2)_3 + 3H_2SO_4 \rightleftharpoons C_3H_5(SO_4H)_3 + 3HNO_3$. The nitro-glycerine dissolved as such was determined by shaking out rapidly with chloroform, and the nitro-glycerine decomposed was estimated by difference. Fig. 44 shows the amount of nitro-glycerine taken up by acid containing water and nitric acid in the constant ratio 1·1 : 1 and varying percentages of sulphuric acid. It will be seen that portions of the curves are represented by shaded lines. This indicates that on attempting to saturate acids in this zone oxidation of the glycerine radicle occurred, and the results were vitiated. An uncontrollable reaction would set in if special precautions were not taken: no acid of a composition in or near this zone should ever be allowed to come in contact with nitro-glycerine in a manufacturing operation. Fig. 45 shows the results that were obtained with acids in which the ratio of sulphuric acid to water was kept constant at 5·8 and the nitric acid was varied. In Fig. 46 the ratio of sulphuric to nitric acid was kept constant at 10·4, and the water was varied. Fig. 47 was obtained with mixtures of sulphuric acid and water only; here again oxidation took place with acids of 50 to 85 per cent. strength. All these solubility determinations were carried out at 20° C. It will be seen that all the curves with mixed acids show a distinct minimum, which points to the fact that there must be a certain composition of acid which will be the most economical to use.

ime of eparation

The time that the nitro-glycerine takes to separate from the acid is liable to vary within wide limits: when the separation is carried out in a special separator, it may be anything from a quarter of an hour up to several hours. Long separations are very inconvenient as they disorganize the whole of the work of the factory. In the early days of the industry they were generally attributed to impurities in the glycerine, and probably with justice. In the Boutmy system of manufacturing nitro-glycerine the glycerine was dissolved first in sulphuric acid, the solution was cooled and then a mixture of nitric and sulphuric acids was added. But as a result of the action of the concentrated sulphuric acid on the glycerine and the impurities in it, products were formed, which greatly impeded the separation: no nitro-glycerine was taken off until twenty-four hours had elapsed, and then the acids were transferred to carboys

---

[1] *See* Nathan and Rintoul, *loc. cit.*

or other vessels, where further separation occurred and might continue for a month.[1]

Since the introduction of good distilled glycerine, one cause of long separa-

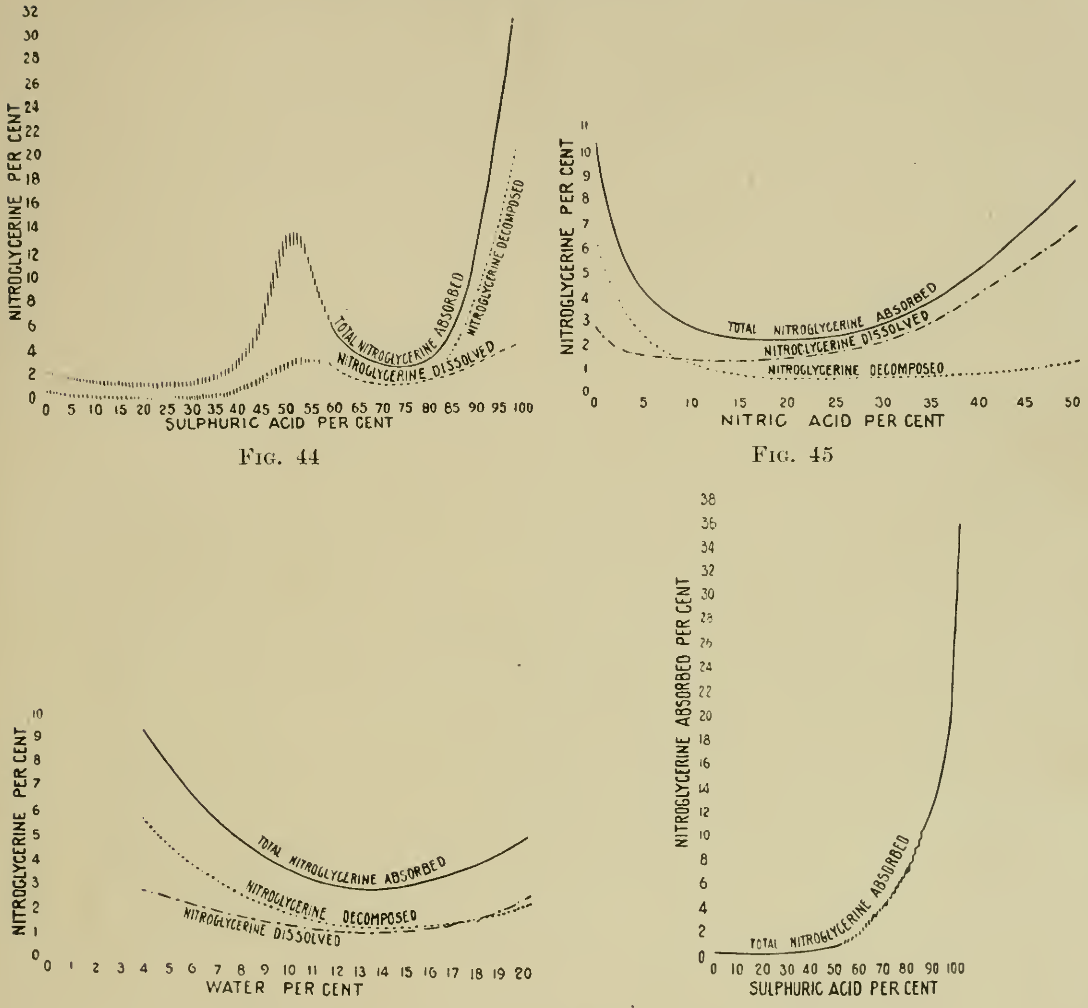


Fig. 44

Fig. 45

Fig. 46

Fig. 47

Figs. 44–47. Solubilities of Nitro-glycerine in Acids

tions has been eliminated, and the source of the trouble is to be sought now rather in the acids. A large amount of suspended matter in the acids causes the formation of numerous small drops of nitro-glycerine, which do not readily

---

[1] For full particulars of this process and its disadvantages, *see S.R.* 48, January 1883.

coalesce, and consequently take a very long time to separate. Hence the importance of allowing the acids to stand for some days after mixing in order to allow time for the insoluble impurities to settle out. These consist mostly of the sulphates of lead, iron and aluminium. But during the nitration process a further quantity is precipitated, mostly lead sulphate, which is considerably less soluble in dilute acids than in concentrated, and this freshly formed precipitate is probably more injurious, as it has not had time to be converted into larger aggregates. The time of separation increases with increase in the percentage of water in the waste acid; this is no doubt due partly to the larger amount of lead sulphate precipitated, but may also be caused partly by the retardation of the nitration reaction by the presence of the water. Just the same trouble with long separations is liable to occur with the nitrator-separator or any other form of plant. It is due to the formation of an emulsion of the one liquid in the other, and is intimately connected with the phenomena of surface tension, but the matter has not been investigated sufficiently to allow of a full and satisfactory explanation. The formation of an emulsion can be prevented by the addition of various substances to the charge: thus R. Moeller, in Ger. Pat. 171,106, claimed the addition of 0·05 to 0·2 per cent. of the weight of glycerine of various fatty substances, such as paraffin, vaseline, the higher fatty acids and their esters. The slow separations have also been ascribed to the presence of silicates, and especially gelatinous silicic acid, and the addition of 0·001 per cent. of sodium fluoride has been proposed to destroy them.[1] The Westfalisch-Anhaltische Sprengstoff A. G., in their Ger. Application 38,595 of December 2, 1911, on the other hand claim the addition of a small quantity of a silicate, such as kaolin or talc, and the Rheinische Dynamitfabrik adds both silica and hydrofluoric acid or sodium silico-fluoride.[2] The addition of either purified petroleum or sodium fluoride undoubtedly accelerates the separation, and the use of these substances is extending.

Conveyance of nitro-glycerine Before the invention of dynamite and blasting gelatine nitro-glycerine was sent long distances in the liquid state. The dangers involved led to numerous accidents, as was inevitable. In America Mowbray froze the material for the purposes of transport, but then it had to be thawed again before use, as it is too insensitive in the frozen state. In Europe liquid nitro-glycerine is now no longer used as such, but in America it is employed for "blowing" oil-wells, for which purpose it has to be sent by road, as the railways will not carry it. In the works the principle is adopted of mixing it with a solid substance at as early a stage as possible, so that the quantity of liquid nitro-glycerine is reduced to a minimum, but until it has been fully washed and mixed, it must of course be conveyed from one house to another in the liquid state. This is sometimes done in closed trucks or trolleys (*see* Fig. 48).

---

[1] Eastern Dynamite Co., Ger. Pat. 181,489; C. L. Reese, Am. Pat. 804,817.

[2] Eng. Pat. 14,586, of June 12, 1912; Germ. Pat. 283,330, of October 10, 1912.

In Germany the tendency is to revert to trolleys on account of the danger of explosions being communicated from one house to another by gutters or pipes. Where small quantities only have to be transferred, as from the after-separating and wash-water-settling houses to the washing house, covered buckets of indiar-ubber, gutta-percha, or papier maché are used, and these are carried in the hand. In England the bulk of the nitro-glycerine is, however, caused to run from one house to another through open gutters, which are usually made of lead. Pipes are not suitable on account of the impossibility of inspecting or cleaning them properly. All wash-waters are also sent down open gutters to the wash-water-settling house, as they carry globules of nitro-glycerine. The fall of the gutters should not be less than about 1 in 65: they should be free from sharp turns and from all inequalities in which nitro-glycerine can lodge. At the Royal Gunpowder Factory they are joined by butt-welding, as this gives a much smoother surface than lap-welding. In order to prevent the nitro-glycerine from freezing in cold weather, the gutter

FIG. 48. Truck for Conveyance of Liquid Nitro-glycerine, Repauno, U.S.A.
(By permission of E. J. du Pont de Nemours Co.)

Gutters.

connecting the nitrating house with the washing house is provided with an outer jacket (*see* section in Fig. 43), and warm water is circulated in this when the outside temperature is low. The gutter is protected by means of a canvas covering fixed along one edge and laced down on the other, so that it can easily be turned back for cleaning purposes. After a charge has been run down, the gutter is wiped along its whole length with a flannel in the direction of the washing house to remove any traces of nitro-glycerine.

When the nitro-glycerine has been mixed with sufficient gun-cotton or other absorbent material to render it non-liquid it is comparatively safe.

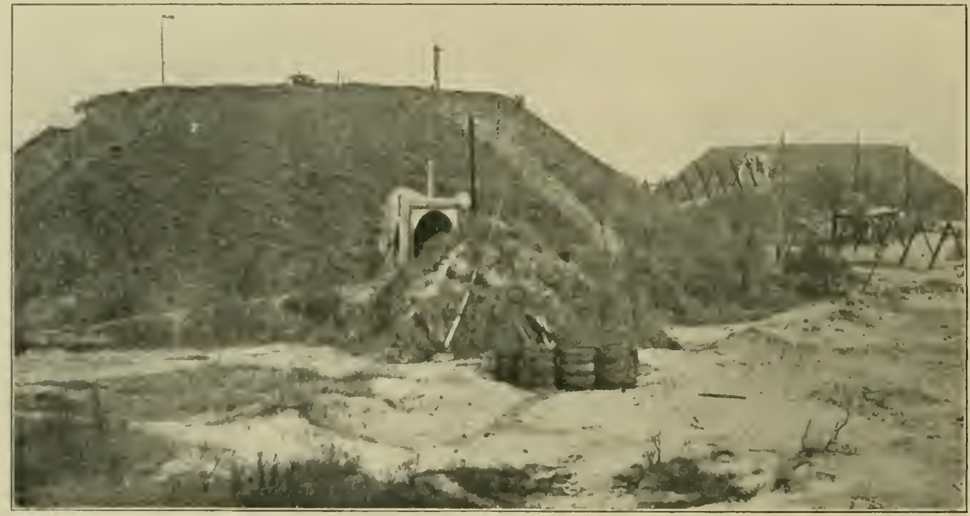


FIG. 49. European Nitro-glycerine "Hills." Forcite Works at Baelen-Wezel (From *Fabrication des Explosifs*, Brussels, 1909)

"Mixed material" for the manufacture of cordite has been transported in very large quantities over considerable distances without mishap. When the nitro-glycerine factory at Waltham Abbey, near London, was destroyed by an explosion on May 7, 1894, supplies were obtained from the Nobel Factory at Ardeer, in Scotland, in this state until a new factory was built. Gun-cotton in the wet state was sent from Waltham Abbey to Ardeer, and was there dried and mixed with the requisite quantity of nitro-glycerine and returned by sea, and so the manufacture of cordite at Waltham Abbey was not brought to a standstill. Similarly, when the nitrating house at Curtis's and Harvey's works at Cliffe, in Kent, was blown up on February 18, 1904, gun-cotton was sent from there to Waltham Abbey, and was there converted into mixed material and sent back. Messrs. Curtis's and Harvey were thus enabled to carry out their Government contract for cordite, which was urgently required for the South African War. The Düneberg Factory, near Hamburg, which makes the nitro-glycerine smokeless powder for the Germany Navy, obtains all its mixed material from the neighbouring dynamite works at Krümmel, which was the first nitro-glycerine factory erected by Nobel outside Sweden.

Location o factory.

Nitro-gylcerine factories are often built on rising ground in order to provide a fall from each house to the next without having to make the nitrating house of great height. With the nitrator-separator, however, the difference of level between the top of the nitrator and the bottom of the wash-water settling tank need not be more than 16 feet, which can easily be provided for on a flat site. One great disadvantage of placing a nitro-glycerine factory on the top of a hill is that it is very likely to be struck by lightning, and if that occurs it does not seem that any system of lightning conductors, however complete, will prevent the explosion of the nitro-glycerine and the consequent total destruction of the building. There have been numerous cases of such catastrophes in Germany and South Africa. In consequence of this the danger buildings of the Hoppecke dynamite factory have been

Fig. 50. American Nitro-glycerine Hill, Haskell, U.S.
(From *Appleton's Magazine*)

built underground in a hill, and Bichel has put forward similar proposals.[1]

That part of the works in which are situated the buildings for the manufacture of nitro-glycerine and other specially dangerous operations should be separated from the rest by a fence, and no one should be allowed within the "danger area" unless his duties take him there.

Air supply. Provision must be made for the stirring of the contents of the nitrator and the washing tanks, etc., in case the air compressor should fail. This can be done by having a large reservoir for compressed air with an automatic inlet valve, so that the contents cannot escape in the direction of the compressor. A cylinder of highly compressed carbon dioxide or nitrogen can also be used as a reserve; it should be provided with a reducing valve and a manometer, or other appliance, to show how much it contains.

Thunder-storms. If a thunder-storm pass over the factory all work must cease in drying and mixing houses, and the men must retire to the mess-room or other place of safety. In the nitrating house no fresh charge should be started whilst there is a thunder-storm anywhere near. All men must leave the building except one to look after the separation, and one for the nitrator if a charge be in the process of nitration. If the storm becomes very threatening, these also should leave after stopping the operations. Charges in the washing tanks may be left with the air turned on. In Germany it is laid down that the electric light and power wires are to be disconnected.

Limit boards. Every nitro-glycerine house, like all other danger buildings, must have a board in the entrance showing the maximum number of workmen and the greatest quantity of explosives that may be in it at one time. In Germany the following are the greatest numbers of men allowed, exclusive of carriers:

Nitrating house	2
Separating house	1
Washing house	2
After-separating house	2
Wash-water house	2
Denitrating house	2

Use-lists. At the Royal Gunpowder Factory, Waltham Abbey, Use-lists are also posted up, showing the total number of loose articles that are allowed in each house. This is a very valuable institution, as there is no doubt that many accidents have been caused by the dropping or falling of some heavy implement, or by the use of some unsuitable tool. It has been found possible to limit the number of loose articles to those which appear in the Table given below. These only are allowed.

General precautions. It need scarcely be said that the most scrupulous cleanliness and tidiness

---

[1] *S.S.*, 1910, p. 182; *Chemische Industrie*, 1912, p. 139.

must be observed in all nitro-glycerine houses. Any nitro-glycerine that may be spilt should be wiped up immediately with a flannel.

The men in the nitro-glycerine section should have special clothes of a different colour from those of other danger building men. There must be no pockets. The boots must be changed on entering a danger building; those worn inside must have no nails or others parts made of iron. Keys and other implements, that have to be brought near the buildings, are to be made of gun-metal or other soft material.

To destroy spilt nitro-glycerine H.M. Inspectors of Explosives recommend the use of a solution of 1 lb. caustic soda in $1\frac{1}{2}$ lb. water to which is added a gallon of wood spirit, or failing that methylated spirit.[1]

Sensitivenes

Nitro-glycerine can be exploded readily on iron or steel by an iron implement, but with some difficulty only with a brass one, or on brass with an iron one. Contrary to what might have been anticipated it is more difficult to explode a thin film than a layer of moderate thickness, such as that formed by a small drop. It is very difficult to explode nitro-glycerine on sheet lead placed on stone by iron or steel implements either by a direct or a glancing blow.[2]

USE-LISTS AT WALTHAM ABBEY.

	Nitrating House	Washing House	Wash-water House	Filtering and Mixing House
Bags, rubber	—	—	—	1
Bottles, gutta-percha . .	—	—	—	12
Buckets, rubber	3	6	6	—
Covers, bucket, gutta-percha .	—	6	6	—
Flannels	4	3	2	2
Gauntlets, rubber . . .	1	—	—	—
Gauntlets, leather . . .	—	—	—	2
Overshoes, rubber . . .	4	3	2	—
Socks	—	—	—	2
Thermometers	3	3	2	—

---

[1] *A.R.*, 1904, p. 62.

[2] *A.R.*, 1902, p. 25; 1903, p. 25.

CHAPTER XVII

LOW-FREEZING NITRO-GLYCERINE

Freezing of nitro-glycerine explosives : Effect of additions : Super-cooling : Dinitro-glycerine : Dinitro-chlorhydrin : Dinitro-acetin : Dinitro-formin : Tetranitro-diglycerine : Dinitro-glycol : Nitroisobutyl-glycerine nitrate

Freezing of nitro-glycerine explosives.

One of the greatest drawbacks attaching to nitro-glycerine explosives is the liability of nitro-glycerine to go solid at moderately low temperatures. The melting-point of pure nitro-glycerine is 13·3° C. or 56° F.,[1] but it can often be kept even in large quantities for considerable periods at temperatures much below this without solidifying, for it shows in a high degree the phenomenon of super-cooling. In the solid state it is much less sensitive to the detonative effect of fulminate, and this is a great source of danger, for frozen cartridges are liable to remain in the bore-hole partly or entirely unexploded, and in the subsequent operations they are very likely to be fired by a blow with disastrous results. Whether frozen nitro-glycerine is more sensitive to blows than when liquid the evidence is somewhat contradictory. H.M. Inspectors of Explosives[2] tried the effect of a falling weight of 5 lb. on little cylinders of dynamite ½ inch diameter and ½ inch high, placed between gun-metal discs, and found that whereas the unfrozen material was sometimes exploded with a fall of 30 inches, the frozen dynamite was never exploded with a single blow of the weight falling 48 inches, but a feeble explosion was produced at the second blow. Later on further experiments were carried out with other nitro-glycerine explosives.[3] Thin slices of the explosive about the size of a shilling and about 0·2 inch thick were placed between brass plates 1 inch square and 1/8 inch thick. The slice thus sandwiched was placed on an anvil, and a 58-lb. weight was allowed to fall on the upper brass plate. The critical or probable exploding points under these conditions were found to be about as follows:

	Unfrozen		Frozen
Blasting gelatine	12′	. .	1′
Gelatine dynamite	7′ to 8′	. .	6′ to 7′
Dynamite	1′	. .	—

The figures give the number of feet of fall of the weight which caused explosion.

---

[1] Kast, *S.S.*, 1906, p. 225; Nauckhoff, *S.S.*, 1911, p. 124; Hibbert, 8th *Int. Cong. App. Chem.*, vol. iv. p. 37. [2] *A.R.*, 1879. [3] *A.R.*, 1889.

The dynamite was in slices about the size and thickness of a sixpence. It was also found that frozen dynamite was very liable to detonate when it was ignited whereas the plastic material merely burnt away under the same conditions. Some hard frozen blasting gelatine laid on a sloping board and fired at with a rifle at 20 yards' range detonated powerfully, whereas unfrozen cartridges under similar conditions did not explode, and cartridges of the explosive frozen only slightly were merely scattered.

On the other hand, Will,[1] in falling weight and shooting experiments, found the frozen nitro-glycerine explosives less sensitive in all cases. The differences in the case of the falling weight experiments were probably due to the use of very much smaller quantities of explosive by Will. It is the increased resistance offered by the frozen explosives that makes them more dangerous to manipulate. If a very thin layer be used it is the resistance of the supporting surface that comes into play and not that of the explosive, and when fired with a detonator also, the hardness of the material has but little influence. But miners have to do with whole cartridges of explosive, and that these have special dangers is shown by the accidents that occur in spite of the warnings that have been issued repeatedly and the regulations that require the use of proper warming-pans. Thus, in the annual report of H.M. Inspectors of Explosives for 1911, the following cases are cited :

No. 2, Jan. 4. Man injured whilst ramming home a frozen charge of gelignite.

No. 32, Jan. 16. A man inserted an iron spike into a cartridge of Samsonite preparatory to attaching the detonator. The cartridge was probably frozen. Two injured.

No. 35, Jan. 3. Man injured breaking a frozen cartridge of Samsonite in two by hand.

No. 66, Jan. 4. A labourer was about to charge a shot-hole when he fell and knocked the explosive against the rock. Apparently the gelignite had not been thawed sufficiently or had become hard again. Man injured.

No. 92, Mar. 22. A man was in the act of breaking a frozen gelignite cartridge with his hands when it exploded. Two injured.

No. 106, Mar. 10. Whilst a miner was handling a congealed gelignite cartridge it exploded and injured him.

No. 117, Mar. 25. A miner dropped a "hard" gelignite cartridge on a tram-rail and it exploded. One injured.

No. 119, Mar. 25. A charge of undoubtedly hard frozen Samsonite exploded whilst being rammed home with a wooden rammer. Two injured.

No. 158, Apr. 11. A chargeman was making a hole for a detonator in a Rippite cartridge when it exploded. Apparently the cartridge had been rather hard, and he rested it on the ground and was pressing or knocking the pointed end of the steel nippers into it. One injured.

Similar cases have occurred in other years, but not always with the same

---

[1] *Zeits. Berg., Hütten-u. Salinenwesen*, 1905.

fortunate absence of fatal injuries. C. Herlin has carried out experiments in which the conditions of some of these accidents were reproduced more closely. He dropped balls of explosive weighing 40 to 110 grammes from various heights up to 12·3 metres on to an iron plate. Frozen explosives went off every time if the quantity and the length of drop were sufficient, but partly thawed balls never exploded, and presumably the unfrozen material did not either.[1]

The following Table shows how certain classes of accident are much more frequent at those times of the year when nitro-glycerine is liable to be frozen. Only those accidents in which an explosive containing over 10 per cent. of nitro-glycerine was involved are shown here.

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sep.	Oct.	Nov.	Dec.
Ramming or stemming charge .	1	—	4	1	—	—	1	1	1	1	—	2
Boring into unexploded charges	—	1	—	2	1	2	1	2	—	1	1	—
Striking unexploded charges in removing debris . . .	—	1	1	—	1	—	—	1	—	—	—	1
Total of above causes, 1914 .	1	2	5	3	2	2	2	3	1	2	1	3
Total in past 14 years . .	75	91	94	58	39	29	31	16	26	21	34	60

In addition to these there were up to the end of 1914 110 accidents in thawing cartridges of frozen nitro-glycerine explosives, causing death to 85 persons and injuries to 143 others. It is true that all except one of these accidents would have been avoided, if the explosives had been thawed in the regulation manner. The one exception was due to the thawing of some unstable explosive, the heat test of which had been masked by the addition of mercuric chloride.

Effect of additions.

These special dangers and the trouble in having to keep the explosives in heated magazines during cold weather, or of thawing them and keeping them thawed up to the time of using them, as well as the great difficulty in preventing the workmen thawing them in an irregular manner, has caused endeavours to be made to manufacture nitro-glycerine explosives which will not freeze so readily. For this purpose use is made of the fact that when a substance is dissolved in a liquid the freezing-point is depressed in accordance

---

[1] *S.S.*, 1914, p. 390.

with the equation $\Delta = E \cdot \frac{m}{M}$, in which Δ is the depression of the freezing-point produced by the addition of m grammes of a substance of molecular weight M to 100 grammes of the solvent, and E is a constant, which represents the depression produced by 1 gramme-molecule. It can be calculated by the formula $E = \frac{RT^2}{100W}$ in which R is the gas constant ($= 2$), T the absolute temperature of the freezing-point and W the latent heat of fusion. As early as 1885 Nobel patented the lowering of the freezing-point of nitro-glycerine by dissolving other substances in it.[1]

The behaviour of nitro-glycerine when cooled was investigated by Nauckhoff,[2] and was found by him to be quite normal. He determined the latent heat of fusion as 23·1 cal. per gramme,[3] and hence $E = 70{\cdot}5$. The following Table gives some of the depressions of the freezing-point observed and calculated by Nauckhoff :

Substance Dissolved	Molecular Weight.	Grammes per 100 g. N/G	Depression of Freezing point	
			Observed	Calculated
Nitro-benzene	123	0·637	0·30°	0·37°
,, ...	,,	1·334	0·73°	0·76°
Dinitro-benzene	168	0·644	0·23°	0·27°
,, ...	,,	1·508	0·59°	0·63°
Trinitro-benzene . . .	213	1·935	0·56°	0·64°
Dinitro-toluene	182	1·057	0·37°	0·41°
Dinitro-naphthalene . . .	218	0·707	0·23°	0·24°

Nauckhoff also determined the freezing-, or rather melting-points of a number of mixed explosives :

Nitro-glycerine	100	100	100	100
Nitro-benzene	19·7	10	5·9	5·7
Nitro-cellulose	10	8	5·1	7·0
Freezing-point	1·0°	5·0°	7·5°	9·0°

---

[1] French Pat. 170,290 of July 24, 1885.

[2] *Ang.*, 1905, pp. 11, 35.

[3] H. Hibbert and G. P. Fuller found the latent heat to be 33·2 cal. per gramme or 7·54 cal. per mol. (*J. Am. Chem. Soc.*, 1913, p. 978).

Nitro-glycerine	50	50	50	50	50	50	50	50	50	50	53
Nitro-cellulose	5	5	4	5	5	5	5	5	5	5	5
Ammonium Nitrate	40	35	40	35	40	34	40	40	40	40	42
Nitro-benzene	5	10	—	—	—	—	—	—	—	—	—
Dinitro-benzene	—	—	5	10	—	—	—	—	—	—	—
o-Nitro-toluene	—	—	—	—	5	11	—	—	—	—	—
p-Nitro-toluene	—	—	—	—	—	—	5	—	—	—	—
Nitro-naphthalene	—	—	—	—	—	—	—	5	—	—	—
o-Nitro-phenol	—	—	—	—	—	—	—	—	5	—	—
Aniline	—	—	—	—	—	—	—	—	—	5	—
Freezing-point	5°	2°	6½°	4°	6°	1½°	6°	7½°	6½°	4°	11½°

The freezing-point of the nitro-glycerine used for these experiments was about 10·5°. Taking into account this fact, and that the law of the depression of the freezing-point is strictly true only for dilute solutions, the figures found agree fairly well with those calculated. The low freezing-point of the original nitro-glycerine was due of course to the presence of some impurity in the nitro-glycerine, probably dinitro-glycerine, of which about 8 per cent. would be required to produce this depression. Nauckhoff considers that 10·5° is the normal freezing-point of commercial nitro-glycerine, but this no doubt depends upon the composition of the acid used and the proportion of acid to glycerine. There is no doubt that much of the nitro-glycerine manufactured is almost pure trinitrate and freezes near 13°.

The melting-points of nitro-glycerine, dinitro-chlorhydrin and mixtures of them were determined by Kast:[1]

Nitro-glycerine	Dinitro-chlorhydrin	Melting-point	
		Observed	Calculated
g.	g.		
24	0	13·4°	—
21	2·1	9·0°	9·6
21	4·2	6·2°–7·0°	6·1
21	6·3	4·0°	2·6
0	30·8	6·6°–6·8°	—

Kast also gives the "freezing-points," but as the liquids were cooled considerably below the true freezing-points before being inoculated with a crystal, the composition had been altered by the separation of crystalline nitro-glycerine before the temperature rose to a maximum, and this consequently

---

[1] *S.S.*, 1906, p. 225.

did not correspond with the true freezing-point. which is, of course, identical with the melting-point. Kast observed that nitro-glycerine can also crystallize in another or "labile" form, the melting-point of which is more than 11° below that of the stable form. Freezing-point determinations were also carried out with mixtures inoculated with crystals of this form :

Nitro-glycerine	Dinitro-chlorhydrin	Melting-point	
		Observed	Calculated
24	0	2·7° to 2·9°	—
12	11·5	about — 12°	—31·5
18·4	5·4	—7° to — 5°	—8·1
21·6	2·6	—0·8° to — 0·6°	—2·0
0	23·1	5·1° to 5·2°	—

A different sample of dinitro-chlorhydrin was used for this series.

Super-cooling.

Nitro-glycerine preparations do not necessarily go solid when the temperature is reduced below the freezing-point, on the contrary they can often be kept for months at a temperature considerably lower without solidifying. This property of super-cooling is intimately connected with a slow rate of crystallizing, when solidification does start, and this again appears to be related to high viscosity. The rate of crystallization of a given substance depends also upon the temperature ; as this is reduced below the freezing-point the rate increases at first, reaches a maximum and then falls again. Nauckhoff gives the following Table :[1]

Substance	Temperature	Super-cooling	Rate of crystallization mm. per min.
Glycerine	0°	10°	0·011
Nitro-glycerine . . .	5°	7·3°	0·145
,, . . .	0°	12·3°	0·183
,, . . .	—4·9°	17·2°	0·267
,, . . .	—17°	29·3°	0·125
Betol	—	—	1 maximum
Guaiacol	—	—	6 ,,
Azo-benzene . . .	—	—	570 ,,
Phosphorus . . .	—	—	60.000 ,,

The rate of crystallization is further reduced, if the nitro-glycerine is

---

[1] *Ang.*, 1905, p. 16.

gelatinized with collodion, but if it is absorbed in kieselguhr its tendency to crystallize is increased. When a cartridge of a nitro-glycerine explosive has once been frozen, it has a much greater tendency to become hard again as soon as the temperature falls below the freezing-point. This is probably due to the separation of globules of practically pure nitro-glycerine, which only mix again with the impurities and other constituents very slowly.

The first attempts to reduce the freezing-point of nitro-glycerine were with nitro-benzene [1] and nitro-toluene.[2] Unfortunately they not only reduce the sensitiveness of the explosive, a difficulty that can be overcome by the use of a stronger detonator, but also diminish the power and the velocity of detonation. For blasting hard rock these drawbacks are of the greatest importance, but for safety explosives for use in coal-mines, etc., far less so; in fact it is necessary to reduce the power and the velocity of detonation in order to make the explosive safe, and for blasting soft rock too high a rate of detonation is undesirable. Hence various nitro-hydrocarbons are used as constituents of many safety explosives. In order to reduce the freezing-point to any great extent it is necessary that the proportion of dissolved substance to nitro-glycerine should be fairly high, and the greater the molecular weight of the addition, the larger must be its proportion. But substances of very low molecular weight cannot be used because they are volatile. Therefore, in order not to reduce the efficiency of the explosive too much, it is desirable to add some substance that is almost as effective an explosive as nitro-glycerine. There are a number of substances closely allied to trinitro-glycerine, which can be used.

Methods for the manufacture of dinitro-glycerine have been devised by Mikolajczak [3] and the *Zentralstelle*.[4] Will has pointed out that dinitro-glycerine is liable to go solid at quite moderate temperatures, and that it has the further disadvantage that it combines with water of crystallization, is soluble in water and acids and somewhat hygroscopic. To what extent these troublesome qualities disappear when it is mixed with several times its weight of trinitro-glycerine there is no published evidence to show, but the results of experience with this substance in France do not appear to have been very favourable.[5]

Dinitro-glycerine.

Dinitro-chlorhydrin is easier and cheaper to prepare and purify, and is now used to a considerable extent for reducing the freezing-point of explosives. It mixes with trinitro-glycerine in all proportions and gelatinizes collodion cotton equally well. As regards power, Roewer found that there

---

[1] Rudberg, Swed. Pat., April 30, 1866.

[2] Volney, Am. Pat., March 5, 1872; Wahlenberg and Sundström, Swed. Pat. 1877.

[3] Am. Pats. 789,436 of September 11, 1906, reissue 12,669 of July 2, 1907, and 830, 909 of January 26, 1909.

[4] Ger. Pats. 181,385 and 175,751.

[5] *See* Vennin, *Poudres et Explosifs,* p. 367.

was little difference between explosives made with nitro-glycerine alone and those made with a mixture in which 20 per cent. of the nitro-glycerine had been replaced by dinitro-chlorhydrin. In the following Table the columns marked A are those obtained with the nitro-glycerine explosives, and B those with the mixtures of nitro-glycerine and dinitro-chlorhydrin :

	Guhr dynamite		Blasting gelatine		Gelignite	
	A	B	A	B	A	B
Trauzl Test, c.c.	300	301	555	541	395	384
Ballistic Pendulum, kg.m. .	74·0	75·9	111·4	111·4	90·8	88·5

The calorimetric figures calculated for 65 per cent. gelatine dynamite (63 per cent. nitro-glycerine or mixture, 2 per cent. collodion cotton, 26 per cent. sodium nitrate, and 9 per cent. cellulose) also give similar results :

	A		B
Heat evolved per kg. . . .	1,244 Cal.	..	1,278 Cal.
Temperature of Explosion . .	2,939°	..	2,835°
Gas produced per kg. . . .	7,168 litres	..	6,872 litres

Dinitro-chlorhydrin

Dinitro-chlorhydrin is a constituent of the following explosives authorized for transport by rail in Germany : Gelatin Astralit, Gelatin Wetterastralit, Gelatin Donarit, Gelatin Westfalit, and Perilit.

In order to make a mixture of nitro-glycerine and nitro-chlorhydrin, the chlorhydrin can be mixed with the glycerine, and the mixture nitrated and washed in the usual way.

Dinitro-chlorhydrin is practically insoluble in acids and water, and is not hygroscopic, but has the disadvantage that on explosion it gives off hydrochloric acid, which makes it unsuitable for use underground, unless sufficient of an alkali nitrate or other compound be added to convert all the chlorine into an inorganic chloride. This difficulty does not occur if the third oxygen atom in the glycerine molecule be combined with the radicle of an organic acid instead of chlorine. Vender has found that the acetyl and formyl derivatives, mono-acetin and mono-formin, can be nitrated and give a good yield, provided that the mixed acid contains more nitric than sulphuric acid.[1] Dinitro-acetin, $C_3H_5(NO_3)_2.(C_2H_3O_2)$, he says, can be obtained with a yield of 95 per cent. by nitrating 40 parts of acetin with a mixture of 100 parts nitric acid and 25 of 25 per cent. oleum. Dinitro-formin may be made by heating 100 kg. glycerine with 50 kg. oxalic acid first at 100° and then

Dinitro-acetin.

Dinitro-formin.

---

[1] Ger. Pats. 209,943 of April 27, 1906, and *S.S.*, 1907, p. 21.

at 140° to 150°, and then nitrating. The product has a specific gravity of 1·57, contains 15·7 per cent. N and consists of 33 per cent. dinitro-formin and 67 per cent. nitro-glycerine. It is unfreezable and gelatinizes collodion as well as, if not better than, nitro-glycerine.

Tetranitro-di-glycerine.

By treating it in various ways glycerine can be condensed to di-glycerine: $2C_3H_8O_3 = H_2O + (CH_2OH.CHOH.CH_2)_2O$, and this on nitration yields a tetra-nitrate $C_6H_{10}N_6O_{13}$, which reduces the freezing-point of nitro-glycerine just as the other substances that have been mentioned. The formation of di-glycerine was studied in the *Zentralstelle*,[1] and it was found that the conversion was best effected by heat alone. By heating glycerine for seven or eight hours at 290° to 295° some 60 per cent. of di-glycerine is formed together with 4 to 6 per cent. of poly-glycerines. The constituents can be separated by distillation at a pressure of 8 to 10 mm. According to Eng. Pat. 24,608 of October 24, 1910, taken out by Nobel's Explosives Co., W. Rintoul and A. G. Innes, the conversion is best effected by heating at a temperature of 245° to 250° in a current of inactive gas, such as carbon dioxide, which carries away the water formed, and keeps the liquid in a state of agitation.

Claessen, in Eng. Pat. 9572 of 1908, claims the use of a small proportion of alkali; by heating to 275° to 280° with 0·5 per cent. the conversion is effected in a comparatively short time.

Pure di-glycerine boils at 245° to 250° under a pressure of 8 mm.; it is a colourless, sweet liquid readily soluble in water: its specific gravity is 1·33 and it is eleven times more viscous than glycerine. Tetra-nitro-di-glycerine is very similar to nitro-glycerine. A mixture of glycerine with about 25 per cent. di-glycerine can be nitrated in the same way as glycerine alone, and the product is unfreezable. Guhr dynamite made with such a nitro-glycerine produced as great an effect in the lead block as ordinary dynamite.

Dinitro-glycol.

Dinitro-glycol $CH_2NO_3.CH_2NO_3$ is used by the Société anonyme d'Explosifs et de Produits chimiques.[2] Its power according to calculation is 4 per cent. greater than that of nitro-glycerine. In the calorimetric bomb the results obtained indicated a superiority of 8 to 20 per cent. according to the method of interpreting the results; by the lead block test the results were about equal. The Société state that at the present high price of glycerine nitro-glycol can be made at a cost not much greater than that of nitro-glycerine. It is more volatile than nitro-glycerine; its specific gravity is 1·496 at 15°.

Nitro-iso-butyl-glycerine nitrate.

If nitro-methane be mixed with 4 parts of 40 per cent. formaldehyde, and a little potassium carbonate or bicarbonate be added, condensation takes place with the formation of nitro-isobutyl-glycerine: $NO_2CH_3 + 3H.COH = NO_2C.(CH_2OH)_3$, a crystalline substance readily soluble in water and alcohol

---

[1] *See* Will, *S.S.*, 1906, p. 231.

[2] *P. et S.*, 16, 1911–12, p. 72.

but less soluble in ether. It melts at 158° to 159°.[1] If this be purified by recrystallization and then nitrated with mixed acid, the trinitrate $NO_2C(CH_2NO_3)_3$ is formed,[2] a liquid of specific gravity 1·68 and very low freezing-point. At present it is not of practical importance on account of the high price of nitro-methane, but if an inexpensive method of making this could be devised, it could be used commercially.

---

[1] Henry, *Compt. Rend.*, 1899, I., p. 1154.

[2] F. E. Matthews, Brit. Pat. 6447 of 1914 ; Hofwimmer, *S.S.*, 1912, p.

PART VI

NITRO-AROMATIC COMPOUNDS

CHAPTER XVIII

BY-PRODUCTS OF COAL DISTILLATION

Aromatic compounds : Distillation of coal : Coal-tar : Nomenclature : Benzol from gas : Distillation of coal tar : Toluene from petroleum : Carbolic Acid : Phenol from benzene : Naphthalene : Yields

Aromatic compounds

Very great and increasing use is made of the nitro-derivatives of aromatic substances as explosives and in the preparation of composite explosives. The principal, but not exclusive, source of the aromatic compounds is the destructive distillation of coal.

Distillation of coal.

When complex organic materials are submitted to destructive distillation they yield as a rule three classes of products : solid, liquid and gaseous. Of the products from coal the gas and solid (coke) are used as fuel. The liquid products are ammoniacal liquor and tar, obtained on cooling the gas and scrubbing it. Until recently ammoniacal liquor was almost the only source of ammonia, but it is now meeting severe competition from synthetic ammonia, for which see Chapter VIII.

Coal-tar.

The quantity and composition of the tar naturally depends upon the sort of coal carbonized and the temperature and type of the retorts. The higher the temperature the greater is the yield of gas, but if the temperature be very high the yield of tar is less, and there is in it a smaller proportion of the simpler aromatic compounds, such as benzene, toluene and phenol. In the large gasworks there has been a tendency to carbonize at higher temperatures than was formerly the practice, and consequently the tars produced have not been of as great value as those from small country gasworks. The modern continuous vertical retort, however, yields a considerable quantity of good tar. The quantity of tar varies from about 4 to 10 per cent. of the coal and averages about 5 per cent. ; it contains generally less than 1 per cent. each of benzene and toluene. The composition of coke-oven tar is similar, but varies between wide limits.

Coal tar is a thick black liquid of specific gravity 1·1 to 1·3. It is a very complex mixture from which various valuable constituents can be separated by fractional distillation combined with treatment with chemicals. Owing to the complexity of the mixture only those substances are, as a rule, separated in a state of comparative purity on the commercial scale which are present in the largest proportions, or which possess some physical or chemical property which facilitates their isolation. Of these substances the most important are the aromatic hydrocarbons, benzene, toluene, naphthalene and anthracene, and the aromatic alcohols, phenol or carbolic acid, and cresol or cresylic acid. All these are used in the manufacture of synthetic dye-stuffs, drugs, etc., and toluene, benzene, phenol and naphthalene are also used in the manufacture of nitro-explosives, especially toluene and phenol. Hence the demand for these substances is sometimes difficult to meet, especially in the case of toluene.

Benzene and naphthalene on the contrary are obtained in abundant quantities. The following are the melting- and boiling-points of the principal substances in coal tar:

Substance	Formula	Molecular weight	Melting-point	Boiling-point
Benzene	C_6H_6	78	5·6° C.	80·2° C.
Toluene	C_7H^8	92	—92	110·7
Phenol	C_6H_5OH	94	43	182
Ortho-cresol . . .	C_7H_7OH	108	30	188
Meta	..	..	4	200·5
Para	..	..	36	201·1
Naphthalene . . .	$C_{10}H_8$	128	80·1	218
Anthracene	$C_{14}H_{10}$	178	216·6	351

Nomenclature. The aromatic hydrocarbon, C_6H_6, was formerly called benzol or benzole, but in scientific English its name is now benzene, the termination *-ol* being restricted to bodies of the nature of an alcoh*ol* and containing a hydroxyl group (OH). The name benzol is applied commercially to volatile distillates obtained by the destructive distillation of coal and rectified so as to boil between about 80° and 130°. The next hydrocarbon of this series, $C_6H_5.CH_3$, has similarly had its name altered from toluol to toluene. Different grades of benzol are distinguished by the percentage which distils over below 100° C. from a plain still or retort without a dephlegmating column, thus 90 per cent. benzol is a liquid of which 90 per cent. distils over below the boiling-point of water. According to Kraemer and Spilker[1] the following are the mean compositions of the benzols used in colour works:

	90 per cent. Benzol	50 per cent. Benzol	30 per cent. Benzol
Benzene	80·9	45·4	13·5
Toluene	14·9	40·3	73·4
Xylene	2·2	12·4	11·7
Impurities	2·0	1·9	1·4

---

[1] Muspratt, *Handbuch der technischen Chemie*, 4th ed., 8, pp. 33 *et seq.*

Benzine is a volatile distillate from petroleum having about the same range of boiling-points as benzol. It consists mostly of hydrocarbons of the paraffin and olefine series. In German benzene is still called benzol; in French it is sometimes called benzine.

The alcohol corresponding to benzene is phenol, C_6H_5OH. Unlike ordinary alcohol it has decided acid properties and is often called carbolic acid, but this term, like "benzol," is more generally applied to commercial products containing other similar substances and impurities as well as phenol.

Benzol fro gas.

The quantities of benzene and toluene contained in the tar are, however, small compared with what is carried away in the state of vapour in the gas. Thus Bunte found that at the Karlsruhe Gas Works the products from the distillation of 100 kg. of coal contained:

Primary Products	Quantity	Containing	
		Benzene	Toluene
Tar	5 kg.	45 g.	40 g.
Gas	17 kg. (=30 cub. m.)	938 g.	312 g.

Very large quantities are now recovered from coke-oven gas, especially in Germany, by scrubbing it with creosote or anthracene oil. The removal of the benzene and toluene from coal gas destroys its illuminating power when burnt in a fish-tail burner, and reduces its calorific power. If these hydrocarbons be removed from gas for town supplies it is necessary to reintroduce the greater part of the benzene. By using a minimum of washing oil it is, however, possible to remove a considerable amount of the toluene with very little benzene without seriously interfering with the quality of the gas. The volatile products are distilled off from the washing oil by means of live steam or by heat alone. The distillate is separated from the accompanying water and fractionated.

Distillation of coal tar.

The tar[1] is first freed as far as possible from ammoniacal liquor, and is then fractionally distilled from an iron boiler fired directly, the products being separated either into four or five fractions. The following are the fractions:

I	Crude naphtha	up to 110°
II	Light oil	110–210
III	Carbolic oil	210–240
IV	Heavy or creosote oil	240–270
V	Anthracene oil	above 270

---

[1] This account of coal tar distillation is taken mainly from *The Manufacture of Organic Dye-stuffs*, by A. Wahl, translated by F. W. Attack (Bell & Sons, 1914).

or

I	Light oil	up to 150°	density less than 1
II	Medium oil	150–210	,, more ,, 1
III	Heavy oil	210–280	
IV	Anthracene oil	above 300	

The residue remaining in the still is pitch, a thick black mass which sets practically to a solid. The naphtha is separated from the water, which passes over with it, and is agitated first with dilute sulphuric acid to remove basic substances, and then with concentrated sulphuric acid to resinify the unsaturated hydrocarbons and absorb the sulphur compounds, such as thiophen. After washing twice with caustic soda and then with water the liquid is again fractionally distilled, preferably through a good dephlegmating column similar to that shown in Fig. 69 (p. 344), giving benzols and solvent naphtha. On redistilling these give more or less pure hydrocarbons: benzene, toluene, xylenes, etc., which generally have still to be further purified.

The light oil is distilled and separated into two portions: the fraction up to 170° is added to the naphtha and the other is added to the carbolic oil, which is worked up for phenols and naphthalene.

The heavy oils are used for impregnating wood, burning for heating purposes, for lighting and for the production of lamp-black, etc. They are also heated ("cracked") for the production of illuminating gas and of more valuable hydrocarbons. On leaving to crystallize anthracene oil gives crude anthracene, and on redistilling the oil gives a further yield of anthracene. This is purified by pressing washing with creosote oil, subliming and recrystallizing. It is used for the manufacture of numerous dye-stuffs.

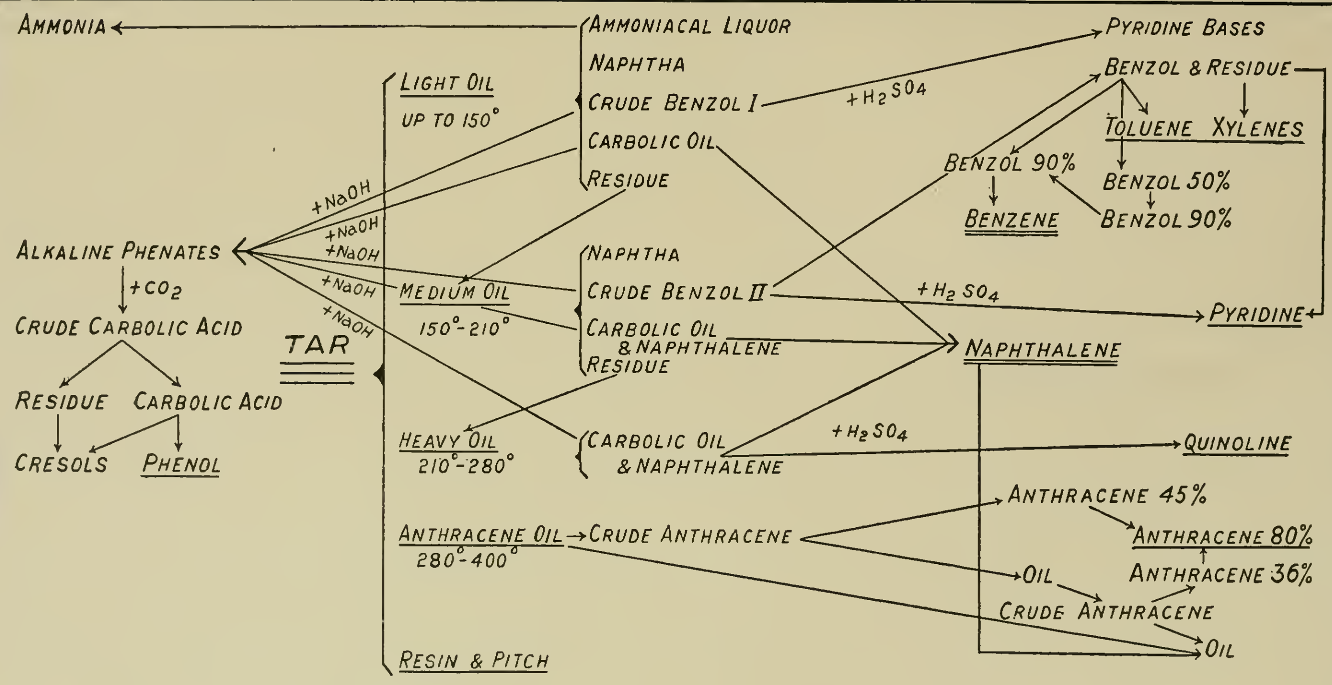
According to Lunge the distillation of a ton of coal tar yields on an average:

Ammoniacal liquor	3·0 gallons
Naphtha	6·3 gallons
Light oils	13·4 to 15·0 gallons
Heavy oils	68 gallons
Pitch	0·54 ton

The treatment of the tar is outlined in the diagram on the next page.

Toluene from petroleum.

Aromatic hydrocarbons are present in petroleums obtained in various parts of the world, but the published information about this is somewhat contradictory. It has been demonstrated by W. F. Rittman and T. J. Twomey of the U.S. Bureau of Mines that if petroleum be heated under pressure to temperatures of 550° C. and upwards considerable quantities of aromatic hydrocarbons are formed. Toluene and xylene are apparently produced most easily. Benzene requires more strenuous cracking, and its formation reaches a maximum at a point where toluene and xylene have already fallen off considerably. Naphthalene begins to form at about the



TREATMENT OF COAL TAR.

from "Farbenchemisches Praktikum" by Möhlau & Bucherer.

Leipzig. 1908.

point where the toluene and xylene content is at a maximum, indicating that it is probably formed by the condensation of two molecules of a monocyclic hydrocarbon. Anthracene is formed under similar conditions to naphthalene, but requires even more severe heating. The production of toluene was in some cases 4 per cent. of the original petroleum and 18 per cent. of the cracked oil. Under manufacturing conditions it would perhaps be possible to obtain considerably better yields.[1] This process is being developed commercially.

W. A. Hall heats petroleum products to about 600° C. in order to obtain motor spirit. It has been found that the product sometimes contains as much as 10 per cent. of toluene and 8 per cent. of benzene.[2]

Carbolic acid. The fraction collected as carbolic oil consists mainly of naphthalene and phenolic substances. The oil is run into tanks and allowed to cool down, whereupon 25 to 30 per cent. of naphthalene crystallizes out. The oil separated from this has a specific gravity of about 1·0025 and contains 25 to 30 per cent. of phenols. It is first concentrated by redistilling it, preferably through a dephlegmating column. First some crude benzol comes over, then a mixture of benzol and water. When the distillate no longer separates into two layers the receiver is changed, and it is collected as crude carbolic acid. A further fraction may also be collected consisting largely of cresols and naphthalene. The residue according to its quality is either run into the creosote oil tank or used for softening pitch.

The rectified carbolic oil is next treated with weak caustic soda to separate the acid from the neutral hydrocarbons. For this purpose a lye is used with specific gravity not greater than 1·075 to 1·10, as a stronger liquor would dissolve some of the naphthalene. If pure phenol be aimed at fractional extraction with caustic soda is generally adopted : a quantity of the carbolic oil is mixed thoroughly with a quantity of caustic solution more than sufficient to extract all the phenol so that it also takes up a small proportion of the cresol. The aqueous solution is then drawn off and mixed with a further quantity of the carbolic oil, when an interchange takes place, the sodium cresylate being converted into sodium carbolate. This method is rendered possible by the fact that phenol has a considerably greater affinity for the soda than the cresols and other homologues ; in other words, it is a stronger acid.

The solution of phenate cr carbolate of soda is purified by boiling and blowing in steam, which removes any naphthalene and various other impurities. It is filtered if necessary and then treated with acid to release the phenol. For this purpose carbonic acid is now generally used, but a little sulphuric acid is added to complete the process. The solution of sodium carbonate thus obtained is reconverted into one of caustic soda by treating it with lime.

---

[1] *J. Ind. Eng. Chem.*, 1916, p. 20. For description of plant see Rittman, Dutton and Dean, *ibid.*, 1916, p. 351. *See also* G. Egloff and T. J. Twomey, *J. Phys. Chem.*, 1916, p. 121.

[2] *See* C. F. Chandler, *ibid.*, p. 75.

Thus not only is the soda saved and used again but the carbolic acid remaining in the solution passes into the process again. The crude phenol separates as an upper layer on the acidified liquor : it is drawn off and further purified by fractionating through a dephlegmating column. At first the distillate consists of water containing only a small percentage of phenol, then practically pure phenol comes over ; [1] at the end of the distillation cresols are obtained. The phenol can be further purified by allowing it to crystallize and pressing out the liquid residue.

Cresol can be separated and in a similar manner from the fractions from which the phenol has already been removed, and it can be purified in the same way. But as a rule, cresol and the other similar bodies are used without exhaustive purification for the preparation of disinfectants, etc. The alkaline washings obtained by treating benzol with caustic soda solution are worked up for phenol or crude carbolic acid in the same way.

Before the war Germany depended largely on England for the supply of carbolic acid, as the coke-oven tars made there contain comparatively little of it, and its extraction consequently could not compete very successfully with the English product made from gas tar. For the rectification of the carbolic oil from coke-oven tar, F. Raschig recommends that it be fractionated *in vacuo* through a very tall dephlegmating column, 14 metres long. This column he fills with small hollow rings of sheet iron, 1 inch long and 1 inch in diameter, with walls of $\frac{1}{32}$ inch thick. These offer a very large surface for the interaction of the vapour and condensed liquid, and consequently improve the fractionation and offer little resistance to the passage of the vapours, and so do not diminish the vacuum. The distillation is carried out at about 120° C. At first an oil passes over containing no phenol, and is shown by the fact that if a portion be shaken with caustic soda its volume is not reduced. After a time the phenol content rises rather suddenly to 30 or 40 per cent. It remains at this for some time, and then falls to 20 or 25 per cent., and naphthalene then crystallizes out from the distillate on cooling. The distillation is now stopped. [2]

Phenol fro benzene.

When the demand for phenol is so great that it cannot be met by the amount obtained from coal tar, the consequent rise in price makes it remunerative to manufacture phenol from benzene by sulphonation and fusion with soda. A. H. Ney has described the process with considerable detail in a lecture [3] in New York : the following description gives the methods briefly. The sulphonation kettle is a cast-iron vessel, fitted with a lid and a condenser

---

[1] For the vapour pressures of mixtures of phenol and water *see* F. A. H. Schreinemakers, *Proc. K. Akad. Wetensch.*, Amsterdam, 1900, p. 1 ; also A. Marshall, *J. Chem. Soc., Trans.*, 1906, p. 1365.

[2] *Ang.*, 1915, i. p. 409.

[3] Reproduced in *Chem. Trade Jour.*, October 16 and 23, 1915 ; also *Met. and Chem. Eng.*, 1915, p. 686.

to condense vapour of benzene and return it to the kettle. It has a good stirrer and a jacket for heating it. Eight parts by weight of concentrated sulphuric acid are placed in it, and three parts of benzene are added with constant stirring. When the temperature ceases to rise, heat is applied and it is maintained near the boiling-point of benzene. After five to nine hours the sulphonation is complete and the contents of the kettle are run into a lead-lined tank and diluted with an equal volume of water. Then milk of lime is added. which converts the benzene sulphonic acid into the calcium salt, which remains in solution, and the excess of sulphuric acid into calcium sulphate, which is precipitated. The latter is filtered off in a filter press and washed: the solution is mixed with sodium carbonate (soda ash), which precipitates the calcium as carbonate and leaves sodium sulphonate in solution. This is evaporated down and the dry salt is heated with fused caustic soda. In a cast-iron vessel are placed 10 parts of caustic soda and a little water. This is melted and heated to about 270°, and 10 parts of the sulphonate are gradually added. The temperature is then raised to about 315°: the sulphonate is thus converted into sodium phenate and sulphite

$$C_6H_5SO_3Na + 2NaOH = C_6H_5ONa + Na_2SO_3 + H_2O.$$

The melt is ladled out, allowed to solidify, broken up, crushed and dissolved in water. Then dilute sulphuric acid is run in until there is a copious evolution of sulphur dioxide, and the liberated phenol is allowed to separate out. It is freed from sulphur dioxide by blowing air through, and is rectified by distillation.

Naphthalene. The naphthalene which crystallizes out from the carbolic oil and various other fractions is subjected to a number of operations to purify it. After allowing it to drain it is heated and pressed in a powerful press to remove the bulk of the oil. Then it is washed with caustic soda solution to dissolve out carbolic acid, and then with hot water. Next it is heated with sulphuric acid of about 1·8 specific gravity, which absorbs various impurities. Then it is washed again with hot water, and afterwards with weak alkali, and finally it is fractionally distilled. It is thus obtained as a white crystalline solid having a characteristic smell.

Yields. The quantities of the different products obtained naturally vary according to the nature of the tar and the processes adopted, but they are usually within the following limits:[1]

Benzene and toluene	1 to 1·5 per cent.
Anthracene	0·25 to 0·45 ,,
Phenol	0·4 to 0·5 ,,
Cresol	2 to 3 ,,
Naphthalene	6 to 10 ,,
Heavy oil	25 to 30 ,,
Pitch	50 to 60 ,,

---

[1] Meyer und Jacobson, *Organische Chemie*, vol. ii. part 1. p. 93.

CHAPTER XIX

NITRO-DERIVATIVES OF AROMATIC HYDROCARBONS

Nitro-benzene $C_6H_5NO_2$: Accidents : Dinitro-benzene $C_6H_4(NO_2)_2$: Trinitro-benzene, $C_6H_3(NO_2)_3$: Nitro-toluene, $C_7H_7NO_2$: Dinitro-toluene, $C_7H_6N_2O_4$: Trinitro-toluene, $C_7H_5N_3O_6$: Waste acids : Purification of trinitro-toluene : The trinitro-toluenes : Accidents : Properties : Density : Mono-nitro-naphthalene, $C_{10}H_7NO_2$: Dinitro-naphthalene, $C_{10}H_6N_2O_4$: Trinitro-naphthalene, $C_{10}H_5N_3O_6$: Tetranitro-naphthalene, $C_{10}H_4N_4O_8$

Nitro-benzen **$C_6H_5{\cdot}NO_2$**

BENZENE is nitrated on a very large scale as a stage in the manufacture of aniline, which is used in the preparation of many dye-stuffs. The process of nitration does not differ in principle from the manufacture of nitro-glycerine, but the mixed acids are generally run into the benzene instead of the benzene into the acids, and as mono-nitrobenzene is not explosive, the same precautions are not necessary. Fig. 51 shows a plant capable of nitrating 500 gallons or two tons of benzene in one charge. It consists of a cast-iron pan *F* having a total capacity of 1600 gallons. It has a strong lid, through which passes a shaft bearing the two propeller agitators *H*, the lower of which is surrounded by a cylinder to increase the upward motion of the acid. On the top of this cylinder is a grid *K* supporting the lead coils *J*, the inlets of which are shown at *N*, *O*, and the outlets at *L*, *M*. These coils are each 2 inches in diameter, and 150 feet long. Through these cooling water can be circulated, or hot water or steam if it be required to raise the temperature of the contents of the pan. Into the acid mixing tank *A* are run 5000 lbs. of nitric acid of specific gravity 1·43 through the pipe *D*, and through *C* 6600 lb. of concentrated sulphuric acid. They are then mixed together by blowing air through the perforated pipe *B* ; but in some works large quantities of acid are mixed at a time in capacious tanks and allowed to settle. The benzene is introduced into the pan and the agitators are revolved at about 60 revolutions per minute, and then the acid is run in in a thin stream, the temperature not being allowed to rise above 60° C. After the whole of the acid has been introduced, agitation is continued for a further 4½ hours to complete the nitration. The waste acid should then contain less than 1 per cent. of nitric acid. The contents of the pan are then allowed to settle, and the waste acid is run into the egg *X*, and blown up through the pipe *V* to the waste acid tank by admitting compressed air through *U*. The nitro-benzene is similarly run into *X*, and blown up through the pipe *S* into the wash-pan *R*, where it is washed first with soda solution and then with water, air being blown in through the pipe *P* to agitate the liquids. After settling, the nitro-benzene is run to a storage tank. The maximum theoretical yield from 100 parts of benzene is 157·6, and the actual yield should not be less than 154·5. The nitro-benzene can be further purified by distillation *in vacuo*.

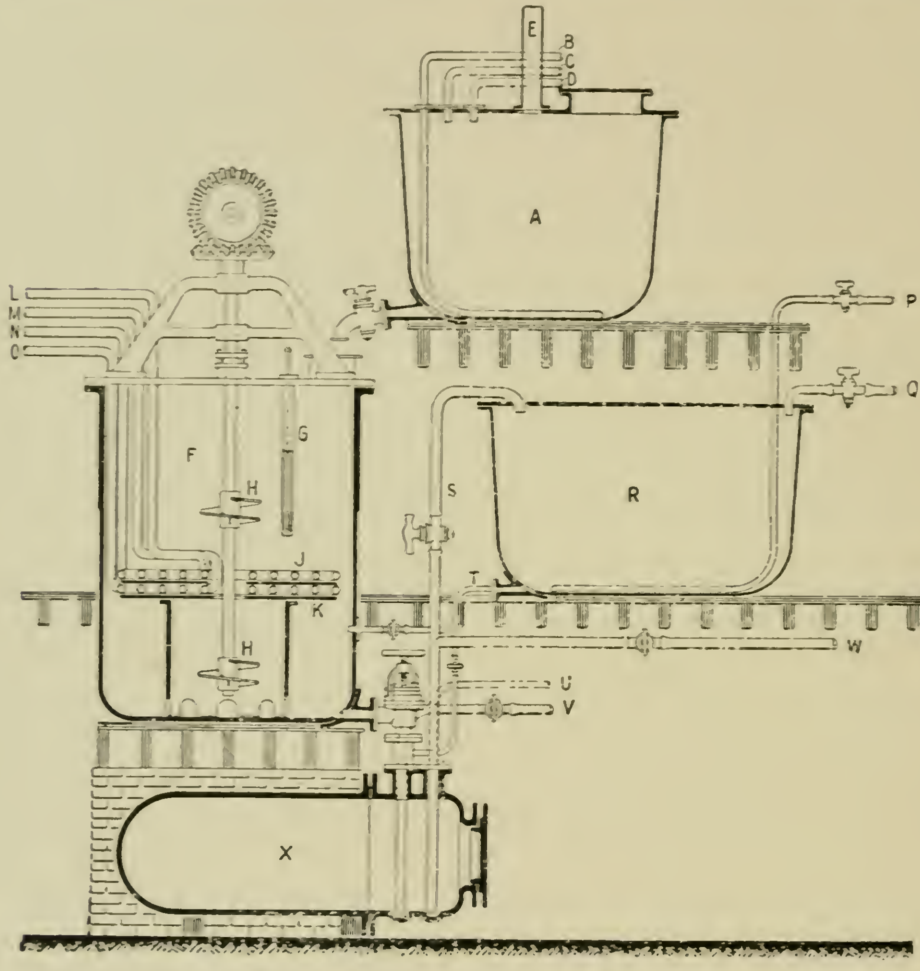


FIG. 51. Benzene Nitrating Plant. (From Thorpe's *Dictionary of Chemistry*)

Nitrobenzene, $C_6H_5NO_2$, is a pale yellow oil slightly volatile at the ordinary temperature and having a characteristic odour. It is slightly poisonous, but is used for perfumery and flavouring under the name of "oil of mirbane." Under atmospheric pressure it boils at 209° C.; it freezes with some difficulty, and melts at 3·6°. Although its use has often been proposed as an ingredient of various explosives it has not been so used very extensively, as its volatility is objectionable, and there are other nitro-compounds available which have more decided explosive properties. It has, however, been used as an ingredient of Sprengel explosives and to reduce the freezing-point of nitro-glycerine. It is practically insoluble in water, but soluble in alcohol ether and other organic solvents.

Accidents.

With ordinary care the nitration of benzene is quite a safe operation, but in February 1914, there was a severe accident at Rummelsburg in the works of the Aktiengesellschaft für Anilinfabrikation whereby eleven people were killed and fourteen injured. The catastrophe seems to have been caused by allowing the acid to run into the benzol without starting either the stirring gear or the cooling water. After a time such an energetic action set in that the top was blown off the pan, and large quantities of benzol vapour escaped, mixed with the air and exploded. Similar accidents occurred at Mannheim in 1907, and Moscow in 1911.

After the Rummelsburg catastrophe a committee of chemical manufacturers assembled in Wiesbaden to consider the steps to be taken to avoid the recurrence of such accidents,[1] and subsequently the Prussian Minister for Trade and Industry passed regulations somewhat similar to those in force in explosives factories, namely:

1. Accumulations of material and persons are to be avoided as far as possible.
2. Arrangements must be made to prevent large quantities of raw materials interacting on one another at one time. The nitration plant should be examined every time before it is started; accidents may be caused by the inadvertent presence of acid.
3. It is undesirable that the plants should be in communication with one another.
4. The nitrators are to be so erected that if large volumes of hydrocarbon vapours are evolved they will be discharged above the roof by an outlet of sufficient size.
5. Arrangements must be made that acid cannot be run in before the stirrer has been started.
6. There must be a device to show whether the liquid is in motion.
7. These rules may be moderated somewhat in the case of continuous processes.

At the meeting of the Wiesbaden Committee, W. ter Meer described a continuous nitration plant, which he has used in his works.[2] This consists of a cylindrical vessel of 3 cubic metres capacity provided with two inlets at the bottom end for benzol and acid respectively. Down the middle of

---

[1] *Chem. Ind.*, 1914, p. 337.

[2] Germ. Pat. 228,544 of July 24, 1909.

the cylinder passes an axle carrying a number of stirrer blades. The path of the liquids is prolonged by a number of diaphragms extending nearly across the cylinder and fixed alternately to the walls and to the axle. The cylinder is provided with a water-jacket and an outlet at the top. The benzol is introduced at the rate of 300 kg. per hour, together with the requisite quantity of mixed acid, about 800 litres in all. They take nearly four hours to pass through the nitrator, and in a twelve-hour shift 4½ tons of good nitro-benzol are obtained.

Neumann described a similar plant in which the reacting liquids are made to traverse an annular space between a fixed and rotating cylinder, both carrying stirrer blades and cooled or heated locally or entirely as required.

Kubierschky's plant is on a different system : it has no mechanical stirrers and the benzol and acid are made to pass in opposite directions through a tower. It is shown diagrammatically in Fig. 52. The benzol flows from the tank *A* into the nitrating tower *I* at the point *a* near the bottom. The mixed acid flows from *B* into the same tower near the top at *b* ; in consequence of its higher gravity it sinks down gradually, nitrating the benzol as it goes. At the bottom of the tower the waste acid separates from the benzol and flows into the tank *C*. The nitrated product flows from the top of the tower through the pipe *d*, and the visible overflow *D* to the washing tower *II*, where it meets a stream of water flowing up the tower, and is thus freed from acid. The flow from the bottom of *II* is regulated by the cock *e* : the nitro-benzol is preheated in *E*, and then flows at *f* into the top of the column *III*. Up to this point the nitro-benzol contains about 10 per cent. of unchanged benzol, an excess having been used to prevent the formation of dinitro-benzol. In *III* this benzol is removed by means of live steam at *g*. The purified nitro-benzol then flows through the cooler *G*, and the visible overflow to the separator *K*, where it is freed from water, carried along mechanically. The distillate from *III* is condensed in *E* and *F*, and is separated in *J* into benzol and water.

The construction of column *I* is shown in Fig. 53. The arrows in the lower portion show the way the benzol circulates and passes in a finely divided state through the acid which is moving in the opposite direction. The nitric acid is thus very fully utilized. The temperature in this column is regulated by means of the coils. The nitration process is followed by taking readings of the density of the crude nitro-benzol by a hydrometer in *D*, and the flow of benzol and acid is regulated accordingly. The column *II* is of similar construction to *I*. This plant is said to work well.

Dinitro-benzene, $C_6H_4(NO_2)_2$

Dinitro-benzene is manufactured in the same way as mono-nitro-benzene, except that twice as much acid is used. The nitration is generally carried out in two stages, the bulk of the waste acid from the first stage being run away before the second lot is run in. For the second stage the acids may with advantage be somewhat stronger and the contents of the nitrating pan are heated, finally to near the boiling-point of water. The waste acid from the second stage may be revivified by the addition of strong nitric acid and used for the preliminary nitration of a further charge of benzene. Of the three isomeric dinitro-benzenes the meta-compound is that principally formed, mixed with only small quantities of ortho- and para-dinitro-benzene. It is separated from the waste acid and washed first with cold water, and then with hot. As it is slightly soluble in the latter, the final wash-water should be kept and used again for the cold washing of a later charge.

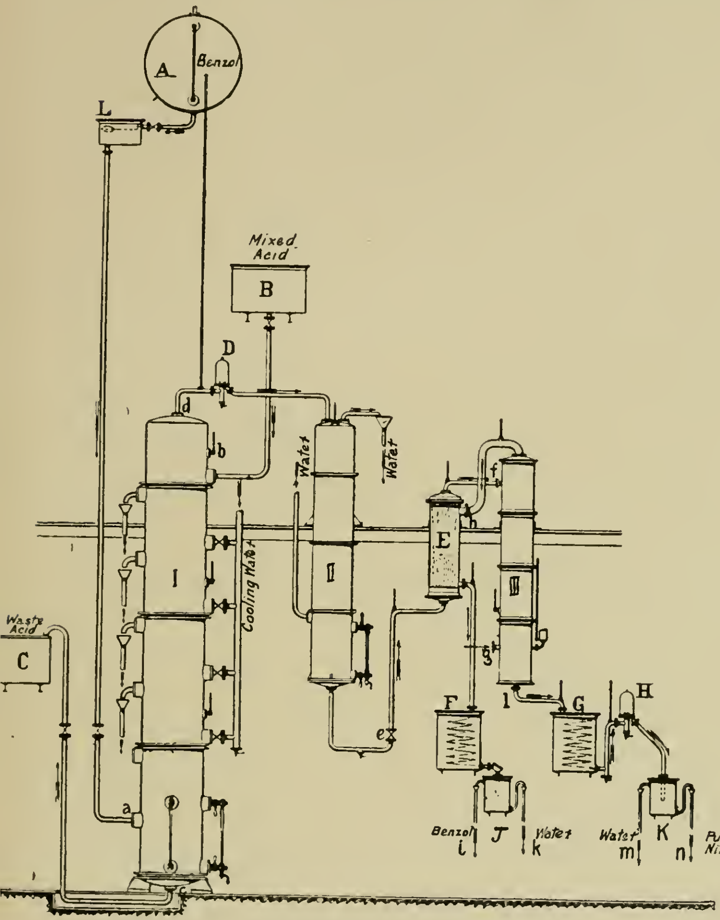


FIG. 52. Kubierschky's Nitrating Plant.

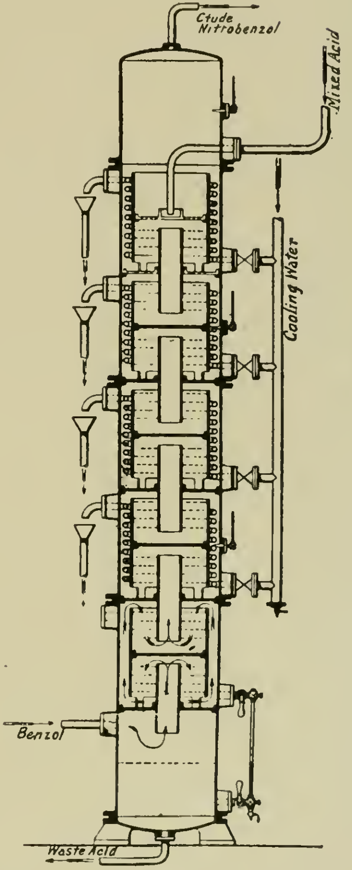


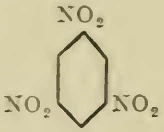
FIG. 53. Kubierschky's Nitrating Tower.

Pure m-dinitro-benzene melts at 89·9°, whereas the melting-points of the o- and p-compounds are 118° and 172° respectively. Good commercial dinitro-benzene melts at 85° to 87°, and is in the form of long shining needles of light yellow colour. It should contain no nitro-benzene and should be odourless. It is readily soluble in alcohol, benzene and other organic solvents, and can be purified by recrystallization from them. It can only be detonated with great difficulty, and consequently is not used an an explosive by itself, but it has been used as a constituent of complex explosives, such as the ammonium nitrate explosives, Bellite and Roburite, and low freezing nitro-glycerine explosives. There has been a tendency of recent years to substitute di- and tri-nitro-toluene for this substance, but the present scarcity of toluene is likely to cause this practice to be reversed. The density of m-dinitro-benzene is 1·369 at 89·1°.

Trinitro-benzene, $C_6H_3(NO_2)_3$

By a further nitration of dinitro-benzene it can be converted partly into trinitro-benzene, but it is necessary to use very strong acids made with oleum, and to carry out the nitration at a high temperature and for a long time. This drastic treatment causes the destruction of much of the material by oxidation, and consequently the yield is poor. It is obtained more easily from trinitro-toluene: this is oxidized by sulphuric acid and bichromate of potash to trinitro-benzoic acid, which is reduced to trinitro-benzene by boiling with water. In either case the manufacture is expensive and troublesome, so that although it is a slightly more powerful explosive than either trinitro-toluene or picric acid it has never come into general use.

There are three possible trinitro-benzenes, but the one that is obtained almost exclusively is the symmetrical or 1 : 3 : 5 compound.



It melts at 121° C.; its explosive properties have been investigated by Dautriche.[1] The 1 : 2 : 4 compound is also known.

Nitrotoluene, $C_7H_7NO_2$

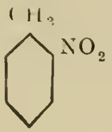
Toluene is nitrated in the same way as benzene, but the nitration proceeds somewhat more rapidly: also less acid is required because the molecular weight is greater. Of the three nitro-toluenes only 2 to 4 per cent. of the meta-compound is formed, about 38 per cent. of the para and 60 per cent. of the ortho, the proportions varying somewhat according to the conditions of nitration.[2] The yield is about 140 parts from 100 parts of toluene, whereas according to theory there should be 149. The product has a specific gravity of about 1·165, and is liquid at the ordinary temperature. By cooling it to about 10° C., part of the para-nitro-toluene can be made to separate out and filtered off on a cooled filter plate, but to effect a separation of the

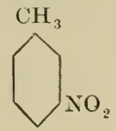
---

[1] *P. et S.*, 16. p. 27.

[2] *See* A. F. Holleman, *Proc. K. Akad. Wetensch.*, Amsterdam, 1908, vol. xi., p. 248; *Rec. Trav. chim.*, 1914, p. 1. H. W. Fischer, *Z. Elektroc.*, 1910, p. 161.

constituents of the liquid residue it is necessary to submit it to fractional distillation *in vacuo*. The ortho-compound distils over first; when the greater part of it has passed over the distillation is interrupted and the residue is run out and cooled, whereupon it deposits the greater part of its para-nitro-toluene. The following are the principal physical properties of the nitro-toluenes:





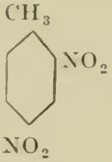
	Ortho	Meta	Para
Specific gravity	1·163 (20°/4°)	1·168(22°)	1·123(54°)
Melting-point	−3·85°	+16·1°	52°
Boiling-point	223·3	230–231	237·7

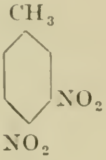
The mono-nitro-toluenes are not explosive in themselves and are not used as constituents of composite explosives, but they are formed in the first stage of the formation of di- and tri-nitro-toluenes, and para-nitro-toluene is used extensively for the manufacture of dye-stuffs.

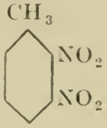
Dinitro-toluene, $C_7H_6N_2O_4$

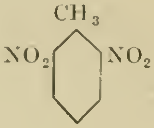
On further nitration para-nitro-toluene gives almost exclusively 2 : 4-dinitro-toluene, and the ortho-derivative gives mostly the same compound, but also some 2 : 6-dinitro-toluene. The meta-derivative is present only in small quantity and nitrates much less readily, and consequently remains unchanged to a considerable extent. Consequently the principal product of the direct nitration of toluene to the second stage is 2 : 4-dinitro-toluene mixed with small quantities of other dinitro-compounds, some mono-nitro-toluene (meta and para) and trinitro-toluene. The mono-nitro-toluenes are only separated from one another before nitration if the para-compound is required for the manufacture of dye-stuffs; in this case the crude ortho-nitro-toluene is taken for nitration. When the nitration is complete the crude dinitro-toluene is allowed to separate from the waste acids in the warm. On cooling it sets to an oily solid. This is often purified by warming it to about 40° C. and allowing the more easily fusible portion to flow away. The purified product is used for the manufacture of dye-stuffs, and sometimes for the preparation of composite explosives such as Cheddite. The more fusible residue is known in Germany as "Binitrotropföl," and is used for the manufacture of trinitro-toluene. From the waste acids on cooling there separates out a further small quantity of nitro-product which floats on the surface, from which it is skimmed off. The waste acid has a specific gravity of 1·75 to 1·77, and contains from 3 to 4 per cent. of nitric acid, whereas the waste acid from the manufacture of mono-nitro-toluene has a specific gravity of 1·66 to 1·67, and contains, according to R. Escales, 1 to 1·5 per cent. nitric acid.[1] If the nitration be properly conducted the yield of dinitro-toluene is not far short of the theoretical.

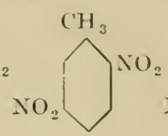
There are six possible dinitro-toluenes, and all of them have been prepared either by nitration of toluene or by more indirect methods.

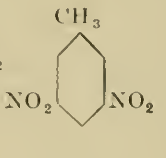












	2 : 4	3 : 4	2 : 3	2 : 6	2 : 5	3 : 5
Melting point	70°	60°	63°	66°	52·5°	92–93°

Of these the first is the only one that is of any commercial importance; ortho-nitro-toluene, however, gives a little of the 2 : 6-compound. Meta-nitro-toluene gives 3 : 4 mixed with smaller quantities of 2 : 3 and 3 : 6.[2] Commercial crude dinitro-toluene contains, therefore, all the above six compounds except the last, but the first predominates. The statement that the 3 : 5-derivative is also formed[3] is doubted by Will.[4] All except the 2 : 3- and 3 : 5-compounds have been found in a by-product from the purification of dinitro-toluene.[5]

In explosive properties all these substances are very similar; they can only be detonated with great difficulty, and are decidedly insensitive. The 2 : 4-compound is used as a constituent of composite blasting explosives, notably cheddite. They possess the disadvantage that they are very poisonous and are liable to affect injuriously those who handle them. From the purification of the crude material a complex mixture can be obtained, which is liquid at the ordinary temperature. This dissolves collodion cotton, and is thereby converted into a thick jelly, which is used in the manufacture of plastic blasting explosives.

Trinitro-toluene, $C_7H_5N_3O_6$

Trinitro-toluene may be made by the nitration either of "Binitrotropföl" or crude ortho-nitro-toluene or from toluene by successive nitration in two or three stages without the separation of any of the nitro-bodies. In any case it is best to conduct the conversion of di- into tri-nitro-toluene as a separate operation as it requires a stronger mixed acid, and if a large volume of strong mixed acid be used to nitrate toluene or mono-nitro-toluene directly to trinitro-

---

[1] *Nitrosprengstoffe*, p. 142.

[2] A. F. Holleman and H. A. Sirks, *Proc. K. Akad. Wetensch.*, Amsterdam, 1906, p. 280; *Chem. Soc. Abstr.*, 1907, i., p. 280.

[3] Häussermann and Grell, *Ber.*, 1895, p. 2564

[4] *Ber.*, 1913, p. 558.

[5] E. Molinari and M. Giua, *Rendiconti del Reale Istituto di Scienze e Lettere*, 1913, vol. 46, No. 11; *S.S.*, 1914, p. 239.

toluene the yield will be low in consequence of its solubility in the waste acid, and by-reactions due to the oxidizing action of the acid. The mixed acid may be made by adding nitric acid cautiously to oleum of 20 per cent. strength. According to F. Langenscheidt the quantities are 1125 kg. of 20 per cent. oleum and 305 kg. nitric acid of sp. gr. 1·5.[1] 500 kg. of binitrotropföl are placed in the nitrating pan and melted and the mixed acid is run in slowly at a temperature of 70 to 75° C. When all the acid has been added the mixture is warmed gradually until at 90° to 100° the reaction sets in and the temperature rises to about 130°. At this temperature it is allowed to remain for an hour and then cooled to 100°. Water is added to the charge to diminish the solubility of the trinitro-toluene in the acid,[2] and the contents of the nitration are run off through a steam-heated cock and kept hot until separation is complete. The trinitro-toluene may be solidified in a suitable state of division by running it on to a jet of air over water. Toluene is nitrated with considerably greater ease than benzene,[3] but it is necessary to use strong acids at a high temperature to make the trinitro-derivative, and there is an appreciable loss by oxidation, with the result that the yield is lower than the theoretical. According to Will trinitro-benzoic acid and tetranitro-methane are liable to be formed,[4] the latter may sometimes be recognized in the factory by its intense smell. The oxidizing action is said to be increased by the presence of metallic salts,[5] sodium nitrate, and especially ammonium nitrate,[6] but the formation of nitro-benzoic acid under manufacturing conditions has been denied by F. Langenscheidt.[7] According to Copisarow, phenolic compounds are liable to be formed by the action of the acids on the metal of the nitration vessel producing hydrogen, and sulphonic acids if the quantity of nitric acid present be insufficient.

Waste acids.

The waste acid contains up to 4·5 per cent. of nitric acid and nitrous acids,[8] and a considerable amount of trinitro-toluene and various by-products in solution. It may with advantage be revivified and used for the manufacture of mono-or di-nitro-toluene,[9] or the nitric acid is distilled off after diluting to density of 1·38, and the residue is further diluted to 1·21 to precipitate the nitro-bodies. It is not advisable to use the waste acid for the manufacture of nitric acid from sodium nitrate because the nitro-

---

[1] *S.S.*, 1912, p. 425.

[2] *See* Germ Pat. 254,754 of July 15, 1909, also Vennin et Chesneau, p. 261.

[3] For measurements of the velocities of nitration *see* J. P. Wibaut, *Rec. Trav. chim.*, 1915, p. 950 ; *J. Soc. Chem. Ind.*, 1915, p. 241.

[4] *Ber.*, 1914, p. 707.

[5] M. Copisarow, *Chem. News*, 1915, vol. 112, p. 247 ; *J. Soc. Chem. Ind.*, 1915, p. 1168.

[6] A. Voigt, *S.S.*, 1914, p. 225.

[7] *S.S.*, 1915, p. 23.

[8] *See* L. Wuyts, *J. Soc. Chem. Ind.*, 1916, p. 149.

[9] *See* F. M. Vásquez, *Memorial de Artilleria*, Sept. 1910 ; *S.S.*, 1911, p. 302 ; also Eng. Pat. 23,181 of 1914, by Craig, Robertson, Farmer and Rotter, *Arms and Explosives* 1915, p. 139.

explosives pass unaltered into the nitro-cake and may cause explosions.[1] Or it may be denitrated in a denitration tower, but in this case a large proportion of the nitro-compounds pass over with the nitrous gases and cause stoppages.[2] The following are the compositions of two waste acids given by M. Copisaroff:[3] in the second one an insufficient quantity of nitric acid has been used:

Colour	yellow	brown
Nitrous acid	0·2	0
Nitric acid	2·05	0
Sulphuric acid	63·46	58·0
Water	34·29	37·28
Sulphonic acids	0	4·72
	100	100

W. McHutchison and R. Wright[4] give the following as the composition of a waste acid:

Colour	brown
Nitrous acid	0·50
Nitric acid	6·71
Sulphuric acid	86·30
Water, etc.	6·49
Specific gravity	1·850 at 17°

On mixing with this an equal volume of water, reducing the specific gravity to 1.489, trinitro-toluene separated, equivalent to 5·8 per cent. by weight. The addition of 4 more volumes of water only increased this amount to 6·2 per cent. The authors recommend that the waste acid be added to the water, and not vice versa, so as to recover the trinitro-toluene in a convenient form.

The nitro-compounds can also be extracted from the waste acid by agitating it with toluene, or by revivifying the acid and using it for the manufacture of mono- or dinitro-toluene. In either case the toluene used to extract the nitro-body is eventually converted into trinitro-toluene.

Purification of trinitro-toluene

The crude product is freed from acid either by boiling it with water or by washing it in a granular condition with warm water with the addition of a little sodium bicarbonate. It is then dried and purified either by washing with alcohol of 95 per cent. strength,[5] or by recrystallization either from alcohol or benzene. According to Langenscheidt,[6] technical alcohol contain-

---

[1] Vennin et Chesneau, p. 260.

[2] F. Langenscheidt, *S.S.*, 1912, p. 426.

[3] *Chem. News*, 1915, p. 247; *J. Soc. Chem. Ind.*, 1915, 1168.

[4] *J. Soc. Chem. Ind.*, 1915, p. 781.

[5] Vennin et Chesneau, p. 261.

[6] *S.S.*, 1912, p. 427.

ing about 90 per cent. C_2H_5OH dissolves at the boiling-point one-ninth of its weight of trinitro-toluene and gives 90 per cent. of it up again on cooling. Benzene dissolves 1·7 times its weight at the boiling-point, and about 78 per cent. of it crystallizes out again on cooling. But the best solvent is alcohol mixed with 5 to 10 per cent. of pure benzene. In a double-walled iron vessel are placed 2300 litres of this solvent, and 500 kg. of trinitro-toluene. The liquid is stirred and boiled, the vapour formed being condensed and returned to the vessel. When solution is complete the liquid is filtered and allowed to cool. The crystals are freed from mother liquor by centrifuging or filtering off in a vacuum press. If the material be recrystallized more than once the mother liquor from the second recrystallization is used for dissolving up a further quantity of crude substance, and so on. The last mother liquors are concentrated in a still and give on cooling some trinitro-toluene of inferior quality, and on further concentration a still more impure material is obtained, which may be liquid at the ordinary temperature, and may then be used for making plastic explosives.

Trinitro-toluene may also be purified by recrystallization from sulphuric acid. This method is used in France for the preparation of material for the manufacture of mining explosives. After this recrystallization it is washed methodically with warm water, neutralized with a dilute solution of sodium carbonate and then rinsed with pure water. The product obtained has a melting-point of 77° to 79°.[1] Vender has patented a process for recrystallizing it from strong sulphuric acid, preferably of 100 per cent. strength. After dissolving at 80° to 100° the acid is cooled and may be diluted. It is claimed that this process gives a large yield of material of good quality.[2]

Another proposal is to use nitro-toluene as a solvent.[3] The trinitro-toluene is heated with a third of its weight of nitro-toluene, allowed to cool, filtered off and washed with alcohol to remove the nitro-toluene. The nitro-toluene containing the impurities is used for the manufacture of a further quantity of trinitro-toluene. The objection to this process is that the nitro-toluene must be nearly as difficult to eliminate as the natural impurities.

Liquid trinitro-toluenes are naturally very variable in composition, an average sample may contain 80 per cent. trinitro-toluene, consisting of the 2 : 4 : 6-compound with one or more other isomers, together with several dinitro-toluenes and only a very small quantity of mono-nitro-toluene.[4] Other substances are probably also present. Nobel and Co. of Hamburg have patented a method for increasing the degree of nitration of this product

---

[1] Vennin et Chesneau, p. 261.

[2] V. Vender, Eng. Pat. 18,281 of 1909, Germ. Pat. 237,738.

[3] Germ. Pat. Announcement 8729, 12 o, Aug. 28, 1913.

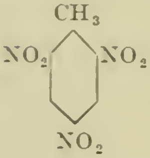
[4] *See* 8th Intern. Cong. Appl. Chem., 1912, vol. 27, p. 44.

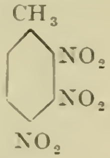
without causing it to solidify at the ordinary temperature.[1] For this purpose they use an acid rich in sulphuric acid and poor in nitric. The following example is given: 100 kg. of a residue from purification, containing about 15 per cent. nitrogen, are heated for a long time at a temperature of 85° to 100° C. with 185 kg. of mixed acid containing 85 per cent. H_2SO_4 and 15 per cent. HNO_3. The resulting product was 87 kg. of liquid trinitro-toluene solidfying at 14°, containing 16·6 to 17·2 per cent. nitrogen and giving a Trauzl test of 250 to 270 c.c., whereas dinitro-toluene contains 15·4 per cent. nitrogen, and trinitro-toluene 18·5 per cent. and gives a Trauzl test of about 290 c.c.

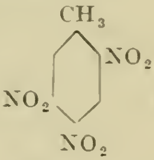
Light has been thrown upon the low melting-points of these products by M. Giua, who has determined the melting-point curves of various binary mixtures of nitro-toluenes.[2] In each case examined he found that a complex compound is formed having a melting-point about 30° lower than that of either constituent. These compounds only exist in the solid state, when melted they dissociate entirely. Mixtures containing three or more constituents would show a still greater depression of the melting-point.

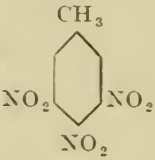
The trinitro-toluenes,

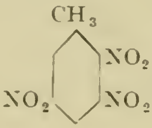
There are six possible trinitro-toluenes, and according to M. Copisarow[3] they are all known and have the following melting-points:

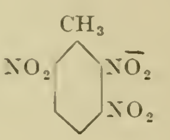












	α	β2	γ2	δ	ε3	θ
	2:4.6	2:3:4	2:4:5	3:4:5	2:3:5	2:36
Melting-point	81	112	104	137·5	97·2	79·5
Coloration with acetane and ammonia	deep red	greenish yellow	blue	orange red	rose red	—

As already stated, commercial dinitro-toluene consists almost entirely of the 2 : 4-compound, and this on further nitration gives only 2 : 4 : 6-trin trotoluene, which consequently constitutes the bulk of crude commercial trotyl. It contains, however, small quantities of 2 : 3 : 4- and 2 : 4 : 5-trinitro-toluene, these being formed from the products of meta-nitro-toluene.[4-5] 2 : 5-dinitrotoluene gives the 2 : 4 : 5-compound and 2 : 3- the 2 : 3 : 4-compound, 3 : 4- a mixture of about 75 per cent. 2 : 4 : 5- and 25 per cent. 2 : 3 : 4-. It is doubtful whether 3 : 5-dinitro-toluene is amongst the products of nitration, but

---

[1] Germ. Pat. 264.503 of Sept. 14, 1910.

[2] *Ber.*, 1914, p. 1718.

[3] *Loc. cit.*

[4] W. Will, *Ber.*, 1914, p. 707.

[5] W. Körner and A. Contardini. *Atti R. Accad Lincei*, 1915, i., p. 888.

it can be prepared indirectly; Will found, however, that it could not be further nitrated to a trinitro-toluene: it either remained unchanged or was oxidized to dinitro-benzoic acid. Only the first three of the above six trinitro-toluenes are therefore known to be formed by the nitration of toluene, and of these the first is by far the most important. It has not hitherto been found possible to make tetra-nitro-toluene.

Trinitro-toluene was made in the laboratory by Hepp as long ago as 1880,[1] and in 1891 C. Häussermann together with the Griesheim Chemical Factory took up its manufacture.[2] Experiments were carried out with it by the German military authorities in the late 'eighties, and early 'nineties, and in 1902 they adopted it for filling shell and other purposes. In 1901 the manufacture was taken up by the Carbonite Co., and other explosive firms soon followed. Other countries soon followed suit, Italy in 1907, and Russia shortly after.

It has been given many names, mostly abbreviations of its scientific one. In the English service it was formerly known as T.N.T., but now as trotyl; in Italy it is called tritolo. Other names are trinol and trilite.

It has largely displaced picric acid for filling high-explosive shell because, although it is not quite so powerful or violent, it has a lower melting-point, is not so sensitive and does not tend to form dangerous metallic salts. It has replaced picric acid and gun-cotton for filling submarine mines and torpedo war heads: over gun-cotton it has the advantage of greater violence and a higher density. It has been substituted for dinitro-benzene in blasting explosives because it is not only more powerful but also less poisonous. It is used in the manufacture of detonating fuse and composite detonators and many other explosive accessories.

The melting-point of the pure substance was at one time stated to be 82°,[3] but this is too high. According to Comey it is 80·5°–80·6°,[4] Molinari and Giua as 80·65°,[5] Rintoul as 80·8°–80·85°,[6] and Escales as 80·6° or 80·7°.[7]

Trinitro-toluene is one of the most stable explosives; when heated it does not ignite until a temperature of about 300° is reached and then it does not explode. Even at 150° there is no perceptible decomposition, but at 180° there is a steady though slow evolution of gas.[8] On June 11, 1910, an Order

---

[1] *See Annalen*, vol. 215, p. 361.

[2] *See* C. Häussermann, *Zeitsch. angew. Chem.*, 1891, p. 508; *J. Soc. Chem. Ind.*, 1891, p. 1028.

[3] Wilbrand, *Annalen*, 128, 1863, p. 178; J. Rudeloff, *S.S.*, 1907, p. 4.

[4] A. M. Comey, *J. Ind. Eng. Che.*, 1910, p. 103.

[5] *Rend. Reale Ist. Scienze Let.*, 46, 1913; *S.S.*, 1914, p. 242.

[6] *J. Soc. Chem. Ind.*, 1915, p. 60.

[7] *Nitrosprengstoffe*, pp. 20, 155, 293.

[8] Verola, *P. et S.*, vol. 16, 1912, p. 40.

in Council was issued under section 50 of the Explosives Act, 1875, exempting it from being deemed to be an explosive during manufacture and storage, unconditionally, and when conveyed and imported provided it is properly packed.

ccidents.

Nevertheless it must not be forgotten that it can explode, and in fact it has caused a number of disasters. In 1906 a fire at the Roburite Factory at Witten led to the explosion of the store-room containing trinitro-toluene and ammonium nitrate; the detonation was so violent that the factory was almost entirely destroyed, and forty-two people were killed, and many injured.[1] In 1908 an explosion occurred at J. W. Leitch and Co.'s works at Huddersfield, whereby five men were injured. The accident was caused by placing a pipe containing trinitro-toluene in a boiler fire to clear the pipe by melting out the contents. In 1909 several men were killed by an explosion in the crystallizing house at Allendorff's factory at Schönebeck, a.E. This accident is somewhat puzzling, as the effects seemed to be too great to be due only to an explosion of vapour, and yet not nearly so great as would have been caused by the explosion of even a small proportion of the trinitro-toluene present in the building.[2] In 1912, 100 kg. exploded from some unknown cause in a cask in the washing house of a German factory, whereby four men were killed and four severely injured. It would seem that the substance is liable occasionally to contain some impurity, which renders it much more dangerous. To a cause of this sort is ascribed a fatal explosion that occurred in 1907 in a vacuum still from which mono-nitro-toluene was distilled.[3] Dupré found that the addition of a little caustic potash caused trinitro-toluene to explode when heated to 160°.[4]

β-and γ-trinitro-toluene are, however, somewhat less stable than the a-compound. Their behaviour with alkali was investigated by W. Will,[5] who found that the β- and γ-compounds when treated with alkali, even an alkaline carbonate, whether in the presence or absence of alcohol, are converted into salts of dinitro-cresol, and these have much the same properties as picrates. This change even takes place when they are heated with lead oxide in the presence of alcohol, lead cresylates being formed. The a- compound, on the other hand, is not attacked by heating with lead oxide and alcohol, and by 1 per cent. soda solution at 95° to 100° it is only attacked a third as rapidly as the other two. Alkali alone converts the a-compound into red colouring matters, and in the presence of an oxidizing agent gives hexanitro-dibenzyl, which is comparatively stable.

---

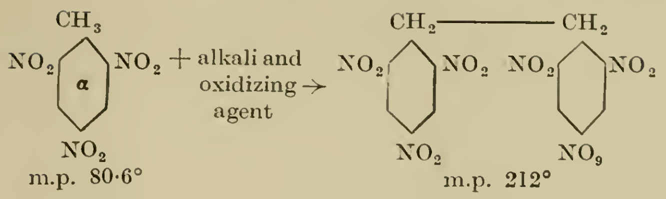
[1] *See S.S.*, 1907, pp. 333, 413, and 416.

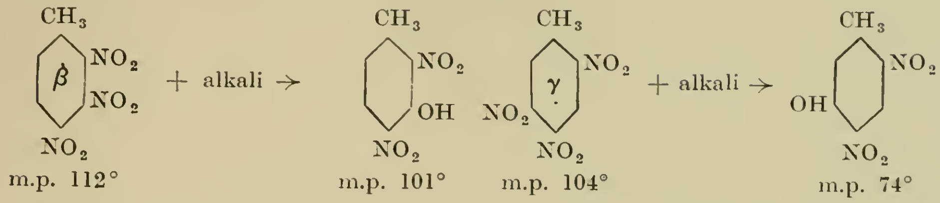
[2] *See S.S.*, 1909, p. 213.

[3] *S.S.*, 1908, p. 298.

[4] *A.R.*, 1903, p. 26.

[5] *Ber.*, 1914, p. 711; *see also* M. Copisarow, *Chem. News*, 1915, vol. 112, p. 283.





Properties.

Except as regards the melting-point the physical properties of the three isomeric trinitro-toluenes are similar. They have about the same specific gravity of about 1·62, the same temperature of ignition, 290° to 310°, the same heat of combustion of about 3660 Calories, give the same result in the Trauzl test, and are about equally sensitive under the falling weight, although the α-compound is slightly less sensitive than the γ.

Density.

Trinitro-toluene, which has been melted, has a density of 1·57 to 1·60; when powdered and compressed Dautriche found that it had the following densities:

Pressure		Mean density
kg./cm.^{2}	tons/in^2	
275	1·75	1·320
685	4·35	1·456
1375	8·73	1·558
2060	13·1	1·584
2750	17·5	1·599
3435	21·8	1·602
4125	26·2	1·610

whence it is concluded that the limiting density for the compressed material is about 1·62.[1]

NITRO-XYLENES, ETC.

The next homologue of the benzene series is xylene, of which there are three isomers, all of which are present in coal tar, and have boiling-points close together between 137° and 142°. It is not practicable to separate them

---

[1] *P. et S.*, vol. 16, 1912, p. 28.

on a commercial scale. Nitro-xylene is a constituent of some blasting explosives, Monachit for instance,[1] but for this purpose the crude mixture is used which is obtained by nitrating the mixture of the three xylenes. As these are nitrated with different degrees of difficulty a mixture tri-, di- and even mono-nitro-xylenes is obtained, and in consequence of the complexity of the mixture it is often liquid. If the crude xylene contain other substances as well, the nitro-product will, of course, be still more complex. The liquid products can be used, like liquid trinitro-toluene, for the manufacture of plastic explosives, the liquid being thickened by dissolving some collodion cotton in it.

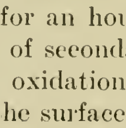
Some inventors have proposed to nitrate wide fractions of coal tar naphtha. Thus C. Distler, E. Blecher and C. Lopez [2] nitrate the fraction boiling between 130° and 170°, and O. Silberrad [3] that between 200° and 350°. There is no published information as to the chemical stability of these complex mixtures of nitro-compounds.

NITRO-NAPHTHALENES

Mono-nitro-naphthalene, $C_{10}H_7NO_2$.

This substance is made by nitrating naphthalene with a mixed acid containing only slightly more than the theoretical amount of nitric acid. The acid is placed in a nitration pot provided with a stirrer and the naphthalene added a little at a time, the temperature being kept below 40°. Then the liquid mixture is heated to 60° for an hour. A considerable amount of red fumes is evolved in consequence of secondary reactions involving the formation of phthalic acid and other oxidation products. On cooling the nitro-naphthalene crystallizes out on the surface of the acid, which is then run off. The product is centrifuged, washed with water and dilute sodium carbonate solution, then with water again and dried at 50°. It may be purified by recrystallization from alcohol or benzol. The yield is about 110 per cent., whereas theoretically it should be 135 per cent.

There are two mono-nitro-naphthalenes, but under ordinary conditions of nitration the α-compound only is formed. The melting-point of this is given variously as 58·5° and 61°, but the commercial product, not being quite pure, melts at about 55°. It is a neutral body, insoluble in water, but soluble in ether, alcohol, carbon bisulphide, petroleum ether, etc. As an explosive its power is small, but it is used in cheddite as a combustible and agglomerant, its softness helping to bind the powder together. Its specific gravity is 1·331 at 4°.



---

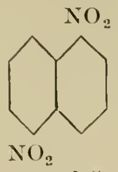
[1] *See S.S.*, 1909, p. 106.

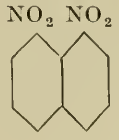
[2] Germ. Pats. 212,906, 214,887, 242,731 ; French Pat. 380,996 ; Eng. Pat. 19,565 of 1907

[3] Eng. Pats. 13,860, 13,861 and 19,381 of 1912.

Dinitro-naphthaler $C_{10}H_6N_2O_4$

If nitro-naphthalene be further nitrated in the same way a mixture of two dinitro-naphthalenes is obtained :


α or 1:5
m.p. 217°


β or 1:8
m.p. 170°

or naphthalene may be nitrated directly to the dinitro-compound if a sufficient quantity of acids of suitable strength be used. The commercial product melts at about 140°. Both isomers are used for the manufacture of dye-stuffs. To separate them advantage is taken of the fact that the α-compound is almost insoluble in many organic solvents, which dissolve the β-compound with ease. The crude product is washed with water, treated with carbon bisulphide to remove nitro-naphthalene, and then with acetone to dissolve β-dinitro-naphthalene. But for the manufacture of explosives it is not necessary to separate the isomers. Dinitro-naphthalene is a constituent of Grisounites made in France, of Ammonite and some other similar explosives. It is decidedly insensitive and not at all powerful as an explosive.

Trinitro-naphthaler $C_{10}H_5N_3O$

This is made by nitrating mono- or di-nitro-naphthalene with moderately strong mixed acid. A mixture of several isomers is obtained melting at about 110°. This is washed, and heated in copper crucibles to a temperature above the melting-point until no more gas is evolved. The molten mass is then poured into water, powdered, centrifuged and dried. It is used in the same classes of explosives as dinitro-naphthalene, and has also been added to smokeless powders as a stabilizer.[1]

Tetranitro-naphthaler $C_{10}H_4N_4O$

This is made by nitrating dinitro-naphthalene with a mixture of nitric acid and oleum. It is a mixture of several isomers and melts at about 220°. It has been but little used in explosives, probably because the yield is small.

M. Patart has in the laboratory nitrated naphthalene with a large number of different acid mixtures, using the acid in the proportion of 30 parts to 1 of naphthalene.[2] The results have been plotted by Saposhnikoff on a triangular diagram similar to that on p. 138.[3] The curves showing the degree of nitration attained take a very similar course to those for nitro-cotton. In practical manufacture the proportion of acid used is very much smaller than Patart employed, but the results may be of value as indicating the composition that the waste acids should have.

---

[1] Vennin et Chesneau, p. 268.

[2] *P. et S.*, vol. ix., p. 38 ; vol. xi., p. 147.

[3] J. Russ., *Phys. Chem. Soc.*, 1914, p. 1102 ; *Chem. Soc. Abstr.*, 1915, i., p. 393.

POISONING BY AROMATIC COMPOUNDS

The aromatic hydrocarbons have a decided toxic action; the vapours of benzene and toluene produce giddiness and finally insensibility when inhaled. Workers who are constantly exposed to the fumes may suffer severely in health. Adequate fans should therefore be provided when these volatile liquids are exposed in open vessels.

The nitro-derivatives of these hydrocarbons are more poisonous than they are themselves, but are not so volatile. Dinitro-benzene and dinitro-toluene are specially poisonous, and their use in explosives is therefore objectionable. Explosives containing them should not be handled with the bare hands, and during all manufacturing operations precautions must be taken to prevent workers inhaling the dust and fumes.[1] A French Commission which reported on this subject in 1912 [2] found that:

1. The workers most frequently affected are generally young people who have not been working long in the factory.
2. Most of these workers are drinkers.
3. Serious attacks are most frequent in July and August, and especially when the weather is thundery, the vapours being liberated to a greater extent the higher the temperature.

The symptoms are drowsiness, sometimes going as far as unconsciousness, gastric troubles, excema, and frontal headache. In mild cases a few hours in the open air may cure the patient. Severe cases may end in death. Workers who show signs of being affected should at once be transferred to other work at any rate for a time.

Trinitro-benzene and -toluene are generally considered to be much less, poisonous than the dinitro-compounds. There have, however, been some cases of fatal poisoning by trotyl, but these may have been due really to the presence of dinitro-toluene.

Picric acid has a disagreeable bitter taste, but is not very poisonous. The chlor-nitro-compounds, on the other hand, are more dangerous than those not containing chlorine. Some of the other nitro-derivatives, such as tetryl and hexa-nitro-diphenylamine, have been found to be decidedly poisonous.

The curative measures adopted in Germany are: immediate removal from the factory, artificial respiration and inhalation of oxygen, and non-alcoholic stimulants. As preventative measures alcohol is forbidden during working hours, and only moderate quantities are allowed at other times. The workers should wear leather gloves, and clothes fitting tightly at the neck, wrists and ankles. Their boots should have wooden soles, and they should

---

[1] *See* Report to the Home Secretary by Dupré and Smith, 1893.

[2] *P. et S.*, vol. xvi., p. 144.

put cotton wool in their ears, and when necessary they should wear respirators. Meals must not be taken in the working rooms, and before eating the worker must wash his face and hands with soap and water and clean his nails with a nail-brush, and rinse his mouth out with a 2 per cent. solution of tincture of myrrh. The workers have daily a douche bath and once a week a tub.[1]

---

[1] R. Escales, *Nitrosprengstoffe*, p. 211; *see also S.S.*, 1908, p. 259.

CHAPTER XX

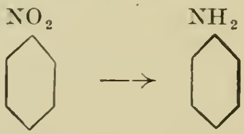
OTHER NITRO-AROMATIC COMPOUNDS

Derivatives of Aniline

Aniline $C_6H_5NH_2$: Diphenylamine $(C_6H_5)_2NH$: Hexanitro-diphenylamine $(C_6H_2N_3O_6)_2NH$: Nitro-anilines : Nitro-methylanilines : Manufacture of tetryl : Properties of tetryl : Higher nitro-derivatives of methyl-aniline : Picric acid, $C_6H_3N_3O_7$: Properties : Higher nitro-phenols : Styphnic acid $C_6H_3N_3O_3$ Trinitro-cresol, $C_6H,OH,CH_3(NO_2)_3$: Picrates and trinitro-cresylates : Trinitro-anisole, $C_6H_2OCH_3(NO_2)_3$: Kinetics of nitration

Aniline, $C_6H_5NH_2$.

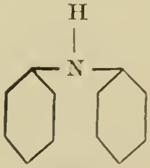
ANILINE is made from nitro-benzene- by treating it with iron borings and hydrochloric acid. The nascent hydrogen replaces the oxygen. When reduction is complete the aniline is distilled in a current of steam, allowed to settle, and purified by distillation *in vacuo*. For details of the processes *see* Thorpe's *Dictionary of Applied Chemistry*, vol. i, p. 260.



Aniline, when pure, is a colourless liquid with a specific gravity of 1·025 at 15°/15° and boiling at 184°. It is used very extensively for the manufacture of synthetic dyes, and some of its derivatives are used in the explosives industry. The substance itself has been used as a stabilizer in smokeless powders, but its strongly basic character and its volatility are serious objections : it has now been replaced for this purpose by other substances, notably diphenylamine.

Diphenylamine, $(C_6H_5)_2NH$.

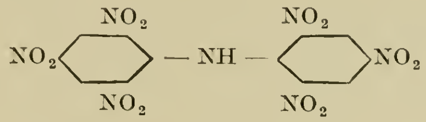
This is made by heating aniline and aniline hydrochloride together in an autoclave for thirty to thirty-five hours at 220° to 230°. The product is extracted with hot dilute hydrochloric acid, which dissolves the unchanged aniline hydrochloride whilst the diphenylamine floats on the surface as free base. The yield is 60 to 70 per cent. of the aniline used. It is a



crystalline solid melting at 54° and boiling at 310°. It is almost insoluble in water, soluble in alcohol, benzene and ether, and only feebly basic. It is used as a stablizer in military smokeless powders, and also for the manufacture of dyes.

Hexanitro-diphenyl-amine, $(C_6H_2N_3O_6)_2$NH.

One of these dyes is the hexanitro-derivative, known as "Aurantia," which is made either by nitrating diphenylamine or by other synthetic methods.[1] It is a powerful explosive,but does not appear to be used much for this purpose, nor is it any longer used much as a dye. It is acid in character and somewhat poisonous. Its colour is lemon yellow, and it melts at 238°. It is more sensitive to blows than tetryl.[2]



Nitro-anilines,

The direct nitration of aniline is liable to give low yields, because by-reactions set in. Therefore it is often combined first with acetic acid to form acetanilide, which is nitrated and then heated with dilute acid or alkali to remove the acetyl group. In this way ortho- and para-nitro-aniline can be made.[3] The meta-compound is obtained by the partial reduction of meta-dinitro-benzene. Various other indirect methods can be used. The mono- and di-nitro-anilines are readily nitrated further. Thus ortho-nitroaniline gives 2 : 4 : 6-trinitro-aniline, or picramide, which, however, is more easily made by the action of ammonia on trinitro-chlor-benzene. This is a powerful explosive, but has not been used on a large scale.

Similarly meta-nitro-aniline gives tetra-nitro-aniline,[4] and Flürscheim has proposed to use this as a commercial explosive[5] as it is more powerful than any substance at present in use. He makes the nitro-aniline by treating commercial dinitro-benzene with sodium bisulphide and water. The product thus obtained, without previous purification, is nitrated with mixed acid at about 70° or lower. The nitration proceeds rapidly. The crystals of tetra-nitro-aniline are filtered off from the undiluted waste acids, washed with water and dried. In this way commercial dinitro-benzene yields almost its own weight of pure tetra-nitro-aniline, whereas theoretically it should yield 1·53 times its weight. Tetra-nitro-aniline is a yellow solid with a specific gravity of 1·867. It cannot be melted without decomposition ; if heated

---

[1] *See S.S.*, 1910, p. 16 ; also T. Carter, *S.S.*, 1913, p. 205.

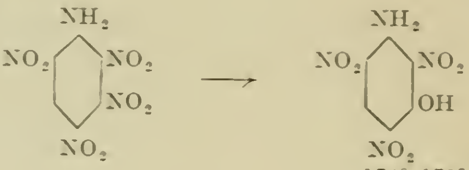
[2] F. Langenscheidt, *S.S.*, 1912, p. 446.

[3] For the proportions and yields *see* A. F. Holleman, J. C. Hartog and T. v. d. Linden, *Ber.*, 1911, p. 704.

[4] B. Flürscheim and T. Simon, *Proc. Chem. Soc.*, 1910, p. 81.

[5] Eighth Intern. Cong. Appl. Chem., 1912, vol. iv., p. 31 ; *S.S.*, 1913, p. 185. Eng. Pats. 3224 and 3907 of 1910 ; Germ. Pats. 242,079 and 241,697.

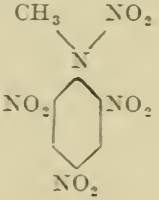
5° a minute it melts at about 216°. It is claimed for it that it is not more sensitive than tetryl, and that it is stable, but on boiling with water it is converted into trinitro-amino-phenol, and the same substance is obtained instantaneously at the ordinary temperature by the action of an equeous solution of sodium acetate.



m.p. 174°–175°

Nitro-methyl-anilines.

Methyl-aniline is made by heating anline hydrochloride or sulphate with methyl alcohol. On nitration four NO_2 groups can be made to enter the molecule without any great difficulty, three combining with the carbon atoms of the benzene ring and one with the nitrogen. This substance is often called tetranitro-aniline, but strictly speaking its scientific name is trinitro-phenyl-nitramine: commercially it is called tetryl or tetralite. It was first described by Romburgh in 1883,[1] and is obtained also on nitrating dimethyl-aniline, which is made in a similar manner to methyl-aniline.



Manufacture of tetryl.

The following is the method of manufacture as described by F. Langenscheidt:[2] The dimethyl-aniline used should be of a high degree of purity; 95 per cent. of it should distil over within a range of 1° or 1¼° C. Its specific gravity is 0·9567 at 23°, and its boiling-point 190°(at 760 mm. ? According to the Tables of Landolt-Börnstein, 1912, the specific gravity is 0·9555 at 20°/4° and the boiling-point 193·1° at 760 mm.) The nitration vessel consists of an enamelled pot provided with an enamelled stirrer, and a jacket through which water or steam can be passed. In it 1000 kg. of colourless lead-free sulphuric acid of 97 to 98 per cent. strength are placed, the stirrer is started and 100 kg. of the dimethyl-aniline is slowly run in: this takes about two hours. The acid in dissolving the dimethyl-aniline becomes coloured light brown, but the colour must not be so dark that one cannot see through a layer 5 cm. thick. A dark colour is generally due to insufficient cooling or too rapid

---

[1] *Rec. trav. chim.*, vol. ii., p. 108.

[2] *S.S.*, 1912, p. 445. *See also* F. M. Vasquez, *S.S.*, 1911, p. 302.

addition of the dimethyl-aniline. The sulphuric acid solution should be nitrated without unnecessary loss of time, otherwise there may be darkening, and the dark colour cannot be removed from the finished tetryl.

The nitration is carried out in the same or a similar vessel. In it are placed first 430 kg. of nitric acid of 47° B. (sp. gr. 1·483, 87·3 per cent. HNO_3) and heated to 40° C., and the sulphuric acid solution is run in in a thin stream. At first the temperature must not be allowed to rise above 44°, but when two-thirds have been run in the temperature may be allowed to rise to 55°. The addition takes eight or nine hours; after it is finished the temperature is maintained for another two hours at 53° to 55° to complete the nitration. The oxidation of one of the CH_3 groups causes the contents of the vessel to froth considerably. When the nitration is complete the mixture is cooled to the ordinary temperature and allowed to stand over night. The tetranitromethyl-aniline separates out on the surface in fine crystals, provided that the nitric acid used is not stronger than as stated above. If stronger acid be used the crystals are larger and cannot be washed properly. Next morning the waste acid is run off; it has about the following composition:

Sulphuric cid	74·04
Nitric acid	11·05
Nitrogen peroxide	2·58
Nitro-bodies	0·24
Water (by difference)	12·19
	100
Specific gravity	1·75

After draining off the waste acid the solid product is washed by means of dilute sulphuric acid on to the plate of a vacuum filter, where it is washed with more dilute sulphuric acid. Then it is removed to another filter, where it is washed with water until it is neutral. To test for this 15 or 20 g. of the wet substance, equivalent to about 10 g. dry, are boiled with 50 c.c. water, cooled, filtered and washed: the filtrate should not require more than 0·2 c.c. N / 10 caustic soda solution to render it neutral to phenol phthalein. This amount is principally due to the faint acid character of the pure tetryl. The substance is then dried. It now has a melting-point of 126° to 127°, and the yield is about 210 kg., whereas according to theory there should be 237 kg. from 100 kg. of dimethyl-aniline.

It is necessary further to purify the tetryl by recrystallization, as small amounts of impurity seriously affect its stability. For this purpose 500 kg. are dissolved by boiling in 1850 kg. of pure benzene and allowed to crystallize out, filtered off and dried. The benzene is recovered from the mother liquor by distillation, but some water is added to the still to prevent heating the solid residue above 100°. About 13 per cent. of the crude tetryl is lost by this process and remains in the still. As this residue is unstable it is destroyed by burning. There are also other methods of purification in use.

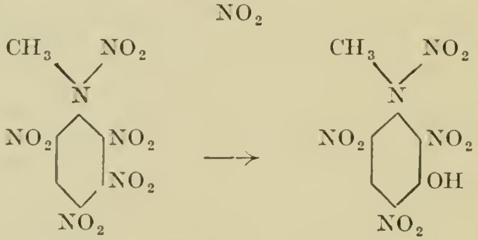
Properties of tetryl.

Pure tetryl looks like flour with a faint yellow colour. The melting-point of the pure substance is 129° to 130°, that of a good commercial material 127·5° to 128·2°.

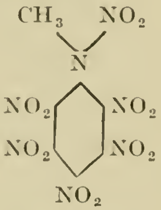
Tetryl is a more powerful explosive than trotyl or picric acid, but it is also somewhat more sensitive, without, however, being dangerously so with ordinary precautions. This makes it very suitable for use as an intermediate detonating agent. It is used in conjunction with fulminate as a filling for detonators, and as a primer for high explosive shell. Detonating fuse has also been filled with it. According to Langenscheidt it gives a Trauzl test of 460 to 480 c.c., and in the falling weight test it requires a weight of 5 kg. falling 30 to 40 cm. to explode it. It is somewhat poisonous, and should not be handled more than is necessary as it is liable to set up skin irritation. It is a component of some ammonium nitrate explosives such as Fortex, but its comparatively high cost of manufacture prevents its extensive use for this purpose.

Higher nitro-derivatives of methyl-aniline.

Still higher nitro-derivatives of methyl-aniline have been prepared, but are unstable. Tetranitro-phenyl-methyl-nitramine is a substance melting at 146° to 147°; on boiling with water one of the nitro-groups is replaced by OH and nitric acid is formed:—



Other reagents produce similar changes.[1]



The corresponding penta-nitro-derivative is a yellow crystalline substance which melts at 132° and explodes at a higher temperature.[2]

---

[1] Romburgh, *Rec. trav. chim.*, 1889, p. 108; Romburgh and Schepers, *Proc. K. Akad. Wetensch.*, Amsterdam, 1913, p. 369.

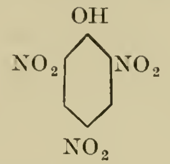
[2] J. J. Blanksma. *Proc. K. Akad. Wetensch.*, Amsterdam, 1902, p. 437.

NITRO-PHENOLS

Phenol (carbolic acid) is nitrated very easily even by dilute nitric acid yielding a mixture of ortho- and para-nitro-phenol, and these on further nitration give 2 : 4-dinitro-phenol, which may also be obtained by the direct nitration of phenol with mixed acid. These compounds are not, however, used as explosives, although they can be detonated with some difficulty.

Picric acid $C_6H_3N_3C_7$.

Picric acid, or 2 : 4 : 6-trinitro-phenol, has, however, been used on a very large scale as a military explosive, and is still, in spite of the fact that trotyl is generally preferred.



This substance is the final product of the action of nitric acid on a large number of substances containing a benzene nucleus, just as oxalic acid is the result of the oxidation of many bodies of the fatty series. Picric acid is obtainable from indigo, aloes, gum-resins, wool, silk, etc., but the common idea that the yellow colour produced by nitric acid on animal tissues, such as skin, wool, etc., is due to the production of picric acid is erroneous : it is due to the formation of xanthoproteic acid.

Picric acid was formerly prepared by the direct action of nitric acid on phenol, but is now made by first dissolving the phenol in strong sulphuric acid and then acting on the resulting phenol-sulphonic acid with excess of nitric acid. Mono- and dinitro-phenol may result if the action is not carried far enough. Picric acid separates from the acid mixture as an oily liquid, which solidifies on cooling.

A. H. Ney in a lecture delivered before the National Exhibition of American Chemical Industries in New York has given the following information about the manufacture of picric acid :[1]

The technical production of picric acid is to-day carried out by two distinct processes :

1. The first and older method, which even to-day is employed almost exclusively, consists in treating phenol with concentrated sulphuric acid at about 100° to 110° until the odour of phenol has disappeared and the reaction product is completely soluble in water, and nitrating the sulphuric acid thus obtained with an excess of nitric acid, preferably in the presence of an excess of sulphuric acid.

---

[1] *J. Met. and Chem. Eng.*, 1915, p. 686 ; *Chem. Trade Jour.*, 1915, p. 385. *See also S.S.*, 1910, p. 15.

2. The second and more modern method employs as starting material chlorbenzol, which is dinitrated to dinitro-chlorbenzene; this product is separated from the spent nitrating mixture, the chlorine atom replaced by hydroxyl by heating with caustic soda, and the resulting dinitro-phenol is nitrated.

The possibility of a third commercial method for the production of picric acid is suggested by an old publication by Hepp,[1] who claims to have obtained, with an excellent yield, picric acid by oxidizing trinitro-benzene in alkaline solution with potassium ferric cyanide, the use of other mild oxidizing agents being also suggested.

In view of the difficulty in obtaining trinitro-benzene with anything like a satisfactory yield, the commercial feasibility of such procedure is open to grave doubt, although the writer has private information that a small plant is at the present time producing picric acid to some extent by a process purporting to be based upon this method.

The chemical and technical literature contains many suggestions and several descriptions for the manufacture of picric acid, all of them, however, being obsolete. Chemically, the preparation of pictic acid is very simple and easy, and, as a matter of fact, it would seem almost impossible for any one placing phenol and nitric acid together, in some form and manner, not to obtain picric acid. Technically, however, the manufacture involves several difficult problems, mainly due to the fact that the handling of unmixed nitric acid is a difficult and dangerous operation excluding the use of materials for receptacles, etc., usually employed in the chemical industry, and the somewhat exaggerated fear of contamination by inorganic salts, detrimental to the stability of the product. The drying and pulverizing of the material is a very dangerous operation, which, however, is now seldom required in chemical factories, the Ordnance works usually requiring delivery of the wet crystals with a moisture content of approximately 20 per cent.

The manufacture of picric acid is carried out as follows:

A large sulphonation kettle of the usual construction, preferably lead-lined, with steam jacket, bottom discharge and agitator, is charged with one part phenol and four parts sulphuric acid, 98 per cent. The mixture is heated under agitation until a sample appears completely sulphonated—that is, soluble in water without turbidity, and having no odour of phenol. The content of the sulphonation kettle is now divided into the nitrators, which are receptacles suspended in a space adapted to have hot or cold water circulated therein. To the content of each kettle an equal part of sulphuric acid is added, and after reducing the temperature to below 20° the nitrating acid is run in. This is preferably a usual mixture of equal parts of sulphuric acid and nitric acid of 62 per cent. strength, but other proportions may be

---

[1] *Annalen* (1882), 215, p. 344.

used. Instead of the three molecules required by the theory, four molecules of HNO_3 are added; the temperature is kept below 40° while the first 30 to 40 per cent. nitric acid is run in, and then gradually increased to 70° or 80°, hot water being circulated towards the end of the operation and one to two hours afterwards. Proper ventilation must be provided. Air may be blown through the nitrators before removing their content in order to remove the nitrous gases formed. The content is now removed into an acid-proof, non-metallic receptacle and diluted with water, about equal volumes having been found to give the best results. After cooling, the picric acid, which separates usually in large crystals, is filtered by means of "nutches" or centrifuges, and washed. The yield is somewhat less than the theoretical. The formation of too large crystals and "caking" should be prevented. It is now usually of sufficient purity, but to obtain it still purer, it may be fused in a steam-jacketed enamelled kettle, from which it is run, if desired, through a sieve of platinum or gold, into a wooden tank with water. It is then filtered off again. The method suggested in the literature of dissolving in alkali, and again precipitating, is irrational and dangerous, and has never been practised by manufacturers.

The material of which the nitrators are made may be cast-iron if the strength of the acid is always kept above 82–85 per cent., otherwise earthenware or enamel receptacles are indispensable. After the nitration the mixture is diluted, and for all final operations, contact with metals, other than precious, must be avoided.[1] Coatings of a pure asphaltum varnish have given satisfaction. Proper agitation devices and ready means for discharging the nitrators and filling the same open a wide field for the ingenuity of the constructional engineer.

The largest manufacturer of picric acid in the world (Hauff in Fuerbach) uses an interesting and highly efficient filtering device. It consists of a filtering box or "nutch," with vacuum below and above, and is adapted to be used as both filter and dryer. The crude picric acid is placed on the filtering surface (a porous stone plate) and suction is applied. After the bulk of the adhering waste acid has been removed, alcohol is sprayed on the material and received in a separate container, from which it is at once rectified and recovered. The filter box is then covered with a specially constructed lid and vacuum applied; the drying proceeds very rapidly, and the resulting product is very pure, due to the fact that it has been washed with alcohol, which is an excellent solvent for the resinous products always formed during high nitration.

Properties. Picric acid forms pale yellow, crystalline needles or scales, of an intensely bitter taste and specific gravity 1·767 at 19°. The pure acid melts at 122°, and the common at a lower temperature, to a brownish-yellow oil, which at

---

[1] Tin and aluminium may be used.—A. M.

a higher temperature partially sublimes, and boils with formation of yellow, bitter, suffocating vapours. The lower melting-point of impure picric acid is probably due to an admixture of dinitro-phenols or of a nitro-cresol. Hence the melting-point of picric acid is a test of its purity.

When strongly heated, picric acid burns rapidly with formation of an intensely black smoke. It does not explode when heated under ordinary conditions, but it can be made to explode by allowing it to fall into a tube heated to a red heat.[1] Picric acid can be detonated by means of other violent explosives; a charge of 1 g. of mercury fulminate suffices to determine the explosion under favourable conditions. Metallic picrates, especially that of lead, or even an imperfect mixture of picric acid with the oxides or nitrates, will detonate violently when heated or submitted to a moderate blow, and the explosion will induce the detonation of neighbouring quantities of picric acid or picrates, even though they be wet. In spite of the comparative insensitiveness of the pure substance, these properties have led to a number of serious accidents, of which the following were particularly disastrous:

Heron Chemical Works, Lancaster, June 7, 1882.[2]

Roberts, Dale and Co.'s Works, Cornbrook, near Manchester, June 22, 1887.[3]

Rheinau, near Mannheim, June 27, 1890.[4]

Read, Holliday and Sons, Huddersfield, May 30, 1900.[5]

Griesheim-Elektron, near Frankfort a. Main, April 25, 1901, twenty-four killed and one hundred and seventy-eight injured.[6]

Woolwich Arsenal, June 18, 1903, sixteen killed and fourteen injured.[7]

For the historical development of the use of picric acid as an explosive, see Chapter III, pp. 44, 49. It is now used only as a military explosive either alone or mixed with a nitrate or with other nitro-compounds. It is not itself used much as a dye now, but it is used in the manufacture of more complex compounds, which are valuable dye-stuffs.

The sensitiveness of picric acid can be reduced by mixing it with inert substances. Under Orders in Council, Nos. 20 and 20A, it is not considered an explosive when mixed with half its weight of water or with three times its weight of the following substances: anhydrous sulphate of soda, crystallized sulphate of soda when in hermetically closed packages, or potash alum.[8] It is also not considered an explosive if in a quantity of not exceeding 2000 lb.

---

[1] M. Berthelot, *Ann. Chim. Phys.*, 1889, vol. xvi., p. 23; *P. et S.*, 1900, vol. x., p. 280.

[2] *S.R.*, 81, p. 20, Home Office Papers A, 17,412.

[3] *S.R.*, 81. [4] *A.R.*, 1890, p. 48. [5] *S.R.*, 139.

[6] *Ang.*, 1901, p. 459; *Chem. Zeit.*, May 1, 1901; *Chem. Trade Jour.*, May 18 and 25, 1901 (Chemical Notes).

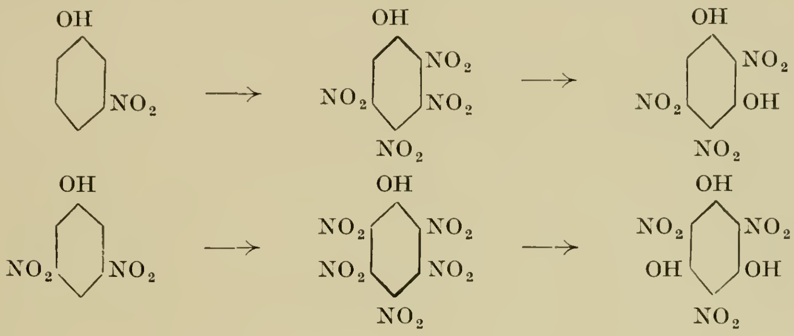
[7] *A.R.*, 1903, p. 51; *Chem. Trade Jour.*, July 4, 1903.

[8] *See Guide to the Explosives Act*, pp. 204–206.

packed in substantial barrels or cases where it is not liable to come in contact with any metal other than aluminium, nor with the oxides or other compounds (other than sulphates) of lead, iron, potassium, barium, calcium, sodium, zinc or copper, nor with any chlorate, nitrate, or other oxidizing agent.

Higher nitro-phenol

Other trinitro-phenols are known, but they are not made so easily, and are probably less stable. Higher nitro-phenols have also been prepared: thus J. J. Blanksma [1] by nitrating meta-nitro-phenol with mixed acid in the cold obtained 2 : 3 : 4 : 5-tetra-nitro-phenol, which melted at 140° and exploded at a higher temperature, but according to R. Nietzki [2] this compound melts at 130°, often with a somewhat violent explosion. In a similar manner Blanksma obtained pentanitro-phenol from 2 : 4-dinitro-phenol. These substances are not very stable and are converted by boiling with water into trinitro-resorcinol and trinitro-phloroglucinol respectively.



Styphnic acid, $C_6H_3N_3O_8$,

Styphnic acid or 2 : 4 : 6-trinitro-resorcinol is made by nitrating resorcinol or some of its derivatives. Resorcinol, or meta-dihydroxy-benzene, can be made from benzene in the same way as synthetic phenol, but its derivatives occur in many gums and wood extracts, and these can be made to yield styphnic acid directly by appropriate treatment with nitric acid.[3] Böttger and Will obtained a yield of 18 per cent. from Brazil wood extract (Fernambukholz-extrakt).[4]

Styphnic acid is a fairly strong dibasic acid, and its salts are more violently explosive than those of picric acid. Its use as an explosive was patented by Hauff in 1894, and in 1897 it was examined by the French Commission des Substances Explosives,[5] who found that it was less powerful and more expensive than picric acid, over which it possessed no advantage. It does not appear ever to have been used commercially as an explosive, but is worthy of notice

---

[1] *Proc. K. Akad. Wetensch.*, Amsterdam, 1902, p. 437.

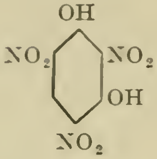
[2] *Ber.*, 1897, p. 181.

[3] *See* Stenhouse, *Annalen*, vol. cxiv., p. 224.

[4] *Annalen*, vol. lviii., pp. 269, 298.

[5] *P. et S.*, vol. ix, p. 139.

in consequence of its formation directly from natural products. Its melting-point is 175·5°.



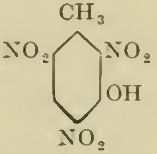
Trinitro-cresol, $C_6H,OH,CH_3(NO_2)_3$

In commercial cresol obtained from coal tar there are three cresols present in about the following proportions :

	Proportion	Melting-point	Boiling-point
Ortho	40	30°	190°
Meta	35	4	200·5
Para	25	36	201·1

Mono- and di-nitro-compounds can be made from all of these, but only meta-cresol gives a trinitro-derivative, the others on continued nitration being oxidized to oxalic acid, etc. It is necessary, therefore, to use meta-cresol as pure as practicable for the manufacture of trinitro-cresol. The ortho-compound can be eliminated by fractional distillation without great difficulty, but the others boil at almost the same temperature. Nevertheless it is said that the meta-compound can be obtained almost pure by fractional distillation.[1] The separation can also be effected by sulphonation with oleum, whereby meta-cresol is converted into a liquid sulphonic acid and the para-compound into a solid one. For other methods of separation *see* Thorpe's *Dictionary of Applied Chemistry*, vol. ii., p. 164.

Trinitro-cresol is made in the same way as picric acid, but the nitration proceeds with greater ease. The yield from meta-cresol is said to be 150 per cent., the theoretical being 225 per cent.



Trinitro-cresol or trinitro-cresylic acid is a very similar substance to picric acid, but is less powerful as an explosive as it contains a smaller proportion of oxygen. It has been used in France under the name of Crésylite for filling

---

[1] Vennin et Chesneau, p. 280.

shell in admixture with picric acid. A mixture of 60 parts with 40 parts of picric acid (mélinite) melts at 85° and is plastic at 65° or 70°.

Picrates an trinitro-cresylates.

The composition and temperatures of ignition of a large number of metallic picrates were investigated by Silberrad and Phillips,[1] and the formation and explosibility of various picrates and trinitro-cresylates by Kast.[2] The picrates of lead, calcium, barium, potassium, and copper explode when heated, the lead compound being much more violent than the others. The picrates of sodium, zinc, silver, magnesium and iron explode with considerably less violence; those of ammonium, mercury and aluminium, like picric acid itself, do not explode when heated in the ordinary way.

The trinitro-cresylates behave very similarly to the corresponding picrates. The lead salts are also by far the most sensitive to blows, being about as dangerous in this respect as nitro-glycerine, blasting gelatine and dry gun-cotton. The salts of the other heavy metals, such as copper, silver, iron, calcium, and barium are also somewhat sensitive: more so than picric acid. The salts of sodium, potassium and ammonium are less sensitive, and those containing water of crystallization are less so than the dried substances.

The action of solutions of picric acid and trinitro-cresol upon different metals was investigated by Kast. Plates of metal 5 × 10 cm. were placed in mixtures of 50 g. picric acid or trinitro-cresol and 200 g. water for four weeks It was then found that the following quantities of the metals had been dissolved:

	Picric acid	Tri-nitro-cresol
Lead	3·91 g.	4·15 g.
Iron	13·71 g.	3·78 g.
Zinc	18·86 g.	0·48 g.
Copper	2·37 g.	1·04 g.
Brass	1·19 g.	1·02 g.
Aluminium	small quantity	small quantity

Saposhnikof tried the effect of molten picric acid on metals under conditions more nearly resembling those that prevail in a shell that is filled with the melted explosive.[3] One gramme of the finely divided metal was placed in a beaker with 2 g. of picric acid and kept at a temperature of 125° for eight and a half to nine hours. The weights of metal that had been dissolved were:

Lead	0·2798 g.
Iron	0·1530 g.
Zinc	0·2046 g.
Copper	0·1754 g.
Aluminium	0·0488 g.
Nickel	0·1862 g.
Tin	—

---

[1] *J.C.S.*, Trans., 1908, p. 474.

[2] *S.S.*, 1911, pp. 7, 31 and 67.

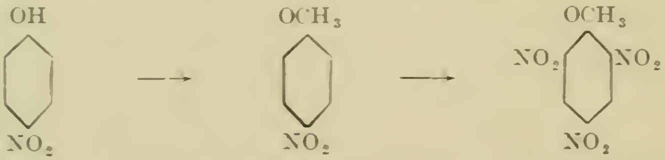
[3] J. Saposhnikof, *S.S.*, 1911, p. 183.

Picrates were at one time much favoured by inventors as ingredients of explosives, but very few of these mixtures achieved any practical success. Designolle's powder consisted of potassium picrate and saltpetre and sometimes charcoal, and was made for a time in France as a cannon powder. Brugere's powder consisted of 54 parts of ammonium picrate and 46 of saltpetre, and was said to give good results in the Chassepôt rifle. A mixture of 43 parts ammonium picrate and 57 saltpetre is used as a detonating agent in lyddite shell, under the name of picric powder. It is made by incorporating the two ingredients together in a ball mill.

Trinitro-anisole, $C_6H_2.OCH_3(NO_2)_3$.

Anisole is made by condensing phenol or sodium phenate with methyl chloride or methyl alcohol in various ways. Experiments on nitrating it have been carried out by A. L. Broadbent and F. Sparre,[1] who found that there is a tendency for the acid to attack the side chain and consequently give low yields. By commencing the nitration with mixed acids at 0°, however, they obtained a yield of 85 per cent. of the theoretical. When one nitro-group has been introduced into the molecule there is no longer any tendency to attack the side chain.

Another possible method of manufacture is from nitro-phenol. Phenol is nitrated in the cold with dilute nitric acid, yielding ortho- and para-nitrophenol and some tar. The ortho-compound is distilled off with steam and used for the manufacture of dyes, etc. The para-nitro-phenol is purified by crystallization from xylene; it is used for the manufacture of phenacetin and some other synthetic compounds, but the demand for it is less than for the ortho-compound. Consequently there is spare material, which can be used for the manufacture of explosives. By treatment with caustic soda, sodium carbonate, methyl alcohol and methyl chloride under pressure it can be converted into nitro-anisole,[2] which on nitration gives trinitro-anisole.



Trinitro-anisole is a yellow crystalline substance with a melting-point of 64° to 65° and a specific gravity of 1·408 at 20°. It has the same composition as trinitro-cresol, but is free from acid character and consequently much safer, but unfortunately it is slowly hydrolysed by water to picric acid. It is more difficult to detonate than trotyl.[3] It has been used by the Germans for filling bombs. In December 1914 the German Railway Commission admitted it to Group A1*b* of their classification, enabling it to be sent in

---

[1] Eighth Intern. Cong. Appl. Chem., vol. iv., p. 15.

[2] *See* L. Paul, *Ang.*, 1896, p. 587.

[3] A. Stettbacher, *S.S.*, 1914, p. 356.

unlimited quantities as ordinary goods. Previous to that date it had not been mentioned in the classification.

Kinetics of nitration.

It is evident from what has been said above that on nitration the NO_2 groups tend always to take up the meta-position with respect to one another, and that when so placed they are more stable than when in the ortho- or para-position. Consequently in all the important trinitro-compounds the three groups are arranged symmetrically round the benzene ring. When the NO_2-groups are next to one another (ortho-position) there is a tendency for one of them to be displaced with ease, and when three of them are together the middle one splits off very readily. On the other hand, the NO_2-groups tend to take up the ortho- or para-position with respect to substituting groups such as CH_3, OCH_3, OH and NH_2, and the presence of these groups makes the nitration more easy and rapid.

The kinetics of the nitration reaction have been investigated by H. Martinsen, who has found that in sulphuric acid the velocity of nitration of nitro-benzene is proportional both to the quantity of nitric acid and of nitro-benzene present.[1] It is trebled for a rise of temperature of 10°, and is at a maximum when the molecular proportion of sulphuric acid to water is 1 : 0·7, as is shown by the following figures :

Per cent. by weight of H_2O or SO_3 in acid	Velocity at 0°	Constant at 25°
3·2 per cent. SO_3	0·036	0·22
5·2 ,, H_2O	0·085	1·50
13·7 ,, ,, ...	0·280	3·22
15·9 ,, ,, ...	0·017	0·18

The velocity of nitration is much modified by the presence of other atoms or groups in substitution for the hydrogen of benzene. Martinsen gives the following scheme :

$$\mathrm{NO_2} > \mathrm{SO_3H} > \mathrm{CO_2H} > \mathrm{Cl} < \mathrm{CH_3} < \mathrm{OCH_3} < \mathrm{OC_2H_5} < \mathrm{OH}$$

Cl sometimes accelerates and sometimes retards nitration ; those on the right accelerate, the further they are to the right the more they accelerate ; those on the left retard, NO_2 most of all. The latter cause the NO_2-groups to take up the meta-position, and those on the right the ortho- and para-positions.[2] J. P. Wibaut[3] gives the following velocities of nitration :

Benzene	0·0025 at 25°
Chlorbenzene	0·0020 ,,
Brombenzene	0·0013 ,,
Toluene	0·0080 at 0°

---

[1] *Zeit. physikal. Chem.*, 1904, vol. l., p. 385.

[2] *Ibid.*, 1907, vol. lix., p. 605.

[3] *Rec. trav. chim.*, 1915, p. 241

Martinsen found that when para-nitro-aniline is nitrated two, nitro-groups are introduced at nearly the same rate giving picramide, 2 : 4 : 6-trinitro-aniline. The rate of nitration of α-nitro-naphthalene is greater than that of nitrobenzene.

If para-nitro-anisole be freshly dissolved in sulphuric acid and nitric acid be then added, one molecule of the latter is taken up instantaneously with the formation of dinitro-anisole. But if the sulphuric acid be allowed to stand for a day before the nitric acid is added nitration is slow. This is ascribed to the gradual formation of the sulphonic acid, which is much more difficult to nitrate. Sulphonation of para-nitro-toluene is much slower than nitration, but is more rapid the stronger the acid. In oleum containing 2·5 per cent. SO_3 the velocity constant is 0·003 and in absolute H_2SO_4 0·0004, and in acid containing a little water much less.[1]

In aqueous solution the nitration proceeds in quite a different way to that in sulphuric acid solution. It commences very slowly and then the velocity increases, being accelerated by the production of nitrous acid in the course of the reaction. The velocity of nitration is increased by the addition of sulphuric acid or potassium nitrate, and to a less extent by sodium or strontium nitrate. A minute quantity of sodium nitrite at the commencement of the reaction accelerates it considerably.[2]

---

[1] *Zeit. physikal. Chem.*, 1908, vol. lxii., p. 713.

[2] H. Martinsen, *ibid.*, 1904, vol. l., p. 385.

PART VII

SMOKELESS POWDERS

CHAPTER XXI

SLOW-BURNING SMOKELESS POWDERS

Drying the nitro cellulose : Alcoholizing : Incorporation : Shaping the powder . Poudre B : Russian powder : Rumanian powder : Belgian powder : American powder : Spanish powder : Ballistite : Filite : Solenite : German powders : Cordite : Weighing the gun-cotton : Measuring the nitro-glycerine : Mixing : Incorporating : Pressing : Drying : Japanese powder : Sporting rifle powders : Axite : Moddite

All smokeless powders that have been manufactured up to the present have one important feature in common : every one of them consists largely of nitro-cellulose in some form, and many of them contain only small proportions of other substances. They may be divided into two principal classes : slow-burning powders for use in rifled fire-arms, and fast-burning for use in shot-guns, etc. Of the former there are two main divisions : those that contain nitro-glycerine, the nitro-glycerine powders, and those that do not contain it, which are called nitro-cellulose powders, although all the powders contain this substance. Powders for rifled fire-arms are required to burn at a uniform rate and not too fast ; this is achieved by converting the nitro-cellulose into a uniform and dense colloid by mixing it with a solvent. Sporting shot-gun powders, on the other hand, are required to burn very rapidly, and as a rule are only partially gelatinized. For nitro-glycerine powders the solvent generally used is acetone, as it readily dissolves all nitro-cellulose even of the highest degrees of nitration, but if the powder contain no nitro-glycerine the colloid yielded by acetone is too hard and brittle. Consequently for nitro-cellulose powders ether-alcohol is generally used, and the nitro-cellulose must be of such a description that it can be gelatinized by this solvent.

Drying the nitro-cellulo

The nitro-cotton or other form of nitro-cellulose comes in the wet state from the factory where it is made. For safety some 30 per cent. or more of water is left in it until it is necessary to dry it for further use. The nitro-cellulose may either be in loose form as it is taken from the centrifugal, in which the greater part of the water has been extracted, or it may be moulded into blocks, slabs or cylinders by compressing it in a hydraulic press with a moderate pressure. The advantage of moulding it is that less dust is formed in the drying stoves and during the operation of weighing the nitro-cellulose. The drying is effected by blowing air by means of a fan through a steam heater and then into the stove. The temperature of the air entering the stove should not exceed 60° C., nor the temperature inside the stove 40°. The best arrangement of the inlet pipes is to provide them with a number of orifices near the top of the building and to direct the air on to the ceiling. The outlets should be near the floor and should have a larger area than the inlets. The reason for blowing the hot air in at the top of the stove is that when the air takes up water vapour from the nitro-cellulose it becomes heavier and tends to sink; although the water vapour itself is lighter than the air, the cooling produced by the conversion of the water into vapour is so great that the air after taking up the water is considerably denser. Thus suppose 1 cubic metre of dry air at 40° C. on coming in contact with the wet gun-cotton to take up 1 gramme of water. The latent heat of water vapour at this temperature is 573 calories per g., the cubic metre of air weighs 1127·5 g. and its specific heat is 0·237 calories per g. Consequently the reduction of temperature of the air is $\frac{573}{1127 \times \cdot 237} = 2{\cdot}14°$ and the volume is reduced to 993·2 litres. The gramme of water vapour occupies a space of 1·4 litre, and therefore the 1128·5 g. of the damp air occupies 994·6 litres, and a cubic metre of it weighs 1134·6 g. Hence by taking up this small amount of moisture the density of the air has been increased 0·63 per cent.: the evaporation of more water will lead to a further increase of density. It is important that the inlets and outlets be well distributed round the ceiling and floor respectively to avoid the formation of dead corners in which the gun-cotton will not be dried properly. If the air is blown in at the bottom, as is often the case, the fresh dry air tends to rise at once to the top and escape through the outlets before it has done as much drying as it should. The stove should not be unnecessarily tall; inside it should be lined throughout with zinc sheet with soldered joints or other suitable material, in order that there shall be no cracks in which dust may accumulate, and so that the stove can be washed out thoroughly from time to time. If the nitro-cellulose has been moulded into blocks, these should be stood on racks with air spaces between the blocks to facilitate drying. If the material is in the form of loose fibres, it should be laid on trays, preferably of copper wire. In either case the racks or trays should be so arranged that they are connected electrically to earth, as dry nitro-cellulose is very liable to become electrified, and a spark may set the powdery material alight. The stoves should not be very near other buildings, as there is always a risk of one catching fire. The stoves are generally constructed of light material. If the nitro-cellulose be in loose fibrous form, it may be dried in twenty-four hours, but if it be moulded, it will take several days. The greatest care must be exercised not to subject the dry nitro-cellulose to friction or blows, especially if it be still warm. The whole stove should be allowed to cool down thoroughly before it is unloaded.

In most instances, when an accident has occurred in a gun-cotton stove, the explosive has merely burnt away extremely fiercely, but without exploding; but on March 10 and 28, 1913, severe explosions took place in stoves situated respectively at Ardeer, in Scotland, and Pitsea, in Essex.[1] In both cases the stoves were being unloaded, and the presumption is that some of the gun-cotton must have been subjected to blows or friction by the workmen. In the former case it is supposed that the explosion was brought about by upsetting one of the racks on which the gun-cotton primers were placed. The explosion caused three other similar stoves in the neighbourhood to explode also, with the result that altogether seven men were killed and ten injured.

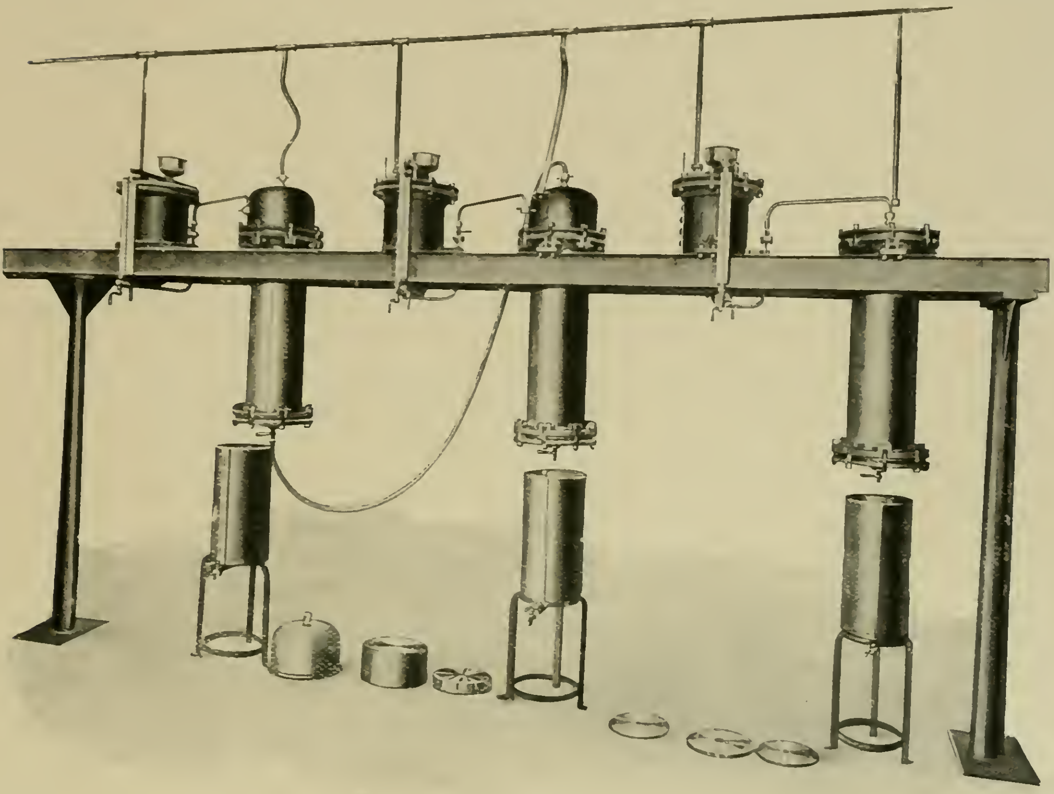


FIG. 54. Alcohol Displacement Plant (Maschinenbau A.-G. Golzern-Grimma)

---

[1] *S.R.*, Nos, 206, 207.

The explosion of these other stoves was probably caused by the buildings being shaken and wrecked, and perhaps by the racks being thrown down in them also. From this accident the deduction may be drawn that these and all other buildings for sensitive explosives should be so strongly constructed that the explosion of a neighbouring building will not wreck them. The racks should be fixed rigidly to the floor.

Alcoholizing.

In the case of powders that are gelatinized with ether-alcohol the troublesome and dangerous operation of drying the nitro-cellulose can be dispensed with, as the water can be displaced by means of alcohol. The wet guncotton is packed into a cylinder (*see* Fig. 54), and then alcohol is forced through it by means of compressed air. First, water flows away and is run to waste, then weak alcohol, which is re-rectified, so that it can be used again, and, finally, fairly strong alcohol, which is used again for the preliminary displacement of another cylinder of nitro-cellulose. The alcohol is always introduced at the top of the cylinder as it is lighter than the water; first alcohol from the final displacement in another cylinder, and then strong alcohol. The displacement takes three to six hours. When the water has been displaced, the surplus alcohol is removed from the nitro-cellulose by means of a hydraulic press. A type of press much used for this purpose in Germany is shown in Fig. 55. It has two cylinders, which swing round together on one of the columns, so that whilst the contents of one are being pressed, the other can be emptied and filled again. Washing with alcohol has the further advantage that it removes the unstable impurities to some extent. According to Guttmann this device of displacing water by alcohol was used in Austria in 1891, but the invention has been claimed for Messier, Ingénieur des Poudres et Salpêtres, in 1892. In this year a patent was also taken out for it in England by Durnford.[1]

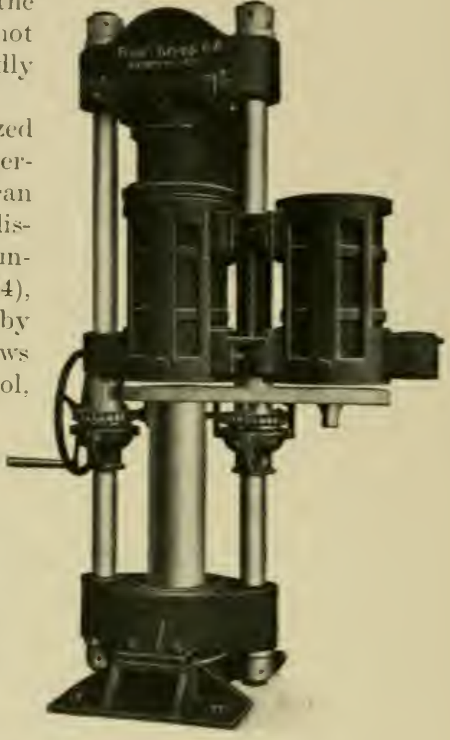


Fig. 55. Press for Alcoholized Nitro-cellulose

ncorporation.

The nitro-cellulose is incorporated with the solvent in a machine which

---

[1] *Manufacture of Explosives*, vol. ii., p. 239. Vennin, *Poudres et Explosifs*, p. 394; Buisson, *Problème des Poudres*, p. 37. Brit. Pat. 20,880 of Nov. 17, 1892.

is constructed on the same principles as the kneading machines used in bakeries (*see* Figs. 56, 57). It consists of a trough, in which two curved blades rotate in opposite directions, one twice as fast as the other, both going downwards in the centre of the trough and upwards by the walls. First, some of the solvent is poured in to moisten the axles and blades, then the nitro-cellulose and other materials, and finally more solvent. The incorporator is then started and kept running for some hours until the constituents of the powder are thoroughly mixed, the trough meantime being kept covered to prevent loss of solvent. The trough is then tilted up and the blades are made to rotate in the opposite direction. The dough falls into a box or other receptacle, and is taken to the buildings where it is pressed into cords, tubes or strip, or is rolled into sheet, according to the form that it is required to give to the finished powder.

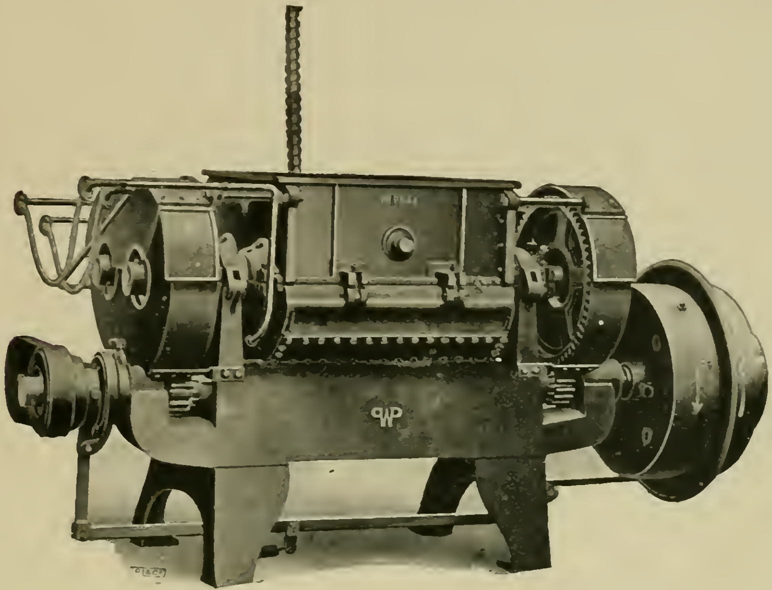


FIG. 56. Incorporating Machine in Working Position
(Werner, Pfleiderer and Perkins, Ltd.)

If the incorporator be driven by an electric motor, this should be placed so that vapour of the solvent cannot possibly be ignited by sparks of the commutator. The motor should be provided with an automatic release to prevent danger of the explosive being fired by the application of too much power. The lid of the incorporator is best made of aluminium, domed somewhat so as to allow of more material being placed in the machine. The aluminium may be surrounded by a wooden frame held down to the rim of the incorporator by butterfly nuts.

haping the owder.

The dough is next formed into the desired shape. Formerly it was in many cases rolled into sheets by passing it repeatedly through rolls resembling a paper-maker's calender. The sheets were cut into strips, which were again cut transversely so as to form cubes or flakes. Now it is more usual to press the dough through a die in a press, which is an adaptation of the machine used for making macaroni. It is thus obtained in the form of cords, strips, or tubes: if desired these can then be cut into flakes of any required thickness.

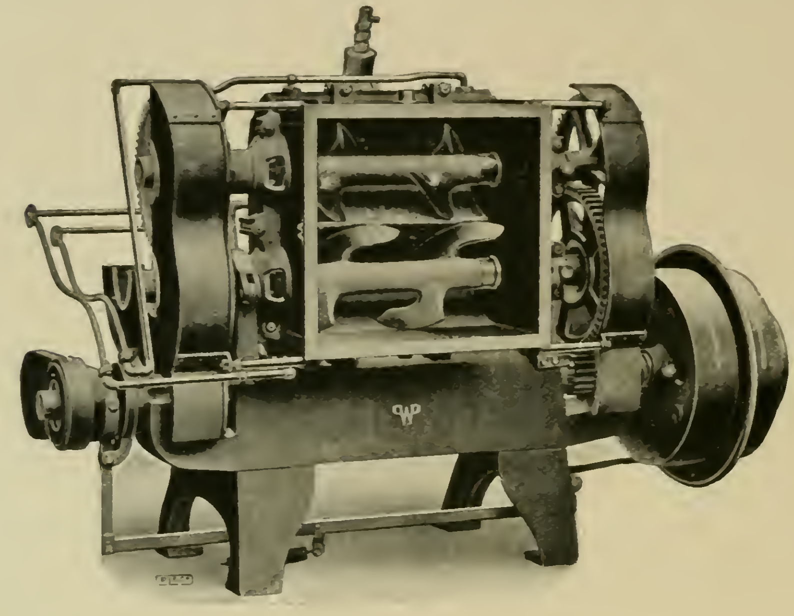


FIG. 57. Incorporating Machine. Trough Tilted, showing Blades

Poudre B.

Poudre B, which was invented by Vieille and adopted by the French Government in 1884 for use in the Lebel rifle, was the first smokeless powder to achieve success in a rifled fire-arm. It is named after the first letter in the name of General Boulanger, who was Minister of War at the time. According to an analysis made by Lieut. Wisser, U.S.N.,[1] its composition was:

Insoluble nitro-cellulose	68·2 per cent.
Soluble ,,	29·8 ,,
Paraffin	2·0 ,,

---

[1] Worden, *Nitro-cellulose Industry*, p. 962.

Apparently it was gelatinized by means of acetic ether. The composition was modified several times; the powder known as Poudre BN consisted of:

Insoluble nitro-cellulose	29·1 per cent.	38·7 per cent.
Soluble ,,	41·3 ,,	33·2 ,,
Barium nitrate	19·0 ,,	18·7 ,,
Potassium nitrate	8·0 ,,	4·5 ,,
Soda	2·0 ,,	3·6 ,,
Volatile matter	—	1·3 ,,

N stands for Nouvelle. Instead of soda, tannin was sometimes used. The powder was gelatinized with ether-alcohol; the first analysis was given by Neumann,[1] the second by Weaver.[2]

All other solid constituents were subsequently abolished, and the powder consisted only of a mixture of soluble and insoluble nitro-cottons gelatinized with ether-alcohol. In order to improve the stability an addition of amyl-alcohol was introduced in 1896–1897, first 2 per cent. and afterwards 8 per cent. These powders received the names $B(AM_2)$ and $B(AM_8)$ respectively. Now diphenylamine is added instead.

Various processes of nitration are in use in the French Government factories: the Abel process, nitrating centrifugals, and at Angouléme there is a displacement plant on Thomson's system. Two sorts of nitro-cotton are made, called CP_1 and CP_2 respectively. CP_1 is a gun-cotton of high nitration giving 205 to 215 c.c. NO per gramme in the nitrometer (= about 13 per cent. N) and having a solubility in ether-alcohol of less than 15 per cent.: in practice it gives 209 to 214 c.c. NO, and has a solubility less than 10 per cent. CP_2 is a soluble nitro-cotton giving 190 to 198 c.c. NO per gramme (= about 12 per cent. N), and having a solubility of over 96 per cent. Limits are also set to the viscosity of the solution in ether-alcohol and to the percentage of matter soluble in alcohol.

The proportions of CP_1 and CP_2 are varied according to the sort of powder that is to be made. For rapid powders, such as BF, 20 to 25 per cent. of soluble nitro-cellulose are used, and in the slowest powders 50 to 55 per cent. CP_1 is not only a more powerful explosive than CP_2, but as the fibres are not gelatinized by the solvent, but only covered with the solution of CP_2, it burns more rapidly.

The nitro-celluloses are boiled and pulped and mixed in the proper proportions, and are then dehydrated with alcohol and pressed. If the pressure be 300 kg. per sq. cm. (2 tons per sq. in.) the alcohol left in the block amounts to about 20 or 25 parts per 100 of nitro-cotton. It is then placed in the incorporator with the solvent, which consists of 1 volume of alcohol to 1·9 volumes ether, allowance being made for the alcohol already present. The quantity of solvent varies according to the sort of powder

---

[1] *S.S.*, 1910, p. 451.

[2] *Military Explosives*, p. 135.

from 140 to 150 parts per 100 parts nitro-cotton. The alcohol used is of 95 per cent. strength by volume (92·5 per cent. by weight, sp. gr. ·8164), the ether is of 65° Baumé (sp. gr. ·7264), and the mixture is of 56° Baumé (sp. gr. ·760). In the solvent is dissolved the stabilizer, diphenylamine, 1·5 to 2 per cent. of the nitro-cellulose. The incorporation lasts from one to three hours, and then the dough is placed in air-tight boxes and allowed to "ripen."

By means of a press it is now squirted through a die which forms it into a strip. Above the die is placed a filter of fine wire gauze to retain impurities. The strip is received on an endless band. Its width varies according to the type of powder from 20 to 150 mm., and its thickness from 0·6 to 8 mm.

The strips must not be dried too rapidly at first, else they will curl up. As they come from the press they have just sufficient tenacity to allow of their being suspended from bars. Thus suspended they are introduced into a chamber where they first meet with air partly saturated with vapour of ether-alcohol. The bars can be moved in the opposite direction to the current of air, so that the Poudre B meets air ever less saturated with solvent vapour. The air may be circulated in a closed circuit: after leaving the drying chamber it passes through a heat regenerator, then through a cooling plant, which is also constructed on the regenerative principle, and in which the temperature is reduced to —20° to —5° C. so as to condense most of the solvent vapour. After this the air passes through the heat regenerator again, then through a heating coil and then is driven by a fan back into the other end of the drying chamber. The powder after this preliminary drying contains 15 to 20 per cent. of solvent, mostly alcohol.

It is now cut to the right size. Artillery powders are merely cut into lengths, usually of 100 to 400 mm. Rifle powder is cut into small flakes, 1·5 to 2 mm. square and about 0·5 mm. thick: the strips are first cut by rotating circular cutters into narrower strips, and these are then cut transversely. Irregular grains are sorted out by means of automatic sieves and re-incorporated with a fresh charge.

The cut powder is then dried in stoves heated not above 55°. It is next immersed in water at or slightly below 80° C. for a period varying from a few hours up to forty-eight hours for powders of the largest size. Finally it is dried again in a stove for one to four days to remove the water and reduce the volatile matter within the limits fixed for each sort of powder, 0·8 to 2 per cent. The water immersion is carried out at such a high temperature in order to reduce the time. A reduction of 10° in the temperature would render it necessary to double the time of immersion, and a reduction of 20° to quadruple it.

The powders are given letters according to the purpose for which they are intended: thus BF and BNF are small-arm powders from the words "fusil" and "nouveau," BC is powder for field guns, the celebrated "soixante-quinzes," from "campagne," BSP powder for siege howitzers from "siège et place," and BGC powder for the larger military guns from "gros calibre." Powders for naval ordnance have the letter M (marine) with an index figure according to the size :

Calibre mm.	Powders
100 and 138·6	BM_5 to BM_7
164·7	BM_5 to BM_9
194	BM_9 to BM_{10}
240 and 274·4	BM_7 to BM_{13}
305	BM_{13} to BM_{17}
340	BM_{13} to BM_{19}

In addition letters and indices are used to indicate the stabilizer added and the percentage : thus AM_8 means 8 per cent. of amyl-alcohol, and D_2 2 per cent. of diphenylamine. Other letters show the place and date of manufacture of the powder and the cartridges. For instance BM_7. AM_8. 01, SM, B, 2, (2 is a naval powder with 8 per cent. amyl-alcohol forming part of the 4th lot of 1901 made at Saint Médard and put into cartridges at Brest in February, 1902. Poudre BC is made in strips measuring 80 mm. × 40 mm. × 0·7 mm. ; the width of the largest naval powders is as much as 150 mm., and the thickness 8 mm. Naval powders are blended into uniform lots of 100 tons each. Poudre BN_3F, in use with the D bullet, is drummed and graphited to restrain the initial rate of ignition. On the other hand, BC, BSP and BM_1 to BM_5 are striated to increase the rate of burning.

The presence of numerous fibres of ungelatinized nitro-cotton probably facilitates the oxidation and consequent deterioration of Poudre B. The extent to which it is porous is indicated by the density, which is only about 1·52, whereas that of nitro-cotton is 1·67. In former years a number of spontaneous ignitions occurred with Poudre B, of which those on the battleship *Jéna* in March 1907, and on the *Liberté* in September 1911, attracted much attention as both occurred in Toulon harbour and destroyed the vessels in the sight of the whole town. Formerly amyl-alcohol was added to the powder to improve its stability, but this substance has no great power of absorbing nitrogen oxides, and the final products are acid and consequently injurious. Old powders were soaked in a mixture of ethyl- and amyl-alcohols to restore their stability. This procedure, called "radoubage," was unsound, and was given up after the *Jéna* disaster in favour of "remalaxage," which consisted of reincorporating the doubtful powder with ether-alcohol containing amyl-alcohol. Further investigation, however, showed that the stability of the nitro-cellulose was not really restored by this process, and a few years ago it also was abolished. No material is now reworked except quite new cuttings, etc.

The cost of production of Poudre B in 1912 was Fr. 6·40 per kg.

Russian powder.

The question of smokeless powders was referred by the Russian Government to the great chemist Mendeléeff, who started work upon the problem in 1891 together with a band of able assistants in the scientific laboratory of the navy, which was founded specially for this purpose. Mendeléeff found that it was possible to make a nitro-cotton totally soluble in ether-alcohol, which had as high a percentage of nitrogen as the mixture of soluble and insoluble nitro-cottons used by the French (*see* p. 295). This, which he called pyro-collodion, when gelatinized with ether-alcohol gives a much more uniform colloid than a powder like Poudre B, as may be seen in the micro-photographs reproduced in Fig. 58.

Pyro-collodion contains about 12·44 per cent. N and therefore has enough oxygen to convert all the carbon into CO and all the hydrogen into water, but as a matter of fact some CO_2 and CH_4 are always formed and some of the hydrogen is evolved as such. According to Buisson, Russian powder contains 1 per cent. of diphenylamine. The general methods of manufacture are similar to those for Poudre B. As the productive power of the Russian factories was insufficient, powder was often obtained from France before the war.[1]

Rumanian powder.

In Rumania a powder resembling Poudre B is made from a mixture of two nitro-cottons containing 13 and 12·5 per cent. N respectively. At a factory at Dudeski a powder is made containing 1 per cent. of diphenylamine and 4 per cent. of centralite, which is a substance used to gelatinize the surface of the powder and so restrain the initial rate of ignition.[2]

Belgian powder.

The powder made by Coopal et Cie. at Caulille was also of the same type. It contained 40 to 60 per cent. of soluble nitro-cotton gelatinized by means of ether-alcohol in the proportion of 1125 parts by weight to 1000 parts of nitro-cotton. The dough was not pressed through a die but rolled into sheets between rollers, doubled over and rolled several times. The sheets were then cut into strips or flakes.[3]

American powder.

The Americans, after experimenting with various sorts,[4] have adopted a

---

[1] *Problème des Poudres*, p. 70. [2] *Ibid.*, p. 59. [3] *Ibid.*, p. 63.

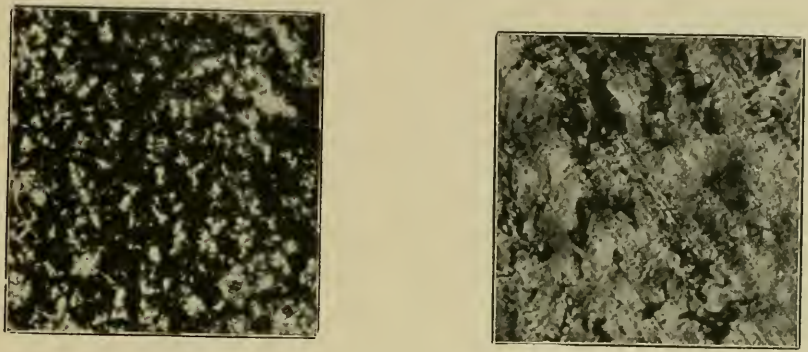
[4] The Maxim-Schüpphaus powders that were used in the American services had the following compositions :

	Per cent.	Per cent.
Gun-cotton	80	80
Soluble nitro-cellulose	19·5	10
Nitro-glycerine	—	9
Urea	0·5	1

They were gelatinized by means of acetone.

The powder for the naval small-arms consisted of nitro-cellulose and the nitrates of barium and potassium, that for the military small-arms contained also nitro-glycerine and a deterrent. (Weaver, *Military Explosives*, 1906, p. 134.)

pyro-collodion powder for all kinds of guns.[1] In the United States the powder is made up into the form of short cylinders which are pierced longitudinally with small perforations, usually seven. The plant and methods of manufacture are described by Worden. The soluble nitro-cotton with 12·6 to 12·8 per cent. N is made as described on p. 180, and boiled to render it stable.[2] The greater part of the water is wrung out in a centrifugal, and the remainder is displaced by alcohol in a hydraulic press. Pressure up to 3500 lb. to the square inch is then applied so as to produce a block weighing about 38 lb., of which 10 lb. is alcohol of 88 per cent. strength. These blocks are broken up with wooden mallets, and three of them are loaded into an incorporating machine, which is run for about fifteen minutes before any ether is added in order that the lumps may be broken up to a fine powder. Then 48·4 lb. of ether are added and 6 oz. of diphenylamine to act as a stabilizer, so that the charge consists altogether of :



Pyroxyline Powder.
Mixture of Soluble and Insoluble
Nitro-cellulose

Pyro-collodion Powder

FIG. 58. Microphotographs of Smokeless Powders (Saposhnikoff, *S.S.*, 1907, p. 163)
Sections 0·05 mm. thick. Magnification 150

Nitro-cotton	84 lb.
Alcohol	26·4 lb.
Water	3·6 ,,
Ether	48·4 ,,
Diphenylamine	6 oz.

The incorporator is kept covered to prevent loss of solvent, and incorporation is continued for forty-five minutes. The white, finely comminuted material

---

[1] *See* Schüpphaus, *J. Soc. Chem. Ind.*, 1895, p. 556 ; Hudson Maxim, *ibid.*, 1897, p. 495 ; Aspinwall, *ibid.*, 1900, p. 315.

[2] *Nitro-cellulose Industry*, pp. 902–926.

is then converted into a compact mass by subjecting it to a pressure of 3500 lb. to the square inch in a hydraulic press. By means of another press it is filtered through a 30-mesh iron wire sieve to remove gross impurities. Then it is compacted again in a third press, and by means of a fourth it is squirted through a die, which forms it into a long multi-perforated cord. The dough is so stiff in consequence of the small proportion of solvent used that a considerable amount of heat is generated in passing through the die, but by means of a water jacket the temperature is kept down to 30° or 35°. It is not advisable to reduce the temperature below 30°, because at lower temperatures the cord becomes too hard to be cut into short lengths in the next operation. In order to prevent fall of temperature and evaporation of ether from the warm colloid, the cord is passed at once to the powder cutter, whence the grains drop into a closed receptacle. This is removed to a drying house, where the drying is carried out slowly at first in order not to distort the grains too much or make them crack. The temperature of drying does not exceed 44° and the process is a long one: for large grain powders it lasts four or five months. Quick drying methods are said not to give a uniform powder.[1] The finished powder is subjected to special physical tests to ascertain that it is not brittle: the ends of the grain are cut off even and perpendicular to the axis, and then it is subjected to a slow pressure: the length must diminish 45 per cent. before the grain begins to crack.[2] If kept for long there must, however, be a gradual though slow loss of solvent, which will make the grain harder and more brittle. If the powder grains break up in the gun, high pressures are generated, and the gun may be injured or even

FIG. 59. American Pyro-collodion Powders (from *Appleton's Magazine*)

---

[1] R. Earle, *Jour. U.S. Artillery*, Sept., Oct., 1914.

[2] Schuhmacher, *S.S.*, 1907, p. 82.

burst. It is stated that there have been numerous cases of such accidents in the United States, but this has been officially denied.[1] Very large quantities have, however, been re-worked with fresh solvent and an addition of diphenylamine; thus at the powder works at Indian Head in 1913, 1,800,000 lb. of new powder were made, and 965,000 lb. were re-worked at a cost 35 per cent. of that of the new powder. Altogether nearly 8,000,000 lb. had been re-worked up to the end of 1910.[2] The quantity of solvent in the ordnance powders when new varies from 3 per cent. in that for the 1 pr., up to 6·8 per cent. in that for the 30 cm. 40-calibre gun. The specific gravity of the powder is 1·563,[3] and the cost of production 2*s.* 4*d.* per lb. To the contractors 1·2 lb. of alcohol is supplied for every 1 lb. of powder accepted. In the finished grain the length is two and a quarter times the diameter, which is ten times the diameter of the holes.[4]

The French, Russian, and American Navies are the only important ones that use nitro-cellulose powders for their large calibre guns. The other Powers are of the opinion that for this purpose powders containing nitro-glycerine offer decided advantages, but for the comparatively small field-guns and for small-arms every Power except Great Britain and Italy uses nitro-cellulose powder. Nitro-cellulose powders are mostly made of soluble nitro-cotton, because ether-alcohol gives a less brittle colloid than acetone. The powders differ somewhat as regards the degree of nitration, also as to the form of the grains, some being rolled into sheets and then cut into small square flakes, others being pressed into cords or tubes and cut off into short lengths; some are coated with graphite and some are not.

Spanish powder.

The Spaniards, after trying a nitro-cellulose powder made at the Rottweil works in Germany, containing about 1 per cent. of camphor and a small proportion of a urea derivative, now make their own powder, which also is of the nitro-cellulose type. For small-arms it is made in the form of flakes, for artillery in long tubes, but they have also experimented with powder in strip form.[5]

Ballistite.

In 1887, a few years after the invention of Poudre B, Alfred Nobel invented a smokeless powder in which the fibrous structure of the nitro-cotton was destroyed not by the use of a volatile solvent, but by dissolving it in another explosive, nitro-glycerine. This substance, to which he gave the name ballistite, is indeed blasting gelatine with the proportion of nitro-cellulose largely increased.[6] At first benzene was added to facilitate the solution,

---

[1] *S.S.*, 1911, p. 136.

[2] *S.S.*, 1911, p. 197.

[3] Schuhmacher, *S.S.*, 1907, p. 82.

[4] Buisson, *Problème des Poudres*, p. 50.

[5] *See S.S.*, 1908, pp. 154, 248, 283; 1910, pp. 161, 188, 416; 1912, p. 479; from *Memorial de Artilleria*, Feb. and Apr. 1908; July, Sept., Oct., Nov., 1909; July 1912, Buisson, *Problème des Poudres*, p. 67.

[6] Fr. Pats. 185,179 of 1887, and 199,091 of 1889, and Eng. Pat. 1471 of 1888.

and was afterwards evaporated off. A better method of incorporation was discovered by Lundholm and Sayers [1], who place the soluble nitro-cotton and nitro-glycerine in hot water and stir it by means of compressed air. Under these conditions the nitro-cotton gradually dissolves in the nitro-glycerine, or perhaps it would be more correct to say that the nitro-glycerine dissolves in the nitro-cotton. The dough thus produced is then passed between rolls heated to 50° or 60° C., whereby the water is pressed out, and the explosive is made into a sheet. This is folded over and passed through the rolls again, and the operation is repeated until the material has been converted into a uniform colloid. It is then cut into square flakes, generally coated with graphite, and finally it is blended. Various additions have been made at different times to make the powder more stable or to improve its physical properties. The first English patent mentioned camphor, but this was dropped on account of its volatility: diphenylamine, aniline and calcium carbonate have also been used much for this purpose. The powder generally contains 40 to 50 per cent. of collodion cotton and 50 to 60 per cent. of nitro-glycerine. It has the advantage that the plant required for its production is comparatively simple, but it causes very severe erosion in the guns.

FIG. 60. American Rifle Powder (Thörner, *S.S.*, 1907, p. 425)

Filite. Ballistite was adopted by the Italian Government soon after its invention, but instead of using it in flake form it was drawn out into cords with the aid of a solvent, and hence was given the name "Filite." Italian ballistite generally consists of equal parts of nitro-glycerine and collodion cotton, together with 0·5 to 1 per cent. aniline or diphenylamine; for micro-photos *see* Paterno and Traetta-Mosca, *S.S.*, 1910, p. 145.

Solenite. In consequence of the severe erosion that ballistite causes in the gun, the Italians reduced the percentage of nitro-glycerine to 33 per cent. It then became necessary to use acetone to assist the gelatinization, and the presence of this solvent made it possible to use a nitro-cellulose only partly soluble in nitro-glycerine or ether-alcohol. From 1 to 3 per cent. of a light-coloured mineral jelly was also inserted, so that the powder, which is called Solenite, does not differ very much from Cordite. The nitro-cotton used contains 12·4 to 12·6 per cent. N, and about 50 per cent. of it is soluble in ether-alcohol. It is pressed into tubes, which are cut into short lengths. The grains thus

---

[1] Eng. Pat. 10,376 of 1889.

obtained are translucent and of a light brown colour, and look somewhat like glass beeds.

German powders.

The Germans adopted ballistite for their navy in 1898 under the name W.P.C /89: it had the same composition as the Italian Filite, but was made up in the form of square flakes or cubes. W.P. stands for Würfelpulver, *i.e.* cube powder. In 1897 and 1900 other powders were introduced less erosive to the guns. These are blackish-grey in colour, and in composition they appear to be much the same as Solenite or Cordite M.D., except that a little diphenylamine is added as a stabilizer as well as mineral jelly. The powders are made in tubular form and are called R.P.C/97 and R.P.C/00. R.P. stands for Röhrenpulver, *i.e.* tube powder. The Germans use nitro-glycerine powder for their large naval guns and for their howitzers, as they consider that they give more regular ballistics in these weapons than nitro-cellulose powders. For their small-arms and 77 mm. field guns, etc., they use nitro-cellulose powder of comparatively high nitration containing diphenylamine as a stabilizer, and sometimes some camphor as an auxiliary gelatinizing agent. The powder for field guns is made in the form of tubes. They have also introduced a progressive powder with the surface gelatinized by means of Centralite.[1]

The following particulars as to German military powders are given by Berlin: [2]

Nitro-cellulose powders. Colour greyish yellow or brown, resembling glue.
S.P. Flake powder for rifle 98 and carbine 98.
Pl.P.P. (Platzpatronen-pulver). Blank powder for same weapons.
Gesch.Bl.P. (Geschütz-Blättchenpulver). Flake powder for the 9 cm. guns 73, 73/88, and the heavy 12 cm. gun.
Gesch.Bl.P. 03
Gesch.Bl.P. (umg.) } Powders made by re-working Gesch-Bl.P. and Gr.Bl.P. to make them milder and more stable.
Gr.Bl.P. 03 (Grobes Blättchenpulver). Large flake powder for use in the 15 cm. ring cannon and 21 cm. do.
Gr.Bl.P. (umg.). Made by re-working the above.
R.G. 96
R.P. 05 } Tubular powders for use in the field gun 96 n/a (127 mm. long).
R.P. 97 and 99 (Röhrenpulver). For use in the various 10 cm. guns (380 mm. long).
R.P. 07. For the 13 cm. gun.
Man.R.P. (Manöver-Ringpulver). Blank ring powder for field guns.

Nitro-glycerine powders. Colour black, due to coating of graphite.
W.P. (½) (Würfelpulver). Cubic powder, edge of cubes ½ mm. for the 3·7 revolver-cannon.
W.P. (2 × 2 × ¾). For the 5 cm. gun.
W.P. (4 × 4 × 1). For the light field howitzer.
W.P. (2). For the heavy field howitzer and 21 cm. bronze mortar.
W.P. (10 × 10 × 1½). For the heavy field howitzer 02, and 15 cm. howitzer, and the 21 cm. bronze mortar.

---

[1] Buisson, *Problème des Poudres*, p. 71.

[2] *Handbuch der Waffenlehre.*

W.P. (12 × 12 × 12). For the 21 cm. mortar.
Rg.P. (Ringpulver). Short tubular powder for mortars.
Man.St.P. (Manöver-Sternpulver). A porous powder easily ignited, made in the form of stars, colour grey with yellow spots, for blank cartridges for manœuvres.

Cordite.

About the time of the discovery of Poudre B, the English Government appointed a committee to investigate and report upon the subject of a suitable smokeless powder for the British service. Samples were obtained of ballistite and all other available powders, but the committee was not satisfied with any of them, and finally devised a new one, to which the name Cordite was given from the fact that it was made in the form of cords. The composition differed from that of ballistite in that gun-cotton was used, insoluble in ether-alcohol, and this was incorporated with nitro-glycerine by means of acetone, which was afterwards evaporated off. Mineral jelly, a semi-solid petroleum product, was added with the idea of lubricating the barrel. It does not have this effect, as it is, of course, entirely consumed in the explosion, but it was a most fortunate addition, as it exercises two most important functions in the powder. Firstly it diminishes the temperature of the explosion and so reduces the amount of erosion of the barrel. At the same time it increases the volume of gas given off and so does not reduce the power of the powder to any great extent. Secondly, it absorbs the nitrous gases which are gradually given off when the powder is stored, and so prevents them from increasing the rate at which the powder decomposes; in this way the mineral jelly adds greatly to the chemical stability of the powder. It also prevents the access of the air to the gun-cotton and nitro-glycerine, and so reduces the amount of deterioration due to oxidation.

The experimental work in connexion with the invention of cordite was mainly carried out in Sir F. Abel's laboratory in Woolwich Arsenal, much of the most important work being done by Dr. W. Kellner, who afterwards succeeded Abel as War Department Chemist. Patents No. 5614 of April 2, 1889, and No. 11,664 of July 22, 1889, were taken out on behalf of the Government by Sir F. Abel and Professor (now Sir) J. Dewar, who were members of the committee, and the same year the manufacture of cordite was commenced at the Royal Gunpowder Factory, Waltham Abbey.

Cordite must be considered one of the most successful smokeless powders, for after a quarter of a century, during which it has been subjected to far more drastic treatment in all parts of the British Empire than the powder of any other Power, it is still giving satisfaction. The Germans meantime have adopted and abandoned a number of different powders, and for their naval guns have finally decided upon a powder of the same type as cordite. The two worst defects of cordite are that it erodes the guns badly, especially those of large calibre, and that when stored at a high temperature its life is a limited one. The erosion is not so severe as that caused by the use of ballistite, because the mineral jelly reduces the temperature of the gases considerably. Nevertheless, the wear of the guns was so bad in the South African War that afterwards the composition was modified in order to reduce the temperature further. The proportion of gun-cotton in the powder was increased, and the explosive thus altered was given the name Cordite M.D. (*i.e.* modified).

	Mk.I.	M.D.
Gun-cotton	37	65
Nitro-glycerine	58	30
Mineral jelly	5	5

As regards the chemical stability it is not possible to say whether there is any other powder which would be more satisfactory, as no other one has been subjected to adverse climatic conditions in such immense quantities. It is, however, certain that all foreign Powers find it necessary to exercise constant vigilance over their smokeless powder, especially if it has to be stored at a high temperature ; if the vigilance be relaxed, catastrophes inevitably follow sooner or later.

A large production of the cordite for the British services is made in the Royal Gunpowder Factory at Waltham Abbey, and it was there that the methods of manufacture were worked out. Under the superintendence of Colonel Sir F. L. Nathan, R.A., a great many improvements were effected in every part of the manufacture, whereby the safety of the workmen was increased, the stability of the explosives was improved, and the cost of production was reduced. Many of these methods have now been adopted by the private contractors, who also supply cordite to the Government.

Weighing t
gun-cotton.

When the stove, in which the gun-cotton has been dried, is quite cool, the men go and unload it. The gun-cotton is weighed out in the porch of the stove. These operations require to be carried out with the greatest care, as dry gun-cotton is very sensitive. The men wear nothing on their feet but socks ; formerly, the gun-cotton was weighed out into brass-lined wooden boxes, but now waterproof india-rubber bags are used. Several explosions have been ascribed to the jar or friction of the edges and corners of such heavy boxes one against the other, especially when the boxes have contained nitro-glycerine. Such accidents can be guarded against to some extent by covering the edges with rubber or leather, but it is better to avoid this danger by using rubber bags ; but if nitro-glycerine is to be poured into them it is essential that they should be absolutely water-tight, and they should be inspected frequently to ensure this. The scales are of such a design as to reduce friction between the knife-edges to a minimum ; the weights are either attached to the scale so as to form an integral part of it, or they are made of gutta-percha bottles filled with the requisite quantity of lead shot. The quantity weighed out into each bag is that which is required for a charge of the incorporator, or if this be of great size, an integral fraction of it. The necks of the bags are tied up, and they are transported by boat or trolley to the mixing house.

Measuring the nitro-glycerine. Formerly the nitro-glycerine was weighed out into india-rubber buckets and then poured on to the gun-cotton in the brass-lined boxes. Now, however, it is measured out in a special burette made of lead, which holds the exact quantity required, and is fixed to the floor. It is a small cylindrical vessel with a conical top ending in a narrow neck ; the bottom slopes down to one side where there is an orifice to which a rubber tube is attached, the other end of which can be passed over a lead plug near the top of the burette, when it is not being emptied. Round the outside of the neck is a channel to catch nitro-glycerine that overflows, and this is conducted by a pipe into a rubber bucket, so that it can be returned to the filter-tank. The burette is filled by means of the rubber pipe attached to the filter-tank, until it is quite full, and then the burette is emptied by means of the similar rubber tube attached to it into one of the rubber bags containing dry gun-cotton.

Mixing. The next operation is to mix the gun-cotton and nitro-glycerine roughly together, and reduce the large primers of the former to the form of powder. At one time this was done by rubbing the material through a $\frac{1}{2}$-inch copper wire sieve, but now a special lead table is made for the purpose. This is pear-shaped and slightly dished out. At one end are a number of $\frac{1}{2}$-inch holes, and underneath is a sort of neck on to which a bag can be attached. The contents of a bag of gun-cotton and nitro-glycerine are placed on the other and larger part of the table ; then a man wearing leather gloves transfers a little at a time to the end where the holes are and rubs it through into the bag below. No unnecessary violence must be used.

Incorporating. The "cordite paste" thus obtained is next taken to the incorporating house. The interior of the incorporator (*see* Figs. 56, 57) is thoroughly moistened with acetone, the charge of paste is added and the rest of the acetone, and the machine is run for three and a half hours, then the mineral jelly is added and the kneading is continued for another three and a half hours. The quantity of acetone used is about 56 per cent. of the weight of the gun-cotton.

Pressing. The cordite dough thus obtained is next pressed through a die, which forms it into a cord. The type of press used depends upon the size of cordite that is to be made. The smaller sizes, such as $3\frac{3}{4}$ which is used for rifles, are pressed in a small press with only a single orifice, and the cord as it emerges is wound on to a small drum, which is then taken to the cordite stove for drying. The larger sizes are made in large presses which have several orifices, and the large cords as they emerge are cut by hand to the lengths required, according to the size of the cartridges to be made ; these sticks are then laid upon trays, which are conveyed to the stove. Inside the press cylinder above the die is placed a piece of fine wire gauze, through which the dough is made to pass in order to remove from it all foreign material as far as possible. The dough is rammed into the press cylinder by means of a wooden rammer. There is only one pressing operation, whereas the American multiperforated nitro-cellulose powder undergoes four.

For pressing cordite in the ordinary round form the die has, of course, a simple round hole. For making tubular cordite a pin is inserted in the centre of the hole. In the case of tubular cordite of small size it is found that the tubes have a tendency to collapse in consequence of the difficulty the air has to pass through a great length of narrow tube. To overcome this difficulty Lloyd and Curtis's and Harvey Ltd. use a perforated pin communicating through the side of the die with the open air.[1]

Occasionally the cordite ignites as it emerges from the press. As a rule no serious damage is done, but on September 17, 1909, an ignition took place at Waltham Abbey whilst pressing cordite Mk.I size 20, which wrecked the press and damaged the building. Two men were injured by broken glass from the windows, which were shattered. The fire was accompanied by two explosions probably of acetone vapour as well as some cordite. The first apparently destroyed the die seating and released the die ; the burning then continued, and the second explosion occurred in the cylinder.[2]

Drying.

The cordite stove consists merely of a building provided with suitable racks and heated by means of steam pipes to a moderate temperature, which depends upon the sort of cordite that is to be dried. Cordite Mk.I size $3\frac{3}{4}$ gives off its moisture so readily that artificial heat is not necessary in the summer time. All that is required is to keep the reels in the stove at a temperature of about 15° C. for a few days. The larger sizes are dried at temperatures from 38° to 43° C. for periods ranging up to a fortnight. Cordite M.D. gives off its moisture much less readily than Mk.I, and consequently requires to be kept in the stove several times as long ; in the case of the largest sizes the stoving occupies months, and is one of the greatest difficulties that have to be contended with in the manufacture. The moisture in the cordite Mk.I must not exceed 0·4 to 0·6 per cent. according to size, but the percentage allowed in M.D. is considerably more. The size of cordite is given by a figure, which is the approximate diameter in hundredths of an inch of the die through which the cordite has been pressed. Thus cordite size 50 has been pressed through a die about ½ inch in diameter. The thickness of the cord is, however, somewhat less than this, as it shrinks considerably in drying. Various particulars about the different sizes of cordite will be found in the *Treatise on Service Explosives*, Appendices V and VI.

It is usual now to recover as much as possible of the acetone that is given off during the drying. The cordite should therefore be placed in an air-tight

---

[1] Eng. Pat. 27,700 of November 28, 1910.

[2] *See* A. R., 1909, p. 33.

receptacle as soon as possible after pressing, and this should be taken to the stove without unnecessary loss of time.

apanese owder.

The Japanese Government formerly bought cordite for its naval ordnance from private firms in England, but after the spontaneous ignition on the *Mikasa* in 1905 it resolved to make its own powder.[1] Powders for field and mountain guns captured by the Russians during the Russo-Japanese war were found to be nitro-cellulose powders with 40 to 47 per cent. soluble in ether-alcohol and 12·5 per cent. N.[1] They were in strip and flake form respectively. The Japanese are said now to be nitrating wood cellulose obtained from the island of Sakhaline.[2]

porting rifle owders.

The smokeless powders used for sporting rifles are practically the same as those used for military small-arms. Ballistite of a suitable size is employed to a considerable extent, as the erosion is not so very severe in these weapons. Cordite is very largely used : most of the principal explosives manufacturers in England make cordite for the Government, and consequently have all the plant and experience required. Several slight modifications of cordite are also made.

xite.

Thus Kynoch Ltd. in axite have replaced a portion of the gun-cotton by means of potassium nitrate or oxalates of potassium and barium. A sample that I examined some years ago had the following composition :

Nitro-glycerine	29·7	per cent.
Gun-cotton	63·1	,,
Mineral jelly and oil	5·1	,,
Volatile matter	0·2	,,
Potassium nitrate	1·9	,,
	100·0	,,

It was made in the form of flat strips. The patents, Nos. 12,892 of June 22, 1905, 15,564, 15,565 and 15,566 of July 26, 1905, cover the use of olive-oil in addition to vaseline or mineral jelly, of flakes and strips with various forms of ribs and knobs to facilitate ignition, and the addition of carbonates. Axite is also sometimes made of a composition resembling that of cordite Mk.I with part of the gun-cotton replaced by potassium nitrate. It is claimed that axite erodes the rifle less than cordite, as the temperature of explosion is lower, and that it does not cause the barrel to rust so much, because the residue remaining in the bore is alkaline.

Ioddite.

Eley Bros. also manufacture a variety of cordite which they call Moddite. A sample, which I examined, had the composition :

Nitro-glycerine	38·7	per cent.
Nitro-cellulose	56·8	,,
Mineral jelly	4·3	,,
Volatile matter	0·2	,,

---

[1] Buisson, *Problème des Poudres*, p. 175.

[2] Saposhnikoff, *S.S.*, 1906, p. 69.

Of the nitro-cellulose 34·5 per cent. was soluble in ether-alcohol. It was made in the form of strip.

Nitro-cellulose powders are also used in sporting rifles. They are generally made of soluble nitro-cellulose containing 12 to 12·5 per cent. N gelatinized with ether-alcohol. Sometimes a few per cent. of some other constituent, such as resin, is added. Usually the powders are made in the form of flakes.

CHAPTER XXII

REQUIREMENTS OF A SLOW-BURNING SMOKELESS POWDER

Rate of burning : Form of powder : Progressive powder : Erosion : Nitro-glycerine *v.* nitro-cellulose powders : Backflash : Muzzle flame : Products of explosion : Testing propellants : Efficiency.

It is required of a powder for rifles or ordnance that it shall give a high-muzzle velocity with moderate pressures, that it shall not cause too much erosion of the bore, and that the ballistics shall be regular, *i.e.* different rounds fired with similar ammunition must give practically the same velocity to the projectile. The speed acquired by the bullet or shell is due to the pressure of the powder gases on its base, as it travels down the bore of the fire-arm, and it is important that the powder shall burn in such a manner that the pressure is suitable during the whole of the time until the projectile leaves the muzzle. Two of the most important facts in connexion with the study of internal ballistics are : (*a*) That the grains of completely gelatinized powders burn away uniformly from the surface, so that they retain their original shape, but get thinner until entirely consumed ; and (*b*) that the rate of burning varies directly with the pressure. From the results of experiments in closed vessels Vieille deduced that the rate of burning v could be calculated from an equation of the form $v = cp^x$, where p is the pressure and c and x are constants. For ordinary black powder $x = 0{\cdot}5$, for highly compressed black prism powder 0·33, for brown prism powder 0·25, for Poudre B 0·67, and for powder containing 50 per cent. nitro-glycerine 0·55.[1] Mansell [2] and Petavel [3] prefer an equation of the form $v = a_0 + ap$, where a_0 is the rate of burning when there is no pressure, and a is the rate of increase of burning per unit of pressure. For cordite $a_0 = 0{\cdot}5$ cm. per sec. and $a = 0{\cdot}018$ cm. per sec. per atmosphere.

Rate of burning.

That the burning proceeds uniformly by layers is shown by the fact that if a gelatinized powder be fired from a gun, which is too short to allow of the total consumption of the explosive, the remains of the grains thrown from the muzzle are found to be in every way similar to the original grains, except that the dimensions are reduced.

---

[1] Vennin, *Poudres et Explosifs*, p. 72.
[2] *Phil. Trans.*, 1907, 207A, p. 243.
[3] *Proc. R.S.*, 79A, p. 277 ; *S.S.*, 1908, p. 166.

FIG. 61. Projectile and Powder Charge for American 16-inch Gun; Weight of Charge, 666·5 lb. nitro-cellulose powder

(From *Smithsonian Report*, 1914, p. 256)

Form of powder.

The result of this is that with a powder made in the form of cords or cubes there is a diminution of the burning surface as the combustion of the charge proceeds, and consequently the pressure falls off rapidly as the projectile approaches the muzzle, although not so much as was the case with black powder, which being porous did not burn entirely by parallel surfaces. In order to overcome this objection other forms are often adopted for the grains of powder. If a strip or flake be used, the width of which is great compared with the thickness, the area of surface remains practically constant until the material is entirely consumed. It has been found, however, that powders made up in these flat forms are liable to give irregular ballistics, and this has been ascribed to the obstacles in the way of regular ignition, when two grains lie flat against one another. Messrs. Kynoch have proposed to remedy this defect by providing the strips or flakes with ribs or knobs.

Constancy of the area of surface can also be attained by making the powder in the form of tubes. There is then no difficulty about the ignition, but the pressure inside the tube is always somewhat greater than outside, because the gases cannot escape very readily, and this excess of pressure may become sufficiently great to split the tubes. If this occur, the ballistics become unreliable, partly on account of the sudden relief of pressure, and partly because the surface is increased in an erratic manner. If the gravimetric density of the powder in the chamber be high, the general pressure is increased, and the difference between the pressure inside and outside the tubes is diminished.

If instead of only one perforation there be several as is the case with the American multiperforated powder, the pressure increases as the burning proceeds, and consequently the pressure is maintained at a higher level whilst the projectile is travelling through the forward portion of the bore. This should not be carried too far, because it is not practicable to have great thickness of metal near the muzzle. To prevent the grains splitting in consequence of the great pressure inside them they are cut into short lengths.

The thickness or diameter of a powder should be such that it is entirely consumed shortly before the projectile reaches the muzzle.

Surface treatment.

The relative rate of burning of the powder charge at different instants can also be regulated by submitting the explosive to an operation, wherein the surface layer of the material is modified. Such "progressive" powder is made at Rottweil by treating the grains of nitro-cellulose powder with an alcoholic solution of "Centralite" (dimethyl-phenyl-urea); this causes the outer layers of the grains to burn more slowly, and so causes the chamber pressure to be less, and that further down the bore to be higher. The same method is being tried in France.[1] Another method is to treat the powder in a drum with a solution of 0·1 to 1 per cent. of paraffin-wax dissolved in benzole. Flake powders for small-arms are sometimes coated with graphite. This

---

[1] *See* Florentin, *S.S.*, 1913, p. 32; *also* Buisson, *Problème des Poudres*, p. 40.

FIG. 62. Cross-Section of Machine-Gun Barrel after firing 3,000 Rounds with Nitro-glycerine Powder

(From *Smithsonian Report*, 1914, p. 257) not only restrains the initial velocity of ignition but also facilitates the loading from loading machines.

Nitro-glycerine v. nitro-cellulose powders.

There has been considerable controversy as to the relative advantages and disadvantages of nitro-cellulose and nitro-glycerine powders. The advantages claimed for nitro-glycerine powders are that they give more regular ballistics, do not give back-flash when fired, are more powerful, are cheaper to manufacture, leave less residue in the gun, and have at least as good chemical stability as nitro-cellulose powders. Their great disadvantage is that the temperature of explosion is high, and consequently the erosion of the bore of the gun is very severe.

In spite of the fact that they erode the guns more, most of the Powers use nitro-glycerine powders in their large guns, and the principal reason for this is that they give more regular ballistics. It is impossible to drive the whole of the solvent out of a colloided nitro-cellulose powder, even though the drying be greatly prolonged, and indeed it is advisable to leave several per cent. in the powder, because otherwise it is too brittle. But this residual solvent is a source of uncertainty, because it gradually diffuses from the centre of the grains or strips, etc., and evaporates, even though the powder be stored in closed receptacles. The loss of this combustible matter makes the powder more powerful, but what is more serious is that the material becomes harder and more brittle, and it may break up when fired, and consequently give high pressures and irregular velocities.

The addition of a considerable proportion of nitro-glycerine to a powder makes it give up its volatile matter much more readily. Apparently the residual solvent passes from the particles of gun-cotton to the adjacent ones of nitro-glycerine, and diffuses through the latter to the outside of the stick or flake much more rapidly than it can through the colloidal nitro-cellulose [1] The result is that the percentage of volatile matter can be reduced without difficulty to 1 per cent. or a little more, and if a fraction of this afterwards escapes, it does not alter the composition of the powder materially, and even the loss of the whole of it does not affect the physical properties of the material. The presence of the nitro-glycerine causes it to remain always a tough or slightly plastic mass according to the percentage. Nitro-glycerine powders are also considerably less hygroscopic. Thus N. L. Hansen found that in a nitro-cellulose powder in strip form 0·78 mm. thick freely exposed the moisture varied from 1·71 to 2·35 per cent. according to the time of year and the amount of moisture in the atmosphere, and in a tubular nitro-cellulose powder 3·70 mm. thick from 0·56 to 1·36 per cent.[2] With a nitro-glycerine powder the

---

[1] It has been found by H. Bechhold and J. Ziegler that whereas in dilute gels diffusion is practically the same as in the pure solvent, in very stiff gels it is much smaller, and may be either increased or diminished by the addition of other substances (*Zeitsch. physikal. Chem.*, 56, 1906, p. 105).

[2] *S.S.*, 1911, p. 461.

amounts of water absorbed and the variations would have been much smaller, as the nitro-glycerine waterproofs the powder.

The smaller bulk of nitro-glycerine powders is of some advantage on board ship, where magazine room is limited. The lighter weight of th cartridges also makes them rather more easy to handle.

Erosio

The question of erosion was investigated by Vieille,[1] who showed that the temperature produced in the explosion was the principal factor. He fired charges of various explosives in vessels, which were closed except for a small orifice drilled through a metal plug, which was weighed before and after the experiment. He found that the erosion increased with increase of length of the orifice, with decrease of the diameter, and with increase of the volume of gas and the pressure. The influence of the nature of the explosive is shown by the following Table :

Explosive	Pressure kg./cm.^{2}	Temperature (calculated)	Erosion cub. mm. per g.
Gunpowder, 75 per cent. saltpetre .	2167	2910°	2·2
,, 78 ,, ,, .	1958	3513°	4·5
Nitro-guanidine	2019	907°	2·3
Nitro-cellulose	2276	2676°	6·4
Solenite (34 per cent. N/G) . .	2449	—	13·8
Dynamite (75 per cent. N/G) .	2084	3161°	18·0
Cordite.	2500	—	18·1
Nitro-mannite	2361	3429°	23·6
Ballistite (50 per cent. N/G). .	2440	3384°	24·3
Blasting gelatine	2458	3545°	31·4

This clearly shows the influence of the temperature of the explosion gases. The lower the melting-point of the metal, the more it is eroded ; the following results were obtained by firing charges of 3·55 grains of ballistite, using plugs of different metals :

Platinum	59·1	cub. mm.
Platinum-iridium	74	,,
Iron	68·2	,,
Cannon steel	84·5	,,
Chrome steel (3·5 per cent.)	98	,,
Copper	98·8	,,
Nickel steel (24 per cent.)	107	,,
Cast iron	131	,,
Silver	230·8	,,
Bronze	279	,,
Brass	326	,,
Zinc	1018	,,

---

[1] *P. et S.*, vol. xi., 1902, p. 157.

It will be seen that the melting-point affects the erosion far more than the hardness of the metal. Similar experiments have been carried out in America,[1] where charges of smokeless powder were fired in an armour-piercing shell, closed with plugs of different metals, which were drilled with holes 3·97 mm. in diameter. The erosion was measured by the number of times the area of the orifice was enlarged :

Wrought iron	4·5 times
Martin steel	4·5 ,,
3 per cent. tungsten steel	4·5 ,,
Martin steel with 3 per cent. tungsten . . .	4·7 ,,
3½ per cent. nickel steel	5·0 ,,
20 per cent. nickel steel	5·9 ,,
Manganese bronze.	23·0 ,,

The erosion is to be ascribed to the fusion of the surface of the metal, which is then swept away by the rush of gas. As regards the influence of pressure Vieille found that up to a pressure of 100 kg./cm.^{2} the erosion was only slight ; it increases very rapidly with rise of pressure from 900 to 2000 kg./cm.^{2}, and then remains practically constant from 2000 to 4000 kg.

Noble carried out an elaborate series of experiments with cordites specially manufactured with varying proportions of nitro-glycerine.[2] These were tested in the calorimetric bomb and also fired from the gun. The results are shown in Fig. 63. It will be seen that when the percentage of nitro-glycerine is increased from 10 to 60 per cent., the quantity of heat increased 60 per cent., but the erosion was greater by nearly 500 per cent.

When only small charges are used, the erosion is not very severe, for both the temperature and pressure in the chamber are much lower. It is largely for this reason that practice with large guns is mostly carried out with reduced charges. It is reckoned that the wear of the gun due to a proof round is equal to that of two full charges, and that a full charge of powder is equivalent to four ¾-charges or sixteen ⅓-charges or sixteen blank charges. One round of cordite Mk.I is equivalent to several of cordite M.D. producing the same ballistics. It is in large ordnance, firing very heavy charges of powder in order to obtain a high muzzle velocity, that the erosion is most severe ; in smaller guns it is comparatively trifling. By properly proportioning the chamber and the length of the gun, and making the powder of the right size and shape, the erosion can be reduced somewhat, but naval guns of large size require re-lining after they have fired a few hundred full charges.

With smokeless powder the erosion mostly consists in washing the surface of the metal smoothly away. With high charges of black powder, which generated temperatures of the same order, the metal was scored into deep ruts, and this has been ascribed to the mechanical action of the solid particles

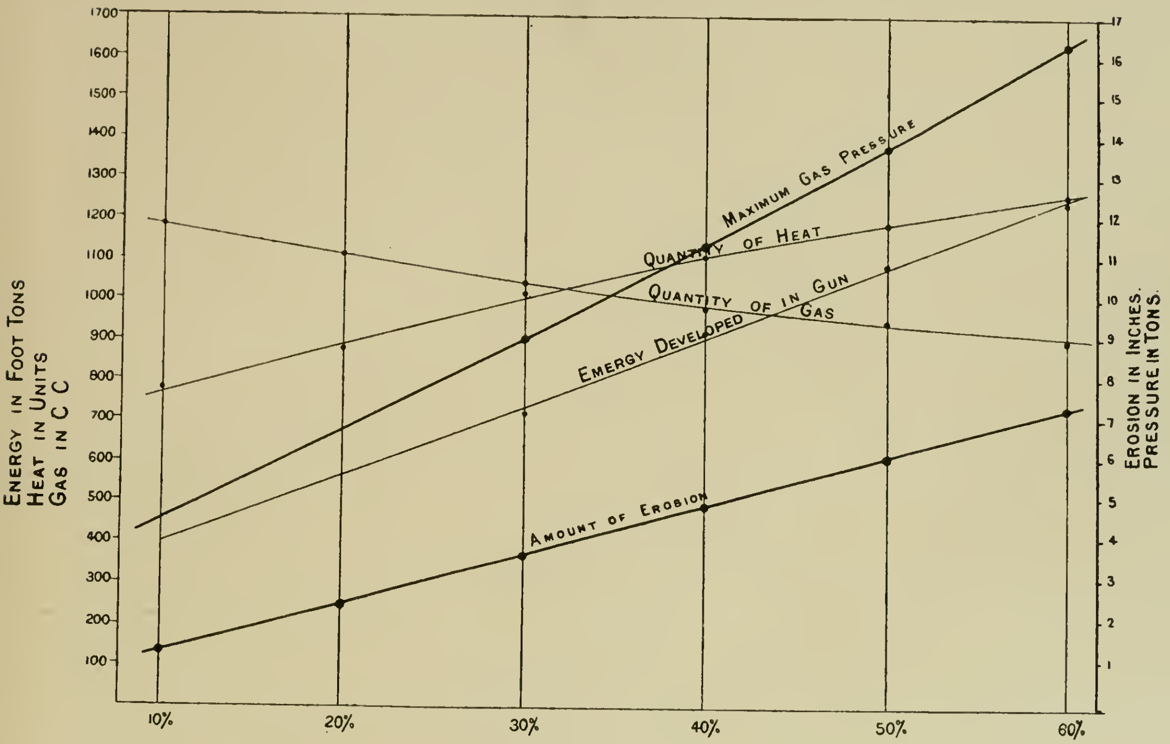
---

[1] *See S.S.*, 1907, p. 211.

[2] *Artillery and Explosives*, p. 534.

in the products of explosion. With smokeless powder there is some scoring, but not nearly so much.

Erosion is most severe, not in the powder chamber, but just in front of it, where the powder gases rush past between the copper band of the projectile and the bore of the gun. Further down the bore the wear is much less, as the pressures are less, the copper bands fit the rifling better, and the projectile is travelling so rapidly, that the escapes of gas have little time to do harm.



Per cent. Nitro-glycerine

Fig. 63. Noble's Erosion Experiments

The inner tubes of guns also occasionally split. This is apparently caused by the alternate heating and cooling of the inner surface of the metal combined with the compression to which it is subjected. The result is that the surface layer of metal is in a state of tension.

Yarnell has shown that just as nitro-glycerine powders cause more erosion than those that only contain nitro-cellulose, so nitro-cellulose powders of high nitration are worse in this respect than those of low nitration, in spite of the fact that a smaller charge is required.[1] Like Vieille he found that the erosion is practically independent of the pressure if it exceed 2000 atmospheres. Yarnell also tried the effect of adding considerable quantities of water or paraffin to the charge. The erosion was greatly reduced thereby, and the pressures were increased. Such additions have been advocated frequently, but apart from the difficulty of carrying them out under war conditions, the presence of cooling material in the lump, so to speak, must render the ballistics uneven. Any addition should be incorporated with the powder during manufacture. The mineral jelly in cordite reduces the temperature of the products several hundred degrees, and in fact cordite M.D. has a temperature of explosion, which is but little higher than that of some nitro-cellulose powders. An addition such as this does not diminish the ballistic efficiency of the powder to any great extent, because the reduction of temperature is partly compensated by the increase in the volume of gas formed.

Vieille (*loc. cit.*) showed the effect of adding nitro-guanidine to powders:

	Erosion per gramme		
	Nitro-cellulose Powder	Cordite	Ballistite
Alone	6·4	18·1	24·3
With 30 per cent. nitro-guanidine .	5·45	13·0	14·2
,, 50 ,, ,, .	3·44	8·44	7·8

The difficulty is to find a substance that can be incorporated with the powder in sufficient quantity without affecting injuriously any of its qualities. Nitro-guanidine, for instance, makes it brittle.[2]

Back-flash. With a low temperature of explosion is always associated a low percentage of oxygen in the powder, and consequently a large proportion of carbon monoxide in the products. When large guns are fired the combustible powder gases are liable to catch light at the muzzle and burn down the bore, and on the breech being opened this flame may emerge, especially if the gun be pointing to windward. In France, where nitro-cellulose powder only is used, a number of disasters have been caused by such flames emerging, and setting light to cartridges in the turret, or standing near the gun. Similar accidents have occurred in the United States, where also nitro-cellulose powders are employed exclusively. This danger is also present with cordite, although not to the same extent, and must be guarded against.

---

[1] *Journ. Amer. Soc. Naval Engineers*, May 1910; *S.S.*, 1911, p. 193.

[2] Bravetta, *S.S.*, 1912, p. 493.

Muzzle flam

When cannon are fired, flames appear at the muzzle due to the ignition of the combustible gaseous products. This is objectionable, because at night it reveals the position of the guns. The flame can be diminished or even abolished in some cases by adding a few per cent. of sodium resinate or other sodium or potassium salt,[1] but the quantity of smoke is thereby greatly increased and this will reveal the position by day, and will obstruct the gunners.

Muzzle flame is due to high temperature of the gases as they emerge from the gun as well as to their composition. With a large charge of powder it is much more difficult to keep this temperature below the ignition point of the gases. The problem of doing away with it has much in common with that of the preparation of coal mine explosives.

Products of explosion.

Numerous analyses of the products from the explosion of cordite and Rottweil nitro-cellulose powder have been published by Noble.[2] The powders were exploded in a calorimetric bomb at various densities of loading, but only the figures for the lowest density, 0·05, are reproduced here, as they probably represent most nearly the composition of the gases evolved in the gun.

	Cordite Mk.I	Cordite M.D.	Rottweil R.R.
Vol. permanent gas, c.c. per g.	678·0	781·8	814·7
Vol. total gas, c.c. per g.	877·8	955·4	993·1
Composition of perm. gas :			
CO_2	27·15	18·15	17·90
CO	34·35	42·60	43·45
H_2	17·50	23·15	24·40
CH_4	·30	·35	·60
N_2	20·70	15·75	13·65
Composition of total gas :			
CO_2	20·97	14·85	14·68
CO	26·53	34·87	35·63
H_2	13·52	18·95	20·01
CH_4	·23	·29	·49
N_2	15·99	12·89	11·19
H_2O	22·76	18·15	18·00
Pressure, tons sq. in.	2·9	2·7	3·35
Heat evolved (water liquid)	1272	1036	896
Tempre. of explosion, ° C.	5151	4056	3488

The temperatures were calculated with very low values for the specific heats and are consequently high and have only relative value.

---

[1] *See* Schildermann, *S.S.*, 1913, p. 126.

[2] *Proc. Roy. Soc.*, 76A, 1905, p. 381.

Macnab and Leighton carried out similar experiments with cordite.[1] The relative temperatures of explosion determined with thermocouples as compared with the sporting powders given on p. 327 were 191 and 168 for Cordite Mk I and M.D. respectively.

According to Schumacher,[2] American multiperforated powder fired at a density of 0·05 gives 664·4 c.c. of permanent gas per gramme having the composition :

CO_2	20·7
CO	46·6
H_2	14·7
CH_4	1·3
N_2	16·7

Sir A. Noble has also given the following figures in *Engineering* :

	Vol. Gas	Heat	$\frac{\text{Vol.} \times \text{Heat}}{1000}$
Cordite Mk.I	875·5	1246	1090
,, M.D.	913·5	1030	941
Ballistite, Italian	810·5	1305	1057
Norwegian 167	999·9	1005	905
Nitro-cellulose	934	924	863
Norwegian 165	909·9	935	851
Blanche nouvelle	822	1003	824
Lyddite	960·4	856	822

Testing propellents.

When a new explosive is being investigated all the usual characteristics of an explosive may with advantage be determined, such as the power, inflammability, residue, volume and composition of gases. The recoil and erosion of the gun may also be measured, and the temperature of combustion calculated. A determination may also be made of the law of combustion, *i.e.* the rate of rise of pressure with time, by means of a spring manometer.[3]

For current supplies of powder the principal tests are : determination of the composition by chemical analysis, stability tests, measurements of the muzzle velocity by means of an electric chronograph, and of the maximum pressure in the chamber of the gun by means of a crusher gauge. The mean and greatest differences of series of these last two are also taken into consideration.

Efficiency.

Of the total energy of the powder from 15 to 40 per cent. is actually utilized as kinetic energy of the projectile.[4] Of the remainder the greater part remains

---

[1] *J. Soc. Chem. Ind.*, 1904, p. 300.

[2] *S.S.*, 1907, p. 84.

[3] Vennin et Chesneau, p. 142 *et seq.*

[4] *Ibid.*, p. 147.

in the powder gases as heat and kinetic energy, but the barrel also absorbs a considerable proportion as heat. An investigation carried out with the German rifle M.98S gave the following distribution :[1]

Heating barrel	22·5	per cent.
Bullet, velocity energy	32·7	,,
,, rotation energy	0·2	,,
Recoil	0·9	,,
Gases, cartridge case	43·7	,,
	100	

---

[1] C. Cranz and R. Rothe, *S.S.*, 1908, p. 303.

CHAPTER XXIII

FAST-BURNING SMOKELESS POWDERS

Shot-gun powders: Condensed powders: Bulk powders: Ingredients: Manufacture of bulk powders: American method: 33-grain powders: 30-grain powders: French powders: German powders: American powders: Austrian powders: Requirements: Testing shot-gun powders: Powders for trench howitzers: Blank powders

Shot-gun powders. THE shot-gun is distinguished from the rifle not only in not having a rifled bore, but also in being generally of considerably greater calibre. To produce a weapon easy to handle it is necessary to make the forward portion of the barrel very light, and therefore there must be but little pressure except near the breech. The distribution of the shot in a uniform manner, *i.e.* the formation of a good pattern, seems to require that comparatively little pressure be exerted on the shot in the forward portion of the barrel. For these reasons a shot-gun powder must burn much more rapidly than a rifle powder, and therefore there must be more surface exposed. These powders are of two kinds: the "condensed" and "bulk" types.

Condensed powders. In the condensed powders the nitro-cellulose is completely gelatinized: they are made in much the same way as rifle powders, but are formed into quite small grains or very thin flakes. Cannonite, Shot-gun Rifleite and Sporting Ballistite are of this type, but the first two of these are no longer manufactured; their composition is given in the Table on p. 327. Cannonite was made in the form of small graphited grains; the process of manufacture was described by Sanford in the first edition of his *Nitro-Explosives*, 1896, p. 182. Shot-gun Rifleite was in the form of thin flakes; Sporting Ballistite is also a flake powder. The advantages claimed for these powders are that they leave very little solid residue when burnt, and are consequently free from smoke and "blow-back," and leave but little fouling in the bore, that they are not much affected by exposure to moist air, are very quick and give little recoil. On the other hand, they require special cartridge cases with a cone of pasteboard filling up part of the base, because otherwise the case would not be entirely filled, and also too much of the powder would be exposed to the flash of the cap. In consequence of the small space occupied by the powder charge very slight variations in the strength of the cap and other conditions produce great variations in the pressures generated, and the gun may therefore be strained dangerously, and difficulties are sometimes experienced in extracting the cartridge cases. These powders are also more difficult to manufacture than those of the bulk type.

Bulk powd

Bulk powders are so made that the charge for a 12-bore gun occupies the same space in the cartridge as the standard charge of 82 grains of black powder occupying a space of 3 liquid drams equal to 10·65 c.c. The first successful smokeless powder was that of Captain E. Schultze, of the Prussian Artillery, who made it from nitrated wood.[1] This was first cut into thin veneers, from which small cylinders were punched, and then it was purified by boiling with soda, bleaching and washing. After nitration the nitro-lignin was boiled with soda, and washed with cold water, and afterwards impregnated with the nitrates of barium and potassium. In the course of time various modifications have been made in the process of manufacture. The wood fibre now used is thoroughly purified by drastic chemical treatment, and is formed into grains by manipulation with solvents after nitration. The treatment with solvent also hardens the grains and makes them more waterproof. For further information about the early development of Schultze powder *see ante*, p. 47, also Guttmann, *Progress*, p. 38 and Appendices, and Griffith's Patents 3294 of 1877, and 11,808 of 1884. Most of the other powder manufacturers use nitro-cotton instead of nitro-lignin, but the Schultze Company have adhered to wood fibre, as they consider that a powder made with it is less sensitive to variations of loading, and gives more satisfactory results under adverse climatic conditions.

Ingredient

Bulk powders frequently contain a small proportion of substances, such as vaseline or paraffin wax, which serve to moderate the action. Starch also is sometimes used ; it helps to hold the grains together. Camphor is somewhat objectionable, as it is volatile and escapes on long storage. The mono- and dinitro-derivatives of benzene and toluene are present in some powders ; like camphor they have the property of assisting the gelatinization of the fibres. Other materials that are added sometimes are lamp-black, wood meal, various gums and potassium ferricyanide. In order to complete the oxidation of such added organic matters, and also to make the rate of burning more uniform, nitrates of barium and potassium are added : the barium salt has the advantage that it produces comparatively little smoke and is not hygroscopic. On the other hand, it leaves a residue in the gun, which is difficult to remove. Therefore it is customary to use a considerable percentage of barium nitrate together with a small proportion of potassium nitrate. A small quantity of aniline dye is also added in many cases to colour the powder. Other powders are coated with graphite, which renders them less liable to become ignited by electrification, although there is little danger

---

[1] *See* Eng. Pat. 900 of 1864.

of this in powders that contain mineral salts. Graphiting also retards the ignition of the powder and so acts as a moderating agent. The nitro-cellulose used generally contains 12·5 to 12·8 per cent. nitrogen, and is partially soluble in ether-alcohol. The addition of calcium carbonate improves the stability of the powder by neutralizing any acid that is given off, but it should be very intimately mixed with the nitro-cellulose, and such intimate contact is best produced by precipitating the carbonate in the fibres by using hard water for the boiling of the nitro-cellulose.

Manufacture of bulk powders.

The incorporation of the ingredients is in many cases performed under edge-runners similar to those used for the milling of black powder. The wet nitro-cellulose, containing some 40 per cent. of water, is roughly mixed with the other ingredients, and these are ground together in the mill, water being added from time to time to keep the mixture moist. The duration of the milling and the amount of water are regulated according to the gravimetric density required in the finished product. The longer the milling and the higher the proportion of water, the greater the gravimetric density. The material is then passed through a sieve with meshes somewhat larger than the finished grain is to be. The moist grains thus formed are then dried in a stove by means of a current of hot air, the powder being spread on trays to a depth of not more than 3 inches. When dry the material should be allowed to cool down in the stove before it is moved. The dust and large lumps are then removed by passing the powder through slope reels.

Fig. 64. English Bulk Powder (Thörner, *S.S.*, 1907, p. 424).

The next operation is the important one of hardening the grain by treating it with solvent. This is frequently done by spraying it with the solvent inside a drum, which can be closed hermetically and rotated about its axis. After a few minutes' rotation the grains are thoroughly moist. The powder is then allowed to steep for some time either in the same vessel or another one, and then it is dried. The preliminary drying may be carried out in a solvent recovery plant consisting of a rotating drum provided with a steam jacket and a hollow axle, which is connected through a condensing coil with a vacuum pump. The coil, pump, etc., are placed in a separate compartment from the drying drum, which is isolated by means of a wall having no openings, in order to minimize the danger of fire. A considerable proportion of the solvent is recovered in this way, and after redistillation may be used again, but in order to obtain a satisfactory recovery it is necessary to cool the coil by means of refrigerated brine to a temperature considerably below the freezing-point of water. The drum is fitted with ribs inside to prevent the powder simply sliding round in a cake. The exit is covered with wire gauze and cotton wool to prevent dust being drawn into the condenser. The man-hole lid fits air-tight, and can be held on by means of thum-screws, but during the drying these screws are removed so that the lid is held on by the vacuum only. If pressure arises at any time during the drying the lid will at once fall off and relieve the pressure. The temperature of the powder should never exceed about 50° C. (122° F.). The powder as it comes from the drums contains 3 or 4 per cent. of water and solvent. The drying is completed on trays in a drying stove. When dry it is sifted so as to remove the grains that are too large or too small: these are added in small proportion to a further charge in the milling operation. Finally, the powder is tested for stability and ballistics, and carefully blended with other batches so as to obtain the standard results. But before the final tests are made the powder should be kept for a month or two in order that it may take up the normal amount of moisture. In case of necessity it can be "aged" artificially by exposing it for a few hours to a hot moist atmosphere, but natural ageing is more satisfactory.

This scheme of manufacture has been varied in many ways. The incorporation, for instance, can be performed in drums with lignum vitæ balls. The mass can then be pressed and broken up into grains of the desired size much as is done with black powder. Granulation can also be effected by sprinkling the powdery material with water and then rotating in a drum. Various solvents have been used by different powder-makers: mixtures of ether and alcohol, acetone and alcohol, and acetone and ether have been employed. Ether is very volatile and consequently the losses are considerable. Ether-alcohol only partially gelatinizes the nitro-cellulose unless the degree of nitration is low. Benzol is sometimes added to moderate the action.

America method.

According to C. E. Munroe,[1] the following method is adopted in America for the production of shot-gun powder with fibres entirely gelatinized. The manufacture is conducted in a stationary still of copper about 5 feet in diameter with conical ends. A shaft extends downwards through a stuffing box in the top to a point near the bottom. At intervals of about 8 inches horizontal arms are attached to this shaft; they extend almost to the walls on either side. Five of these are square in cross-section and about 1 inch thick, but the sixth bar, which is the top one, is flattened out so as to form paddles which slant in the direction of motion of the shaft in such a way as to smooth down the surface of the contents of the still. The height from the bottom to the top stirrer blades is about 6 feet 3 inches.

The orifice at the bottom of the still having first been closed, the vertical shaft is set in rotation at a speed sufficient to maintain the particles of gun-

---

[1] *U.S. Census Bull.*, 92, 1908, p. 84.

cotton in mechanical suspension in the solution: this rotation is maintained during the whole of the process. Water in which 5 per cent. of barium nitrate and 2 per cent. of potassium nitrate have been dissolved is then pumped into the still, and finely pulped gun-cotton is thrown in through an opening in the upper part. In all 450 lb. of fresh gun-cotton and some 250 lb. of dust and fine grains from previous granulations are introduced. More of the nitrate solution is pumped in, and finally the opening is closed, and an emulsion is pumped in consisting of 25 to 50 per cent. amyl-acetate in nitrate solution. The surface of the liquid should now be up to the top stirrer blades.

The material now begins to granulate, and the progress of the granulation is observed by withdrawing a little of the mixture through a small orifice near the bottom of the still. When granulation has been effected throughout the mass, which is within five minutes of the time when the introduction of the emulsion into the still was commenced, steam is turned into the jacket surrounding the lower portion of the still. Heating is continued for five or six hours, by which time practically all the amyl-acetate has been distilled over together with some of the water. This is condensed and the amyl-acetate is separated. A gate valve in the bottom of the still is now opened, and the mixture of water and granulated powder is drawn off into a draining tank. After draining it is dried, sized, blended and packed. The strength and amount of the emulsion used depend upon the amount and quality of the gun-cotton; the best proportions are ascertained by experience. The finished powder is coloured to suit the taste of customers.

Forty-two grain powders.

The older powders, Schultze and Amberite, are 42-grain powders, that is to say the charge required for an ordinary 12-bore cartridge is 42 grains, and this quantity occupies the same space in the cartridge as 82 grains of black sporting powder. Other 42-grain powders are Ruby, Felixite, Primrose Smokeless, Cooppal No. 1 and K.S. Some of these are still used extensively, but there is a growing demand for powders of which smaller charges are required, the principal advantage of which is that they give a decidedly lighter recoil, for the powder products are ejected from the muzzle of the gun with higher velocity than the shot. It is also claimed that they are quicker. Reduction of charge is effected by using a nitro-cellulose of higher nitrogen content, and reducing the proportion of the other constituents. These changes increase the rate of burning, so in order to prevent the production of dangerous pressures in the gun it is necessary to gelatinize the nitro-cellulose more completely. A 33-grain powder can be made in much the same manner as is described above, except that after the grains have been formed and hardened a portion of the nitrates is washed out by steeping the materials in water. A well-known 33-grain powder of English manufacture is Smokeless Diamond; Henrite is another of this class: both these are in the form of black grains. E.C. No. 3 is a 33-grain powder too; it is coloured yellow with aurine. Other

Thirty-three-grain powder.

33-grain powders are Empire, K.S.G., Lightning, Red Star, Stowmarket Smokeless, Viemos and Emerald.

Thirty-gr
powder.

By taking a further step in the same direction the charge can be reduced to as little as 30 grains. The nitro-cellulose is mixed with a small proportion of "reducers" and several times its weight of barium and potassium nitrates. It is then incorporated in a Werner and Pfleiderer machine with sufficient acetone or other suitable solvent to gelatinize it entirely. The dough is then formed into small cubes or prisms by processes similar to those employed for rifle powders, and after drying, the mineral nitrates are dissolved out as completely as possible with warm water. Only about 5 per cent. are left in. Schultze Cube Powder is an instance of a 30-grain powder produced by a process of manufacture of this sort.

	Imperial Schultze	Amberite	S.S.	E.C.	Schultze	Kynoch's Smokeless	Cannonite	Shot-gun Rifleite	Walsrode	Sporting Ballistite
Nitro-glycerine . . .	—	—	—	—	—	—	—	—	—	37·6
Nitro-cotton . . .	—	71·0	59·2	79·0	—	52·1	86·4	94·0	98·6	62·3
Nitro-lignin . . .	80·1	—	—	—	62·1	—	—	—	—	—
Dinitro-toluene . . .	—	—	15·7	—	—	19·5	—	3·5	—	—
Potassium nitrate . .	—	1·2	1·3	4·5	1·8	1·4	—	—	—	—
Barium nitrate . . .	10·2	18·6	17·0	7·5	26·1	22·2	5·7	—	—	—
Camphor	—	—	—	4·1	—	—	—	—	—	—
Wood-meal . . .	—	1·4	5·2	3·8	—	2·7	—	—	—	—
Vaseline	7·9	5·8	—	—	4·9	—	2·9	—	—	—
Starch	—	—	—	—	3·5	—	—	—	—	—
Lamp-black . . .	—	—	—	—	—	—	1·3	—	—	—
Pot. ferricyanide . .	—	—	—	—	—	—	2·4	—	—	—
Calcium carbonate . .	—	—	0·6	—	—	—	—	—	—	—
Ash	—	—	—	—	—	0·9	—	0·9	—	—
Volatile matter . . .	1·8	2·0	1·0	1·1	1·6	1·2	1·3	1·6	1·4	0·1
Calories per g. . . .	742	745	755	762	786	807	845	896	1014	1286
Permanent gas, c.c. per g..	763	635	695	718	576	600	725	705	669	591
Aq. vapour, c.c. per g. .	152	156	131	158	160	126	146	169	206	234
Total vol. gas N.T.P. .	915	791	816	876	736	726	871	874	875	825
Compn. permanent gas p.c. :										
CO_2	8·9	12·0	11·8	11·9	15·5	14·8	14·6	19·0	21·3	32·2
CO	52·7	50·0	51·3	52·1	46·7	49·5	49·9	45·3	48·2	37·1
CH_4	1·0	0·4	0·8	0·5	0·8	0·7	0·6	0·8	0·4	0·4
H_2	27·0	25·5	23·7	23·9	23·0	18·8	22·2	21·5	10·1	10·1
N_2	10·4	12·1	12·4	11·6	14·0	16·2	12·7	13·4	14·8	20·2
Relative temperature .	106	123	135	136	137	139	150	160	161	204

The above Table, published in 1904 by Macnab and Leighton,[1] gives the composition of the principal shot-gun powders at that time in use in England, together with the amount of heat generated in the calorimetric bomb and the composition of the products of explosion. Of these, Shot-gun Rifleite, Sporting Ballistite and Cannonite were condensed powders. S.S., Shot-gun Rifleite and Cannonite are no longer made.

Sporting ballistite is made in much the same manner as rifle ballistite, except that after the sheets have been rolled out, acetone is added and the rolling is repeated, so that the finished sheets are only about 0·005 inch thick and look like oiled silk. These are cut into small flakes. The normal charge of a 12-bore cartridge is only 26 grains.

French powders.

In France the manufacture of sporting powders forms part of the State monopoly of explosives. The following Table gives the composition of the powders made :

Poudre	S.	J.	M.	T.
Nitro-cotton	65	83	71	100
Barium nitrate	29	—	20	—
Potassium nitrate	6	—	5	—
Am. bichromate		14	—	—
Potassium bichromate	—	3	—	—
Camphor	—	—	3	—
Binding material	—	—	1	—
Moisture	2	3	—	1·5
Price . . . . Fr.	28	28	30	32

The following details of manufacture are given in *P. et S.*, 1912, xvi., pp. 99, 100, and Vennin et Cheneau, *Poudres et Explosifs*, pp. 434–437 :

Poudre S. The nitro-cotton consists of 37 parts of CP_1 and 28 of CP_2. The materials are incorporated under light edge runners, dried and partly gelatinized with 35 per cent. of ether-alcohol. The dough, which is not very coherent, is formed into grains by simply passing it through a sieve. The grains are dried, sifted, hardened if necessary with ether-alcohol and again dried and sifted.[2]

Poudre J. A mixture of nitro-cottons is used containing 30 per cent. soluble in ether-alcohol. This is dehydrated with alcohol and mixed with the bichromates in an incorporator. Then 14 per cent. of ether-alcohol (56° B, sp. gr. 0·760) is incorporated in, and the resulting dough is pressed

---

[1] *J. Soc. Chem. Ind.*, 1904, p. 298.

[2] For earlier method *see P. et S.*, 1890, vol. iii., p. 13.

into strips which are cut into cubes. These are then converted into grains of irregular shape in a granulator consisting of grooved cylinders, and then the powder is drummed, sifted and dried with cold air. The finest siftings are used for pistols and practice ammunition. The presence of bichromates makes the powder sensitive and unpleasant to manufacture. It is cheaper than Poudre M. The gravimetric density is 0·65 to 0·70.

Poudre M. The nitro-cotton used has a solubility of only 15 to 20 per cent. After drying to 5 per cent. moisture it is gelatinized with 50 per cent. of ether-alcohol of 56° B. This, aided by the camphor, causes a superficial gelatinization and coats the nitrates. The mass is ground under edge runners weighing 500 kg. with the addition of water and alcohol coloured yellow with auramine. Then it is granulated and drummed. During the latter process the grains are sprayed with ether-alcohol containing 1 per cent. of collodion cotton and 1 to 2 per cent. of camphor, which causes a further gelatinization of the surface. The powder is then dried and re-drummed, several times if necessary, until the required ballistics are obtained. It is sifted and only the grains between 1·4 and 0·65 mm. are retained. There are about 3500 of these to a gramme. The gravimetric density is 0·465 to 0·485. This is the most used of the French sporting powders.

Poudre T. Gun-cotton CP_1 is completely gelatinized with acetone, 2 per cent. of saltpetre being added. The dough is pressed into strips 1·5 mm. thick, which are then rolled down to 0·15 mm. and cut into small squares of 1·5 mm. side. The powder is then steeped in water and dried like Poudre BF, and finally drummed with a little gum and graphite to make it more progressive. There are about 400 flakes to the gramme, and the gravimetric density is 0·55 to 0·58. This powder is superior to the other French sporting powders but more expensive.

The following are the normal charges of a 16-bore gun :

Powder	Charge
Black	4·5 grammes.
J	2·6 ,,
M	2·1 ,,
T	1·9 ,,

Dissatisfaction has been expressed with regard to these French sporting powders, and in 1908 the Minister of War instructed the Committee of the service of " Poudres et Salpêtres " to compare them with foreign powders. Comparative experiments were carried out with Poudre T, Sporting Ballistite and the German condensed powder Mullerite, and it was admitted that the results from the French powder were more irregular. The sales of Poudre T amounted to 22,358 kg. in 1909 and 20,123 in 1910.

German powders.

The following are some of the principal German shot-gun powders:

Rottweil. Square flakes with metallic lustre. Charge 2·22 g. (34·3 grains).

Saxonia. Square flakes, bluish green. Charge 1·90 g. (29·4 grains).

Mullerite. Thin square flakes, green. Charge about 35 grains. Contains no inorganic salts.

Walsrode. Small grains, greyish-white and greyish-green, mixed. Charge 2·27 g. (35·0 grains).

Adler-Marke. Small cylinders, grey. Charge 2·00 g. (30·9 grains).

Wolf-Marke. Grains, white and yellow, mixed.

Fasan (Pheasant). Grains, greyish-yellow. Charge 2·65 g. (40·9 grains).

Tiger. Grains, blue-black. No lustre. Charge 2·73 g. (42·1 grains).

American powders.

The American explosives industry is largely in the hands of the E. I. du Pont de Nemours Powder Co., who make the following:

Condensed powders: Infallible and Sporting Ballistite.

Bulk powders: Du Pont Smokeless, E. C. Improved, New Schultze, Empire and Lesmok.

Austrian.

In Austria there is a State monopoly of explosives. Information about the sporting powders is given in *S.S.*, 1909, p. 413, but their quality has been decried.[1]

Requirements.

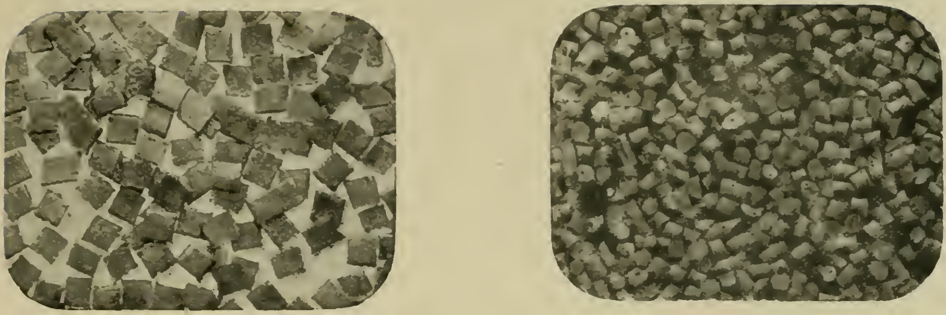
The requirements of a good shot-gun powder are: (*a*) That it shall be reliable and constant in its qualities: this is as important as in the case of other gunpowders, and somewhat more difficult to attain; great care in manufacture and thorough blending are necessary. (*b*) It should burn cleanly, leaving little residue in the gun, and what residue there is should be alkaline in reaction and easily removed. (*c*) It should give good results, even when loaded into cheap cartridge cases, with indifferent wadding and light shot charges. (*d*) It should be quick in ignition: a delay of a few thousandths of a second in the time that elapses between pulling the trigger and the shot leaving the muzzle makes a considerable difference in the accuracy of the shooting; smokeless powders burn considerably faster than black. (*e*) It should not be greatly affected by exposure to hot or moist air. (*f*) It should occupy about the same space as the equivalent charge of black powder: in the manufacture of cartridges the charges are measured and not weighed, and if the powder be very dense, there is considerably greater danger of an extra large charge being introduced accidentally.

Testing shot-gun powders.

To test shot-gun powders they are loaded into cartridges, the ballistics of which are then measured. The velocity of the shot is determined usually over a range of 20 yards from the muzzle by means of an electric chronograph. One of the currents passes through a wire before the muzzle of the standard gun, and the other through a wire screen or a spring contact on the back

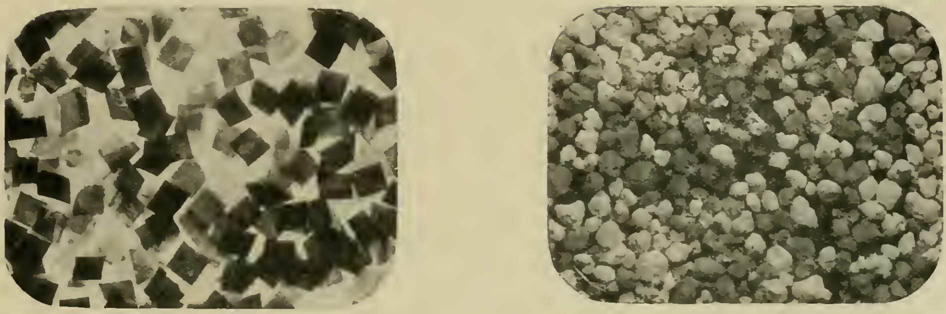
---

[1] *See S.S.*, 1910, p. 320.



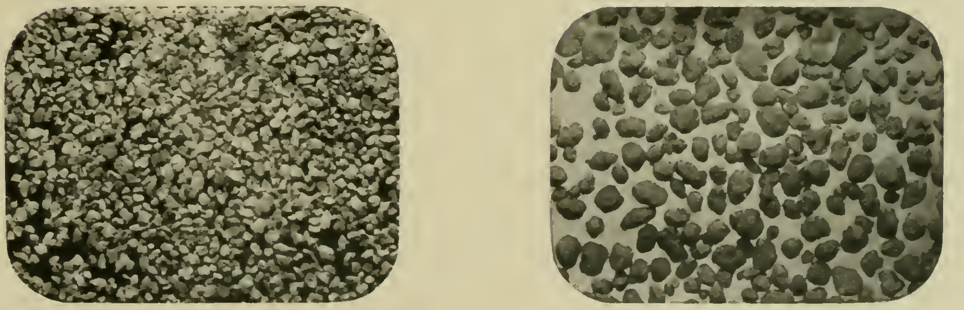
Rottweil

Adler-Marke



Saxonia

Wolf-Marke



Walsrode

Fasan

Fig. 65. German Smokeless Shot-Gun Powders (Thörner, *S.S.*, 1907, p. 423).

of an iron target. An advantage of the spring contact is that the second current cannot be interrupted prematurely by one or two shot going ahead of the bulk of the charge.

The pressures are measured by firing cartridges in a special gun of solid construction. At 1 inch and 2½ inches or 6 inches from the breach there are plugs passing through the walls of the gun; on these plugs are placed crushers which are held down by screws. In England lead crushers are generally used for testing shot-gun powders instead of the copper crushers used with slow-burning powders, as they are found to give more satisfactory results with the very variable pressures obtained. The subject of pressure measurements will be dealt with more fully in Chapter xxix.

The "pattern" of the shot is determined by firing cartridges from a gun of standard choke at a whitewashed iron plate generally at a range of 40 yards. The marks of the shot should be fairly evenly distributed. and about two-thirds of the shot should be within a circle of 30 inches diameter.[1]

The penetration of shot can be measured by firing under standard conditions at a number of pieces of cardboard placed one behind the other and counting the number of pellets that penetrate the different cards.

The recoil of the standard gun can also be measured and forms a useful check on the other determinations, especially the velocity. In Fig. 66 is shown the *Field* proof gun for taking simultaneously the recoil and the pressures at 1 inch and 6 inches from the breech. The velocity and pattern can also be taken at the same time. The gun weighs 50 lb., and is suspended 5 feet below its supports; it is fired by means of a pneumatic bulb in order not to disturb the gun. With this gun numerous investigations have been carried out on behalf of the *Field* newspaper.

The cartridges for the 12-bore and most of the other shot-guns are 2½ inches long. The base and the powder usually occupy just 1 inch, so that the hole bored to admit the powder gases to the base of the pressure plug is bisected by the first wad. Over the powder is placed a thin card wad. then a greased felt wad. then another thin card, then the charge of shot. and finally a thicker card wad. The space above the shot wad should be about ¼ inch: this is turned over inwards by means of a special machine so as to hold the shot wad in place. and a pull of about 50 lb. should be required to extract it. The cartridges are usually adjusted to give a velocity over the 20 yards range of 1050 to 1080 feet per second with a chamber pressure of 3 to 3·3 tons per square inch. If the velocity be higher than this the shot are deformed and scattered too much, if lower the killing power of the pellets is reduced; it is, however. better for the velocity to fall below these limits than to rise above them. as shooting is generally at short ranges. If the pressure be too low

---

[1] For special appliances for analysing patterns see Vennin et Chesneau, *Poudres et Explosifs*, p. 149, also O. Maretsch, *S.S.*, 1915, p. 261.

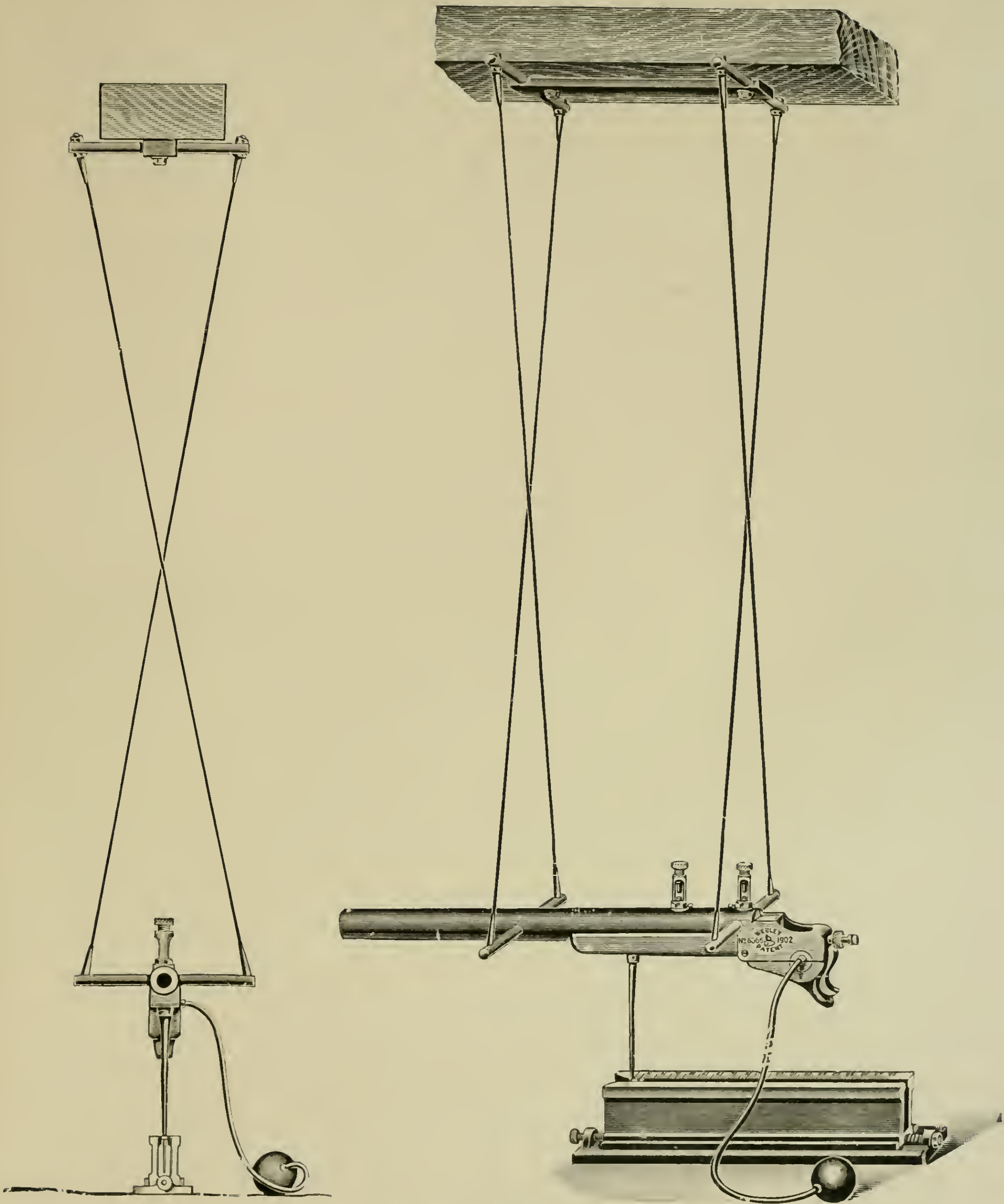


Fig. 66. *Field* Proof Gun

From *Arms and Explosives*, 1911, p. 5 (Webley & Scott) the patterns are bad, if too high the gun may be spoilt or even burst. The recoil of the sportsman's gun should be about 16 feet per second, whereas that of an express rifle is usually about 17 feet per second, and that of a military rifle, which is fired much more rapidly, is 10 feet per second.[1] The French smokeless powders only give a velocity of 755 feet per second over a range of 15 metres (16·4 yards) in a 16-bore gun with the standard loading.

The pressure is increased by using felt wads that are harder or slightly larger in diameter or by having a longer or harder turnover. The velocity is also increased slightly by the same alterations. The opposite changes, of course, produce the opposite effects. The ballistics are affected also by the strength and nature of the cap in the cartridge case. If by adjusting these elements it is not possible to produce the desired result it is necessary to alter the weight of powder or shot, or both.

Powders for trench howitzers.

The propellant for a trench howitzer has to fulfil much the same requirements as that for a shot-gun: a heavy projectile has to be given a comparatively low-muzzle velocity and the gun cannot withstand a high pressure. The difficulty is to obtain constant ballistics with this low pressure in the chamber. It is overcome by using powders of the same types as those for shot-guns.

Blank powder.

Blank powders are used for firing time and other signals, for manœuvres and displays, such as *feux de joie*: in all cases, in fact, where it is required to make the noise of firing without ejecting a projectile. Difficulty is caused by the fact that there is no heavy projectile to offer resistance to the expansion of the powder gases: consequently as soon as the envelope containing the powder is burst the pressure falls almost to nothing. With black powder this does not matter very much, as the rate of burning is not affected to the same extent by the pressure: gunpowder can be used indeed for this purpose which is not good enough for ordinary cartridges. The rate of burning of nitro-powder, on the other hand, is greatly affected by the pressure: there is danger therefore if the envelope offer a little too much resistance or the primer be too strong, that dangerous pressures may be set up in the gun: and if the resistance or the ignition be too weak the report will be insufficiently loud.

As in the case of shot-gun powders the rapidity of burning is attained either by using a partially gelatinized material, or a completely gelatinized one in a fine state of division. In the British service the small-arm blank cartridges have a charge of 20 grains of cordite size 20 S.C. S.C. stands for "sliced," and this powder is made by passing strands of cordite about 0·20 inches in diameter through a machine, in which it is cut transversely by rapidly rotating knives into small discs having a thickness of about 0·0055 inch. For ordnance, however, black powder is still used generally. In France

---

[1] *Arms and Explosives*, 1908, p. 8.

a special powder is manufactured known as Poudre EF, which is made of nitro-cotton and binding material in much the same way as Poudre M.[1] In Spain a nitro-cellulose flake powder is used for small-arm blank ammunition.[2]

In order to offer greater resistance to the powder gases the cartridge is often provided with a " mock shot " made of hollow wood or other suitable material which breaks up at the muzzle of the gun. A disadvantage of these is that they are liable to lead to accidents, men being shot at short range during manœuvres. In Germany a large proportion of the wounds thus caused formerly proved to be fatal because the patients developed tetanus. The source of this disease was, however, traced to the felt wads used under the mock shot. This danger is now guarded against by sterilizing the felt wads.[3]

Blank powder for rifles is called in Germany " Gewehrplatzpatronenpulver " (Gew. Pl. P.P.), and that for machine guns " Maschinengewehrplatzpatronenpulver " (M. Gew. Pl. P.P.). The latter is more violent in order to give sufficient recoil to work the Maxim gun, and with the same object a piece is fixed to the muzzle with a narrower bore. In order to prevent accidents an appliance is sometimes fixed on to the muzzle to break up the mock bullet and deflect it. In Austria blank cartridges are called " Exerzierpatronen."

---

[1] *P. et S.*, 16, 1912, p. 100.

[2] *S.S.*, 1908, p. 284.

[3] E. Neumann, *S.S.*, 1915, p. 220.

CHAPTER XXIV

SOLVENTS

Solvents available : Ether-alcohol : Nature of colloids : Manufacture of acetone : Permanganate test : Impurities : Acetone from starch : Acetone from acetylene : Recovery of solvents : Acetone recovery : Volatility of nitroglycerine : Vapour explosions : Toxicity of vapours

Solvents available. In the powders first introduced, Schultze, E.C., Poudre B, the solvent used was a mixture of ether and alcohol, which had been employed in making collodion solutions for many years. When the English Government introduced cordite in 1888, they adopted a solvent, which had been but little used previously except in the laboratory, namely, acetone. This possesses the advantage that it can dissolve gun-cotton even of the highest degree of nitration.

In the lacquer and celluloid industries various solvents for nitro-cellulose are used in order to obtain different specific effects. Amyl-acetate especially is much employed in the preparation of lacquers. Its great value lies in the fact that it boils at a high temperature ; consequently the surface does not become cooled by rapid evaporation, and so condense water from the air. Moreover, from a mixture of amyl-acetate and water the latter evaporates proportionally much faster than the former. Consequently the solution of nitro-cellulose gradually sets to a clear solid film, as the amyl-acetate evaporates, whereas if only very volatile solvents such as ether and alcohol are used, water accumulates more and more, until it precipitates the nitro-cellulose in an opaque form.

In the manufacture of military and rifle powders there are not many different solvents used. If gun-cotton with some 13 per cent. of nitrogen be the base, either acetone or ethyl-acetate is used, generally the former. If a " soluble " nitro-cotton be the base, ether-alcohol is usually employed. In Poudre B amyl-alcohol was formerly added for a purpose somewhat similar to that for which amyl-acetate is used in lacquers. For sporting shot-gun powders a somewhat wider range of solvents is in use, and they are often mixed in order to produce certain specific effects.

The subject of the solubilities of nitro-celluloses in the various simple and mixed solvents has never been thoroughly investigated, although it is of considerable practical and theoretical importance. De Mosenthal gave a long list of solvents that have been mentioned in patent specifications,[1] but in the absence of information as to the sort of nitro-cotton or the conditions under which it is dissolved, the list is not of great value.

Gun-cotton containing about 13 per cent. nitrogen only dissolves to a small extent in ether-alcohol, but is totally dissolved or gelatinized by acetone and other ketones, by aldehydes such as benzaldehyde and furfurol, by esters such as ethyl-acetate (acetic ether), by acid anhydrides such as acetic anhydride, and by some nitro-compounds such as nitro-toluene. On the other hand, it is not dissolved by nitro-benzene, nitro-phenol, or organic acids such as acetic or formic. Excepting nitro-toluene all the above solvents for gun-cotton contain the group :CO connected with two other radicles other than hydroxyl, —OH.

Etheral-cohol

"Soluble" nitro-celluloses are distinguished from gun-cotton by the fact that they are soluble in a mixture of ether and alcohol: of any ether and any alcohol; whereas they are practically insoluble in the ether alone and only dissolve with difficulty in absolute alcohol. From determinations of the viscosity of mixtures of various alcohols and ethers F. Baker[2] finds evidence of the formation of compound molecules such as C_2H_6O, $C_4H_{10}O$, and it is these apparently which have the property of dissolving the nitro-cellulose; but Bingham has pointed out that the evidence is not conclusive.[3] An alternative theory is that the ether only plays a passive part in causing the associated molecules of alcohol (R.OH)n to split up into simple molecules R.OH, which latter dissolve the substance. But this theory is inconsistent with some of the facts: other liquids which are known not to combine with the alcohol, such as benzene, cannot be substituted for ether; then again the most associated alcohols, methyl- and ethyl-alcohols, have the greatest solvent powers when mixed with ether; also the solvent power of a mixture of ether and alcohol is increased by reduction of temperature.[4] All these facts are consistent with the theory that it is the compound molecules of ether-alcohol that have the solvent power, but not that this property resides in the unassociated molecules of alcohol. The solubility in various mixtures has been investigated by Stepanow,[5] who found that the maximum solubility is obtained when the proportion of ether to alcohol is 3 : 2, *i.e.* when the two liquids are mixed in about equi-molecular proportions. The addition of solvents such as acetone or ethyl-acetate, increases the solubility in ether-alcohol, but indifferent substances such as benzene, toluene, pyridine, phenol,

---

[1] *J. Soc. Chem. Ind.*, 1904, p. 295.

[2] *J. Chem. Soc.*, 101, 1912, p. 1409.

[3] *J. Chem. Soc.*, 103, 1913, 964.

[4] W. Macnab succeeded in dissolving highly nitrated "insoluble" gun-cotton in ether-alcohol by reducing the temperature to that of solid carbon dioxide.

[5] *S.S.*, 1907, p. 43.

chloroform diminish the solubility, the diminution being proportional to the quantity added. Other substances, such as water and acids, also affect the solubility, but not proportionally.

Soluble nitro-cellulose or collodion cotton is also dissolved by nitro-glycerine, acetic acid, etc. In the celluloid industry use is made of the solvent power of camphor, and there are a number of other substances, solid at the ordinary temperature, which have the same property : the dissolution is greatly promoted by the addition of alcohol. It has been stated by Bernadou that at a low temperature nitro-cellulose is dissolved by ether alone.

Lunge and Bebie[1] found that a nitro-cotton containing about 11 per cent. N was soluble in absolute alcohol, but insoluble in 95 per cent. alcohol. Ennea-nitro-cellulose (12 per cent. N) only dissolved to the extent of 70 per cent. in absolute alcohol, whilst a deka-nitro-cellulose (12·75 per cent. N), although completely soluble in ether-alcohol, only dissolved in absolute alcohol to the extent of 1·3 per cent. With a nitro-cotton containing 11·5 per cent. N the following results were obtained with the ether and alcohol in varying proportions :

Ether : Alcohol		Ether : Alcohol	
1 : 3	Dissolves readily	—	
1 : 6	Less readily, 93 per cent. after treating twice.	6 : 1	Dissolves readily.
—		9 : 1	Less readily, 95 per cent.
1 : 12	More readily, 96 per cent. after treating once.	12 : 1	92·1 per cent. dissolved.
1 : 24	95·6 per cent.	27 : 1	7·3 ,, ,,

Similar experiments have been carried out by A. Matteoschat with a nitro-cellulose of medium solubility containing 12·95 per cent. nitrogen.[2] The solvents used consisted of pure ether and pure alcohol containing varying percentages of water mixed in different proportions. To prevent surface gelatinization of the nitro-cellulose the alcohol was added first and then the ether. The following were the solubilities found :

	Strength of Alcohol by Volume			
Ether : Alcohol	99·5%	95%	90%	80%
1 : 2.	32·4	—	—	—
1 : 1.	52·3	42·3	28·7	14·2
2 : 1.	40·5	52·4	53·9	45·0
3 : 1.	25·0	42·4	53·0	57·5

It will be seen that in mixtures rich in ether the solubility is increased by the addition of a moderate proportion of water. T. Chandelon has found that the addition of water also diminishes the viscosity of the solution of nitro-cellulose in ether-alcohol, and that it makes no difference whether wet

---

[1] *Ang.*, 1901, p. 537.

[2] *S.S.*, 1914, p. 105.

nitro-cellulose be dissolved in water-free solvent, or dry nitro-cellulose in ether-alcohol containing water, provided that the final composition of the solution be the same.[1]

Nature of colloids.

The dissolution of a colloidal substance, such as nitro-cellulose, differs fundamentally from that of crystalline substances, such as sugars or the ordinary mineral salts. Strictly speaking colloids do not form solutions, but with suitable liquids they form what are termed "sols," which are intermediate between solutions on the one hand and suspensions and emulsions on the other. The latter consist of small particles of solid or liquid respectively suspended in a liquid medium, the particles being of such size that they can be seen under moderate magnification. In a true solution the dissolved substance consists of individual molecules floating about in the solvent. No sharp line of distinction can be drawn between sols and solutions on the one hand and emulsions and suspensions on the other. A molecule has a diameter of about a ten millionth of a millimetre in the case of the simplest compounds up to rather more than a millionth in the case of very complex substances. The extreme limit of visibility through a microscope is about a ten-thousandth of a millimetre. The size of the disperse particles in a sol may be considered to be comprised between the limits of a thousandth to a millionth of a millimetre. If not smaller than about 5 millionths they can be detected as bright spots when illuminated by a powerful beam of light against a dark ground in the ultra-microscope. One of the properties of particles of this size is that they show a continuous oscillating movement, known as the Brownian movement, when observed under the microscope or ultra-microscope. Colloid substances are divided into two classes, suspensoids and emulsoids, according as their sols resemble suspensions and emulsions respectively. Colloidal metal sols belong to the former class; silicic acid, gelatine and other organic colloids, including nitro-cellulose, belong to the emulsoid class. When a colloid of the latter class is immersed in a suitable liquid it swells up. Thus hide substance when soaked in water swells up without passing into the liquid phase, and india-rubber behaves similarly in ether. Gelatine swells up in water in a similar manner, but if the mixture be heated a sol is obtained which on cooling sets again to a "gel." Unvulcanized rubber in chloroform or benzene swells up and at the same time forms a sol, and nitro-celluloses behave similarly with solvents. When a colloid swells there is always evolution of heat and the volume is always smaller than the combined volume of the colloid and the liquid before the swelling took place. From this it may be deduced according to le Chatelier's theorem, that heat must hinder swelling whilst cold and pressure favour it. There is a considerable rise of temperature when acetone or ether-alcohol is added to gun-cotton, but only a slight rise with alcohol alone and none with ether. It

---

[1] *Bull. Soc. chim. Belg.*, 1912, no. 11, *S.S.*, 1914, p. 194.

is supposed that the sol of an emulsoid consists of two liquid phases differing from one another considerably in composition, but as the temperature is raised the compositions of the two phases approach one another, as is the case with partially miscible liquids. Many gels when examined under the microscope show a cellular or webbed structure, whence it is concluded that they also consist of two phases, but this structure has only been observed in gels obtained by coagulating sols by heat or the addition of some other substance. When the gels are prepared by cooling the gel or evaporating off the solvent this structure is not observed, and it is with such gels as these that we are concerned in the case of smokeless powders and blasting gelatine. When a gel is subjected to pressure under such conditions that the solvent alone can escape, some of the solvent escapes, the amount depending upon the pressure applied and the composition of the gel; the larger the quantity of solvent present the more easy it is to express part of it. The last portion of solvent is however very difficult to remove by pressure or even by heat, and this difficulty is increased by the fact that diffusion is very slow in a stiff and concentrated gel, although in a sol containing much solvent it is almost as rapid as in the pure liquid.

Manufacture of acetone.

Acetone is made by the dry distillation of acetate of lime, which in turn is a product of the dry distillation of wood. Beech, birch and the American maple are the trees most concerned, as they yield comparatively large quantities of acetic acid on distillation. Coniferous trees, the fir and pine, on the other hand yield little acetic acid: the most valuable product from their distillation is turpentine. Even from the most suitable woods the yield of acetone is small: only 8 to 10·5 parts of acetate of lime of 80 per cent. strength are obtained from 100 of dry wood, and this in turn only yields about 20 per cent. of acetone. Moreover, fresh felled beech or maple contains about 40 per cent. of moisture. Consequently it requires from 80 to 100 tons of wood to produce 1 ton of acetone, and the manufacture is dependent on the supply of very large quantities of wood. Attempts have been made to manufacture acetate of lime and other products by the distillation of sawdust, waste wood and other woody materials, but most of these undertakings have hitherto proved unremunerative. The charcoal obtained from these waste materials is generally of little value, and the yield of acetate and wood spirit is considerably less than from good new wood.

"Grignon," the residuum left after pressing the oil from olives, is now distilled on a large scale in Spain. It yields about 4 per cent. of acetate of lime and 1·2 per cent of crude wood spirit. Other waste products consisting principally of cellulose and lignin might be utilized similarly: coffee husks, for instance, and the wood from which tannin and dye extracts have been made, such as quebracho chips. In course of time these materials will no doubt be utilized, but only where very large supplies of them are available.

The first necessity of a wood distillation plant is a plentiful supply of wood, the second is a ready market for the charcoal. As a rule a plant will not be remunerative, unless the selling price of the charcoal covers the cost of the wood used.[1] The value of the by-products, acetate, wood spirit and tar, then only has to provide the cost of working, interest and profit.

Charcoal, although it weighs only about one-third as much as the original wood, occupies nearly as much space. Moreover, it is decidedly brittle, and if it has to be transported very far by road or rail, a large proportion of it is converted into powder, which has a comparatively small value. Therefore a wood distillation plant should be situated where there is a plentiful supply of suitable wood, a ready market for the charcoal, and good means of communication. The by-products, acetate, crude wood spirit and tar, are comparatively light and can be transported over considerable distances to a central chemical factory to be worked up.

These conditions are present in many parts of India. Nevertheless charcoal is still produced there in small kilns and the valuable by-products are allowed to escape. The reason is that technical knowledge is deficient, and capital is not available through want of enterprise. Most of the acetate of lime and acetone are manufactured in the United States,[2] but there are also large plants for their production in Hungary, Sweden, Russia, and Canada.

By the destructive distillation of wood three different classes of products are obtained: solid, liquid and gaseous. The solid, charcoal, remains in the kiln or oven; the liquid, crude pyroligneous acid, is recovered from the mixture of gas and vapour by means of a suitable condenser; and the gases pass on and may be used either for heating, or to drive a gas-engine, but a further quantity of methyl-alcohol and acetic acid can first be recovered from them by scrubbing with water in a tower. By distillation and treatment with milk of lime the crude pyroligneous acid is further separated into tar, acetate of lime and commercial wood spirit.

The acetate of lime is not as a rule worked up further at the carbonization works, but is sent to a chemical factory where large quantities are collected and worked up into acetone, acetic acid, and various acetates and derivatives of acetic acid. There are two varieties of commercial acetate of lime, brown and grey, which differ from one another in that grey acetate has had the tar removed as far as practicable, and the brown has not. Brown acetate is not made now on a very large scale, as it gives very bad yields of acetone and acetic acid. Grey acetate generally contains 80 to 82 per cent. of calcium acetate as determined by analysis, and 4 to 7 per cent. of water, the remainder being made up of various impurities. Of the 80 to 82 per cent., however, several per cent. consist of formate, propionate and salts of other organic acids.

---

[1] Klar, *Holzverkohlung*, second ed., p. 62.

[2] For statistics *see J. Soc. Chem. Ind.*, 1914, p. 345.

The conversion into acetone is effected by simply heating the acetate at a temperature of about 300° C., when the following reaction takes place: $Ca(CO_2CH_3)_2 = CaCO_3 + CH_3CO.CH_3$, but the other organic calcium salts react in a similar manner: formic acid yields aldehydes, propionic acid yields methyl-ethyl-ketone and diethyl-ketone, and the higher homologues the corresponding higher ketones.

The distillation of the acetate of lime is usually carried out in a shallow circular retort heated by direct fire. Fig. 67 is a view of a retort at the Royal Gunpowder Factory, Waltham Abbey; it is provided with a stirring arrangement, *B*, and man-holes *A* and *C*, for filling and emptying. The tubes for the gases and vapours have rods, *K*, to remove any obstruction of tar, coke or dust. The charge of such a retort is from 300 to 700 lb. After fastening down the man-hole the stirring mechanism is started and the retort is gradually heated up, care being taken to avoid overheating as far as possible, as it causes the formation of tar and coke, and a corresponding diminution of the yield of acetone. It is not practicable to dry the whole of the moisture out of the acetate before charging it into the retort, as acetone begins to be given off even at a moderate temperature. Consequently the first runnings of the retort consist of water with only a little acetone. The decomposition of the acetate does not become active until the temperature reaches about 380° C.; the bulk of the distillate comes over between 380° and 400° C. At the end of the distillation steam is blown through to remove the last portion of the distillate, and to render the residue in the retort non-inflammable.

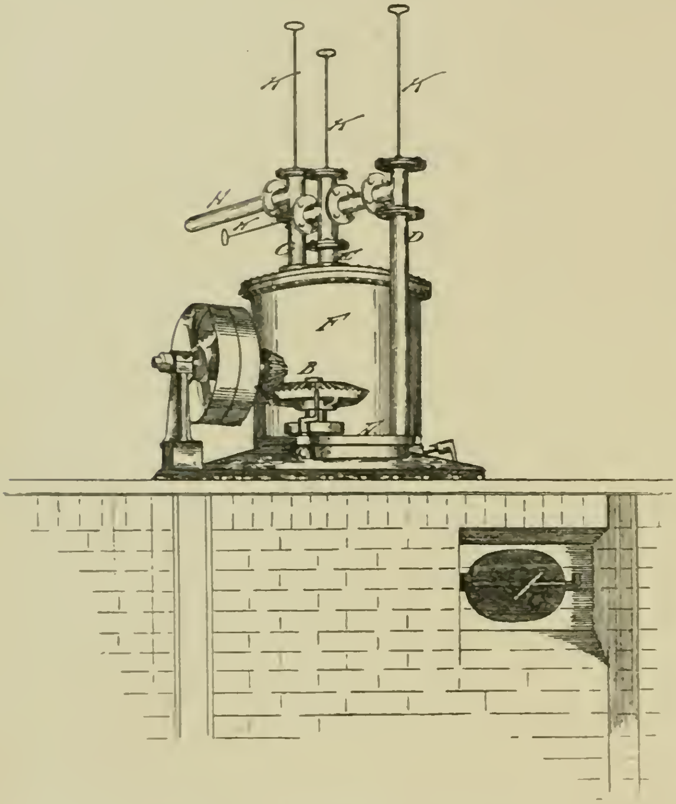


Fig. 67. Acetate of Lime Still.

Attempts have been made to heat the retorts in a bath of lead in order to make the heating more uniform and so improve the yield, but trouble was caused by the oxidation of the lead, with the consequence that heat was lost, and the special object of the bath was not attained. Heating in a stream of superheated steam has also been tried: a better yield is thus obtained, but the consumption of fuel by this process is considerably greater; moreover, it is only possible to work sifted, dust-free acetate, which makes it very expensive. Another process, that has been tried and abandoned, was the conversion of the acetic acid of the crude pyroligneous acid directly into acetone without the preliminary formation of acetate. This was done by passing the acid over heated baryta or lime. A plant was erected on this principle in Woolwich Arsenal, but it did not prove successful, and was soon abandoned. The yields by this process were very poor; the crude acetone was mixed with much unchanged acetic acid, which had to be recovered and worked over again.

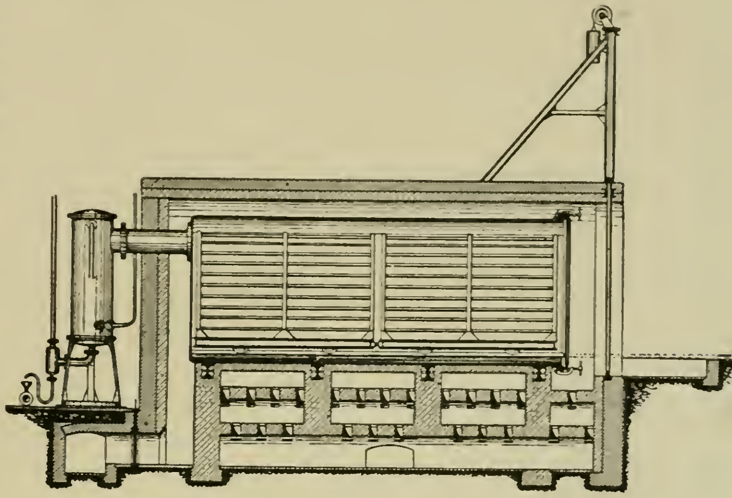


Fig. 68. F. H. Meyer's Plant for the Dry Distillation of Acetate of Lime.

Recently an improvement has been effected by heating the acetate in thin layers, that are not in direct contact with the hot walls of the retort. Fig. 68 shows a retort on this principle made by F. H. Meyer, of Hanover. The trays of acetate are placed on trolleys, two of which are wheeled bodily into the retort. The latter is heated as uniformly as possible by means of a number of fires. When the charge is finished, the trolleys are wheeled out and two fresh ones are run in at once. Thus loss of heat is avoided, and the disagreeable operation of drawing the very dusty spent lime from the retort is much improved.

From the retort the vapours are led to a condenser, which must be so constructed that the tubes can easily be cleaned, as they are liable to become choked with tar and dust. The crude distillate separates into two layers, the heavier of which consists mostly of water and acetone with some methyl-ethyl-ketone and other impurities, the lighter one of methyl-ethyl-ketone and tarry matter with impurities such as dumasin, and there is some water and acetone dissolved in it. The mixture is pumped into a tank rendered alkaline with caustic soda and allowed to settle. The heavier layer is then run off, and the lighter is washed several times with water. These collected liquors are then pumped into a still, such as that shown diagrammatically in Fig. 69. The essential feature of this is that part of the vapour is condensed in the tubular condenser, *D*, and returned to the column, *C*, where it flows over a number of perforated plates. The passage of the vapour through each of these plates is equivalent to a fresh fractionation. The remainder of the vapour passes down the tube, *F*, to the condenser, *D*. From this the liquid flows through the still-watcher, *H*, to a drum or other receiver. Continuous working stills are made on the same principle.

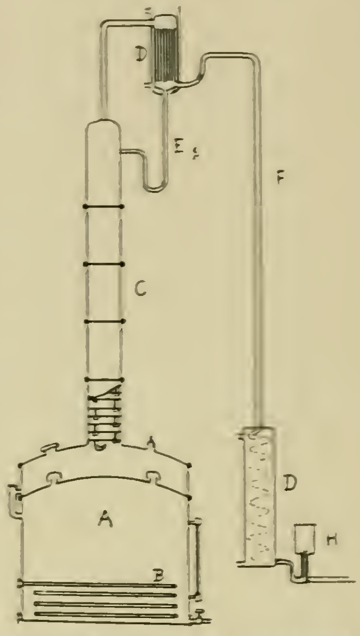


Fig. 69. Still for Rectifying Acetone or Alcohol.

With such a distilling plant there is no difficulty in getting the acetone free from water, but the removal of the other impurities causes considerable trouble. As the distillate runs through the still-watcher, continuous observations of the specific gravity are taken by means of a hydrometer floating in the liquid: all that shows a higher gravity than ·800 is run into a separate receptacle for impure acetone, but it is afterwards redistilled to recover the good acetone.

Permanganate test.

One of the principal tests applied to acetone is the "permanganate test": according to the specification of the English Government 1 c.c. of a 0·1 per cent. solution of potassium permanganate is added to 100 c.c. of acetone, and the characteristic colour of the permanganate must persist for at least half an hour. Only the middle portion of the distillate will stand this test. The soda added to the crude acetone combines with all free acid, so that the distilled acetone contains no acid except a little carbon dioxide. The greater part of the aldehyde is also removed by the soda, as it converts it into resinous bodies, which are not volatile, and consequently remain in the still; the distillate only contains traces of aldehyde.

Impurities.

There are other impurities, however, which pass over and greatly affect the permanganate test. Moreover, it is found that acetones, which pass the test with ease when quite fresh, fail after having been kept some time. The fall of the test is often very rapid at first, but becomes slower after a time, but even after years the fall may still continue. The fall of the permanganate test is generally accompanied by an alteration in the colour of the acetone, which assumes a brown colour instead of remaining colourless. Such deteriorated acetone is considered unfit for the manufacture of cordite and similar explosives, and has to be redistilled before use. As the English Government maintains a large reserve of acetone, amounting to several years' consumption, this redistillation became a serious matter not only on account of the actual cost of redistillation. but also because there was a considerable loss of acetone during distillation, and in the first and last runnings. The cause of the deterioration was therefore investigated and was found to be intimately associated with the presence of basic substances such as methylamine in the acetone. If after the first distillation in the presence of soda the acetone is distilled again, but this time with the addition of a small excess of sulphuric acid to the liquid in the still, all basic substances are entirely removed ; the redistilled acetone gives a much better permanganate test, which, moreover, falls off little or not at all even after storage for several years.[1]

Amines. Of the various amines that may be present in acetone, the primary and secondary amines are those that have the most deleterious effect on the keeping powers of acetone, e.g. methyl-amine, ethyl-amine, butyl-amine, amyl-amine ; dimethyl-amine, diethyl-amine. On the other hand, ammonia and tertiary amines such as trimethyl-amine have little or no effect upon it. The principal amine present in acetone that has not been distilled over acid, is mono-methyl-amine together with some ammonia, and the amount is usually between 0·0005 and 0·005 per cent. Although these quantities are small, they are sufficient in the presence of quantities of aldehyde of the same order to cause a decided deterioration of the acetone. Ammonia and the primary amines form more or less stable compounds with acetone, which are only gradually decomposed again during distillation, with the result that the amine comes over in varying quantities in all parts of the distillate instead of only in the first runnings. It is not the formation of these compounds, however, that causes the deterioration of the acetone, but the action of the amines on the traces of aldehyde and other impurities, or perhaps simultaneous action on these substances and acetone.

Aldehydes The acetate of lime contains a considerable proportion of calcium formate, and this in the dry distillation gives rise to aldehydes. Acetaldehyde is probably the principal one, but there are also formaldehyde, propionic aldehyde, and other higher members of the series. Formaldehyde readily changes into a mixture of methyl-alcohol and formic acid during the dry distillation, and also during the distillation with soda. The formic acid, of course, remains in the still as sodium formate, but the methyl-alcohol passes over into the distillate, and is found especially in the first runnings. Acetaldehyde, when acted upon by the alkali, is largely converted into aldol and other high-boiling condensation products and into resinous bodies, which remain in the still.

---

[1] *See* Marshall, *J. Soc. Chem. Ind.*, 1904, p. 645.

Propionic and other aldehydes behave very much in the same way as acetaldehyde. The destruction of the aldehydes is not complete, however, and consequently small traces are to be found in the acetone even after several distillations.

The presence of small traces of aldehyde can be detected in acetone by the application of Schiff's reagent. Acetone itself gives a purple coloration, but if there be 0·005 per cent. of aldehyde or methylal in it, the colour is distinctly stronger.

Methyl-alcohol.

Methyl-alcohol, as has already been pointed out, is produced from the formaldehyde. There are many other reactions by which it can be formed from the constituents of crude pyroligneous acid. As methyl-alcohol has a boiling-point, 65·5°, considerably higher than that of acetone, 56·1°, and has practically the same specific gravity, 0·796, it might be thought that the alcohol would pass over in the last runnings of the distillation, and that its presence would not affect the specific gravity of the acetone. The reverse is, however, the case. When the two liquids are mixed together, there is a contraction, and consequently the mixture is more dense than the constituents. Moreover, mixtures containing much acetone boil at a lower temperature than acetone itself; the mixture of minimum boiling-point contains 86·5 per cent. of acetone, and 13·5 per cent. of methyl-alcohol, and boils at 55·9°.[1] This mixture has a specific gravity of 0·7997; it cannot be separated into its constituents by fractional distillation; on the contrary it behaves much as a simple liquid. Moreover, as its boiling-point is so near to that of acetone the constant boiling mixture cannot be entirely separated from the acetone. Consequently methyl-alcohol occurs mostly in the first runnings, but is also present throughout the distillation. It is possible that methyl-alcohol may have a deleterious effect upon the stability of explosives with which it is mixed, through its liability to become oxidized to formaldehyde, but as there is no method known for the ready determination of the amount of it in acetone, nor any process for separating it on a manufacturing scale without greatly increasing the cost of the solvent, no particular attention has hitherto been paid to the matter.

Hydro-carbons, etc.

Besides these impurities the first runnings also contain some substances that are insoluble in water: if this acetone be mixed with twice its bulk of water these separate out partly. The liquid thus obtained is a complex mixture with a specific gravity of about 0·78 and boiling over a range of 50° to 110°, it apparently contains various hydro-carbons saturated and unsaturated, and also substances such as furan C_4H_4O and sylvan C_5H_6O. Furan would be formed by the dry distillation of the calcium salt of pyromucic acid, one of the constituents of the crude pyroligneous acid.

The effect of these substances upon the permanganate test is very similar

---

[1] Pettit, *Jour. Phys. Chem.*, 1899, 3, 349.

to that of aldehyde, but not nearly so great. The addition of 0·2 per cent. reduces the permanganate test of pure acetone from many hours to about 100 minutes, and in the presence of basic substances there is a further slow fall, which, however, is not nearly so rapid as in the case of aldehydes. If 0·2 per cent. be present the acetone becomes cloudy on the addition of two volumes of water. Those impurities can be separated by a special process of distillation, for which *see* Part XII. There are also chemical reactions by which these substances can be detected and estimated: such as the iodine test given in Part XII which enables one to estimate the amount of the substances to within 0·002 per cent. Commercial acetones usually contain from 0·02 per cent. to 0·10 per cent., average 0·04 per cent. There appears to be no reason to think that these small quantities can have any appreciable effect on the stability of explosives, either beneficial or otherwise.

The presence of these substances insoluble in water is not confined to the first runnings: there is almost as much of them in the last runnings, and even the middle fractions contain usually 0·02 to 0·04 per cent., as may be ascertained by the application of the tests just mentioned.

When the main bulk of the acetone has distilled over, the temperature of the still-head and the specific gravity of the distillate commence to rise: after a short time the temperature reaches about 73·5° and the specific gravity 0·840, and there they remain steady for some time. The distillate now consists almost entirely of a mixture of water and methyl-ethyl-ketone, the next homologue to acetone, in the proportion of 11·4 of water to 88·6 of ketone. This mixture distils unchanged, and the water can only be separated from it by treatment with a dehydrating agent such as calcium chloride or solid caustic soda. In the intermediate fractions, when the boiling-point and the gravity are rapidly altering, the distillate contains much impurity, substances insoluble in water and perhaps ethyl-alcohol. Afterwards, when the boiling-point becomes constant, the constant boiling mixture comes over in a state of considerable purity. Then after a time the boiling-point rises again, and a distillate is obtained which still separates out into two layers, the lighter of which consists mostly of higher ketones with a small proportion of water and impurities, and the lower largely of water.

Methyl-ethyl-ketone, when freed from water, gelatinizes gun-cotton as well as acetone, and has no bad effect upon it. It would be possible to add a considerable proportion of it to acetone without causing it to fail in any of the usual specification tests, but it is more usual to sell it separately for denaturing spirit and dissolving resins. The heavier acetone oils are also used for making lacquers, etc., but do not command a very good price.

Acetone fr
starch.

It has been discovered by Fernbach that starch can be submitted to a process of fermentation whereby it is converted into a mixture of fusel oil and acetone, and it has been proposed to convert the fusel oil into artificial rubber, whilst the by-product acetone is purified and placed on the market.[1] It has been stated that from 100 parts of dry potato substance a yield of 22 parts of rubber and 14 of acetone can be obtained.

Acetone from acetylene. Acetone can also be made from acetylene and this method has been suggested in Germany during the War.[2] If acetylene be led into sulphuric acid of about 44 per cent. strength, and the product be boiled with water, it is converted into aldehyde.[3] The change is also effected by passing the acetylene through boiling sulphuric acid of this strength. The reaction is assisted by the presence of a little mercuric oxide.[4] The aldehyde may then be oxidized to acetic acid, which is converted into acetone by heating barium or calcium acetate, or by passing the vapour over heated barium oxide.

Recovery of solvents. As but little of the solvent is allowed to remain in the finished powder, it is advisable to recover as much as possible in order that it may be used again. A considerable proportion is lost during the operations of forming the dough into cords, strips, tubes or flakes, and hitherto there has been little attempt to recover this portion, as the difficulties introduced into the carrying out of the operations would absorb too much of the profit on the recovery. It is only from the drying stoves that recovery is attempted as a rule. When the solvent is ether-alcohol difficulties are introduced by the great volatility of the ether: by drawing the air away from the stoves through cooling coils only alcohol is recovered generally. A greater bulk of condensate can be obtained by using refrigerated water or brine, but if the temperature of the coils be reduced much below 0° C. there is danger of the coils being choked with ice. In the manufacture of artificial silk by Chardonnet's process attempts have been made to recover the solvent by passing the air up towers, where it is scrubbed with a mixture of sulphuric acid and water or with oil. T. Chandelon proposes to use the chlorine, bromine or nitro-derivatives of aliphatic or aromatic hydrocarbons for the recovery of ether and alcohol from air.[5] In Spain sulphuric acid is used.[6] It has also been proposed to compress, cool and re-expand the air in a regenerative machine as is done in Linde's plant for the manufacture of liquid air, but whether recovery of the solvent by such a process would prove remunerative seems doubtful.[7]

At the French Government works at Saint-Medard the solvent is recovered from Poudre B by the following method: A trolley charged with strips of powder is run over a metal chamber; a door opens in the top of the chamber just large enough for the trolley to pass through: it is let down and the door

---

[1] *See* Perkin, *J. Soc. Chem. Ind.*, 1912, p. 616; also *C.T.J.*, June 29, 1912.

[2] F. G. Donnan, *Nature*, March 23, 1916, p. 83.

[3] Lagermark and Elterkow, *Ber.*, 1877, p. 637.

[4] Erdmann and Köthner, *Zeitsch. Anorg. Chem.*, 1898, p. 48.

[5] Germ. Pat. 254,913 of February 22, 1912.

[6] *S.S.*, 1913, p. 395.

[7] *See* Worden, pp. 492–496.

is closed, and the vapours of alcohol and ether are given off in the air-tight chamber. They are drawn off by a steady current of air, condensed by refrigeration and collected. When the drying is sufficient the trolley is removed. It is stated that the recovery is satisfactory.[1]

A higher yield of recovered solvent can be attained, if the air after passing through the condenser is returned to the stove, so that it passes constantly round a closed circuit. The evolution of solvent is rapid at first, but becomes slower and slower as the powder gets dryer: large-sized powders for heavy ordnance may have to remain in the stove for months, during the greater part of which time the quantity of solvent vapour given off is hardly appreciable. In laying out works it is advisable to place a few stoves fitted with recovery plant near the press-houses, so that the powder can be transferred to them expeditiously, and dried there for a few days. After this preliminary drying the powder can be transferred to other stoves situated at a distance, where no attempt is made to recover the solvent. Where considerable quantities of powder of large size are made, the area covered with stoves may extend over many acres, and to connect them all up with a recovery plant would be very costly.

Acetone recovery.

For the recovery of acetone from cordite and other materials Robertson and Rintoul have taken advantage of the fact that the vapour is very readily absorbed by a solution of sodium bisulphite, with which it forms a compound, $C_3H_6O, NaHSO_3$.[2] A very simple and satisfactory method has been worked out, by which practically the whole of the acetone in the air of the stove is recovered in a very pure condition. The air is drawn away from the stove through wide zinc pipes to the recovery house where it is caused to pass up a series of towers, down which a 30 per cent. solution of the bisulphite is flowing. Towers were designed specially for this purpose,[3] and they have proved very successful not only for this, but for many other purposes also, such as purifying air (*see* Fig. 70), as they afford a maximum surface of contact between the air and the liquid, and offer a minimum of resistance to the passage of the former. The towers are square in section and lined with lead: inside there are frames, which are wound with strands of wool zig-zag fashion. At the top of the tower each strand dips into a trough, which is kept supplied with bisulphite solution. The top of the tower is closed by means of a glass plate, and there is also a glass window near the bottom, so the action of the tower can be watched. There are, of course, various pumps or eggs and tanks, so that the solution can be raised again and passed down the same tower again, or the next one nearer the stove. When the solution is nearly saturated with acetone it is transferred to a still, where it is simply heated to

---

[1] *P. et S.*, 16, 1912, p. 108.

[2] Eng. Pat. 25,994 of 1901; U.S. Pat. 723,311 of 1903.

[3] Eng. Pat. 25,993 of 1901.

drive the acetone off again, as it has been found that practically the whole of the acetone can be distilled off before the bisulphite begins to decompose.

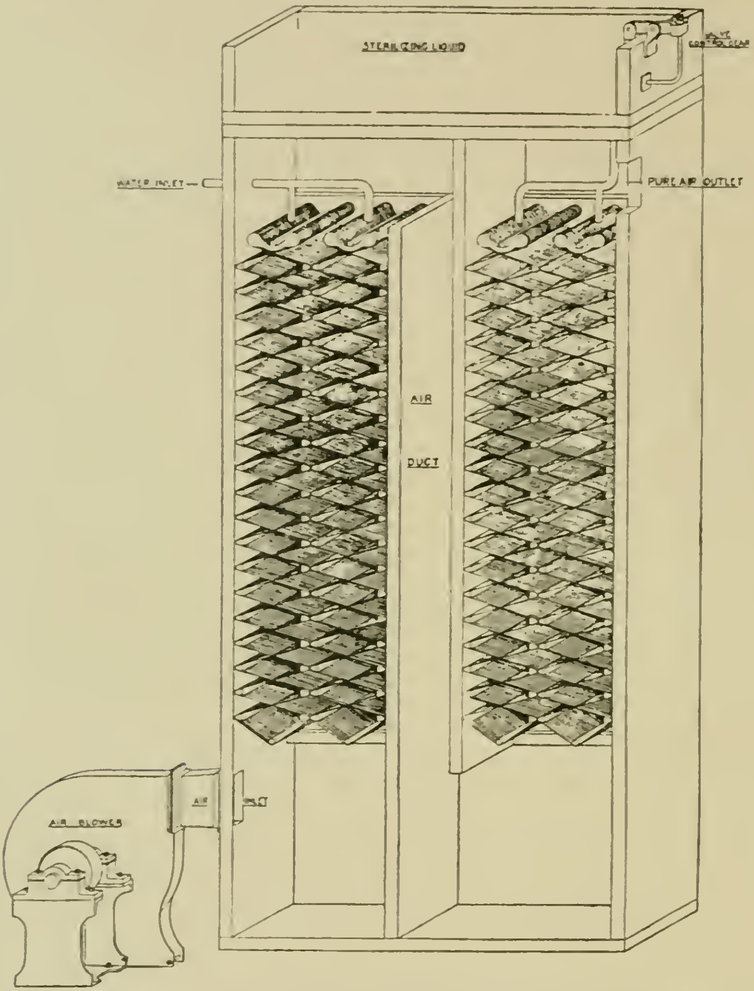


FIG. 70. Scrubbing Towers (Robertson and Rintoul's Patent).

A little sodium carbonate or caustic soda is added, however, to diminish the amount of sulphur dioxide that passes over, and to combine with any free sulphurous acid that has been formed by the oxidation of the bisulphite, and the consequent formation of sodium sulphate. The crude distillate thus obtained is mixed with water and a little sodium carbonate, and distilled again from a still such as that shown in Fig. 69. It is thus obtained in an extremely pure state ; it contains no detectable quantity of any impurity except some ethyl-methyl-ketone, which is harmless, and a trace of carbonic acid. The bisulphite solution is prepared by passing sulphur dioxide into a solution of sodium carbonate, the sulphur dioxide being made by burning sulphur in a small burner in a current of air.

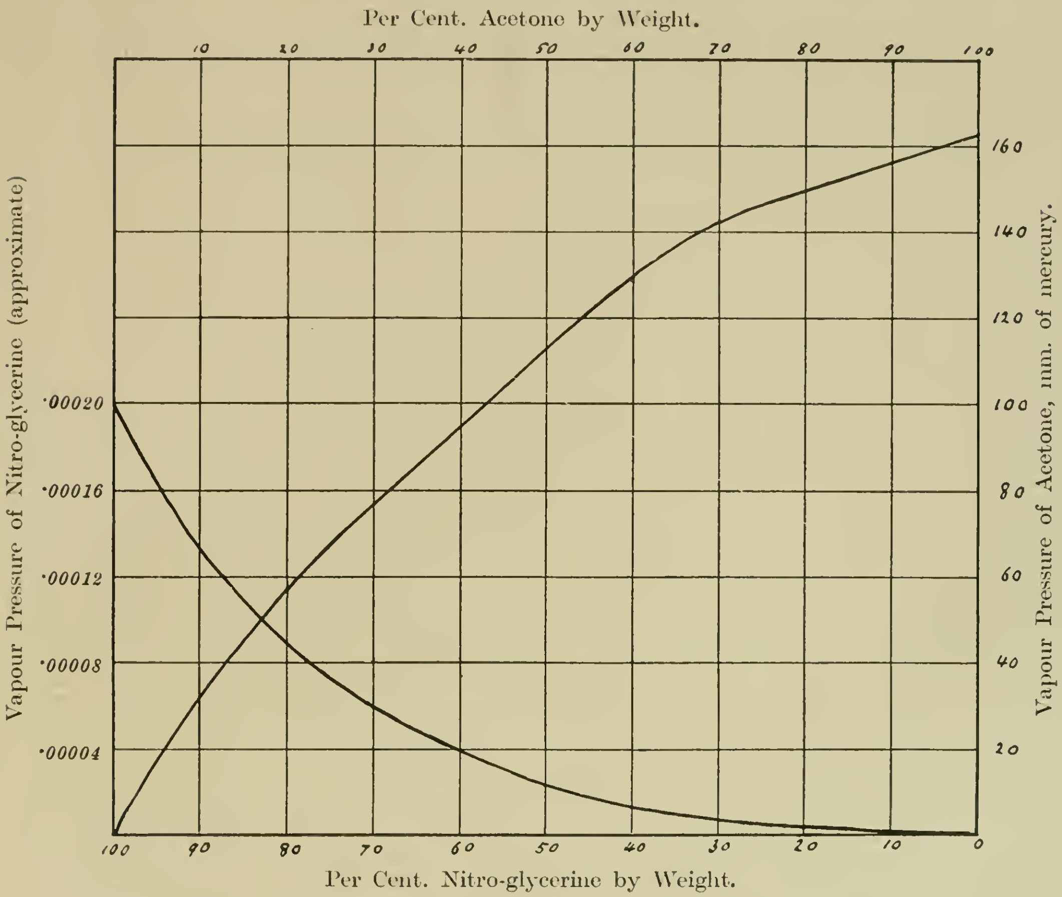


Fig. 71. Vapour Pressures of Mixtures of Acetone and Nitro-glycerine at 18° C.

Volatility o the nitro-glycerine.

Another reason for not attempting to recover the acetone from the last stages of the drying of a nitro-glycerine powder is that nitro-glycerine is given off much more readily when the greater part of the acetone has been removed. Fig. 71 shows how rapidly the vapour tension of the nitro-glycerine rises when the percentage of acetone is very small.[1] In the case of cordite the problem

---

[1] Marshall, *Trans. Chem. Soc.* 1906, 89, p. 1350 ; *Proc.* 1913, p. 157.

is complicated by the presence of gun-cotton, and the vapour pressures of mixtures of gun-cotton and acetone have not been determined. It is probable, however, that in the freshly pressed cords, containing a fairly large percentage of acetone, a considerable proportion of it is dissolved in the nitro-glycerine, thus reducing the vapour pressure of the latter, but when the percentage of acetone has been reduced to a small amount by drying, nearly the whole of it is dissolved in the gun-cotton, so that the nitro-glycerine exerts nearly its full vapour pressure. The result of this is, that in the early stages of the drying there is little or no danger of nitro-glycerine being deposited in the pipes leading from the stove to the recovery house, but in the later stages it will be deposited. Care must be taken therefore in laying the pipes that the nitro-glycerine will only accumulate in places from which it can be drawn off. At all the lowest points of the pipe-run small draining tubes must be provided; these can be closed with rubber corks, so that the nitro-glycerine can be drawn off daily into a rubber or gutta-percha bottle or beaker.

Vapour explosions.

Another danger that has to be guarded against is the communication of fire from one stove to another through the pipe-lines. In Robertson and Rintoul's system protection is afforded by the introduction of traps, in which fine wire gauze is interposed to prevent the further travel of the flame. They are so arranged that a gas explosion in the pipe will blow out a disc of thin material and so relieve the pressure.

It is not only in the pipe-lines that the explosibility of mixtures of vapour and air has to be guarded against, but wherever combustible and volatile liquids are used: in the incorporating and press houses, stoves, magazines and solvent store-houses, great care must be taken that no flame or spark may ignite a mixture of air and vapour. The following Table gives the explosive limits for a number of volatile liquids as determined by Kubierschky:[1]

	Percentages by Volume		Per cent. by Weight corresponding to 1 per cent. by Vol
	Lower Limit	Upper Limit	
Benzene	1·4	4·7	2·77
Toluene	1·4	—	3·20
Ethyl-alcohol	4·0	13·6	1·61
Methyl-alcohol	7·8	(18·0)	1·12
Acetone	2·7	—	2·02
Ether	1·8	5·2	2·56
Carbon bisulphide	4·1	—	2·64
Benzine	2·6	(4·8)	—
Pentane	2·5	(4·8)	2·51

[1] *Ang.*, 1901, p. 130.

If the percentage of vapour fall below the lower limit or rise above the upper, the mixture is no longer inflammable, but these limits depend upon the conditions under which the experiment is carried out. In a large flask the limits are wider than in a narrow tube, and a small spark often will not ignite a mixture that can be caused to explode by the application of a powerful spark or a flame.[1] The limits are much narrowed by the introduction of carbon dioxide or other indifferent gas. It has been shown by Olié [2] that the introduction of a jet of steam will extinguish a large quantity of fiercely burning alcohol in a few minutes, and it is recommended that buildings containing considerable quantities of inflammable liquids be fitted up so that a fire can be extinguished by this means. It must not be forgotten that vapours may be ignited by electric sparks generated by the friction of driving belts, and precautions should be taken to dissipate any charges that may be thus formed.

Even the empty drums which have contained liquids may give rise to serious accidents if the last traces are not removed. On March 30, 1904, a drum that had contained acetone exploded, killing two men and injuring several others at Prince's Dock, Glasgow. The drums when emptied should be left without their bungs and should be placed upon racks in the open for a few days with the bungholes downwards: if at the end of that time it is found that the smell of the solvent is still perceptible in the drum, the last traces can be removed by directing a jet of compressed air into the drum for a minute or so, relying on the absence of smell as an indication that the removal is complete. The bungs should then be replaced and screwed up so tightly by means of a key that it is impossible to remove them by hand, or for them to work loose during transit.[3]

Toxicity of vapours.

The vapours of many of the liquids used as solvents are injurious to the health of those exposed to them. Benzene is very poisonous, but is not used much for making smokeless powders. Acetone has no very serious effect. That of the alcohols increases with the molecular weight; amyl-alcohol is decidedly the worst of those generally used. It has been found that the following doses are fatal per kg. of animal:[4]

Methyl-alcohol	6·00 g. per kg.
Ethyl ,, (absolute)	7·75 ,, ,,
Propyl ,,	3·75 ,, ,,
Butyl ,,	1·85 ,, ,,
Amyl ,,	1·50 ,, ,,

A mixture of the vapours of ether and alcohol is more poisonous than that of either of the substances separately. For this reason also buildings in which amyl-alcohol or ether-alcohol vapours may be present should be well ventilated.

---

[1] *See also* Bunte, *J. f. Gasb.*, 1901, p. 1835; *J. Soc. Chem. Ind.*, 1902, p. 33.

[2] *P. et S.*, 15, 1910, p. 160.

[3] *A.R.*, 1904, p. 94.

[4] *P. et S.*, vol. xvi., 1912, p. 128.

PART VIII

BLASTING EXPLOSIVES

CHAPTER XXV

NITRO-GLYCERINE HIGH EXPLOSIVES

Kieselguhr : Manufacture of dynamite : Properties of dynamite : French dynamites : American dynamite : Ligdyn : Ammonia dynamite : Judson powder : Dynamite Nos. 2 and 3 : Gelatinized explosives : Boxes for jelly : Diminution of sensitiveness and stability : Exudation : Gelignite : Gelatine dynamite : Wrappers : 40 per cent. dynamite : American gelatin dynamites : Forcite : French gelatinized explosives : Low freezing explosives : Safety explosives containing nitro-glycerine : Carbonites

Kieselgu

The first attempts to use liquid nitro-glycerine for blasting proved so disastrous, that it became necessary to find some means of converting it into a solid, unless its wonderful power was to be lost to the world. Many of the principal countries had indeed passed laws forbidding the use of nitro-glycerine, when in 1866 Nobel discovered that it could be rendered comparatively safe by absorbing it in kieselguhr. This at once gave a great impetus to the high explosives industry and laid the foundations of the great fortune, which Nobel afterwards increased by other inventions and by his financial ability. Kieselguhr or guhr is a fine siliceous earth consisting of the remains of diatoms and other microscopic animals. It should have the power of absorbing three times its weight of nitro-glycerine, and should be free from gritty particles. It is found in the Lünerburger Heide, to the north of Hanover, also in Austria, Scotland, Norway, and Australia. The following analyses show its composition :

	From Oberlohe (Hanover)		Dried	Calcined
	Top Stratum	Second Stratum		
	(Gody)	(Gody)	(Sanford)	(Hagen)
Silica	87·85	74·48	94·3	96·34
Calcium carbonate . .	·73	·34	—	—
Lime	—	—	—	1·64
Magnesia	-	—	2·1	—
Iron oxide	·73	·39	1·3	·5
Alumina	·13	—	—	1·5
Organic matter . . .	2·28	24·42	·4	—
Moisture	8·43		1·9	

A sample of the guhr used at Ardeer in 1884 was analysed by Dupré (*S.R.* 61): it was of pale red colour and passed entirely through a 20-mesh sieve; it consisted of:

Soluble silica, oxide of iron	95·69
Insoluble silica, sand and grit	2·00
Loss on ignition	0·60
Moisture	1·71
	100·00

In consequence of the cessation of supplies from Germany and Austria steps are being taken to develop deposits in Victoria and New South Wales. Those at Lillicur, north-west of Ballarat, are said to be suitable for the manufacture of dynamite.[1]

Guhr is decidedly hygroscopic and cannot be dried effectively except at a high temperature: it is necessary to calcine it at a low red heat. The organic matter is thus destroyed also. Sometimes, however, the guhr is only charred, in which case a considerable percentage of carbonaceous matter will remain. The guhr may be mixed with some ochre, mica, talc or barium sulphate without impairing its absorptive powers. Ochre gives the dynamite a uniform red colour. Carbonate of ammonium, sodium, magnesium or calcium is added up to 2 per cent. of the finished explosive, in order to neutralize the acid formed by the decomposition of the nitro-glycerine on storage. The carbonates of magnesium and calcium are best, as the others have a decomposing action on the explosive.

Manufacture of Dynamite.

The carbonate and other additions should be mixed very intimately with the guhr, which is then passed through a 30-mesh sieve to remove all foreign bodies. The material is then weighed out into a lead, brass or copper-lined box, or a rubber bag, and nitro-glycerine is poured on in the proportion of not more than 75 parts by weight to 25 of the absorbent. After standing for a time the material is kneaded or mixed by hand in much the same way as is done with cordite paste. The mixture is then conveyed to a cartridge hut in which are erected two to four, but preferably only two, cartridge machines. Each of these consists of a brass plunger working vertically through two sleeves or guides (Fig. 72). It is worked by means of a hand-lever, and is shod at the lower end with lignum vitæ or ivory. This lower end works in a thin brass tube of the same diameter as the finished cartridge is to be. The upper end of the tube forms the apex of an inverted cone or hopper of soft leather (not shown in the illustration), having a capacity of about a pound of dynamite, the upper edges of this hopper being connected by three or more cords to a boss higher up on the plunger. The plunger works easily through the guides, so as to minimize the friction, and there is a good

---

[1] *Chem. Trade Journ.*, May 13, 1916, p. 426.

clearance between it and the tube. Sometimes it carries an inverted bell to prevent the explosive working up into the lower guide. To work the apparatus a girl wraps a paper cartridge wrapper round the outside of the tube, leaving sufficient paper at the bottom to turn in and close the end. Holding this in position with one hand she works the pump handle with the other; the effect of each upward stroke is to jerk the soft leather hopper by means of the cords, and cause the contained dynamite to fall into the tube, whence it is forced by the ensuing downward stroke into the paper wrapper at the lower end of this tube; this is repeated until the cartridge is of the required length, when it is removed, and the upper end of the paper is folded in.

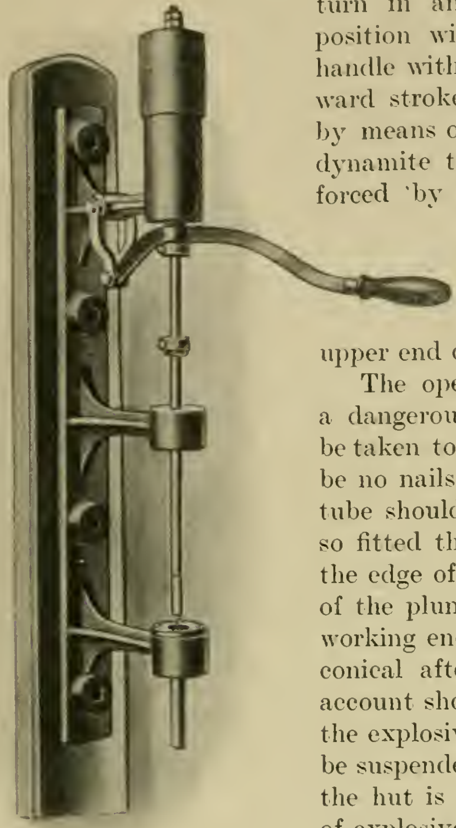


FIG. 72. Dynamite Cartridge Machine.

The operation of making these cartridges is a dangerous one, and the greatest care should be taken to minimize the danger.[1] There should be no nails in the machine; the mouth of the tube should be bevelled and faced with leather so fitted that an untrue plunger cannot strike the edge of the tube; the diameter of the body of the plunger should be less than that of its working end; and the tube should be slightly conical after the first short distance. On no account should any attempt be made to work the explosive when it is frozen, and work should be suspended altogether if the temperature inside the hut is below 50°. Only a small quantity of explosive should be allowed in the hut at one time, the remainder being kept in a cupboard outside. The huts should be at least 40 yards one from another, and surrounded with good mounds.

Properties
Dynamite,

The material thus made is a plastic mass varying in colour from buff to reddish brown. Direct contact with water causes the nitro-glycerine to separate from it; therefore great care must be exercised when using it in wet places. It freezes somewhat more readily than liquid nitro-glycerine. When ignited in small quantities it simply burns away fiercely, but fatal accidents have arisen in considerable number from persons supposing that,

---

[1] *See S.R.*, 61, Nos. 145 and 184.

as it is reasonably safe to ignite a few cartridges of unfrozen dynamite, it is equally safe to warm it upon a shovel, in an oven, in a tin over a fire, or in various other ways, which usually lead to a verdict of "Accidental Death." Frozen dynamite is much more susceptible to explosion by simple ignition, but it is less sensitive to detonation, as also to a blow or friction under some conditions, but the annals of explosives are full of instances of the fatal unexpected explosion of frozen nitro-glycerine explosives, which had not been treated with proper respect. The density of dynamite is stated to be 1·4 to 1·5,[1] but I have found it to be about 1·62. If there were no air spaces in it the density would be 1·77. The temperature of ignition is given as 182°.

The following are analyses made by Dupré in 1901 of two samples from Ardeer :

Nitro-glycerine	73·62	73·98
Kieselguhr	25·70	25·00
Ammonium carbonate	0·19	0·16
Other soluble matter	0·11	0·24
Moisture	0·38	0·62
	100·00	100·00
Containing sand, calculated on dynamite	0·1	0·15
,, ,, ,, Kieselguhr	0·39	0·61

Both samples were of a light brick red colour and gave heat tests of over thirty minutes.

This material is called in Great Britain Dynamite No. 1, or Kieselguhr Dynamite, or simply Dynamite, and in Germany the nomenclature is much the same, but in America it is called Giant Powder, and the term dynamite is usually applied to a mixture of nitro-glycerine, wood pulp and sodium nitrate, which is not authorized in England at all. Dynamite No. 1 is not made very extensively now, as it has been replaced by various gelatinized nitroglycerine mixtures, but it possesses the advantage that it is more stable when stored at high temperatures, as the acid products of decomposition are immediately neutralized by the carbonate present. I have examined dynamite that had been stored for a considerable number of years at Aden, and could find no signs of instability, whereas a gelatinized explosive under the same conditions would have given a very low heat test.

Besides infusorial earth other siliceous materials have been used for the manufacture of dynamite ; in France, for instance, a material called Randanite, which is found in Auvergne, and has been formed by the weathering of feldspar. Berthelot proposed the use of a special artificial silica made by decomposing silicon fluoride with water and having a very high absorptive power. Nobel, in his patent specifications, mentioned a number of materials

---

[1] Chalon, p. 302 ; Vennin et Chesneau, p. 365.

such as powdered brick, dry clay and plaster. During the siege of Paris coal-ashes were used, and in America magnesium carbonate has found some favour.

Formerly a number of special mixtures of this kind were made in France,[1] but now the only nitro-glycerine explosive with inert base used there largely is dynamite No. 1 containing 75 per cent. of nitro-glycerine and 25 per cent. of guhr. More rarely dynamites Nos. 2 and 3 are employed containing 35 and 25 per cent. of nitro-glycerine respectively.[2] Dynamites are not allowed to be transported in France if they are more than twelve months old.[3]

As nitro-glycerine contains an excess of oxygen even after all the carbon has been converted into dioxide, the idea naturally occurred to mix it with an organic absorbent : cork charcoal has a very great absorptive power, but the material that has been used most is wood pulp. The "Atlas Powders" introduced from America by the Fenians in 1883 and 1884 for their criminal attempts were of this type. Two of the samples analysed by Dupré had the following composition :

American dynamite

Nitro-glycerine	29·8	Nitro-glycerine	71·6
Wood sawdust slightly charred in parts	63·8	Wood sawdust and a little chalk .	24·9
Moisture	6·4	Moisture	3·5

But these mixtures contained an excess of oxidizable matter. It is more economical to add another oxygen carrier. In America sodium nitrate is used very extensively for this purpose. In the Bureau of Explosives Report No. 2, Beistle gives the results of the analysis of a large number of American dynamites, which are summarized in the following Table :

Grade	Nitro-glycerine	Wood Pulp	Sodium Nitrate	Moisture
60 per cent.	53·5–65·1	14·2–21·0	16·0–29·8	1·16–3·18
50 ,, ...	49·3–50·1	11·6–13·4	32·6–33·8	1·97–2·00
40 ,, ...	34·8–41·9	7·7–13·9	38·4–50·2	0·80–3·60
30 ,, ...	29·7–32·5	7·9–10·2	52·6–60·1	1·09–1·69

It will be seen that the variations in composition in each grade are considerable ; the figures for the 50 and 30 per cent. grades are based on two analyses each only, but those for the other grades on a considerable number. Many of the dynamites evidently contained a few per cent. of some other constituents

---

[1] See 1st edition of this work, p. 281.

[2] Vennin et Chesneau, p. 363. *See also P. et S.*, vol. xvii., p. 158.

[3] Vennin et Chesneau, p. 365.

undetermined, but those in which there was a considerable deficit have been excluded from the above summary. The following are two examples of American 40 per cent. dynamites :

	Straight dynamite	Hercules
Nitro-glycerine	40	40
Wood-pulp	11·75	11
Sodium nitrate	47·25	45
Calcium carbonate	1	—
Magnesium carbonate	—	1
Sodium chloride	—	1
Moisture	—	2

Hall and Howell give the following as the composition of typical American "straight" dynamites :[1]

Strength	15 per cent.	20 per cent.	25 per cent.	30 per cent.	35 per cent.	40 per cent.	45 per cent.	50 per cent.	55 per cent.	60 per cent.
Nitro-glycerine	15	20	25	30	35	40	45	50	55	60
Combustible material [2]	20	19	18	17	16	15	14	14	15	16
Sodium nitrate	64	60	56	52	48	44	40	35	29	23
Calcium or magnesium carbonate	1	1	1	1	1	1	1	1	1	1
	100	100	100	100	100	100	100	100	100	100

Ligdyn.

A similar explosive is manufactured in South Africa under the name of Ligdyn. The 40 per cent. grade has the composition :

Nitro-glycerine	40
Wood-meal	13
Sodium nitrate	45
Wheat flour	2

The cartridges are made in the Quinan packing machine, which works on the same principle as the hand machine shown in Fig. 72, but it is operated by power, and makes thirteen to fifteen cartridges at one time. On January 3, 1913, the contents of one of these machines exploded and killed nine persons and injured two others.

mmonia ynamites.

In America Ammonia Dynamites are also made, in which a large proportion of the nitro-glycerine is replaced by ammonium nitrate.

---

[1] Bureau of Mines, *Bulletin* No. 48.

[2] Consisting of wood-pulp, flour, and sulphur for grades below 40 per cent. ; wood-pulp only for other grades.

The following Table shows the compositions of typical ammonia dynamites of various grades[1]:

Strength	30 per cent.	35 per cent.	40 per cent.	50 per cent.	60 per cent.
Nitro-glycerine	15	20	22	27	35
Ammonium nitrate	15	15	20	25	30
Sodium nitrate	51	48	42	36	24
Combustible material[2]	18	16	15	11	10
Calcium carbonate or zinc oxide	1	1	1	1	1

Judson powder.

An explosive of a somewhat different type, which is also used extensively in America, is Judson Powder, which was patented in 1876 by E. Judson. This is made with percentages of nitro-glycerine varying from 5 to 20 per cent. Judson Powder R.R.P. has the composition:

Nitro-glycerine	5
Sodium nitrate	64
Sulphur	16
Cannel coal	15

or

Nitro-glycerine	5
Sulphur, coal and resin	35
Sodium nitrate	60

The sodium nitrate is mixed with the combustibles and the mixture is heated beyond the melting point of the sulphur and resin. The slightly porous mass thus formed is coated with nitro-glycerine, which accelerates the explosion of the mixture and so makes it considerably more violent.[3] It is really a sort of crude gunpowder containing a little nitro-glycerine. It is fired with a priming cartridge of dynamite.

The great objection to these mixtures is that sodium nitrate is decidedly deliquescent, and ammonium nitrate still more so: even from a moderately dry atmosphere they take up moisture and become liquid, and the solution thus formed displaces the nitro-glycerine and causes it to exude, thus giving rise to a very serious danger. For this reason such explosives have not been authorized in England. It is noteworthy that for the work on the Panama Canal, in which many millions of tons of dynamite have been used, the Isthmian Canal Commission only accepted explosives containing potassium

---

[1] Hall and Howell, *loc. cit.*

[2] Consisting of wood-pulp, flour, and sulphur.

[3] Bureau of Mines, *Bulletin* No. 48, p. 6.

nitrate and free from sodium nitrate, magnesium salts and other impurities which would make the material hygroscopic. Two samples of Atlas Powder used in the construction of the Panama Canal were analysed by Stillman and had the composition :

	B+	C+
Nitro-glycerine	61·1	45·7
Wood-pulp	14·1	10·5
Potassium nitrate	21·6	40·9
Magnesium oxide	3·0	—
Chalk	—	1·9
Moisture	0·2	1·0

Dynamite Nos. 2 and 3.

The early demand for an explosive that was milder and slower than Dynamite No. 1 was met in England by the manufacture of Dynamite No. 2, which was recommended for work in coal-mines and quarries. This consisted of not more than 18 per cent. of nitro-glycerine mixed with some 10 per cent. of charcoal and 72 per cent. of saltpetre, and sometimes a little paraffin. It was practically gunpowder in which nitro-glycerine had been substituted for sulphur. Dynamite No. 3 was a more powerful explosive, and consisted of a mixture of equal parts of kieselguhr dynamite and a mixture of saltpetre and wood-meal.

Gelatinized explosives,

In 1875 Nobel made a further advance of the very first importance by his discovery that by dissolving 7 or 8 per cent. of collodion cotton in nitro-glycerine it is converted into a gelatinous solid. The discovery arose from the fact that Nobel had cut his finger and collodion had been used to cover the wound : whilst the inventor was experimenting with nitro-glycerine some of it got mixed with the collodion. In the following year patents were granted in the principal industrial countries protecting the invention, but it was some years before the difficulties of manufacture had been overcome. In Great Britain the manufacture was licensed in 1878, and in 1880 the manufacture was commenced on a large scale in the Continental factories of the Nobel Syndicate, but considerable difficulty was found in fulfilling the requirements of H.M. Inspectors of Explosives. The first products exuded nitro-glycerine, and manufacture was suspended for some years : afterwards, when this difficulty had been overcome, the blasting gelatines failed to pass the heat test, and it was not until 1887 that the manufacture was in full swing in Great Britain. A great demand for the material sprang up at once in consequence of its enormous power and convenient nature. For blasting hard rock it has proved very serviceable, especially when, as in tunnelling, it is not necessary to get the rock out in large pieces.

Manufacture.

The collodion cotton is thoroughly dried and reduced to a fine state of division. It should not contain more than 1 per cent. of water. A weighed quantity is placed in a brass-lined box, and the requisite quantity of nitro-glycerine is poured on. The materials are mixed together by hand and allowed to stand for some hours or overnight. The box is then taken to the mixing house, where the material is heated to about 50° C. and gently mixed until solution is complete, which takes about an hour. At first the mixing was done entirely by hand with wooden stirrers, but now the final mixing is generally performed in incorporating machines similar to those used in the manufacture of smokeless powders (*see* Figs. 56, 57). At the Ardeer Factory of Nobel's Explosives Co. and some other works McRoberts's machine is used (Fig. 73). This has a number of narrow stirrer blades mounted on two vertical spindles, which are driven from above. The trough containing the explosive mixture is wheeled in below and raised by means of suitable gearing. There are stops to prevent the bottom of the trough coming in contact with the stirrers. The trough has a double wall, through which hot water can be circulated from a tank outside the building maintained at a temperature of 50° C. The actual temperature of the mixture is 40° to 45°. After about an hour the trough is removed and the gelatine is allowed to stand to get cool and become stiffer, but not too stiff. In 1914 and 1915 two severe explosions occurred in the mixing houses of the Nobel Co. at Ardeer. They may have been caused by dropping a lead apron into the mixer.[1] It is advisable that the machinery be not running whilst the trough is being filled. If the stirrers are driven electrically there should be an automatic cut-out to the motor to prevent the use of too much force.

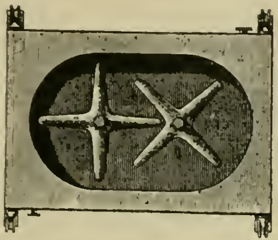


Fig. 73. Plan of McRoberts's Incorporator for Blasting Gelatine

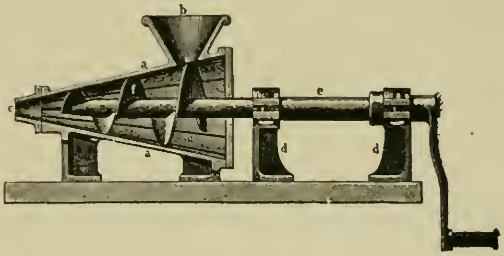


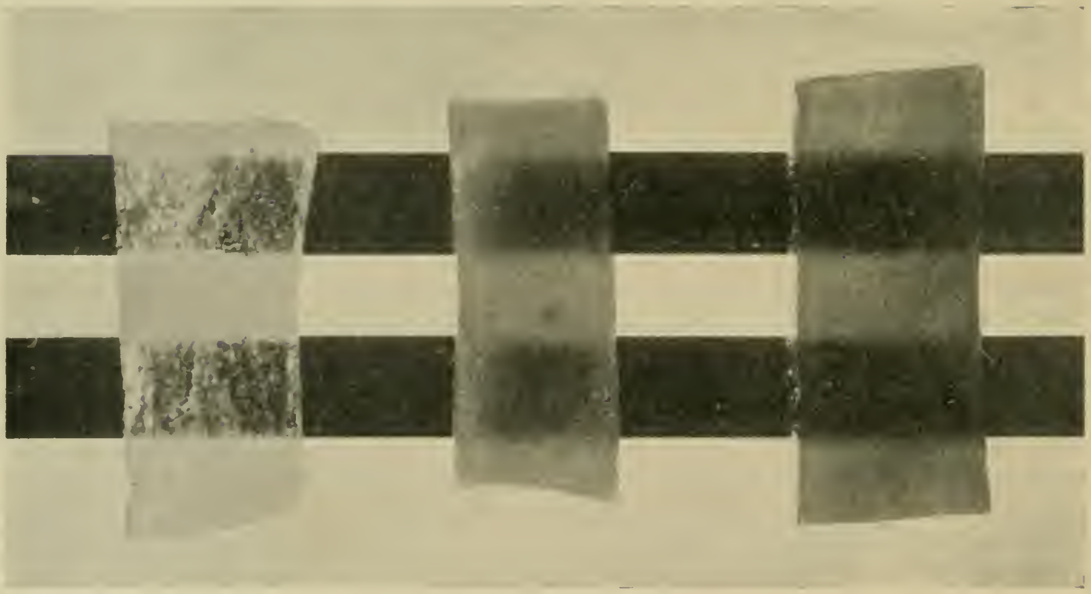
Fig. 74. Cartridge Machine for Gelatinized Explosives

Starting from the theory that blasting gelatine has a webbed structure, W. A. Hargreaves, Inspector of Explosives in South Australia, has arrived at the opinion that it does not possess sufficient sensitiveness unless there be a considerable amount of liquid nitro-glycerine between the webs. He hence concludes that the gelatine is best made by first mixing the nitro-cotton thoroughly in the cold with part of the nitro-glycerine, and then after gelatinization adding the rest of the nitro-glycerine. It is claimed that in this way

---

[1] *See S.RR.* Nos. 209, 213.

Reflected light



Transmitted light

FIG. 75. Photographs of Blasting Gelatines
(From Report to Parliament of W. Australia by A. E. Mann)

FIG. 76. Photographs of Gelignites
(From Report to Parliament of W. Australia by A. E. Mann)

FIG. 77. Photographs of South African Gelignites
(From Report to Parliament of W. Australia by A. E. Mann)

blasting gelatine has been manufactured which is less liable either to become insensitive or on the other hand to exude.[1]

Blasting gelatine may be made into cartridges in the machine shown in Fig. 72, or the "sausage machine" illustrated in Fig. 74 may be used for this and other gelatinous explosives that are not too stiff. The gelatine is fed in through the hopper, *b*, whilst the handle is turned. The Archimedean screw forces the material forward and out of the nozzle, the diameter of which corresponds with the size of cartridge to be produced. It is necessary that the jelly should be warm during this operation, as otherwise it breaks up. The following is the approximate output of cartridges of gelignite, gelatine dynamite or blasting gelatine in a day of $7\frac{1}{2}$ hours by a gang of four girls, one working the cartridge machine and the other three rolling cartridges :

Size of cartridge	Output, lb.
$\frac{7}{8}$, 10	1,000
$\frac{7}{8}$, 2	1,200
$1\frac{1}{4}$, 4	1,500

There are grooves inside the body to prevent the material rotating. In all machines used for working these substances it is essential that only bronze or other suitable alloy be used, and all bearings must be so arranged that the nitro-glycerine cannot get into them. When the nitro-glycerine is hot it is decidedly more sensitive than when cold.

oxes for jelly. The boxes for conveying the mixture of nitro-glycerine and collodion cotton are usually made of wood lined with copper, brass, lead or rubber, or of heavy copper tinned inside and provided with rubber rims. They should be so constructed as to prevent, as far as possible, those surfaces which are liable to have explosive on them from coming in contact with one another, or with the supports on the bogie on which they are carried. The boxes should be cleaned thoroughly at frequent intervals. An explosion that occurred at Arklow on August 4, 1911, is ascribed to the neglect of these precautions.[2]

iminution of ensitiveness, After manufacture blasting gelatine continues to stiffen for a considerable time and, unfortunately, as it gets stiffer it becomes less sensitive to detonation, so that old blasting gelatine may give a missfire. Thus Soddy found that gelatines which gave results of 570 to 600 c.c. in the lead block when first tested, after keeping for a year gave only 340 to 420 c.c. when fired with a No. 6 detonator, but gave normal results again when a No. 7 detonator was used.[3] Indeed, it is not easy to produce a collodion cotton which has the

---

[1] *J. Soc. Chem. Ind.*, 1914, p. 337.

[2] *S.R.*, No. 201.

[3] *A. and E.*, 1912, p. 22.

right degree of gelatinizing power and is at the same time sufficiently stable to stand transport through the tropics, to Australia, for instance. In 1909 125,000 lb. of gelignite were condemned in Western Australia alone on chemical grounds. **and stability.**

Diminution of sensitiveness of the gelatine is accompanied by increase of stiffness, but the reason of these changes is not well understood. Hargreaves's theory has been mentioned above, but it is not by any means certain that a gel such as blasting gelatine has a webbed or cellular structure. The alteration must of course be due to some change in the structure of the particles, but there is no direct evidence to show what this structure is. It is, however, a general property of gels to set slowly and stiffen gradually when cooled again after being heated, and the longer and stronger the heating, the slower is the setting in many instances. The heating causes a diminution in the size of the particles and prolonged storage in the cold may produce the reverse change. The stiffening may therefore be due to increase in the size of the particles, or it may be due to more perfect absorption or adsorption of the nitro-glycerine.

Exudation.

When a colloid swells up by imbibition of a liquid it can be made to exert great pressure on the walls of the containing vessel. Conversely, if sufficient pressure be applied under such conditions that the liquid can escape part of it will be expressed until equilibrium is again established. This shows that the imbibition is a reversible process, but does not throw much light otherwise on the process. The pressure required is small when the gel is very swollen. Some blasting gelatines require so little pressure to deprive them of some of their nitro-glycerine that the weight of the cartridges is sufficient to cause some of it to exude into, or even through, the wrapper of vegetable parchment.

Blasting gelatine may contain anything up to 12 per cent. of collodion cotton, but usually 7 or 8 per cent. To increase its stability 1 or 2 per cent. of calcium or magnesium carbonate may be added, or a fraction of a per cent. of vaseline.

Gelignite.

For most purposes blasting gelatine is considered too expensive and is too violent and local in its action, and consequently explosives are used in which it is rendered milder by the addition of other materials. Gelignite is an explosive which is very largely employed: it consists of 56 to 63 per cent. of nitro-glycerine thickened with nitro-cotton to a thin jelly and mixed with potassium nitrate and wood-meal, with the addition sometimes of calcium carbonate or mineral jelly.

Gelatine dynamite.

Gelatine dynamite is a mixture very similar to gelignite except that it contains a larger proportion of blasting gelatine: there may be from 70 to 77 per cent. of nitro-glycerine in it.

The following Table shows typical compositions for these three standard gelatinized explosives :

	Blasting Gelatine	Gelatine Dynamite	Gelignite
Nitro-glycerine	91·5	74·5	60·5
Collodion cotton	8	5·5	4·5
Wood-meal	—	4	7
Potassium nitrate	—	15·5	27
Calcium carbonate	0·2	0·2	0·2
Moisture	0·3	0·3	0·8

The wood meal used for the manufacture of these explosives should not be too fine, otherwise there is difficulty in obtaining complete detonation. In some factories it is only sifted through a mesh of eight holes to the linear inch, but in other factories it is finer. Apparently the air vesicles in the coarse meal assist the detonation, and at the same time reduce the density of the explosive. The saltpetre and other ingredients, if any, are ground more finely, to pass a 50- or 100-mesh sieve. The mixture should contain sufficient oxygen to convert the whole of the carbon present into carbon dioxide, so that none of the poisonous carbon monoxide shall be formed to foul the air in mines. It has been shown by Mann (Report to the Western Australian Parliament, 1911) that if the paper wrappings on the cartridges are removed very little carbon monoxide is formed ; not more than 2 per cent. of the carbon is converted into this gas, but with the wrappers on from 7 to 14 per cent. is formed. In Great Britain wrappers of parchment paper are used, but on the Continent and in America they are often of paraffined paper. A wrapping of metal foil would have far less reducing action, but the finely divided metallic oxide would itself have a poisonous action. Impregnation of the paper with nitrates or similar means would make the cartridges considerably more inflammable. For the avoidance of this danger of poisoning with carbon monoxide the most effective means is undoubtedly efficient ventilation of the mines.

Wrappers.

Forty per cent. dynamite.

Dynamite No. 4 or 40 per cent. dynamite is a somewhat similar mixture : it contains not more than 39·5 per cent. of nitro-glycerine gelatinized with not less than 0·75 per cent. of nitro-cotton and mixed with sodium nitrate and not less than 16·5 per cent. of dry wood-meal and a little magnesium carbonate. It is sometimes sold under the name of " Farmer's Dynamite " for breaking up sub-soil, making holes for trees and other agricultural purposes, for which an inexpensive explosive is required. It differs from the ordinary American 40 per cent. dynamite in that the nitro-glycerine is gelatinized and a larger proportion of wood-meal is used: the danger of exudation is thus greatly reduced.

American gelatin dynamites.

In America these explosives are called "gelatins" or gelatin dynamites; according to Hall and Howell [1] they generally have compositions approximating to the following:

Ingredients.	30 per cent. strength	35 per cent. strength	40 per cent. strength	50 per cent. strength	55 per cent. strength	60 per cent. strength	70 per cent. strength
Nitro-glycerine . .	23·0	28·0	33·0	42·0	46·0	50·0	60·0
Nitro-cellulose . .	0·7	0·9	1·0	1·5	1·7	1·9	2·4
Sodium nitrate . .	62·3	58·1	52·0	45·5	42·3	38·1	29·6
Combustible material [2]	13·0	12·0	13·0	10·0	9·0	9·0	7·0
Calcium carbonate .	1·0	1·0	1·0	1·0	1·0	1·0	1·0
	100·0	100·0	100·0	100·0	100·0	100·0	100·0

A sample of 40 per cent. gelatine dynamite analysed by W. C. Cope was found to contain:

Nitro-glycerine	30·70
Nitro-cellulose	0·88
Sodium nitrate	54·27
Wood-meal	8·58
Sulphur	3·08
Zinc oxide	1·02
Moisture	1·47
	100·00

To prevent the formation of poisonous gaseous products of explosion Munroe and Hall advise the omission of the sulphur.[3] They recommend the following as a well balanced formula:

Nitro-glycerine	33
Nitro-cellulose	1
Sodium nitrate	54
Flour	11
Calcium carbonate	1
	100

---

[1] Bureau of Mines, *Bulletin* 48.

[2] Wood-pulp is used in 60 and in 70 per cent. strength gelatine dynamite. Sulphur, flour, wood-pulp, and sometimes resin are used in other grades. Some manufacturers replace a small percentage of the nitro-glycerine in these grades with an equal amount of ammonium nitrate. This replacement, however, offers little, if any, advantage other than reducing the cost of manufacture.

[3] Bureau of Mines, *Bulletin* No. 80, p. 27.

Forcite.

The name "Forcite" is also employed sometimes for ordinary gelignites containing potassium or sodium nitrate and wood-meal, but sometimes also for mixtures in various proportions of a thin blasting gelatine with an absorbent having the composition :

Sodium nitrate	76
Sulphur	3
Wood-tar	20
Wood-pulp	1

In Belgium Forcites were manufactured at Baelen-sur-Nèthe, having the following compositions :

	Extra	Supérieur	No. 1	No. 2
Nitro-glycerine	64	64	49	36
Nitro-cellulose	3·5	3	2	3
Sodium nitrate	—	24	36	35
Ammonium nitrate	25	—	—	—
Wood-meal	6·5	8	13	11
Magnesia	1	1	—	1
Rye-bran	—	—	—	14

They are also made with corresponding percentages of potassium nitrate.

French gelatinized explosives.

In France explosives containing nitro-glycerine are excepted from the State monopoly : a large number of different compositions have been authorized for manufacture in the private works. The following are some examples (Chalon) :[1]

	Dynamite-gomme			Gélatine			Gomme E	Gelignite
	Extra forte	Potasse	Soude	A	B-potasse	B-soude		
Nitro-glycerine	92–93	82–83	82–83	64	57·5	57	49	58
Nitro-cellulose	8–7	6–5	6–5	3	2·5	3	2	2
Potassium nitrate	—	9–10	—	—	32	—	36	28
Sodium nitrate	—	—	9–10	24	—	34	—	—
Wood-meal	—	2–3	2–3	8	8	6	10	9
Flour	—	—	—	—	—	—	3	3

Low-freezing explosives.

Any of the nitro-glycerine explosives can be made with low-freezing nitro-glycerine (*see* Chapter XVI). The methods of incorporating the explosives are the same as if ordinary nitro-glycerine were used. In England, where

---

[1] Vennin et Chesneau, p. 369. *See also* Chalon, p. 295. For similar explosives made in Switzerland see B. Zschokke, *S.S.*, 1909, pp. 143, 144.

the winters are not so very severe, reliance is placed rather on keeping the magazines warm than on making additions to the explosive mixtures, but on the Continent and in America a considerable number of such explosives are in use. In Germany and Switzerland several "special" blasting gelatines and gelignites are made containing a percentage of liquid nitro-toluene or other nitro-aromatic compounds, or glycerine esters. In Austria the following are manufactured :

	Dynamit I schwerfrierbar	Dynamit II schwerfrierbar
Nitro-glycerine	55	38·5
Nitro-cellulose	2	1·5
Nitro-toluene	10	8
Wood-meal	8	4·16
Rye flour	—	3·12
Sodium nitrate	24	43·68
Lamp-black	—	0·52
Caput mortuum	0·5	0·52
Sodium carbonate	0·5	—

The following is a French explosive of this class :

Nitro-glycerine	66·4
Nitro-glycol	16·6
Nitro-cotton	5
Potassium nitrate	10
Wood meal	2

In America low-freezing dynamites are made which differ from the corresponding "straight" dynamites in that about a quarter of the nitro-glycerine is replaced by nitro-substitution compounds.[1] The Red Cross dynamites made by the E.I. du Pont de Nemours Co. are explosives of this class.

The following are the compositions of typical low-freezing dynamites as given by C. E. Munroe and C. Hall : [2]

Strength	30 per cent.	35 per cent.	40 per cent.	45 per cent.	50 per cent.	55 per cent.	60 per cent.
Nitro-glycerine	23	26	30	34	38	41	45
Nitro-substitution compounds	7	9	10	11	12	14	15
Combustible material	17	16	15	14	14	15	16
Sodium nitrate	52	48	44	40	35	29	23
Calcium or magnesium carbonate	1	1	1	1	1	1	1

The composition of the combustible material is similar to that in the corresponding "straight" dynamites.

---

[1] *See* Hall and Howell, Bureau of Mines, *Bull.* 48, p. 7.

[2] Bureau of Mines, *Bulletin* No. 80, p. 22.

The use of these low-freezing nitro-glycerine explosives diminishes the danger of solidification, but does not overcome it entirely. If the weather be very cold it is still necessary therefore to make use of thaw-houses and warming-pans to prevent accident.

Safety explosives containing nitro-glycerine.

There are a number of explosives made which consist practically of gelignite in which part of the potassium nitrate has been replaced by ammonium-oxalate, or a compound containing much water of crystallization such as magnesium sulphate, so as to slow down the explosion and reduce the temperature of the flame. These are mostly used for blasting coal. The most largely used of all the "Permitted Explosives" in Great Britain was at one time Saxonite, made by Nobel's Explosives Co. The consumption in 1907 under the Coal-Mines Regulation Act was 1,721,193 lb. But in 1909 it failed when re-tested in the testing gallery and was removed from the list. It was promptly replaced by Samsonite, in which the limits of composition are considerably narrower, and of which 1,071,143 lb. were used in 1910. Saxonite is still used, however, where permitted explosives are not compulsory, and in 1911 the consumption was 135,548 lb.

	Saxonite	Samsonite
Nitro-glycerine	42·5–62	57 –60
Nitro-cotton	2·5– 5	3 – 4
Potassium nitrate	16 –27·5	17 –19
Wood-meal	3·5– 8	5 – 7
Chalk	0 – 0·5	– –
Ammonium oxalate	9 –27	12·5–14·5
Moisture		0 – 1·5

Whilst the "Woolwich Test" was in force a number of other explosives very similar to Samsonite were on the Permitted List: Arkite, Rippite, Stowite, Cornish Powder, Swalite, amongst others.

To pass the more severe "Rotherham Test" it has been found necessary to reduce the percentage of nitro-glycerine and increase the amount of nitrate and oxalate. The following are on the Permitted List:[1]

	Arkite, No. 2	Duxite
Nitro-glycerine	32	32
Nitro-cotton	1	1
Potassium nitrate	27	—
Sodium nitrate	—	28
Wood-meal	10	10
Ammonium oxalate	30	29
Moisture		
Maximum charge, oz.	40	12
Power (swing of bal. pend.)	2·41"	2·45"

---

[1] In the *Explosives in Coal Mines Orders* the limits of composition are published. Here only the approximate means are stated, the wood-meal, etc., being given in the "natural dry" state with about 10 per cent. of its weight of moisture.

The following have passed the Belgian test and are on the list of "explosifs S.G.P.":

	Dynamite antigrisouteuse V.	Grisoutite
Nitro-glycerine	44	44
Cellulose	12	12
Sodium sulphate	44	—
Magnesium sulphate	—	44
Charge limite	650 g.	300 g.
Equivalent, dynamite No. 1	359	179

There is also Grisoutine II, which is practically the same as Dynamite Antigrisouteuse V.

Carbonite.

One of the earliest and most successful safety explosives was Carbonite, which was made by Bichel and Schmidt first about 1885, and after undergoing some modifications gave satisfactory results at the Neunkirchen testing station in 1887. It consists of nitro-glycerine, about 25 per cent., absorbed in wood-meal and mixed with nitrates. The proportion of wood-meal is so high that a large proportion of the carbon is only oxidized to monoxide:

Nitro-glycerine	25
Potassium nitrate	30·5
Barium nitrate	4
Wood-meal	40
Soda	0·5

The composition has been varied by the substitution of other nitrates for those mentioned, and of rye starch and other carbo-hydrates for wood-meal. The composition has been imitated by many other manufacturers. The following are some of the explosives of this type that passed the Woolwich test:

	Carbonite	Tutol	Kolax
Nitro-glycerine	26	25	25
Potassium nitrate	33	33	26
Barium nitrate		2	5
Wood-meal	40½	40	34
Starch	—	—	10
Sulphuretted benzene	¼	—	—
Calcium carbonate	¼	—	—
Sodium carbonate		—	—
Sodium bicarbonate	—	¼	—

There are a number of explosives of this type on the Belgian list of "explosifs S.G.P." :

	Kohlen-carbonite	Minite	Antigel de Sûreté	
Nitro-glycerine	25	25	Nitro-glycerine	25
Potassium nitrate	34	35	Sodium nitrate	20
Barium nitrate	1	—	Dinitro-toluene	15
Flour	38·5	39·5	Ammonium sulphate	5
Tan-meal	1	—	Cellulose	35
Soda	0·5	0·5	Wood-meal	35
Charge limite	900	750	Charge limite	900
Equivalent	501	405	Equivalent	524

Minerite and Colinite antigrisouteuse have the same composition as Kohlen-carbonite. and Securophore III only differs from it in having 1 per cent. wood-meal instead of tan-meal : its "charge limite" is 850 grams, equivalent to 548 grams Dynamite No. 1. Ingélite is identical with Antigel de sûreté.

To pass the Rotherham test it has been found necessary to add a cooling agent such as ammonium oxalate :

	Cambrite	Super-Kolax		Britonite No. 2.
		No. 1	No. 2	
Nitro-glycerine	23	25·5	28·5	24
Collodion cotton	—	—	1	—
Potassium nitrate	27	25·5	16·5	30
Barium nitrate	3·5	5	5	—
Wood-meal	38	30	31	38
Starch	—		8·5	—
Ammonium oxalate	8	7	9·5	8
Calcium carbonate	0·5	—	—	—
Maximum charge, oz.	30	30	32	24
Power (swing of bal. pendulum, inches)	1·98	2·10	2·21	2·26

Some ammonium nitrate explosives also have a small percentage of nitro-glycerine added to render them less insensitive, and to make it possible to compress them to a higher density without making them too difficult to detonate. These are dealt with in Chapter XXVII. The potassium perchlorate explosives dealt with in Chapter XXVI also generally contain nitro-glycerine.

CHAPTER XXVI

CHLORATE EXPLOSIVES

Chlorate dangers : Sprengel explosives : Prométhée or O3 : Rack-a-rock : Cheddite : Steelite : Silesia : Potassium perchlorate explosives : Permonite : Alkalsit : Polarite : M.B. powder : Ammonium perchlorate explosives : Yonckite : Blastine

Chlorate dangers.

THE substitution of potassium chlorate for saltpetre in an explosive mixture increases its power and violence, but also its sensitiveness. A favourite mixture has been "white gunpowder," for which the following proportions have been recommended :

	Augendre	Pohl	Reveley
Potassium chlorate	50	49	48
Potassium ferrocyanide	25	28	29
Sugar	25	23	23

Mixtures of chlorate and sulphur or a sulphide are specially sensitive. Hence the early attempts to make gunpowder with chlorate led to disaster. Such mixtures are used for percussion caps, and for other purposes where a high sensitiveness is required. They have also been used for the manufacture of coloured lights and other similar fire-works, but in England this is now forbidden. Means have been found, however, to make blasting explosives containing chlorate, which are not more dangerous than other explosives. The perchlorates are much less sensitive than the chlorates, and as they are now manufactured at moderate costs, their use in explosives is extending rapidly. Mixtures containing sodium chlorate are more dangerous than those containing potassium chlorate.[1]

Under ordinary circumstances chlorate of potash, when unmixed with combustible matter, is not dangerous, but on May 12, 1899, a large quantity of it exploded during the progress of a fire at the works of the United Alkali Co. at St. Helens, and did an enormous amount of damage.[2] This led to a more thorough examination of the behaviour of potassium chlorate when heated. Berthelot[3] showed that if it be subjected to a blow combined with

---

[1] *See A.R.*, 1904, p. 28.

[2] *S.R.*, No. 135.

[3] *P. et S.*, vol. x., 1900, p. 280 ; *Compt. Rend.*, 1899, vol. 129, p. 926.

sudden intense heat it explodes; he devised the following experiment: A glass tube 25 to 33 mm. in diameter, closed at one end, is supported in a nearly vertical position, and heated in the flame of a large gas-burner, until the lower part has attained a perceptible red heat. A glass rod is drawn out to the thickness of a coarse thread, then introduced into a quantity of pure potassium chlorate, which has been melted in a porcelain crucible, withdrawn and allowed to cool until the salt begins to solidify. The operation is repeated several times until a few decigrammes of solidified salt are accumulated in the form of an oval lump on the end of the glass thread. When the glass tube is quite red, the glass rod is introduced until the potassium chlorate is within about 10 mm. of the bottom, care being taken that it does not touch the tube anywhere. After a short time the chlorate melts and falls, drop by drop, on to the red-hot bottom of the tube. Each drop explodes at the instant that it comes in contact with the glass, producing a very distinct sound and a cloud of white smoke.

Dupré [1] showed that heat alone suffices to explode the chlorate, if it be applied with sufficient suddenness. A bead of potassium chlorate, supported in a loop of thin platinum wire, can be made to explode by heating it rapidly either in a gas flame or by means of an electric current.

Since the St. Helens disaster there have been several other instances in which considerable quantities of potassium chlorate have exploded in the course of conflagrations. On July 27, 1908, an explosion of this sort occurred on the premises of a carrying company in Manchester: [2] and on July 21, 1910, another at the match-works of Messrs. Bryant and May, at Seaforth, near Liverpool.[3] In 1912 an explosion took place during repairs to a drying machine, five men being killed.[4] Although potassium chlorate is not classified officially as an explosive, yet where large quantities are stored they should be kept in an uninflammable building, separate from all combustible materials. The intense inflammability of wood and other organic matter, when impregnated with chlorate, should be borne in mind. The explosibility of chlorate is caused by the fact that heat is liberated when it decomposes into potassium chloride and oxygen. It does not explode with great violence.

Sprengel explosives.

Chlorate explosives may be rendered reasonably safe by adopting the device of Sprengel and issuing the chlorate separately from the combustible matter. The potassium chlorate is made up into porous cartridges, and a liquid combustible is used; the former is dipped into the latter just before use. These explosives are not allowed in Great Britain, as this dipping operation is considered to constitute a process of manufacture, and consequently may only be carried out in a duly licensed factory.

---

[1] *J. Soc. Chem. Ind.*, 1902, p. 217.

[2] *S.R.*, No. 185.

[3] *A.R.*, 1910, p. 41.

[4] *A.R.*, 1913, p. 39.

Promêthêe or O3.

A Sprengel explosive is made in France under the name of "Explosif O3" or "Prométhée"; either the oxygen carrier or the combustible can be varied:

	a	*b*	*c*		
Potassium chlorate .	95	90	80	Oxygen carrier .	92 to 87 per cent.
Manganese dioxide .	5	10	20		
	1	2			
Nitro-benzene .	50	60		Combustible .	8 to 13 ,,
Turpentine . .	20	15			
Naphtha . .	30	25			

Any combination of *a*, *b* or *c* with 1 or 2 can be used. The explosive is sold at the price of Fr. 3 per kg. The amount of liquid combustible taken up by the solid oxygen carrier may vary from 8 to 13 per cent. This irregularity is a serious defect and may cause incomplete detonation.[1]

There is also a factory for Prometheus explosive at Sant. Eusebio, near Genoa, in Italy, where a severe explosion took place on May 10, 1909, killing the manager, head foreman, a customs officer and eight workmen, and injuring three others.[2]

Rack-a-ro

Rack-a-rock, which has been used very extensively in America, Siberia, and China, consists of cartridges of chlorate of potash, which are dipped just before use into a combustible oil. For this purpose nitro-benzene is used, or "dead oil," which consists chiefly of hydrocarbons from coal tar, or a mixture of the two. The chlorate cartridges are enclosed in small bags of cotton: before use these are placed in a wire basket suspended from a spring balance and dipped into a pail containing the liquid, until a quarter to a third of the weight of the chlorate has been taken up. The chlorate sometimes contains an addition of a few per cent. of iron oxide. Considerable quantities of Rack-a-rock were in store at Port Arthur and Dalny at the commencement of the Russo-Japanese War, and were used in the early operations.[3]

Prométhée is similarly issued in the form of compressed cartridges, and the French Government has refused to make it in the form of grains, as the danger of ignition by friction during manufacture and use would be greatly increased.[4] The Government has also refused to issue it ready impregnated with the "combustible," as it would then possess no advantage over Cheddite.[5]

[1] Vennin et Chesneau, p. 356.

[2] *A.R.*, 1909, p. 35.

[3] *S.S.*, 1908, p. 19.

[4] *P. et S.*, vol. xv., 1910, p. 130.

[5] *P. et S.*, vol. xv., p. 148.

An explosive of this sort has, however, been introduced recently in Germany in order to economize nitrates during the war.[1]

If a charge of Sprengel explosive be fired with a primer of black powder, it should be so made up that admixture is impossible: a compressed pellet of black powder wrapped in impermeable paper may be used for instance. The primer of black powder should be not less than 10 per cent. of the weight of the charge with a minimum of 25 g. (say 1 oz.).

Cheddite. It was discovered by E. A. G. Street, of the firm of Bergés, Corbin et Cie, that the dangerous sensitiveness of chlorate mixtures could be reduced by coating the chlorate with an oily material, such as castor-oil thickened by having a nitro-hydro-carbon dissolved in it.[2] Explosives made on this principle have been examined from time to time by the French Commission des Poudres et Salpêtres, and the manufacture of several has been undertaken by the State.[3] They are called Cheddites from Chedde, the place in Haute Savoie, where the above-named firm manufactures chlorates by electrolytic methods. It has been found necessary to keep the proportions of the various constituents within certain limits in order to produce an explosive that shall possess the right degree of sensitiveness and shall not be liable to exude oil. It was also found that the velocity of detonation of Cheddite varies considerably with the density to which it is compressed: with increase of density the velocity of detonation rises until it reaches a maximum and then falls rapidly. This fall is due to the fact that the explosive becomes very insensitive to detonation when the density exceeds a certain critical value, and this difficulty can only be overcome to a slight extent by the use of a stronger detonator. Some of the earlier preparations were found to increase in density on keeping and consequently to diminish in sensitiveness, but this was traced to the use of dinitro-toluene which had been insufficiently purified.[4] The nitro-body should not melt below 60°. else there is danger of exudation.[5] The explosives are easily compressed, and therefore there is danger of diminishing the sensitiveness too much if charges are rammed hard in the bore-hole.

Various attempts have been made to produce a satisfactory Cheddite in which the potassium chlorate is replaced by the cheaper sodium salt, which contains a larger percentage of oxygen, but the mixtures first made were found to be too insensitive, when the density exceeded quite a moderate amount, and very compressible. Moreover, sodium chlorate is very hygroscopic, and when ground gives rise to a great deal of dust, which makes the

---

[1] *S.S.*, 1915, pp. 55, 56.

[2] Eng. Pat. 9,970 and 13,724 of 1897; Ger. Pat. 100,522 of 1897.

[3] *P. et S.*, vol. xi., p. 22: vol. xii., p. 122, 130: vol. xiii., pp. 29, 144, 282; vol xiv., p. 33; vol. xv., pp. 212, 247.

[4] *P. et S.*, vol. xiv., p. 33.

[5] *P. et S.*, vol. xiii., p. 144.

worker's clothing and similar materials very inflammable.[1] The workers with this substance in the powder works at Vonges are obliged not only to change their clothes, but to have a complete bath when they leave off work.[2] However, it was found that a mixture containing 16 per cent. of dinitrotoluene and no nitro-naphthalene could be fired up to a density of 1·65 and was more powerful than the other types.[3] The following Cheddites are authorized in France :

	O1 Typ 41	O1 Typ 60 bis	O2 Typ 60 bis M	O5
Potassium chlorate . . .	80	80	79	—
Sodium chlorate . . .	—	—	—	79
Castor-oil	8	5	5	5
Mononitro-naphthalene . .	12	13	1	—
Dinitro-toluene	—	2	15	16
Paraffin	—	—	—	—
Price, Fr. per kg. . . .	2·10	2·10	2·30	—

The Cheddites most made in France are 0·2 (otherwise Cheddite No. 4), according to formula 60 bis M, and 0·5 (otherwise Cheddite No. 1).

Manufactu

In making Cheddite the nitro-compounds are first dissolved in the castor-oil at 80° C., and the finely powdered dry warm chlorate is then added gradually, whilst the mass is stirred with a wooden rod. The incorporation of a charge of 25 kg. lasts about ten minutes. The material is then carried to another building, where it is further mixed on a wooden board in a half-cold condition for another ten minutes, so as to get it in a suitable granular condition. Each particle of chlorate should be entirely coated with the oily mixture. The material is next sifted, and what is too fine is added to a later charge. That which is of the correct size is made into cartridges by ramming it into wooden moulds, from which it is transferred to paper cases. If the explosive contain sodium chlorate, the cases should then be dipped into molten paraffin to prevent the absorption of water. If the percentage of moisture rise above 1 per cent., the explosibility is impaired.

Cheddite is a soft yellowish material of fine grain, but is sometimes artificially coloured. In consequence of its plasticity it can easily be compressed. It is generally put up into cartridges 22 cm. long and 2·5 cm. diameter. Ched-

---

[1] *P. et S.*, vol. xiv., p. 26 ; vol. xv., p. 135.

[2] Vennin et Chesneau, p. 123.

[3] *P. et S.*, vol. xvi., p. 66.

dite 41 is a slow mild explosive, which splits rocks rather than shatters them. Cheddite 60 is more violent, and the Sodium Clorato Cheddite, O5, still more so. The velocity of detonation of Cheddite 60 was measured by Lheure [1] and found to be 3175 metres per sec., about half of that of picric acid, blasting gelatine, and other very high explosives, and that of O2 2750 metres per sec.[2]

Many other mixtures on the same principle as cheddite have been tried in France and elsewhere, such as O4, a mixture of 90 parts potassium chlorate and 10 paraffin wax.[3] Sébomite containing tallow and dinitro-benzene or nitro-toluene [4] O6 or minélite containing heavy petroleum, mineral jelly and paraffin wax.[5]

teelite.

"Steelite" consists essentially of potassium chlorate, the particles of which are enveloped in oxidized resin, which is made as follows: 9 parts of ground colophony are mixed with 1 part of starch, and to this mixture nitric acid of 1·41 specific gravity (67·5 per cent. HNO_3) is added at the ordinary temperature, without the addition of any sulphuric acid. An oxidized yellow amorphous mass is thus formed, which floats on the top of the acid. This is broken up, washed with water, dried at a moderate temperature, and ground up. It is not explosive without the addition of chlorate, and only burns with difficulty. It is mixed with the ground chlorate and other constituents in a drum with lignum vitæ balls. The mixture is spread on a zinc sheet in quantities of 1 to 5 kg. and sprinkled with methyl-alcohol, whilst it is raked about, so that a paste or dough may not be formed. It is kept in gentle motion with a wooden tool until it is dry.

Several samples of Steelite were examined by the French Commission des Substances Explosives, but it was decided not to undertake its manufacture on the ground that it possessed no advantages over Cheddite, than which it was more sensitive and less dense.[6] Colliery Steelite containing a small percentage of castor-oil passed the Woolwich test for safety explosives and was formerly on the English "permitted list."

ilesia.

In Germany this explosive is called "Silesia": unoxidized resin is apparently used in it sometimes, and to make it pass the Continental tests for safety explosives a considerable proportion of sodium chloride is added. The following are some of the compositions that have been made:

---

[1] *P. et S.*, vol. xii., p. 117.

[2] Vennin et Chesneau, p. 359.

[3] *See P. et S.*, vol. xv. pp. 212, 247, also 1st ed. of this work, p. 298, and Vennin et Chesneau, p. 359.

[4] *P. et S.*, vol. xiii., p. 280, and vol. xv., p. 136.

[5] *P. et S.*, vol. xv., p. 212; Vennin et Chesneau, p. 360,

[6] *P. et S.*, vol. xv., p. 181,

	Colliery Steelite	No. 3	No. 5	Silesia IV 22	Silesia 4
Potassium Chlorate .	72·5–75·5	75	79·2	70	80
Oxidized resin . .	23·5–26·5	25	15·8	8	20
Castor-oil . . .	0·5– 1	—	—	—	—
Aluminium . .	—	—	5	—	—
Sodium chloride . .	—	—	—	22	—
Moisture . . .	0 – 1	—	—	—	—

The Silesia explosive has a large excess of chlorate, and the gases produced contain 14·2 per cent of free oxygen.[1]

In Austria a chlorate explosive called Chloratit has been sanctioned for use in coal mines during the war.[2] It gives rise to bad fumes and is hygroscopic.

Chlorates should never be mixed with ammonium salts, as ammonium chlorate would be formed, and this is liable to explode spontaneously. Mixtures with picric acid or trinitro-cresol also should not be made, as they are very sensitive.

POTASSIUM PERCHLORATE EXPLOSIVES

The perchlorates possess the advantage over the chlorates, that they are more stable and less sensitive, although they contain a larger proportion of oxygen. Consequently explosives containing perchlorates do not require to have each particle encased in fatty matter, as is the case with chlorate explosives. Since the introduction of electrolytic methods of manufacturing perchlorates, these explosives have been used extensively. A certain amount is obtained as a by-product in working up Chili nitrate: 55 tons of potassium perchlorate were exported from Chile in 1914.

Permonite.

Explosives containing potassium perchlorate and ammonium nitrate together with trinitro-toluene, starchy matter and wood-meal, are made by the Sprengstoff-A.-G. Carbonit under the name of "Permonite." One of these compositions was formerly on the English "permitted list," and another is on the Belgian list of Explosifs S.G.P. Gesteins-Permonit is used in potash and ore mines. The following are the compositions, together with other particulars as stated by the makers:

---

[1] *See* Escales, *Chloratsprengstoffe*, 1910, p. 143.

[2] *S.S.*, 1915, p. 294.

	Permonit I or Gesteins-Permonit	Permonite S.G.P.	Permonite (Permitted List)
Potassium perchlorate	30	24·5	31 –34
Nitro-glycerine	—	6	3 – 4
Collodion cotton	—	—	0·5– 1
Ammonium nitrate	40	29	39 –43
Sodium nitrate	7	—	—
Trinitro-toluene	15	7	11 –13
Sodium chloride	—	25	—
Flour	4	4	—
Starch	—	—	5 – 9
Wood-meal	3	3	1·5– 3·5
Jelly	1	1	—
Moisture	—	—	0 – 2·5
Influence test	70 mm.	100 mm.	80 mm.
Trauzl test	320 c.c.	205 c.c.	365 c.c.
Velocity of detonation	3470 m/sec.	2326 m/sec.	—
Sensitiveness, 2 kg. weight	70 cm.	80 cm.	20 cm.
,, 10 kg. ,,	5	10	—

The "charge limite" of Permonite S.G.P. is 900 g., equivalent to about 570 g. of dynamite No. 1.

The "jelly" is a mixture of 1 part glycerine and 3·5 parts gelatine: the influence test consists in ascertaining the distance over which detonation is conveyed from one 30 cm. cartridge to another lying on the ground. Another German explosive similar to Permonit, but not so powerful, is Wetter-Persalit.

Alkalsit, Polarite, Another very similar explosive made in Germany is Alkalsit. Polarite, a non-freezing explosive of high power, is used in England as a substitute for Gelignite.

Several explosives containing potassium perchlorate have passed the Rotherham test, and are on the English Permitted List. They differ from the Permonites in that they contain a larger proportion of nitro-glycerine and wood-meal, and the ammonium nitrate has been replaced by oxalate, so that they are not hygroscopic. The result is that instead of an excess of available oxygen they contain a slight deficit.

The general method of manufacturing these explosives is as follows: The oxalate, perchlorate and wood-meal are all sifted and placed in a pan and mixed together roughly by hand. The nitro-glycerine, which has been partially gelatinized with the collodion cotton the day before, is poured on top, the last portion of jelly being wiped out with some wood-meal which has been kept back for this purpose. The composition is then incorporated in a gelatine incorporator for about an hour at a temperature not higher than 30°.

	Dynobel	Neonal	Neonal No. 1	Ajax Powder	Swale Powder
Potassium perchlorate . .	27	37	14	37·2	37·5
Nitro-glycerine . . .	32·5	21	40	22·5	19
Collodion cotton . . .	0·7	0·8	2·8	0·8	1
Di- and tri-nitro-toluene . .	—	0·2	—	3·5	4
Ammonium oxalate . . .	29·5	25	39	25	28
Wood-meal	10·3	16	5	11	10·5
Maximum charge . . .	22 oz.	16 oz.	30 oz.	12 oz.	20 oz.
Power (swing of bal. pend.) .	2·61″	2·56″	2·51″	2·69″	2·50″

The addition of nitro-toluenes renders the explosives less liable to freeze.

M.B. powder

A different type of perchlorate explosive is represented by M.B. Powder (Modified Black), which consists of black powder in which part of the saltpetre has been replaced by potassium perchlorate. It is made in much the same way as Safety Blasting Powder was, that is to say the ingredients, after a preliminary mixing, are incorporated together in a steam-jacketed pan. On November 25, 1911, a severe fire occurred in the house where this operation was being carried out, whereby three men were killed and one was injured. It was ascribed to friction on dry caked material in the steam-heated incorporator. Another similar explosive is Roslin Giant Powder.

AMMONIUM PERCHLORATE EXPLOSIVES

As a constituent of an explosive, ammonium perchlorate possesses the advantage that it contains a high proportion of available oxygen and only produces gaseous products, but unfortunately these include the poisonous gas hydrogen chloride. The formation of this can be prevented by adding an equivalent quantity of some substance such as sodium nitrate, which will yield a base to combine with the chlorine. In 1906 the French "Commission des Substances Explosives" investigated two Cheddites containing ammonium perchlorate, and although it was decided not to undertake their manufacture some of the experiments are instructive.[1] The explosives had the compositions :

	I.	II.
Ammonium perchlorate	82	50
Dinitro-toluene	13	15
Sodium nitrate	—	30
Castor-oil	5	5

---

[1] *P. et S.*, vol. xiv., pp. 192, 206.

No. I burns with dangerous rapidity when ignited, but II is quite safe in this respect. Fabrics impregnated with ammonium perchlorate are more inflammable than when potassium chlorate is used, but not so much so as with sodium chlorate. Ammonium perchlorate is a mild explosive by itself, but is only exploded with difficulty and incompletely: at ordinary temperatures it is stable, but at 150° decomposition sets in after a time and proceeds according to the equation: $NH_4ClO_4 = Cl + O_2 + N + 2H_2O$ (gaseous) + 38·3 cal. The reaction is apparently auto-catalytic.[1] It is very important that ammonium perchlorate be kept quite separate from the chlorates of sodium and potassium, as dangerous double decompositions are liable to

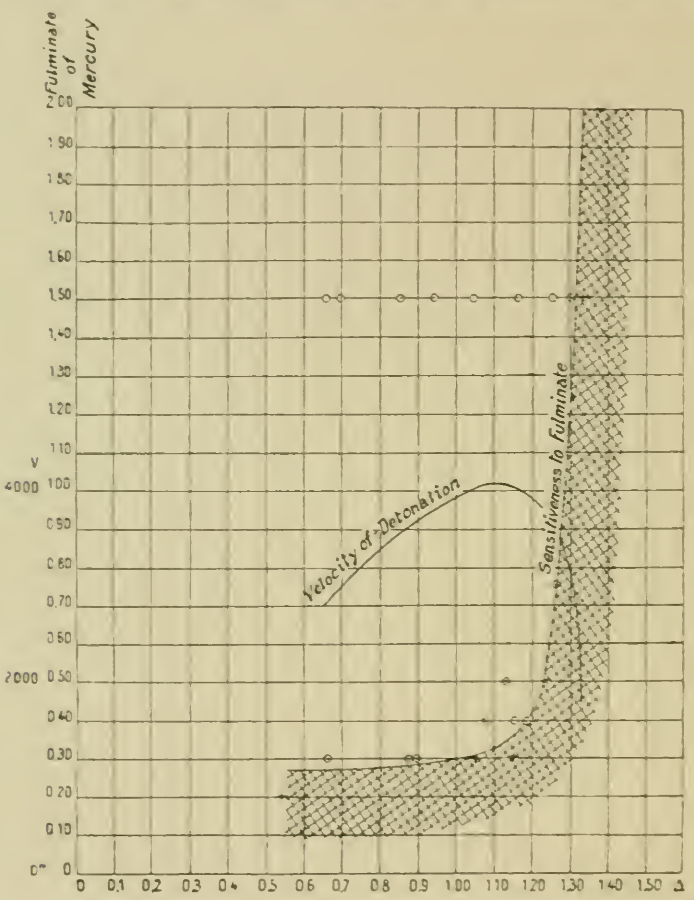


FIG. 78. Detonation of Ammonium Perchlorate Cheddite at Different Densities

---

[1] *See* Girard and Laroche, *Moniteur scientifique*, April, 1909; *S.S.*, 1910, p. 134.

occur. Ammonium perchlorate has about the same degree of sensitiveness to impact as picric acid: a 5 kg. weight falling 50 c.m. causes explosion sometimes. As in the case of other Cheddites the velocity of detonation rises with increase of density to a maximum, after which it falls in consequence of the diminution of the sensitiveness to detonation. This is clearly shown by the curves in Fig. 70, which gives the velocities of detonation and the weights of fulminate required to detonate explosive I, when loaded into cartridges at different densities.

Yonckite.

A number of explosives of this type were made in Belgium under the name of Yonckites. One of these No. 10 bis is on the Belgian list of Explosives S.G.P., No. 13 is of a more brisant type:

	10 bis	13
Ammonium perchlorate	25	20
Ammonium nitrate	30	27
Sodium nitrate	15	27
Barium nitrate	—	6
Trinitro-toluene	10	20
Sodium chloride	20	—

The "charge limite" of 10 bis is 900 g., equivalent to 540 g. dynamite No. 1. To make these explosives the perchlorate and nitrates of sodium and barium are milled together, as also are the ammonium nitrate and trinitro-toluene. The two mixtures are then incorporated together in a Pfleiderer machine. These explosives were examined by the French Commission des substances explosives, but it was decided that they possessed no marked advantage over the Cheddites.[1]

Blastine.

An explosive which is now being used extensively is Blastine, in which ammonium perchlorate and sodium nitrate are mixed with the combustible matters, dinitro-toluene and paraffin wax.

---

[1] *P. et S.*, vol. xvii., p. 170; Vennin et Chesneau, p. 362.

CHAPTER XXVII

AMMONIUM NITRATE EXPLOSIVES

Favier explosives : Grisounites : Ammonals : Sabulite : Grisoutine

ATTENTION was first drawn prominently to the use of ammonium nitrate as a constituent of explosives in consequence of the numerous explosions of coal damp and dust in mines. The low temperature of explosion of mixtures containing large proportions of ammonium nitrate indicated its use for this purpose. Ammonium nitrate explosives are used now very extensively, not only in coal mines, but also for general blasting work, and the introduction of synthetic methods for the manufacture of ammonia and nitric acid is likely to lead to further developments in this direction. In 1884 and 1885 Favier took out patents for mixtures of ammonium nitrate with mononitro-naphthalene, paraffin and resin.[1] The manufacture was soon afterwards undertaken by the French Government and is still continued under the name of Explosifs N, or Explosifs Favier, or Poudres de sûreté.

Favier explosives.

Manufacture.

The ammonium nitrate is first dried and then ground in a mill, the pan of which is heated by steam or hot water. The nitro-naphthalene is then added, and the incorporation is carried on for an hour or two in a warm dry room. The mass is then allowed to cool and is ground to a powder, after which it is loaded into cartridges.[2] In some cases the cartridges are formed under considerable pressure, but in that case it is necessary to remove the core and introduce a primer of the powdered explosive, because if the density be too high, the explosive is very difficult to detonate. In other cases the cartridges are formed under a moderate pressure only, such as that produced by an Archimedean screw working against a slight resistance. The cartridges are contained in wrappers of metal-foil or paper rendered waterproof by dipping in a bath of paraffin-wax. According to the German regulations for the manufacture of ammonium nitrate explosives the temperature of the wax bath must not exceed 100° C. Waterproofing is absolutely necessary because ammonium nitrate is extremely hygroscopic.

Explosifs N or Grisounites.

The composition of the Favier explosives made in France has been varied

---

[1] Ger. Pat. 31,411 of May 27, 1884 ; Eng. Pat. 2139 of February 16, 1885.

[2] *See also P. et S.*, vol. iv., p. 159.

from time to time. The following were the authorized compositions of Explosifs N according to Vennin et Chesneau, pp. 345, 562.

	Grisou-naphtalite-couche		Grisou-naphtalite-roche		Grisou-tetrylite-couche	For mines free from fire-damp, etc.
	N_1a	N_4	N_1b			N_1c
Ammonium nitrate . .	95	90	91·5	86·5	88	87·4
Potassium nitrate . .	—	5	—	5	5	—
Dinitro-naphthalene . .	—	—	8·5	8·5	—	12·6
Trinitro-naphthalene . .	5	5	—	—	—	—
Tetryl	—	—	—	—	7	—

The Grisounites-couches are used in the coal seams as they have theoretical temperatures of explosion of 1500° or less, but N_1a has been replaced to a considerable extent by N_4; these are both coloured with methylene green B. The Grisounites-roches have theoretical temperatures of explosion of 1900° or less, and are for use in the rocks in coal mines; N_1b is dyed rose colour, and N_1c pale yellow.

The sensitiveness of these explosives diminishes rapidly with increasing density; thus for the detonation of an explosive composed of 90 per cent. ammonium nitrate and 10 per cent. mononitro-naphthalene detonators containing the following weights of fulminate were required:[1]

Density of explosive	Weight of fulminate
0·9	0·4 g.
1·0	1
1·1	2
1·2	5
above 1·2	misfires

The following are some of the principal explosives that passed the Woolwich test and so obtained a place on the Permitted List:

	Ammonite	Westfalite		Bellite		Roburite
		1	2	1	3	3
Ammonium nitrate . .	88	95	91	83·5	93·5	88
Potassium nitrate . .	—	—	4	—	—	—
Dinitro-naphthalene . .	12	—	—	—	—	—
Dinitro-benzene . .	—	—	—	16·5	6·5	11
Chloro-naphthalene . .	—	—	—	—	—	1
Resin	—	5	5	—	—	—

---

[1] Gody, p. 594.

In order to pass the Rotherham test, in which the explosive is fired without stemming into the gas mixture, the compositions have had to be modified somewhat :

	Ammonite	Bellite		Faversham Powder	Negro Powder	Roburite
	No. 1	No. 2	No. 4	No. 2	No. 2	No. 4
Ammonium nitrate . .	75	61	66	47·5	57	61
Potassium nitrate . .	—	—	—	24	—	—
Trinitro-toluene . .	5	—	—	10	15	16
Dinitro-benzene . .	—	12	14	—	—	—
Ammonium chloride . .	—	—	—	18·5	—	—
Sodium chloride . .	20	27	20	—	27·5	23
Graphite	—	—	—	—	0·5	—
Limit charge . . .	24 oz.	32 oz.	18 oz.	24 oz.	24 oz.	18 oz.
Power (swing of bal. pend.)	2·42″	2·42″	2·92″	2·61″	2·21″	2·86″

In Belgium the following are on the list of Explosifs S.G.P. :

	Densite 4	Favier 3 bis	Densite 3	Poudre blanche Cornil 1 bis	Favier 2 bis	Fractorite B	Minolite anti-grisouteuse
Ammonium nitrate . .	18	60	74	77	77·6	75	72
Potassium nitrate . .	45·5	11	—	1	—	—	—
Sodium nitrate . .	—	—	22	—	—	—	23
Potassium permanganate .	—	0·5	—	—	—	—	—
Lead chromate . .	—	—	—	1	—	—	—
Trinitro-toluene . .	19	8·5	4	—	—	—	3
Trinitro-naphthalene .	—	—	—	—	—	—	2
Dinitro-naphthalene .	—	—	—	3	2·4	2·8	—
Flour	—	6	—	—	—	—	—
Ammonium oxalate . .	—	—	—	—	—	2·2	—
Alum	—	5	—	—	—	—	—
Ammonium chloride. .	17·5	4	—	18	20	20	—
Barium carbonate . .	—	5	—	—	—	—	—
Charge limite g. . .	850	750	700	500	500	450	400
Equivalent, Dyn. No. 1	549	452	310	305	293	286	236

The following are the results given by some German safety explosives tested at the Gelsenkirchen testing station :[1]

	Roburit		Neu-Westfalit	Glückauf	
	II[2]	III		AI	AIII
Ammonium nitrate	71·5	55	70·3	70·4	82·7
Potassium nitrate	5	9·5	—	10	—
Potassium permanganate . . .	0·5	0·5	—	—	—
Dinitro-benzene	—	—	—	1	1
Dinitro-toluene	—	—	10·9	—	—
Trinitro-toluene	12	12	—	—	—
Wood-meal	—	—	—	6·4	11·5
Flour	6	6	2	—	—
Fennel (?)	—	—	—	7·2	—
Ammonium chloride . . .	—	5	—	—	—
Sodium chloride	5	7	16·8	—	—
Magnesite	—	5	—	—	—
Copper oxalate	—	—	—	5	4·8
Limit charge, g. . . .	350	650	540	400	450
Trauzl test, c.c.	325	257	309	312	341

Other German Favier explosives are :

	Dahmenit	Dorfit		Aldorfit	Fulmenit	Wetter-Fulmenit
		I	II			
Ammonium nitrate . .	91·3	65	61	81	86·5	76·5
Potassium nitrate . .	—	5	5	—	—	—
Potassium bichromate .	2·2	—	—	—	—	—
Gun-cotton	—	—	—	—	4	4
Trinitro-toluene . .	—	6	15	17	5·5	5·5
Paraffin oil	—	—	—	—	2·5	2·5
Rye flour	—	4	4	2	—	—
Naphthalene	6·5	—	—	—	—	—
Charcoal	—	—	—	—	1·5	1·5
Sodium chloride . . .	—	20	15	—	—	10
Limit charge, g. . .	—	532	300	—	—	—
Trauzl test, c.c. . .	—	172	219	—	—	—

---

[1] *S.S.*, 1907, p. 13.

Of these Aldorfit and Fulmenit are not intended for use in dangerous coal-mines. Dorfit and Wetter-Fulmenit differ from them in containing considerable percentages of sodium chloride which reduces the temperature of explosion. Monachit contains crude trinitro-xylene made by nitrating a fraction of benzol. The nitro-product may be solid or liquid, but must not contain more than 60 per cent. of trinitro-bodies :

	Monachit I	Monachit IId
Ammonium nitrate	81	64
Potassium nitrate	5	3
Sodium nitrate	—	
Trinitro-xylene	13	12
Collodion cotton	—	1
Flour	1	—
Charcoal	—	1
Alkali chloride	—	19

Monachit IId has a limit charge of more than 500 grammes.[1]

Under the name of Raschit, Raschig has recently introduced a number of explosives containing ammonium nitrate and highly soluble organic substances such as ammonium mononitro-cresol-sulphonate, sodium cresol-sulphonate, or the residue obtained in the manufacture of wood cellulose. The incorporation is carried out by dissolving the constituents in water and evaporating the solution rapidly on a rotating steam-heated drum.

An ammonium nitrate explosive manufactured in Denmark under the name of Aerolit has the composition :

Ammonium nitrate	78·125
Potassium nitrate	7·5
Sulphur	8·75
Fat (beef suet)	2·5
Sago flour	1·25
Manganese dioxide	1·25
Resin	0·625
	100

The sulphur, fat, resin and manganese dioxide are melted together, and the potassium nitrate and flour stirred in, and the mass is allowed to cool and is powdered. Then the ammonium nitrate is added and the mixture is again melted, cooled and powdered.[2]

The Austrian Government manufacture as safety explosives :

	Dynammon	Wetter-Dynammon
Ammonium nitrate	87–88	94
Potassium nitrate	—	2
Charcoal	12–13	4
Density	0·9	0·85

---

[1] *S.S.*, 1909, p. 106. For the velocity of detonation of Monachit I, *see* H. Kast, *S.S.*, 1913, p. 136.

[2] Danish Pat. 19,858, *S.S.*, 1905, p. 295.

The idea of utilizing the great amount of heat energy that is liberated in the oxidation of aluminium has formed the subject of patents taken out by G. Roth, of Vienna,[1] and mixtures of ammonium nitrate, aluminium, and other substances have been brought on the market mostly under the name of Ammonal. In spite of the high temperature produced by the oxidation of aluminium three of these compositions were able to pass the Woolwich test. **Ammonal.**

	Ammonal B	Ripping Ammonal	St. Helens powder
Ammonium nitrate	93–95·5	84–87	92–95
Aluminium	2·5–3·5	7–9	2–3
Charcoal	2–3	2–3	—
Trinitro-toluene	—	—	3–5
Potassium bichromate	—	3–4	—
Moisture	0–1	0–1	0–1

For safety in coal-mines it is necessary to keep down the percentage of aluminium. In Ripping Ammonal the safety is increased by the addition of potassium bichromate, and consequently the proportion of aluminium can be increased.[2] For ordinary blasting purposes compositions such as the following are used:

Ammonium nitrate	72	47
Aluminium	25	22
Charcoal	3	1
Trinitro-toluene	—	30

Ammonal is an explosive of considerable power.[3] The velocity of detonation of an Ammonal was found by Bichel to be 3450 metres per second. The aluminium powder used for making ammonal should not be too fine.[4] The density of ammonal is usually about 1 or slightly more.

Two explosives of this class are manufactured in Germany under the name of Gesteins-Westfalit B and C: B contains dinitro-benzene and C dinitro-toluene. Roth's Ammonal patent has been contested in Germany, but on June 24, 1911, it was confirmed by the Courts.

In Switzerland an explosive similar to Gesteins-Westfalit C is made under the name of Telsit A.

---

[1] Ger. Pat. 172,327 of June 28, 1900; Eng. Pat. 16,277 of September 13, 1900.

[2] Eng. Pat. 16,514 of 1905, W. Macnab and Ammonal Explosives Ltd.

[3] *See* Bichel, *Ang.*, 1905, p. 1889; also *S.S.*, 1906, p. 26; Rudolph, *Kriegstechnishe Zeitschrift*, 1907, p. 233; Bravetta, *S.S.*, 1906, p. 199, and 1907, p. 13.

[4] P. Hess, *Ang.*, 1904, p. 551.

The Ammonals manufactured at the Felixdorf Powder Works in Austria (G. Roth A.G.) have the following composition :

	a	b	c	d
Ammonium nitrate	80·75	90	88	80
Aluminium	15	4	8	18
Charcoal	4·25	6	4	2

Ammonal is not allowed to be used in fiery mines, but only where dynamite would be permitted.[1]

The effect of adding aluminium to an ammonium nitrate explosive was investigated by Bichel,[2] who obtained the following results :

	Dynammon	Ammonal
Explosive :		
Ammonium nitrate	95·5	72·0
Aluminium	—	23·5
Charcoal (red)	4·5	4·5
Density	·865	·900
Velocity of detonation, m/sec.	3380	3450
Heat of explosion in calorimeter	727·0	1600·5 Cal.
Products of explosion :		
Carbon dioxide	13·14	7·00
Carbon monoxide	—	4·57
Water	49·60	14·14
Oxygen	2·60	—
Nitrogen	34·66	28·47
Methane	—	0·25
Hydrogen	—	1·19
Aluminium oxide	—	44·38
Volume of permanent gas, N.T.P.	360	418 litres/kg.
,, water vapour	617	176
Total volume	976	594
Explosion pressure (calculated)	6338	9425 kg/sq.cm.
Trauzl test	250	329 c.c.

Bichel considers that the results of the Trauzl test are misleading, because the great heat of the explosion in the case of the aluminium explosive melts the surface of the lead and so makes the apparent expansion of the hole greater. The Felixdorf Powder Works contend, however, that ammonal is a very powerful explosive : when exploded on top of a small lead cylinder, it compresses it considerably more than a gelignite containing 65 per cent. nitro-

---

[1] *S.S.*, 1910, p. 54.

[2] *Ang.*, 1905, p. 1889.

glycerine, and it breaks up a shell more than an equal weight of cast picric acid.[1] The French Commission des Substances Explosives found that the addition of aluminium does not greatly increase the useful effect on rock, but it makes the explosive easier to detonate even if only 3 per cent. be present.[2]

Sabulite.

A somewhat similar explosive is Sabulite which contains calcium silicide and trotyl with or without the addition of potassium nitrate and ammonium chloride, the latter constituents being added to make it safe in coal mines. On the Belgian list of Explosifs S.G.P. is:

	Sabulite antigrisouteuse A
Ammonium nitrate	54
Potassium nitrate	22
Calcium silicide	5
Trotyl	6
Ammonium chloride	13
Maximum charge	900 g.
Equivalent to	596 g. dynamite No. 1.

Grisoutine

The only explosives allowed in the more dangerous French coal-mines, in addition to the Grisounites, are the Grisoutines (otherwise Grisou-dynamites), which consist of ammonium nitrate mixed with blasting gelatine. As the State monopoly does not extend to explosives containing nitro-glycerine, these are made by private firms, but the compositions are regulated by the State. In 1911 the "Commission des Substances Explosives" resolved that the compositions should be unified as follows:

	Couche	Couche au Salpêtre	Roche	Roche au Salpêtre
Nitro-glycerine	12·0	12·0	29	29
Collodion cotton	0·5	0·5	1	1
Ammonium nitrate	87·5	82·5	70	65
Potassium nitrate	—	5·0	—	5

The calculated temperatures of explosion of the Grisoutines Couche are below 1500°, those of the Grisoutines Roche below 1900°. The addition of 5 per cent. saltpetre instead of the same quantity of ammonium nitrate has been found to increase the safety, probably because the potassium compounds formed are dissociated and vaporized at the temperature of explosion, and afterwards give up again the energy they have absorbed, so that the effect is not very much less. It is estimated that the explosives with 5 per cent. potassium nitrate are about 5 per cent. weaker than the others.[3]

A number of explosives similar to these passed the Woolwich test and

---

[1] *S.S.*, 1906, p. 26. *See also* Rudolph, *Kriegstechnische Zeitschrift*, 1907, p. 287; *S.S.*, 1907, p. 314.

[2] Vennin et Chesneau, p. 314.

[3] *See P. et S.*, xv., pp. 189, 190.

were formerly on the Permitted List. Monobel, one of the principal ones, had the composition :

Nitro-glycerine	9–11
Ammonium nitrate	78–82
Wood-meal	8–10
Moisture	0·5–2·5

To pass the more severe Rotherham test it has been found necessary in most cases to add sodium chloride or ammonium oxalate :

	Monobel		Super-Excellite			Monarkite
	No. 1	No. A1		No. 2	No. 3	
Nitro-glycerine	8·5	10	74·5	5	9·5	12
Collodion cotton	—	—	—	—	0·5	0·3
Ammonium nitrate	68	60	75·5	50	59	49·7
Potassium nitrate	—	—	7	20	—	—
Sodium nitrate	—	—	—	—	—	7·5
Wood-meal	8·5	10	—	—	—	—
Starch	—	—	3·5	5	4·5	4
Ammonium oxalate	—	—	10	15	10·5	—
Sodium chloride	15	—	—	—	15	24·5
Potassium chloride	—	20	—	—	—	—
Ammonium chloride	—	—	—	5	—	—
Castor oil	—	—	—	—	1	—
Mineral jelly	—	—	—	—	—	2
Limit charge	10 oz.	28 oz.	10 oz.	14 oz.	36 oz.	26 oz.
Power (swing of bal. pend.)	2·81″	2·78″.	2·74″	2·72″	2·73″	2·61″

On the Belgian list of Explosifs S.G.P. are the following :

	Fractorite D	Flammivore III	Ammon-carbonite
Nitro-glycerine	4	6	4
Ammonium nitrate	75	70	82
Potassium nitrate	—	—	10
Sodium nitrate	10	—	—
Ammonium oxalate	7	—	—
Carbohydrates	4	8	4
Ammonium sulphate	—	9	—
Barium sulphate	—	7	—
Charge limite	700	650	300
Equivalent, Dyn. No. 1	420	382	191

There is also Colinite antigrisouteuse B, which is a gelignite containing ammonium nitrate and other constituents

Nitro-glycerine	25
Collodion cotton	1
Ammonium nitrate	20
Potassium perchlorate	6
Trinitro-toluene	12
Cellulose and flour	29
Magnesium sulphate	7
Charge limite	800
Equivalent, Dyn. No. 1	460

Of German Grisoutines the following may be mentioned:

	Salit	Tremonit	Donarit	Ammon-karbonit I
Nitro-glycerine	11·8	—	3·8	4·0
Dinitro-glycerine	—	33·0	—	—
Collodion cotton	0·5	1·0	0·2	0·2
Ammonium Nitrate	53·6	26·5	80·0	80·3
Potassium nitrate	—	—	—	5·0
Dinitro-toluene	8·5	—	—	—
Trinitro-toluene	—	2·5	12·0	—
Sodium chloride	23·1	25·0	—	—
Carbohydrates	2·5	12·0	4·0	4·5
Coal dust	—	—	—	6·0
Charge limite	660	730	130	300
Trauzl test	287	268	450	355

	Astralit	Wetter-Astralit
Nitro-glycerine	4	4
Ammonium nitrate	84·5	74·5
Sodium chloride	—	10
Trinitro-toluene	7	7
Wood-meal	1	1
Charcoal	1	1
Paraffin oil	2·5	2·5

Gelatine-Westfalit is a low-freezing safety nitro-glycerine explosive containing not more than 50 per cent. dinitro-chlorhydrine and 5 per cent. nitro-glycerine gelatinized with a small proportion of collodion cotton, and containing ammonium nitrate, not more than 10 per cent. saltpetre, together with hydrocarbons, vegetable meal, neutral salts and nitro-compounds.

In Austria an explosive called Pannonit is made:

Nitro-glycerine	25·5
Collodion cotton	1·5
Ammonium nitrate	37
Dextrin	4
Glycerine	3
Nitro-toluene	5
Alkali chloride	24

A little caput mortuum is added as colouring matter, and the explosive is fired with a special detonator containing trotyl.[1] It replaced a former explosive consisting of ammonium nitrate, aniline hydrochloride and sometimes ammonium sulphate.[2]

---

[1] *S.S.*, 1913, p. 398.

[2] *S.S.*, 1907, p. 112.

INDEX OF NAMES

INDEX OF SUBJECTS

Butler & Tanner Frome and London

D

5/4/01
H