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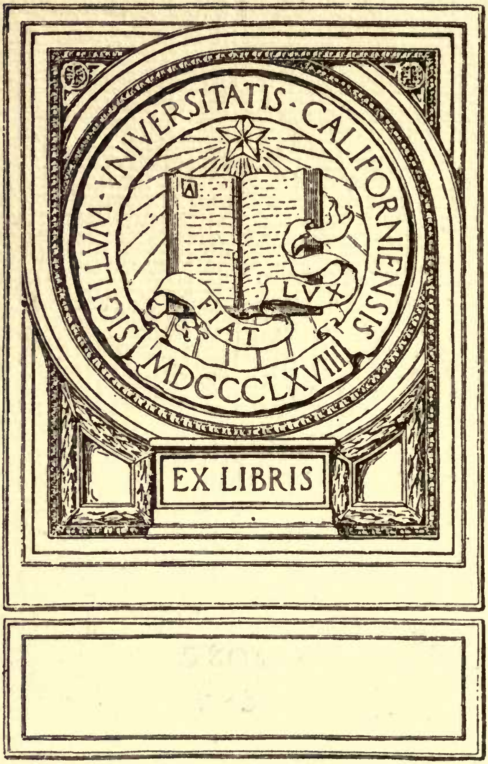
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# CHEMICAL MONOGRAPHS

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## No. III

# The Chemistry of Rubber

# CHEMICAL MONOGRAPHS

EDITED BY A. C. CUMMING, D.Sc.

THE progress of Chemistry is so rapid that it is becoming a matter of ever-increasing difficulty to keep abreast of the modern developments of the science. The volume of periodical literature is so enormous that few can hope to read, far less assimilate, all that is published. The preparation of summaries has therefore become a necessity, and has led to the publication of various well-known journals devoted to the abstraction of original papers. For obvious reasons, however, these do not fully supply the wants of advanced students and research workers, and it is now generally recognised that monographs on special subjects are also needed.

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# THE CHEMISTRY OF RUBBER

BY

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*Castle Mills, Edinburgh.*

GURNEY & JACKSON
33 PATERNOSTER ROW, LONDON, E.C.
1913

# AUTHOR'S PREFACE

THE author hopes that this monograph will be found to contain a concise and accurate account of the Chemistry of Rubber.

In the colloid industries the problems which confront both the manufacturer and the chemist are exceedingly complex, and the scientific knowledge available for their solution is in many cases very incomplete.

In almost every direction there is ground for controversy. Every endeavour has been made in the following pages to give an impartial review of the published work, and at the same time views have been advanced which, in the judgment of the author, are most in accord with the facts.

The monograph is intended for those interested in rubber from a chemical point of view, and the description of technical practice has, therefore, been limited to the details which are necessary for a clear insight into the chemical questions involved.

The author desires to express his thanks to Mr F. D. Miles, B.Sc. (Lond.), A.R.C.Sc., who is responsible for Sections II. and IV., and to Mr B. D. W. Luff, F.I.C., for much valuable advice and criticism. He wishes also to acknowledge his great indebtedness to Mr Alexander Johnston, General Manager, and Mr W. A. Williams, F.C.S., General Works Superintendent, North British Rubber Co., Ltd.

B. D. PORRITT.

Castle Mills,
Edinburgh, *June* 1913.

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# The Chemistry of Rubber

## SECTION I.

### The Properties of Crude Rubber.

India Rubber, Rubber or Caoutchouc * is a hydrocarbon prepared from a watery emulsion termed "Latex" present in the bark of many tropical and sub-tropical trees. Gutta-percha and Balata, obtained in a similar manner, are closely related to rubber, but differ somewhat in their physical properties. In certain cases, however, such as the Guayule shrub and some African roots, the rubber is found deposited in the wood, and for its removal suitable mechanical treatment or the use of solvents is necessary.

Vegetation producing rubber latex is of a very varied character, belonging chiefly to the following botanic orders:—Euphorbiaceæ, Apocynaceæ, Urticaceæ, Compositæ. Amongst commercial rubber-producing trees we may notice such diverse examples as the *Hevea Brasiliensis,* which reaches 60 feet high

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* Throughout this monograph the term "Rubber" will be applied to the technical product, while "Caoutchouc" will be reserved for the chemically purified substance.

and requires a moist, tropical climate such as prevails in the Amazon Valley; the *Manihot Glaziovii*, or Ceara tree, of equal size, which will thrive on rocky and dry situations; the Guayule shrub, from 2 to 3 feet high, suited by almost desert conditions; and the *Landolphias*, a very varied family of vines, often encircling the tops of the highest trees in the moist, tropical climate of many portions of Africa.

The function of the latex in the physiology of the plant is evidently of importance, as is evidenced by the wide distribution of rubber-yielding vegetation. No satisfactory explanation of its function has been put forward, but it may be reserve food material,[33] provide a protection against bark injury,[55] or be a waste product of metabolism.

The latex as obtained by making incisions in the bark is an opaque white liquid, consisting of an emulsion of rubber globules in a watery fluid. The size of these globules varies, according to the species, from 0·5 to 3 $\mu$.[57]

The composition and yield of the latex probably depend on the season of the year, the age of the tree, and the frequency of tapping, but the following figures give a general indication of its composition :—

| | Ceylon.[171] | | *Funtumia elastica.*[172] | *Ficus elastica.* | *Castilloa elastica.* |
|---|---|---|---|---|---|
| | A. | B. | | | |
| Rubber . | 41·29 | 32·00 | 40·72 | 37·3 | 31·2 |
| Resin . | ... | 2·03 | 4·46 | 2·4 | 5·0 |
| Protein . | 2·18 | 2·03 | 3·25 | 0·4 | 0·2 |
| Ash . . | 0·41 | ... | 0·99 | 0·4 | 0·9 |
| Sp. gr. . | ... | ... | 0·979 to 0·988 | ... | ... |

**Coagulation.**—By suitable treatment the globules of rubber may be caused to coalesce; the methods generally employed by the collector to obtain the rubber from the latex are :—heat and smoking (Para), boiling (Funtumia), natural drying on the bark (Ceara), dilution with water (Kickxia), and treatment with acid, the last being in general use for plantation rubbers.[154]

The stability of the latex, like that of any other emulsion, depends on a number of factors, such as the mass and electrical charge of the particles, the presence of protective colloids, etc.

On examining the methods used for coagulation of rubber latex, we shall see that in general they depend on the removal of proteins or peptones, which in this instance serve as the protective colloid,[56] and the neutralisation of the electrical charges of the suspended particles.

Usually the addition of a small quantity of acid is sufficient to ensure coagulation, but Funtumia latex is interesting in that it fails to respond to the usual methods of coagulation.[41] The explanation of this was found to lie in the presence of a peptone and not a protein, and if this protective agent is removed by the addition of formalin or mercuric chloride coagulation takes place readily. At the same time the stability of Funtumia latex appears also to depend on the small size of the globules, for Spence has removed the peptone by treatment with trypsin without coagulation resulting,[135] and a similar result has been found in the case of the protein in Castilloa latex.[68]

On examining latex under high magnification the globules are seen to be in rapid random motion, a phenomenon termed "Brownian movement." This property has been utilised by V. Henri[173] to study the effect produced on Hevea latex by the addition of different reagents. The velocity of the particles was greatly diminished by acids and, to a less extent, by alkalis. On increasing the acidity the particles could be seen to range themselves in chains forming a network. A certain amount of "agglutination" took place with alkalis and salts, but this was reversible and differed from the permanent coagulation produced by acids, alcohol, and acetone.

The method of coagulation and the quantity of reagent used appear to be important factors in determining the quality of the resultant rubber,[23, 117, 130, 62] and special attention requires to be paid to this point to obtain a uniformly good product. Whether this is due to differences in the reticular structure formed by the globules, or the state of aggregation of the molecules, cannot as yet be decided. It is remarkable that Para rubber, produced by a primitive process in the Amazon, should be superior to that prepared under careful scientific control and supervision from the same species of tree in Asia.

## Constituents of Crude Rubber.

As ordinarily obtained from the latex, rubber is far from being a simple substance; under the most careful conditions of collection and coagulation which obtain on plantations, the resultant product will not contain more than 95 per cent. of pure caoutchouc, and for wild rubbers the figure falls much lower. Some of the following substances which may be derived from either the latex or sap vessels will be found present in crude rubber from any source:—

(1) Resins.
(2) Nitrogenous bodies, proteins, peptones.
(3) Carbohydrates and colouring matters.
(4) Inorganic matter.

At the same time the following substances may or may not be present, according to the method and care exercised in coagulation:—

(5) Dirt, bark, and sand.
(6) Moisture.
(7) Free acid and mineral matter introduced by coagulating agents.

**Resins.**—The function served by the resins is at present uncertain. At first sight they would be put down as oxidation products of the rubber, but, as the amount is a constant for each variety, this appears improbable. In contrast to caoutchouc, the majority are found to be optically active, a fact which renders such a view almost untenable and also provides a means for the location of the botanical source of the crude material.[92]

| Variety. | $[\alpha]_D$. | Variety. | $[\alpha]_D$. |
|---|---|---|---|
| Para | nil | Pedang | +28°-30° |
| Upper Congo | +12°-13° | Guayule | +11°-15° |
| Manaos | +16°-18° | Kassai | +29°-30° |
| Peruvian | +29°-31° | Balata | +26°-28° |
| Dead Borneo | +49°-50° | Gutta-percha | +46° |

A considerable amount of work also has been done on the iodine values and products of hydrolysis of the resins from a variety of crude rubbers.[92]

Resins exert an undoubted influence on the course of vulcanisation, and they constitute a considerable bye-product in the preparation of certain rubbers, for instance, Gutta-percha and Balata (50 per cent.), Pontianak, Jelutong or Dead Borneo (70 per cent.), and Guayule (20 per cent.), which are deresinated on a commercial scale. In view of these facts, resins have recently attracted a considerable amount of attention.

Up to the present, unfortunately, little commercial use has been found for these products, and consequently their value is small.

The resins from Balata have been found to consist largely of analogues of the higher aliphatic alcohol, cholesterol, $\beta$-amyrin acetate predominating.[155, 43]

Recently an extended investigation by Hillen[86] has established that the resins from a variety of crude rubbers resemble those from Balata, and it therefore appears that the presence of amyrin acetate is also characteristic of resins from these sources.

The resin from Guayule rubber has been examined by Alexander[1] and found to contain a sesquiterpene alcohol and an essential oil responsible for the characteristic strong odour.

Rubber resins are readily soluble in acetone, and as a result of a quantitative study of their rate of extraction by this solvent, Spence[136] was led to the conclusion that they are absorbed and not dissolved in the rubber.

**Nitrogenous Matter.**—The presence of this impurity had been noted by early investigators, who regarded it as an "insoluble modification" of rubber.

From the reactions of the latex it is evident that, generally, soluble proteins and, occasionally, peptones are present; but owing to the complicated nature of the vegetable proteins and their lack of crystalline properties, it is exceedingly difficult to isolate these substances in a state of purity and to characterise them.[113] For this reason the nitrogenous matter in rubber has been little investigated.

We have already seen that the protein functions as a "protective colloid" in rendering the latex stable; it is, in addition, usually associated with enzymes, which are responsible for the marked colour changes which take place on sheeting and drying crude rubber.

In the case of Para the enzyme was found to be a *peroxidase*, that is to say, one which is active only in the presence of hydrogen peroxide;[137] in Funtumia latex a direct oxidising enzyme or *oxygenase* is present, whilst in *Ficus elastica* a clotting enzyme resembling rennet is stated to occur.[40] The exact function served by these enzymes is at present uncertain.[39]

It has been found that the presence of protein exercises a beneficial effect on the physical strength of the rubber and on the course of its vulcanisation.[24] For this reason it has been proposed to add a proportion of nitrogenous matter to isoprene and its homologues previous to polymerisation, in order to ensure the presence of this constituent in synthetic caoutchoucs.[84]

**Carbohydrates.**—The presence of carbohydrates in various brands of rubber has been known for a considerable time, having been first noticed by Girard in 1866. He obtained three sugars from different sources and determined their melting-points, optical activity, and composition. These, on examination by later investigators, were found to be derivatives of *inositol* or hexahydroxyhexamethylene.[60, 104]

Besides these, the presence of considerable quantities of a carbohydrate has been noticed in rubber and latex derived from *Hevea Brasiliensis.*[125] This proved to be monomethyl *l*-inositol, $C_6H_6(OH)_5(OCH_3)$, m.p. 191°-192°, $[\alpha]_D = -80°$, which on treatment with methyl iodide yields *l*-inositol, m.p. 237°. In certain instances the amount of this constituent present in the crude rubber was as high as 2·5 per cent.

The occurrence of this type of sugar is somewhat rare in nature, and it is somewhat remarkable to find this constituent present in the latex. These sugars are very stable and therefore not adapted, like glucose, for transformation into cellulose, starch, and other materials by the enzymes and protoplasm of plant cells, and it is somewhat difficult to trace any relation between them and caoutchouc.

## Purification of Crude Rubber.

In order that the rubber may be fit for manufacturing purposes it must be freed as far as possible from mechanical impurities, and to this end it is ground between heavy revolving steel rollers under a constant stream of water. The resultant sheet is then hung up to dry in a *dark*, well-ventilated room, at a temperature of 80° F., for three weeks or more. It may also be dried *in vacuo* at higher temperatures, but this procedure, in spite of the manifest advantages of saving space and time, does not appeal to manufacturers generally. Whether due to the comparatively high temperature used (about 140° F.), or to some physical change taking place during maturing in the drying-room, there is certainly a marked difference in the "feel" and "milling qualities" of vacuum and air-dried rubber. The reduction in weight caused by the above treatment is referred to as the "loss on washing."

There remain, however, mineral matter, resins, and proteins; as has been mentioned, the resins are occasionally removed by treatment with suitable solvents, especially from Guayule and Pontianak, but the mineral matter and protein can be extracted only on a laboratory scale, and involve a somewhat troublesome operation.

In the following table the average figures are given for the loss on washing, ash, resins, and protein for a few of the more common rubbers.

| Rubber. | Loss on Washing, Calculated on Crude. | Ash. | Resin. | Proteins * =($N_2$×6·25). |
|---|---|---|---|---|
| | | Calculated on dry washed material. | | |
| | % | % | % | % |
| Para, Fine Hard . | 17-19 | ... | ... | ... |
| Hard Entrefine . | 18-20 | ... | ... | ... |
| Soft Cure . . . | 20-22 | 0·25-0·5 | 2·5-3·5 | 2·5-3·0 |
| Coarse Entrefine | 22-25 | ... | ... | ... |
| Weak Fine . . | 14-16 | ... | ... | ... |
| Plantation . . . | 1 - 2 | 0·25-0·5 | 1·5-3·0 | 2·5-3·0 |
| Ceara Scrap . . . | 28-32 | 1·0-1·75 | 4·5-5·5 | 5·0-6·0 |
| Java . . . . . . | 23-30 | 0·25-0·75 | 9·0-10·0 | 1·5-2·0 |
| Amazon Ball . . | 20-24 † | ... | 4·5-5·5 | ... |
| Para Negrohead . | 40-50 | ... | 4·5-5·5 | ... |
| Assare Scrap . . | 35-50 | ... | 4·5-6·0 | ... |
| Cameroon Ball . . | 26-30 | 0·5-1·0 | 9·0-11·0 | 3·0-4·0 |
| Benguela Niggers . | 30-40 ‡ | 1·0-2·0 | 5·0-6·0 | ... |

---

* Based on the average figure for nitrogen content in vegetable proteins.

† Formerly 25-28, but quality improving owing to more careful methods of collection.

‡ Formerly 25-30, but apparently less carefully collected than in the past.

It is therefore evident from a study of this table that much care and experience are essential in buying crude rubbers, for not only must the manufacturer consider the actual caoutchouc content, but he must never lose sight of the physical strength, vulcanisation qualities, and colour, which vary greatly in rubbers from different sources. It is exceedingly difficult to account for the high prices which some dirty and resinous African rubbers at present command, even granting that a proportion may be useful in certain classes of mixings.

Possibly conservatism on the part of the manufacturer, unwilling to alter his mixings, may have something to do with this, but the following concrete examples should convince such that "bargains" in low-grade rubbers at present prices are illusory.

| Rubber. | Crude Price, pence per lb. | Loss on washing (on crude weight), per cent. | Resins, per cent., on dry sample. | Cost per lb., washed, dried, and deresinated. |
|---|---|---|---|---|
| Plantation, 1st Latex . | 54 | 1 | 2·5 | 55·95 |
| ,, 2nd Latex . | 51 | 1 | 2·5 | 52·85 |
| Loango Ball . . . | 35 | 30 | 24 | 65·80 |
| Gold Coast Lump . . | 24 | 63 | 24 | 85·35 |
| Java . . . . . | 43 | 27 | 8 | 64·03 |

The above figures are based on actual samples submitted for sale.

Fine Hard Para and other high-grade rubbers may be kept hanging for years in a cool, dark, well-ventilated store without undergoing any deterioration, whereas many low-grade varieties must be used up immediately they are sufficiently dry lest oxidation and resinification set in.

## Properties of Rubber.

"**Tackiness.**"—Low-grade rubber is usually characterised by its soft, sticky character or "tackiness," and frequently the sheets melt and run in the vacuum drier, or soften and drop off the supports in the drying-room. The behaviour of a rubber in this respect is a point of great importance in the factory, where a material which readily assumes the consistency of bird-lime is, for obvious reasons, looked on with disfavour.

It is somewhat interesting to notice that the presence of alkali greatly diminishes the adhesive qualities of crude rubber, and Para may be ground into a powder instead of sheets should alkaline wash water be used. It has been proposed to make use of this property to neutralise the "tack" of synthetic caoutchouc,[17] but as the alkali is retained with extreme tenacity and greatly affects vulcanisation, this must be regarded as a somewhat dangerous remedy.

Although many explanations have been advanced to account for tackiness, the subject must be regarded as still open to discussion. Neither bacterial action nor the presence of carbohydrates appears a probable explanation, and the issue seems to lie between "depolymerisation," due to imperfect coagulation or storage in unsuitable quarters, and oxidation. The facts that the solutions of tacky rubbers show a low viscosity,[128] and that a sound and tacky sample of the same rubber give identical figures on elementary analysis,[138] point to the explanation being in the size of the colloidal aggregates. Some experiments by Fickendey,[58] however, on the exposure of rubber in air and other gases to sunlight, support the opposite view.

"**Perishing.**"—The oxidation of rubber is a matter of great practical interest, and is technically known as "perishing." It has already been mentioned that many inferior rubbers possess this defect; after a time a characteristic acid smell becomes evident, the material softens and finally changes to a hard, brittle resin.

Vulcanised rubber behaves in a similar manner, but the problem is here complicated by the undoubted effect exerted by inorganic filling agents (particularly copper salts or oxide of iron)[27] and the method and degree of vulcanisation.

The earliest recorded work on perishing was carried out by Spiller,[133] who extracted some perished rubber and determined the composition of the resin. The results corresponded to $C_{30}H_{48}O_{10}$ or $C_{10}H_{15\cdot7}O_{3\cdot22}$, but are probably vitiated by the presence of the original rubber resin.

Two recent investigations remain to be noticed in which purified material and exact methods were employed. Herbst[85] treated Para dissolved in benzene at its boiling-point for several days with a current of purified air. After evaporation of the benzene two substances were isolated:—

$C_{10}H_{16}O_3$, an amorphous substance constituting only 1·7 per cent. of the oxidation products;

$C_{10}H_{16}O$, a syrup constituting 86·4 per cent.

This latter probably represents the first stage of perishing.

Peachey's work[119] is on the same lines, but the rubber (Plantation Crepe) was a thin film deposited from a solution inside a weighed flask, and this was treated with oxygen at a temperature of 85°. Samples, both natural and resin-free, were used and the rate of oxidation contrasted. It was also found that oxidation was much assisted by the removal of the resins. The resultant body was shewn to have the composition $C_{10}H_{16}O_4$, which is more nearly in agreement with Spiller's figures than those of Herbst.

Perishing is therefore an oxidation phenomenon depending on the action of light and heat and on the quality of the rubber; several compounds may result depending on the conditions, the final product being $C_{10}H_{16}O_4$.

## Preparation of Pure Caoutchouc.

For the preparation of a sample of pure caoutchouc on the laboratory scale it is best to start from the raw material before it has been washed and sheeted, otherwise the protein is broken up and will be found extremely difficult to separate.

As clean a sample as possible is obtained, washed in frequent changes of water until dirt and soluble impurities are removed, then dried, and freed from resins by extraction with boiling acetone for ten hours. The residue is then treated with a caoutchouc solvent—chloroform, carbon tetrachloride, benzene, etc.—for some time, and the dissolved caoutchouc carefully decanted from the undissolved protein and obtained pure, either by precipitation with alcohol or by evaporation of the solvent.

## Physical Properties of Caoutchouc.

The pure caoutchouc is a colourless, transparent substance; its analysis corresponds to the empirical formula $C_5H_8$, but owing to its being non-crystalline, without definite melting-point, optically inactive, and a typical member of a class of bodies termed "colloids," no physical methods are available to determine whether it is a simple substance or whether the same caoutchouc is obtained from rubbers of different botanical origin.

To appreciate fully the properties of caoutchouc, a general acquaintance with the nature of colloids is necessary. This is outside the scope of this work, and for fuller information on the subject reference must be made to other sources. (*Chemistry of Colloids*, Pöschl.; "B. A. Report on Colloids, 1908," Proctor; *Grundriss der Kolloidchemie*, Wo. Ostwald; *The Physics and Chemistry of Colloids*, E. Hatschek.)

The properties of caoutchouc indicate that it is an "Emulsion Colloid," and for this reason its physical constants are somewhat uncertain; moreover, the majority of the published figures are based on vulcanised rubber of unstated composition, so that deductions therefrom are of little value.

The density appears to vary with the previous physical treatment, and has been given as 0·900. For another series of samples of plantation rubber values were obtained varying from 0·9097 to 0·9261. Its optical properties were determined by Gladstone and Hibbert in connection with its constitution, and will be referred to subsequently.

Particularly in the unvulcanised condition, caoutchouc is somewhat sensitive to low temperatures, and when treated with liquid air it loses all elasticity and may be powdered.

Their insulating properties render rubber and gutta-percha of immense value in electrical work generally, and though no figures in this connection are available for pure caoutchouc, it is noteworthy that ebonite, for certain purposes, is required to stand a breakdown pressure of not less than 125,000 volts per millimetre thickness.[118]

On treatment with liquids, caoutchouc swells and takes up considerable quantities. In the case of solvents, such as benzene, chloroform, carbon-tetrachloride, etc., the action goes further, a jelly being formed which slowly merges into an apparently homogeneous, viscous solution. The rate of solution is considerably influenced by the previous mechanical treatment and the age of the sample. Harries has studied the solubility of rubber in ether, and obtained three different modifications (see p. 21).

According to Spence, heating does not greatly assist solution. Mechanical working, by which either the proteid network is broken up or the colloid aggregate simplified, has a marked accelerating effect, and rubber which has been so treated is technically known as "masticated."

The viscosity of caoutchouc solutions has been investigated by several workers.[61] Dilute solutions of various rubbers were prepared with benzene, filtered, and the viscosity measured with an apparatus of the usual Ostwald type.[129] The results appear to be influenced by the age of the solution,[167] temperature, light, and other factors, and though interesting and apparently closely correlated with the physical strength, cannot yet be used as a criterion of the quality of a rubber.

The passage of gas through rubber membranes is of considerable historical and practical interest. The general law obeyed by gases is that the rate of diffusion varies inversely as the square root of the density. Graham,[65] who enunciated this law, obtained the following figures for a rubber membrane. (The values of $\sqrt{D} \times$ Diffusion are added for comparison.)

| Gas. | Density ($H_2=1$). | Diffusion ($N_2=1$). | $\sqrt{\text{Density}} \times$ Diffusion. |
|---|---|---|---|
| Nitrogen . . . | 14 | 1·000 | 3·741 |
| Carbon Monoxide . | 14 | 1·113 | 4·164 |
| Air . . . . | 14·43 | 1·149 | 4·365 |
| Methane . . . | 8 | 2·148 | 6·075 |
| Oxygen . . . | 16 | 2·556 | 10·224 |
| Hydrogen . . | 1 | 5·500 | 5·500 |
| Carbon Dioxide . | 22 | 13·585 | 63·710 |

The condition in which the dissolved gas is held has been investigated by Reychler[126] for the case of sulphur dioxide and found to be that of a simple solution. The abnormal diffusion of carbon dioxide has recently been confirmed by Steinitzer.[144]

From the above table it is evident that Graham's law is not generally obeyed by gases passing through a rubber membrane, and it would therefore appear that two factors are concerned, firstly, diffusion proper, and secondly, the solubility of the gas in rubber.

The behaviour of rubber to hydrogen is of great practical importance in the construction of balloon cloths, because the least diffusion obtainable for a rubbered fabric is about 5 litres per square metre per twenty-four hours, whereas goldbeater's skin and oiled fabric give far lower results. The reader is referred to the reports issued by the Advisory Committee on Aeronautics for information on this subject.

## SECTION II.

### CONSTITUTION AND DERIVATIVES.

BEFORE the chemical and physical properties of natural caoutchouc can be investigated the methods of purification outlined in Section I. must be applied. Resin, protein, etc., having been removed, the question arises whether the remaining material is a simple substance of which the chemical constitution and properties are independent of the source from which it has been derived. Neither natural nor artificial caoutchouc possesses a definite melting-point. Neither can be crystallised from solution. This colloid indefiniteness is possessed by all the derivatives except the ozonide and makes comparison of specimens from various sources extremely difficult. It is also easy to see that a mixture containing two or more caoutchoucs, differing only slightly in physical properties, would be practically impossible to resolve.

The problem of identification has been partially solved by the study of the products which all caoutchoucs form in combination with ozone. In this way some evidence has been obtained that certain Congo caoutchoucs have chemical constitutions slightly different from that of Para.[78] No other differences between natural products have been detected, and no method other than that of examining the products of ozonation has been found capable of detecting such differences at all. It is therefore justifiable, if its behaviour to ozone be excepted, to discuss natural caoutchouc as a chemical individual.

The artificial caoutchoucs and their homologues will also be shortly discussed. For the present the issue may be confined to the natural substance.

**Empirical Composition.**—Ultimate analyses made by Faraday, Berzelius, Ure, and others, proved that caoutchouc was a hydrocarbon and that its formula was $C_5H_8$, or some multiple of this; by analogy with the terpenes the form $C_{10}H_{16}$ has been generally used. The first important research on its chemical nature was that of Gladstone and Hibbert.[64] These investigators purified their material by dissolving in chloroform and precipitating with alcohol, but were unable to free it, "except in the case of one small piece," from an oxygen containing material which they understood to be a modification of rubber. In this case the results of analysis were:—

Found: $C = 87{\cdot}46$, $H = 12{\cdot}00$.
Calculated for $C_5H_8$: $C = 88{\cdot}24$, $H = 11{\cdot}7$.

In all other samples 3 per cent. or more of oxygen was present.

Even at the time of the earliest analyses no one seems to have doubted that the formula of rubber was some multiple of $C_5H_8$. This might be inferred from the constitution of the products which are formed on destructive distillation and receives absolute confirmation from the synthesis by the polymerisation of isoprene $C_5H_8$. It is perhaps fortunate that such a piece of evidence should be forthcoming; many of the published analyses, even the later ones, leave something to be desired.

**Molecular Weight.**—The determination of the molecular weight is a problem which so far has not been solved. A colloid substance has no appreciable osmotic pressure, and the freezing-point and boiling-point methods are therefore useless. It has been generally assumed that the caoutchouc molecule is a very large one, and that its formation is due to the union of nuclei, containing five or ten carbon atoms and possessing chemical affinity for each other. Adopting these views, Bary and Weidert[11] have attempted to determine the molecular weight. They explain the vulcanisation of caoutchouc as an addition of one atom of sulphur to each end of a chain of $C_{10}H_{16}$ complexes. On this hypothesis the quantity of sulphur, which is just sufficient to form a disulphide of the formula $(C_{10}H_{16})_nS_2$, should also suffice to secure complete vulcanisation and to render the whole material insoluble. The percentage of sulphur required for this is about 2·5 per cent., and from this figure the numerical value of $(C_{10}H_{16})_n$ is found to be about 2500. An interesting point in this view of the matter is that further vulcanisation must be preceded by depolymerisation.

It will be evident later that, although the synthesis of caoutchouc from isoprene may be held to consist in the extensive polymerisation of the isoprene molecule or of the $C_{10}H_{16}$ nucleus formed immediately from it, there is no necessity to assume that the caoutchouc molecule contains more than ten carbon atoms, if its chemical reactions alone are to be accounted for. Further, the two derivatives of which the molecular weights have been determined—the ozonide and one of the nitrosites—are found to contain respectively ten and twenty carbon atoms. There seems to be no reason why this number should be much higher in the molecule of the parent substance.

In the liquids usually employed to dissolve it, caoutchouc is present in the colloid state, and each particle of solute probably consists of a large aggregate of molecules. Just as in the case of starch, which has been found to have the constitution $(C_6H_{10}O_5)_4$ in formamide solution,[156] future experiments may reveal a solvent which is capable of yielding a true solution of caoutchouc by resolving the colloid aggregates. The molecular weight would then be determinable; that the determination cannot be carried out with the solvents known at present is no evidence that the molecule is large.

**Physical Modifications.**—The physical properties of caoutchouc are widely variable; considerable changes in tenacity or in solubility can be induced in the same specimen by suitable treatment. This behaviour is characteristic of organic colloid substances. Harries claims to have obtained three distinct modifications of caoutchouc from specimens of the ordinary "a" material which have been purified by precipitation with alcohol. The "b" modification is distinguished by entire insolubility and forms slowly when the "a" variety is kept for a long time. The third, or "c," modification is an oil which dissolves in ether and may be prepared by keeping a solution of "a" at a temperature slightly above atmospheric. These transitions are said to be reversible by suitable means.[75] Each of the three modifications is probably the product of an increasing colloid aggregation by which the material becomes more and more insoluble.

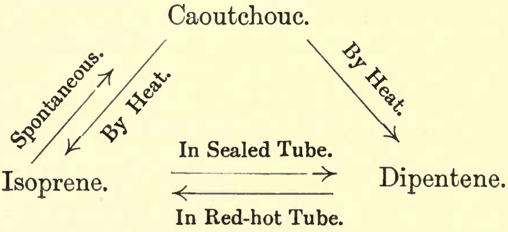
**Caoutchouc in the Latex.**—The caoutchouc in the latex is probably in the very soluble "c" form. By means of ether extraction Harries obtained from *Ficus* latex an oily substance which changed into rubber on keeping.[73] Weber had found previously that the hydrocarbon of the latex could be removed by ether, and on this observation and the supposed insolubility of caoutchouc in the same solvent, he based a theory that the globules of the latex consisted of a diterpene, $C_{20}H_{32}$, surrounded by a sheath of protein. The coagulating agent, besides removing the protein which had acted as a protective colloid, was supposed to cause polymerisation of the terpene to caoutchouc.

This theory never had much in its favour, and was finally disposed of by an investigation made to determine the molecular weight of the hydrocarbon of the latex.[88] The latex was extracted with benzene, and the depression of the freezing-point of the benzene due to dissolved matter was measured, the influence of the resin being separately estimated. In this way the caoutchouc in the latex was found to have an apparent molecular weight of over 3000. It is almost certain that the hydrocarbon was present in colloidal solution, and was therefore not a diterpene.

**Destructive Distillation.**—Much early work, from the time of Dalton onwards, was done on the destructive distillation of rubber. For full information the reader is referred elsewhere.[123]

The first treatment of the subject by a modern scientific method was that of Greville Williams in 1860. He distilled rubber in an iron vessel, keeping the temperature as low as possible, and obtained, after refractionation, two liquids, one boiling at 37°-44°, and another of boiling-point 170°-180°. The first consisted mainly of isoprene, and the second contained caoutchine (identical with the substance described by previous workers under the same name). Williams shewed that the vapour density of caoutchine was twice that of isoprene.

Isoprene was investigated by Bouchardat,[30] who found that in a sealed tube at 280°-300° it gave rise to a substance having a lemon-like odour. Wallach[163] shewed subsequently that this substance and caoutchine were identical with the optically inactive hydrocarbon now called dipentene. Since Tilden demonstrated the decomposition of dipentene into isoprene, and the spontaneous polymerisation of isoprene to caoutchouc was observed by Wallach and by Tilden,[153] the relations of the three compounds may be represented thus—



Besides these, the destructive distillation of rubber gives, according to Harries,[70] two other hydrocarbons. He examined the fraction of the distillate boiling between 150° and 200° and found that dipentene was never present in greater quantity than 33 per cent. of the whole. The residue consisted of other liquids of the composition $C_{10}H_{16}$. One fraction (b.p. 147°-150°) he considered to be a hydrocarbon, which probably had the formula—

$$CH_2 : C(CH_3) . CH_2 . CH_2 . CH : C(CH_3) . CH : CH_2,$$

and was possibly identical with myrcene, obtained from Bay Oil. Another fraction (b.p. 168°-169°) gave no tetrabromide and no nitrosite, and was consequently not dipentene. It has been suggested that this body is the hydrocarbon, caoutchouc in its unpolymerised form ($C_{10}H_{16}$).

In view of the fact that the transition from isoprene to dipentene may be brought about so much more readily than the reverse change, it seems probable that isoprene and, according to Harries, di-isoprene, are the first products of distillation. Dipentene and the others are probably formed by repolymerisation, and the final yield of isoprene is small. Whether this can be said to apply to the fractions of higher boiling-point is uncertain. According to Ditmar,[47] those boiling over 300° may be distinguished from the others by the formation of an amorphous nitro-compound when treated with nitric acid. E. Fischer and Harries[59] also shewed that at a pressure of 0·25 mm. no isoprene or dipentene was formed at all, but only hydrocarbons boiling at 180°-300° under the pressure given.

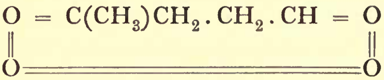
Very few conclusions regarding the constitution of the caoutchouc molecule can be drawn from its behaviour on distillation, though its relation to isoprene is some evidence that there cannot be more than one double bond to every five carbon atoms.

**Unsaturated Nature of Caoutchouc.**—Caoutchouc is an unsaturated hydrocarbon. Gladstone and Hibbert[64] concluded from measurements of refractive and dispersive power that three double bonds were present to every ten carbon atoms. They described, in support of this, a chlorine compound, $C_{10}H_{14}Cl_8$, and a bromine compound, $C_{10}H_{15}Br_5$, the formation of which was best explained by assuming the original addition of six atoms of halogen. These compounds were not of very certain composition and were contaminated by some oxidised impurity. They do not seem to have been examined further.

The most certain indication of the ethylene linkages in rubber was obtained by Harries, who applied the method of ozonation he had previously used to make clear the constitution of oleic acid and other unsaturated compounds. Passing ozone into a chloroform solution of purified Para rubber, he obtained an explosive oil which solidified *in vacuo* to a glassy substance (m.p. 50°). A very notable fact is that its molecular weight was found to be in agreement with the formula $C_{10}H_{16}O_6$. As previous investigations had made it clear that in similar ozonides three atoms of oxygen were associated with each double linkage, there is strong evidence that the rubber molecule has only two such linkages for every ten carbon atoms.

Recently Harries has shewn that by using the concentrated (11 to 14 per cent.) ozone, which is produced by Berthelot tubes run at a tension of 8200 volts, and possibly contains oxyozone ($O_4$), many unsaturated bodies are converted into oxyozonides. Caoutchouc gives the dioxyozonide $C_{10}H_{16}O_8$. In order to prepare the diozonide the concentrated ozone may be used, if it is freed from the more active constituent by washing with concentrated sulphuric acid and with sodium hydrate.

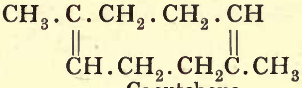
**Hydrolysis of Ozonides.**—At first Harries[72] stated that the action of water on the diozonide caused decomposition into hydrogen peroxide and a keto- or di-aldehyde, lævulinic acid, and another acid of melting-point 195° C. being formed on long boiling. He explained this by assigning to caoutchouc an open chain constitution. In a later paper[74] he shewed that the substance accompanying the lævulinic acid was a primary product of hydrolysis, and was not an acid, as at first supposed, but lævulinic aldehyde. The other primary product was found to be the peroxide of lævulinic aldehyde—



$$\begin{array}{ccc} O & = C(CH_3)CH_2 . CH_2 . CH = & O \\ \| & & \| \\ O & \rule{8cm}{0.4pt} & O \end{array}$$

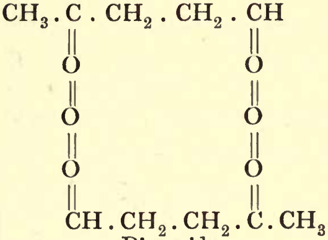
This substance, together with the aldehyde, was formed by the action of steam on the diozonide for a short time. Further hydrolysis decomposes it into lævulinic acid and hydrogen peroxide.

The first products of hydrolysis are therefore lævulinic aldehyde and its peroxide. To account for these being the only substances formed from the diozonide and for the presence of two double bonds to every ten carbon atoms in the caoutchouc molecule, it is necessary to regard the molecule as a cyclic one. If it were an open chain, however long, the diozonide would give two hydrolysis products oxygenated at only one end of their chains. Harries therefore suggested the constitution of 1:5 dimethyl*cyclo*octadiene for caoutchouc—



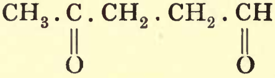
$$\begin{array}{lcl} \mathrm{CH_3.C.CH_2.CH_2.CH} \\ \quad\ \ \| \qquad\qquad\quad \| \\ \quad\ \mathrm{CH.CH_2.CH_2C.CH_3} \end{array}$$

Caoutchouc



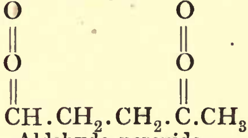
$$\begin{array}{ccc} \mathrm{CH_3.C} & \mathrm{.\,CH_2\,.\,CH_2\,.} & \mathrm{CH} \\ \| & & \| \\ \mathrm{O} & & \mathrm{O} \\ \| & & \| \\ \mathrm{O} & & \mathrm{O} \\ \| & & \| \\ \mathrm{O} & & \mathrm{O} \\ \| & & \| \\ \mathrm{CH} & \mathrm{.\,CH_2\,.\,CH_2\,.} & \mathrm{C\,.\,CH_3} \end{array}$$

Diozonide



$$\begin{array}{ccc} \mathrm{CH_3.C} & \mathrm{.\,CH_2\,.\,CH_2\,.} & \mathrm{CH} \\ \| & & \| \\ \mathrm{O} & & \mathrm{O} \end{array}$$

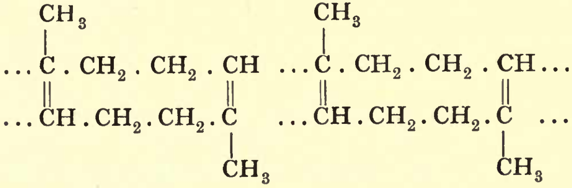
Aldehyde



$$\begin{array}{ccc} \mathrm{O} & & \mathrm{O} \\ \| & & \| \\ \mathrm{O} & & \mathrm{O} \\ \| & & \| \\ \mathrm{CH} & \mathrm{.CH_2.CH_2.} & \mathrm{C.CH_3} \end{array}$$

Aldehyde peroxide

It is possible that the caoutchouc molecule is larger than this formula indicates. Harries proposed that polymerisation took place by reason of the unsatisfied partial valencies which, according to Thiele's theory, are possessed by the double bonds of the octadiene ring, an indefinite number of rings being doubly linked together.

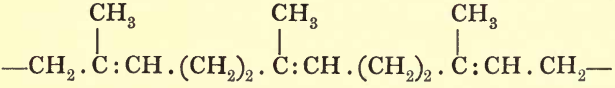


$$\begin{array}{lcclcc} & \mathrm{CH_3} & & & \mathrm{CH_3} & \\ & | & & & | & \\ \ldots & \mathrm{C\,.\,CH_2\,.\,CH_2\,.} & \mathrm{CH} & \ldots & \mathrm{C\,.\,CH_2\,.\,CH_2\,.} & \mathrm{CH}\ldots \\ & \| & \| & & \| & \| \\ \ldots & \mathrm{CH\,.\,CH_2\,.\,CH_2\,.} & \mathrm{C} & \ldots & \mathrm{CH\,.\,CH_2\,.\,CH_2\,.} & \mathrm{C}\quad\ldots \\ & & | & & & | \\ & & \mathrm{CH_3} & & & \mathrm{CH_3} \end{array}$$

*Cis-trans* isomerism could evidently arise in this way, and since the number of possible isomerides was indefinitely large, there was ample scope for explaining the many supposed differences between rubbers from different sources.

**Pickles' Criticisms.**—This view was severely criticised by Pickles,[124] who pointed out that the assumption of partial valencies was unsatisfactory. If the polymerisation were purely chemical in character, the polymeride should be relatively less unsaturated than the simple molecules from which it is formed. This is not the case; and the bond is evidently of so loose a nature that ozone is capable of breaking it before forming the simpler ozonide ($C_{10}H_{16}O_6$). On the other hand, the tetrabromide is an example of other derivatives which are formed apparently without initial depolymerisation of the caoutchouc. Although four atoms of bromine are added for every ten carbon atoms, the molecular weight still remains high and the polymerising influence is still active. Again, destructive distillation of the hydrocarbon would be expected to yield the simple dimethyl*cyclo*octadiene, but this resolution does not take place; under reduced pressure the simplest substances obtained have at least twenty carbon atoms in the molecule.

Pickles therefore suggested that the unsaturated nuclei ($C_5H_8$) unite to form long chains of the structure—

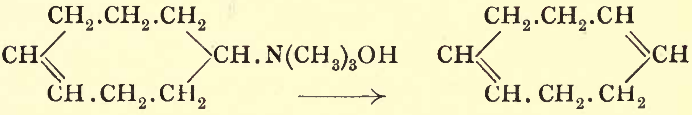


$$—\mathrm{CH_2.\overset{\overset{CH_3}{|}}{C}:CH.(CH_2)_2.\overset{\overset{CH_3}{|}}{C}:CH.(CH_2)_2.\overset{\overset{CH_3}{|}}{C}:CH.CH_2}—$$

The oxidation results require that the ends of such a chain should be linked together. The number of complexes in a chain could vary, but might be supposed constant for any particular kind of rubber. The polymerisation could thus be regarded as strictly chemical. The origin of rubber from isoprene and the formation of the ozonide were simply accounted for; in the case of the ozonide two complexes are capable of holding together; in the case of the bromide there are many more than two. The bromine is united to the molecule in the same way as the molecules themselves are connected.

Pickles' configuration is free from the chief difficulty of the dimethyl*cyclo*octadiene formula, and seems to have been accepted by Harries[75] as an alternative to the latter; but the results of the most recent work on the question are nevertheless strongly in favour of the eight-membered ring.

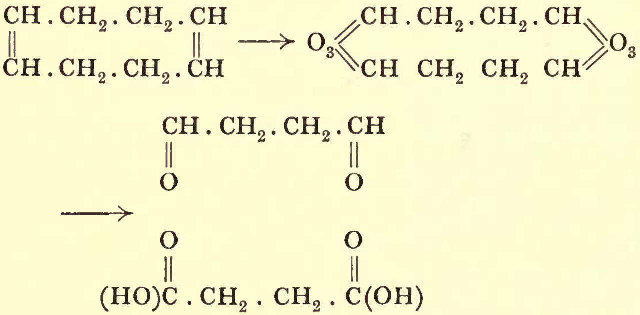
Harries had pointed out that the parent hydrocarbon —*cyclo*octadiene—was already known. Willstätter[165] had prepared it by distilling the methonium hydroxide of *des*-dimethylgranatanine (a decomposition product of the alkaloid *pseudo*-pelletierin)—



*Cyclo*octadiene so obtained was described by Willstätter as a colourless oil which rapidly polymerised to di-*cyclo*octadiene or to a higher polymer, both these substances being crystalline. That *cyclo*octadiene contained a ring of eight atoms was confirmed by its reduction to *cyclo*octane and the oxidation of this to suberic acid—

$$COOH . CH_2 . CH_2 . CH_2 . CH_2 . CH_2 . CH_2 . COOH.$$

The importance of this now appears. If two molecules of isoprene condense to dimethyl*cyclo*octadiene, two molecules of the simpler butadiene should yield *cyclo*octadiene comparable with the substance obtained by Willstätter. A comparison of the ozonides of butadiene caoutchouc and of *cyclo*octadiene, by a method to be discussed below, has been made by Harries, and the two ozonides have been found to be identical so far as their behaviour on hydrolysis is concerned. Succindialdehyde and succinic acid are formed in the same proportions in each case—

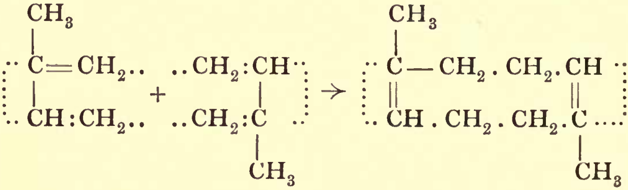


There is some difficulty in separating the butadiene caoutchouc from a terpenoid substance—$C_8H_{12}$—which also forms a diozonide, but the manner of hydrolysis of the two ozonides discussed is so similar that the statement has been made with some confidence that ordinary caoutchouc contains an eight-membered ring.[78]

The two conceptions of the constitution of caoutchouc may now be discussed in connection with the remarks made earlier on the molecular weights of colloids (p. 21). The chief advantage of Pickles' suggestion is that it avoids the vague and unsatisfactory idea of polymerisation by partial valencies, but in attempting to account for the chemical, and to some extent the physical, properties of caoutchouc by means of a chain of $C_5H_8$ nuclei it is no less open to objection than Harries' idea of a chain of loosely connected dimethyl*cyclo*octadiene rings. Both hypotheses represent the molecule as indefinitely large, a supposition which has been seen to be needless. The ozonide contains only ten carbon atoms; there is no evidence that the tetrabromide contains more. Although it must be admitted that the molecules of caoutchouc and those of many of its derivatives are associated with each other to a very high degree, the nature of the association of molecules is too little understood, even in connection with crystalloids, to justify our explaining it by polymerisation and the action of definite chemical affinities, in connection with colloids.

The dimethyl*cyclo*octadiene constitution is necessary and sufficient explanation of the chemical reaction of "normal" caoutchouc. The only simple addition-product which forms a true solution has a structure of ten carbon atoms. In the almost entire absence of any evidence to the contrary, it seems highly probable that the molecule is represented by the formula $C_{10}H_{16}$. The molecular weight has so far not been satisfactorily determined, but this is the smallest aggregate of atoms which is known to react as a whole. It is true that distillation under reduced pressure yields compounds of higher molecular weight, but the mode of formation of these is unknown.

If the *cyclo*octadiene constitution be accepted, the polymerisation of isoprene and similar hydrocarbons is most simply explained by an assumption that seems to have been due originally to Hewitt. Each conjugated double linkage possesses, according to the theory of Thiele, two free "partial" valencies, which are the chief factor in the polymerisation—



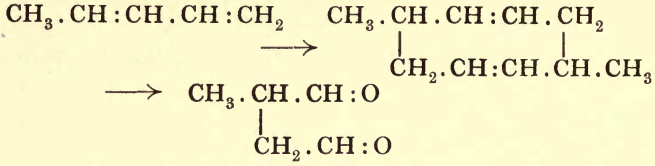
The change only involves the number and position of the double bonds; on any other hypothesis than the one employed, transfer of hydrogen would have to be assumed. In a similar way the formation of butadiene and of dimethylbutadiene-caoutchouc may be formulated.

## Constitution of Synthetic Caoutchoucs.

The hydrolysis of the diozonides has been elaborated into a method by which very close comparison can be made of these substances and indirectly of caoutchoucs of different origin. The action of the water is fairly slow, and data can be obtained for a curve giving amount of undecomposed ozonide plotted against time. The form of this curve is a characteristic of the caoutchouc employed.[77]

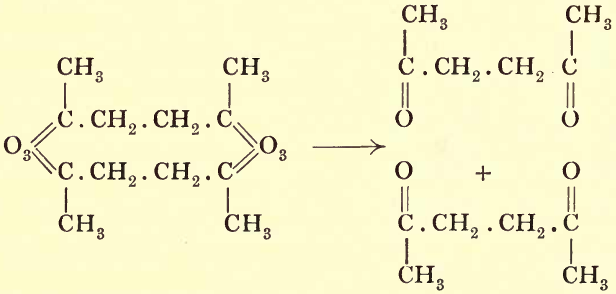
When purified Para and the artificial isoprene-caoutchoucs are examined in this way, no difference whatever can be detected between the curves of Para and of caoutchouc made by auto-polymerisation. The curve of the isoprene material made by the acetic acid process is slightly different. Further, these three substances answer to the tests recently proposed by Harries[76] for the identification of a true caoutchouc. (1) They are all soluble, when freshly prepared, in ether, benzol, and other solvents, not too easily nor yet with difficulty, and on keeping they all become slowly insoluble. (2) They form diozonides, $C_{10}H_{16}O_6$, which give on hydrolysis two molecules of lævulinic aldehyde for every one of acid; and (3) can be converted by concentrated ozone into dioxyozonides, which yield the same products but in exactly the reverse proportion. So far as present knowledge goes they are therefore identical. The ozonide of the "sodium" isoprene caoutchouc, on the other hand, is formed much less readily and gives other products than lævulinic acid and aldehyde. Its curve of hydrolysis is quite different. The constitution of all the "sodium" caoutchoucs is still unknown, though that of the compound from isoprene is believed to be a dimethyl*cyclo*octadiene with conjugated double linkages.

The case of piperylene-caoutchouc is an interesting one on account of its isomerism with and physical resemblance to the natural substance. Hydrolysis of its diozonide is found to yield mainly a substance which is probably methylsuccindialdehyde—

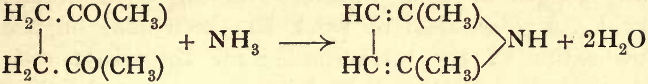


$$\mathrm{CH_3.CH:CH.CH:CH_2} \longrightarrow \begin{array}{l} \mathrm{CH_3.CH.CH:CH.CH_2} \\ \qquad\ | \qquad\qquad\qquad | \\ \qquad \mathrm{CH_2.CH:CH.CH.CH_3} \end{array} \longrightarrow \begin{array}{l} \mathrm{CH_3.CH.CH:O} \\ \qquad\ | \\ \qquad \mathrm{CH_2.CH:O} \end{array}$$

This result indicates that the position of the double bonds is quite different from that which they occupy in "normal" caoutchouc. Butadiene-caoutchouc has already been shown to yield succindialdehyde and succinic acid by ozonation and subsequent hydrolysis. "Normal" dimethylbutadiene-caoutchouc diozonide yields mainly acetonylacetone by similar treatment.



It is thus evident that the diozonide of any "normal" rubber, whether natural or artificial, is decomposed by hydrolysis into products containing carbonyl groups in the 1 : 4 position. Such substances can be readily converted by heating with alcoholic ammonia into pyrrol derivatives, which may be readily recognised by Knorr's reaction. Acetonylacetone, for instance, yields dimethyl pyrrol—



$$\begin{array}{l} H_2C.CO(CH_3) \\ \quad| \\ H_2C.CO(CH_3) \end{array} + NH_3 \longrightarrow \left.\begin{array}{l} HC:C(CH_3) \\ \quad| \\ HC:C(CH_3) \end{array}\right\rangle NH + 2H_2O$$

## Derivatives of Caoutchouc.

With the exception of the diozonide there seems to be no derivative of caoutchouc of quite constant composition.

Gladstone and Hibbert brought forward evidence for the existence of two compounds, $C_{10}H_{14}Cl_8$ and $C_{10}H_{15}Br_5$. Weber[158] claimed to have obtained a tri-iodide, $C_{10}H_{16}I_3$. Spence and Galletly[139] have recently prepared an amorphous chromyl-chloride compound, $C_{10}H_{16}2CrO_2Cl_2$. Apparently no nitrosyl-chloride compound can be obtained (Weber, *Chem. of Indiarubber* (1906), p. 40). Compounds of caoutchouc with hydrogen chloride, bromide, and iodide have recently been obtained by Harries.[76] They have the general formula $C_{10}H_{18}X_2$, and it is indifferent whether natural or "normal" synthetic caoutchouc or gutta-percha be employed. When the halogen hydride is extracted from combination with any one of these hydrocarbons by the action of an organic base, a substance resembling "sodium" isoprene-caoutchouc remains.

Of the remaining derivatives the *Tetrabromide* is the most definite. It was first obtained by Gladstone and Hibbert by the action of bromine on caoutchouc in chloroform solution. More or less hydrobromic acid is formed during this reaction, and it is very difficult to obtain analytical results[75] in agreement with the formula $C_{10}H_{16}Br_4$. It is insoluble in most other solvents, and cannot be heated above 60° for any length of time without evolving hydrobromic acid. A great deal of work has been done on the utilisation of the tetrabromide for the direct estimation of caoutchouc in both raw and vulcanised rubber, but it cannot yet be said that the bromination of rubber is to be relied upon as a method of analysis.

By the action of a mixture of nitric oxide and peroxide on caoutchouc one or more *Nitrosites* are formed according to the conditions. When the fumes generated by the action of concentrated nitric acid on arsenious oxide are thoroughly dried and passed into a dry benzene solution of Para, an insoluble substance approximating in composition to $C_{10}H_{16}N_2O_3$ is precipitated. This is nitrosite "a." It is insoluble in any medium. By the continued action of the nitrous gases it is oxidised to nitrosite "c." This substance is soluble in acetone. Its composition and molecular weight have been found to be in agreement with the formula $(C_{10}H_{15}N_3O_7)_2$. It is said to possess a constant decomposition-temperature of 158°-162° C., and for this reason to be available for the recognition of pure caoutchouc.[75] Harries states that another nitrosite ("b"), having the empirical composition $C_{10}H_{15}N_3O_8$, is formed by the action of chlorine or nitrosyl chloride which the nitrous gases may contain if chlorides are present in the materials from which they are produced.[71]

According to Alexander, the reaction between caoutchouc and oxides of nitrogen is attended with loss of carbon dioxide. Though, in his opinion, the substance produced is not a simple substance, its composition is always in fair accordance with the formula $C_9H_{12}N_2O_6$.

Proposals have been made to estimate caoutchouc directly by means of Harries' nitrosite "a" or "c," but before such methods can be regarded with any confidence, the contradictory accounts of the formation and composition of these substances must be reconciled.

# SECTION III.

## METHODS OF VULCANISATION.

THE marked changes in the physical properties of rubber caused by heating with sulphur are of vital importance from a technical point of view, and from a scientific one provide an interesting problem for which it has been found difficult to supply a solution.

The growth of the modern rubber industry may be considered to date from 1839, when Goodyear, in the United States, discovered the process of hot vulcanisation. Hancock, in England, obtained samples of his product about 1842, and began at once a long course of experiments from which any kind of scientific method was conspicuously absent. He wrote: "I made no analysis of these little bits, nor did I procure, either directly or indirectly, any analysis of them. In making my experiments I depended entirely and solely on my own exertions, having some confidence in an experience of upwards of twenty years of unceasing application to the manipulation with my own hands of the substance I was dealing with."

He was, nevertheless, successful, and found after some time that strips of rubber when immersed in sulphur heated to a little over its melting-point were converted, to a depth which was increased by longer immersion, into a substance which differed from the original by not being hardened when cooled in ice.

In 1846 the process of vulcanisation by treatment with sulphur chloride was patented by Parkes. These two processes—the "Hot Cure" of a rubber with which sulphur has been mechanically mixed, and the "Cold Cure" with sulphur chloride in dilute solution, are in use, with various modifications, for the production of the great majority of rubber goods. The first-named is by far the most important, and any remarks which follow may be taken to refer to it, unless otherwise stated.

**Effect of Vulcanisation.** — That the technical utility of rubber should depend entirely on its relation to a particular element is a surprising fact, and in many ways recalls the part which carbon plays in the iron-carbon alloys known as steels. The use of pure iron, if it could easily be obtained, would be strictly limited by its softness and lack of elasticity; by the introduction of carbon in suitable proportions, materials can be produced having a wide range of hardness, elasticity, and tensile strength.

The elasticity of raw rubber varies with the quality and previous treatment; it is in general low, and a strip which has been stretched returns very slowly or not at all to its original form. Many specimens are quite adhesive at ordinary temperatures, and all become so at a moderate heat, while cooling has a hardening effect. As already remarked, the raw material is dissolved by many solvents. When vulcanisation has taken place, the elasticity is enormously improved, and between wide limits there is no permanent set on stretching. The product is insensitive to heat or cold over a long range, and adhesiveness has entirely disappeared. It is insoluble in any solvent that does not decompose it, and, in addition, is much more resistant to oxidation and much less liable to "perish."

No substance has, so far, been found capable of replacing sulphur in the hot cure, though attempts seem to have been made to use iodine and bromine, or mixtures of one of them with sulphur. Selenium seems to be without effect.[48] For the cold cure process, hypochlorites or hypochlorous acid have been used. Obviously, only the very thinnest films can be cured by immersion, especially when water is the solvent. A solution of bromine in carbon disulphide has been stated to give fairly satisfactory results.[158]

The nature of the vulcanisation change will be discussed later. In this place it is sufficient to say that the reaction, whether chemical or physical in character, consists in the absorption of sulphur. There is no replacement of the hydrogen of the caoutchouc molecule, for the evolution of hydrogen sulphide is not perceptible under normal conditions. The sulphur added in making soft rubbers may vary from 2 to 10 per cent., calculated on the weight of rubber, and of this an amount generally not above 3 per cent. is found to have become so firmly combined with the caoutchouc that it cannot be extracted by any method which does not destroy the material. Finished goods may therefore contain, besides *combined* sulphur, varying proportions of *free* sulphur which can be extracted by solvents, and often the excess of this is apt to crystallise out on the surface of the articles as a pale yellow deposit, an occurrence which is known as "blooming."

In the case of ebonite, or hard rubber, the total sulphur is much higher, usually about 30-35 per cent. This material is the product of vulcanisation pushed almost to its extreme. An interesting point is, that however high the amount of added sulphur may be, the combined sulphur is never found in practice to exceed 32 per cent.

**Constituents of Mixings.**—Although certain varieties of goods are compounded of nothing but rubber and sulphur—elastic thread and golf-ball tape are examples—the great majority are made from "mixings," which contain various inorganic constituents. The ingredients, including the sulphur, are incorporated with the rubber by working through mixing rolls.* The product is soft and plastic and can be moulded into any form, or even "forced" through a die.

The physical properties of the finished article depend largely on the mineral matter which has been added, as well as on the quality of the crude rubber employed and its previous mechanical treatment. The influence of the mineral matter may extend further than this.

The speed of the vulcanisation can be increased by the addition of certain substances, chief among which are litharge, slaked lime, and magnesia—the first-named being much the most important. In

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* For details of the practical manipulation of rubber, the reader is referred to *India Rubber and its Manufacture*, by H. L. Terry (Constable).

many cases the vulcanisation can be controlled by a proper adjustment of the proportion of a mixing containing one of these *accelerators.* It will thus be evident that the nature of the mixings requires careful consideration in practice, and that the mineral ingredients are selected not only as weighting materials but also in view of the process of vulcanisation to be employed and the purpose for which the rubber is designed. The mixings in use by manufacturers have been arrived at mainly by experience, and many of them naturally are jealously guarded trade secrets. The following list of substances in common use may be given:—*

(*a*) **Accelerators of Vulcanisation.**—Litharge, calcium hydrate, magnesium oxide or carbonate.

(*b*) **Colourless Fillings.**—Whiting, barium sulphate, lithopone (finely divided barium sulphate and zinc sulphide), French chalk, and zinc oxide.

(*c*) **Coloured Fillings.** — Antimony, arsenic or mercuric sulphides, red lead, lead peroxide, ferric oxide, chromic oxide, lead chromate (cold cure), ultramarine, Prussian blue (cold cure), graphite, and lamp-black.

(*d*) **Organic Fillers.**—Paraffin wax, pitch, rosin, tar, and rubber substitutes (white and brown).

Both hot and cold vulcanisation may be carried out by several methods, each having its particular application.

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* It is difficult to find adequate reasons for the use of some of these.

## Hot Vulcanisation (with Admixed Sulphur).

**Steam Heating** is employed for such articles as sheetings. The material is rolled round a drum after dusting with French chalk to prevent adhesion, covered with a steam-proof wrapper and placed in an iron heater which can be filled with steam. The time and temperature required depend mainly on the constituents of the mixing. In this process both temperature and pressure are of importance. The pressure is considerably above atmospheric. The large heating capacity of saturated steam is no doubt the reason that curing takes place so quickly, but at no time should the steam actually come into contact with the material.

If a mixing were found to vulcanise too slowly, or if it were required to keep down the percentage of sulphur to prevent "blooming," an accelerator would be added, but litharge could not be used for a white or red article, since the lead sulphide formed during the cure would colour it grey or black. In such a case it would be necessary to make use of lime or magnesia. If, on the contrary, the colour were no objection, with litharge present, the total sulphur could be reduced very considerably without any danger of under-vulcanisation.

**Press Cure.**—For massive articles the press cure is generally preferred. In this the article is treated by heating while under pressure, either in a mould or, as in the case of sheet, between plates. Here the high temperature and pressure are again influential. The pressure is otherwise necessary to secure soundness in a large mass of material. Large articles cannot be satisfactorily treated by steam heat.

**Dry Heat Cure.**—In the dry heat cure, used extensively for shoes, coats, and other black goods, the articles are hung in large air-tight chambers which can be slowly heated by steam-pipes. The time of cure is about six or seven hours.

The most notable point here is that without litharge the cure cannot be performed, at least in the time usually taken. When steam is used the high specific heat of the saturated vapour and its latent heat of condensation are probably responsible for the rapidity of curing. The pressure also seems to have a considerable influence, in fact a mixing containing no litharge can be cured by heating under pressure in an indifferent gas. In dry heat curing these factors are not at work, and the presence of an accelerator is therefore necessary. Litharge is always a constituent, as it is the only substance which is sufficiently active and will prevent the "blooming" which has to be carefully guarded against in making this class of goods.

The advantage of both steam and dry curing have been combined in a recent patent, which claims to secure quick initial heating by the use of steam, and the preservation of the good surface characteristic of dry curing by subsequent heating in an indifferent gas under pressure. Air cannot be used, as oxidation proceeds too rapidly.

Owing to the presence of lead, only black goods are made by dry heating. They are found to be of very good wearing quality, but compared with steam-cured products are deficient in elasticity and strength.

### Cold Cure (with Sulphur Chloride).

In some instances, in order to avoid "blooming" and the alteration of colour which is caused by steam and dry heating, the *cold cure* with sulphur chloride has the preference.

The material, which must be very thin to secure penetration by the liquid, is dipped in or passed through a dilute solution of sulphur chloride in carbon bisulphide or carbon tetrachloride. Some of the chloride is found to have been absorbed, and treatment of the material with ammonia to destroy the excess has no effect on certain amounts of sulphur and chlorine which are left in combination with the rubber. Goods thus cured have a soft velvety surface, but are, unfortunately, liable to perish. When resistance to wear and long exposure is required another process should be chosen.

A modification is known as the *vapour cure.* The articles, which here also must be very thin, are suspended in a room in which the vapour of sulphur chloride can be produced by heating small pots of the liquid. As in the cold cure, after-treatment with ammonia is necessary.

From this outline of the processes in general use it is evident that the proper control of vulcanisation, in order to secure the best possible results in regard to strength, elasticity, durability, colour, and other properties, is a matter requiring extensive experience and a scientific knowledge of the changes which occur. The quality of the raw rubber must be taken into account, particularly in the case of dry heat goods.

The course of hot vulcanisation is found to be largely dependent on the resin and protein which may be present in the raw material. This is especially the case with regard to the first-named, for it has been found that using rubber from which the resin has been completely removed, litharge and other accelerators are without effect.[160]

An explanation of this curious fact has been suggested by Seidl.[131] In his opinion the acceleration is due to the heat of reaction between the litharge and the hydrogen sulphide generated by the action of sulphur on the resin. This theory has been severely criticised,[52] and it is not at first sight a very probable one. Even two per cent. of litharge has a marked accelerating action, and it is hardly conceivable that the transformation of so small a quantity into lead sulphide, with consequent formation of water, should have so much thermal influence. However this may be, the author has found that the absence of resin, if it does not entirely prevent vulcanisation, certainly renders the accelerator inoperative. The protein impurity is probably not without bearing on this point as well as on the strength of the finished articles.[24]

Sufficient has been said to indicate how important is the part played by some of the mineral constituents in vulcanisation. They also have a marked and often a beneficial effect on the physical properties.[22]

## SECTION IV.

### THEORIES OF VULCANISATION.

FROM a purely scientific point of view the most urgent question regarding vulcanisation may be stated thus:—Is the transformation due to the formation of a chemical compound between caoutchouc and sulphur, or is it due to some physical process, such as adsorption? This section will be devoted to a discussion of the answers which have been suggested, and to the experimental work on which they are based.

The subject has suffered much from inexact experiment, and the literature contains many unreliable data as a consequence. Initial purification is absolutely necessary, though in the case of such a colloid as caoutchouc it is a matter of extreme difficulty. The modifications of the vulcanisation process that may be initiated by impurities, derived from the latex, have already been noticed. Research carried out with imperfectly purified materials or with technical mixings is valueless for the present purpose.

The difficulty of the problem is largely due to the fact that very few of the data are established beyond dispute. If nothing be admitted which is in any way open to reasonable doubt, the facts concerned may be stated thus:—

(*a*) A mixture of caoutchouc and sulphur is converted by heat into a material which differs markedly from the original in chemical and physical properties. A certain amount of the admixed sulphur is altered in such a way that it can no longer be extracted by acetone. This is known as *combined* sulphur: that which is capable of extraction as *free* sulphur. So far, no process has been discovered by which the combined sulphur can be removed and the original caoutchouc regenerated (see p. 62).

(*b*) The influence of increased temperature in hastening the process is very marked. Even between 50° and 60° it proceeds slowly and, as the temperature rises above 60°, with rapidly increasing velocity.

(*c*) Caoutchouc which has been vulcanised with sulphur chloride contains besides possible *free* sulphur, *combined* sulphur and *combined* chlorine. Neither combined sulphur nor chlorine can be extracted without destroying the material.

Vulcanisation, particularly the modification using sulphur chloride, has many points in common with dyeing and tanning. A still closer analogy may be found in the coagulation of albumen by mercuric chloride, or of peptone by formaldehyde. In all these instances the action of a particular reagent gives rise to an insoluble combination, and, in general, it is not possible to regenerate the original substance. Here, as in the case of vulcanisation, there is a clear possibility of these reactions being chemical ones, and it might be concluded that chemical influences alone were at work, however indefinite the bond between the reagents, if the advance of chemistry of colloids had not revealed many instances in which this result is simulated by the effect of forces which seem to be mainly physical in nature.

Given that two bodies enter into a loose combination, there are two possibilities alternative to this being a chemical compound, *i.e.*, it may be—

(*a*) A *solution*, even though both reagents are solids.
(*b*) An *adsorption* of the one by the other.

In order to decide between these three hypotheses a quantitative investigation by physico-chemical methods may be required.

The explanation of vulcanisation as a process of solid solution has not met with much support. The impossibility of extracting the combined sulphur is sufficient to condemn it. That adsorption plays the principal part is still maintained by many chemists, and it is between this view of the matter and the older and more definite one of chemical action that the decision lies, though, of course, it is possible that taking the vulcanisation transformation as a whole, both methods of combination may be involved.

Some slight preliminary discussion of adsorption will not be out of place. The formation of a solid solution implies a complete inter-diffusion of the two materials. Examples of this are found in isomorphous mixtures of salts, in numerous alloys, and apparently in the behaviour of vulcanised rubber to many gases. Adsorption, on the other hand, far from involving complete inter-diffusion, is a surface effect, and takes place between an insoluble material—the *adsorbent*—and some substance which is attracted to its surface from solution, until the portion adsorbed is in equilibrium with that which remains dissolved. The adsorption of iodine by charcoal is a typical case. It is characteristic of adsorption equilibria that with increasing concentration of the solution phase the amount adsorbed does not increase in proportion, but more slowly, and in many cases tends towards a maximum, beyond which increase of solution concentration is without effect.

It is found that in many cases the adsorbed material per gram of adsorbent is in direct proportion to the *n*th power of the solution concentration, $n$ being less than unity. This relation is purely empirical and takes no account of a possible maximum. For a discussion of adsorption formulæ the reader is referred elsewhere.[178]

## Cold Vulcanisation.

The problem here is to decide whether the sulphur chloride is chemically combined with the caoutchouc, or is adsorbed by it. Since both these substances can be dissolved in benzene or other suitable solvent, definite evidence on the point can be obtained by estimations of the sulphur chloride in solution, and in combination with the caoutchouc, as the amount of sulphur chloride is progressively increased. If it is found that the quantity attached to the caoutchouc attains a maximum when the two are in simple molecular proportion, there is strong evidence that the combination is chemical. If, on the other hand, there is over a considerable range of concentration an equilibrium between the free and combined sulphur chloride, adsorption is indicated. Here also the amount of combined chloride may reach a maximum; but the probability that this maximum will occur when the reacting substances are in simple molecular ratio is a small one.[161]

The first experiments in this direction were made by Weber, who treated a 5 per cent. benzene solution of rubber with excess of sulphur chloride and extracted the resulting jelly with benzene and acetone. After drying he obtained a friable product, to which he gave the formula $C_{10}H_{16}S_2Cl_2$, stating that its composition was not affected by increasing the excess of chloride in the reaction. In order to explain the properties of cold vulcanised rubber, which contains very much less sulphur than this, Weber suggested that there existed a series of other compounds, the extreme members of which he formulated as $(C_{10}H_{16}S_2Cl_2)_{24}$ and $(C_{10}H_{16})_{24}S_2Cl_2$. Subsequent work has shewn that Weber's results were due to faulty experiment, and that there is no evidence for the existence of this very improbable series.

Hinrichsen and his assistants[87] made experiments in which the presence of moisture was avoided and carefully purified caoutchouc was used.

They found that, allowing for experimental error, the concentration of chloride had, within certain limits, no effect on the composition of the body formed.

Their experiments therefore point to a chemical combination, the formula of the compound being $(C_{10}H_{16})_2S_2Cl_2$.

This conclusion is supported in every respect by the more recent work of Bernstein,[25] whose experiments were controlled by viscosity measurements of the very dilute mixtures used. No substance of the composition $C_{10}H_{16}S_2Cl_2$ seems to exist, and it is interesting to note that the two compounds obtained by Guthrie[67] from ethylene and amylene were of the type of Hinrichsen's compound—$(C_2H_4)_2S_2Cl_2$ and $(C_5H_{10})_2S_2Cl_2$.

So far none of the work discussed has given any indication of the condition in which the elements of sulphur chloride exist in cold vulcanised rubber. According to Bysow,[34] who attempted to deal directly with this question, Para rubber absorbs the sulphur chloride. He immersed strips 0·5 mm. thick in benzene solutions containing 0·1 to 0·4 grm. chloride in 100 c.c. and determined the combined sulphur in the strips when the chloride had ceased to be attracted to the rubber. The results are said to be conclusive for the adsorption theory, but it is very doubtful whether a real equilibrium would be attained without vigorous agitation in such dilute solutions. On the other hand, it was not decided whether the absorption ever came to an end when the amount of sulphur chloride present was from 0·6 to 3·6 grms. Another serious objection to this method is that the adsorbing surface of caoutchouc cannot be considered a constant on account of the swelling action of the benzene. The matter is also complicated by the possibility of the vulcanised material containing more or less sulphur than is equivalent to the chlorine combined with caoutchouc, and by the possible presence of moisture in the original substances.

So far, it cannot be said that investigation has made clear the far-reaching effect of a few per cent. of sulphur chloride on caoutchouc. If adsorption has occurred the change should be reversible; if partial formation of the compound $(C_{10}H_{16})_2S_2Cl_2$ has taken place, the insolubility of the entire material in any solvent is not easy to explain, though it is probable that the conversion of part of the caoutchouc into a different substance causes such a great increase in the colloidal aggregation of the rest to occur, that the whole becomes insoluble.

## Hot Vulcanisation.

In this field as in the other the first systematic experiments were made by Weber. Laying some stress on the additive character of the reaction, he concluded that under conditions in which excess of sulphur was present the definite compound $C_{10}H_{16}S_2$ was formed from Para rubber. Such a substance should contain 32·00 per cent. sulphur, and that his products contained slightly more in proportion to the time they had been heated, he explained by supposing that substitution began to occur after or towards the end of the addition process.

He also made experiments with various brands of rubber in order to obtain information on the progress of the reaction. His mixtures contained 9·1 per cent. sulphur and were vulcanised in an autoclave at fixed temperatures between 120° and 130°. Samples were withdrawn for analysis every hour or half-hour and their combined sulphur estimated. The curves obtained by plotting percentages of combined sulphur against time represented the progress of the vulcanisation, and shewed, especially in the case of Para, curious sharp bends, the arrangements of the bends being characteristic of any particular brand. These curves have been much discussed. It has been stated[93] that Weber accepted them as evidence of chemical combination, but his opinion really was that they indicated rather physical than chemical changes.[158]

Nevertheless, on the ground that the effect of combined sulphur is not only evident but of most practical importance when from 2 to 2·5 per cent. only is present, Weber assumed, without further justification, the existence of a series of compounds with probably a polyprene sulphide, $C_{100}H_{160}S$ ($S=2·35$ per cent.), as the lower, and $C_{100}H_{160}S_{20}$ as the higher limit. Such views of the matter are no longer of much importance; but with respect to the disulphide $C_{10}H_{16}S_2$, they have received considerable support from some recent work.

For scientific purposes it is evidently an advantage to have both reagents, if possible, in a homogeneous solution. Stern[145] attempted a study of the dynamics of vulcanisation in liquid naphthalene solution, but did not obtain any decisive results. These experiments, together with those of Weber and a few made by Hübener on the curing of technical mixings, were almost all that were available up to 1910, when a striking development of the subject occurred.

## Adsorption Theory of Vulcanisation.

In this year the adsorption theory of vulcanisation was proposed by Wo. Ostwald.[116] Besides giving many reasons for considering this explanation more convenient than the chemical one, he recalculated the results of Stern and Hübener, and claimed that they supported his contention. The main lines of his argument were as follows:—

It was urged that Weber's idea of the series of intermediate compounds had received no support, and indeed, according to Ostwald, the evidence for the existence of a definite individual substance limiting the series—$C_{10}H_{16}S_2$—was not satisfactory. This is the most important point, because if it were found that the fixation of sulphur never came definitely to an end, the fact would certainly indicate adsorption.

It was also stated that ordinary vulcanised rubber always contained—as would be expected from the existence of an adsorption equilibrium—some free sulphur. No matter how little was present before vulcanising, some always remained uncombined at the end. That an equilibrium was in evidence was also borne out by the belief that the extraction of free sulphur could never be sharply distinguished from the extraction of the combined (adsorbed) material. No matter how long the extraction was carried, a suitable solvent was said always to dissolve a little more. Vulcanisation was therefore a reversible process.

From a consideration of Weber's results on vulcanisation at different temperatures, Ostwald concluded that the temperature coefficient of the transformation, being less than would be expected for a chemical reaction, was more in agreement with his explanation.

Many of the statements made in this important paper were much in need of experimental proof. Very few satisfactory investigations on vulcanisation had been made and the numerical data available were unsatisfactory. More recently the work of Bysow[35] has been adduced in support of the adsorption hypothesis. This chemist vulcanised various mixings of rubber and sulphur at a steam pressure of 50 lbs., and finding that attainment of equilibrium required a long time, secured comparable results by heating for about two and a half hours in each case. After this treatment 0·19 per cent. sulphur, for example, remained uncombined in an instance where 3·5 per cent. had originally been added. There is every reason to believe that further treating would have caused complete fixation of all sulphur present, and in any case it is difficult to see how an equilibrium equation can hold where the equilibrium has admittedly not been attained.

### Adsorption or Chemical Combination?

Leaving aside the minor arguments, the questions of the nature of the vulcanisation change and the ability of the adsorption theory to explain it are seen to hinge on two points: (1) Does the addition of sulphur reach a limit with the formation of the compound $C_{10}H_{16}S_2$? and (2) Is the reaction reversible? By the decision on these two points the adsorption theory must stand or fall.

Take, in the first place, the question of the limit. Recent experiments support Weber's statement of the formation of the disulphide $C_{10}H_{16}S_2$. Spence and Young,[142] working with a mixture of Para and sulphur (37 per cent.), found that at 135° the combined sulphur reached a limit of 31·97 per cent. in twenty hours and did not increase with ten hours' further heating. The margin of uncombined sulphur (3·80 per cent.) is perhaps rather narrow, and Wo. Ostwald points out that in a more rigorous investigation he would use 60 per cent. or more of initial sulphur.

More recently still a substance of the same empirical composition has been found to be the uniform result of the action of sulphur, in varying excess, on caoutchouc in cumol solution at 170°.* [90] The relative amount of sulphur was more than twice as high as that employed by Spence and Young. In no case did the product contain more than 32 per cent. of combined sulphur.

An additional argument for the disulphide is furnished by the results of bromination experiments. By treatment of rubber with bromine in carbon tetrachloride solution a tetrabromide, $C_{10}H_{16}Br_4$, arises. Vulcanised rubber gives a product containing both sulphur and bromine in such proportions that it may be imagined that only the pure rubber present reacts, the compound $C_{10}H_{16}S_2$ remaining unaffected.[140] This is evidence not only for the formation of the disulphide but for its presence in ordinary vulcanised rubber. It is, therefore, very probable that the maximum amount of sulphur capable of combination with caoutchouc is 32 per cent. of the whole. There is no evidence whatever that this limit can be exceeded.

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* This temperature is too high for confidence that the disulphide was formed from actual caoutchouc.

The second question concerns the possibility of reversing the reaction. The statement that the free sulphur in vulcanised rubber was necessary to maintain the combined in equilibrium, and could not be eliminated by long heating, has been contradicted by Spence and Young.[142] They vulcanised samples containing 10 per cent. sulphur at 135° and 155° C., and in no case found any free sulphur remaining after sufficiently long cure. It is interesting to notice in passing that a sample of Balata gave very similar results.

These chemists[141] have also investigated the mechanism of acetone extraction of the sulphur. By treating vulcanised material with successive equal quantities of hot acetone and determining free sulphur in the rubber and in the solution, after heating in each case long enough to secure equilibrium, they obtained results which justified the conclusion that the free sulphur is adsorbed in the caoutchouc. They were also able to distinguish between adsorbed and mechanically mixed sulphur, so that this element appears to be present in three distinct states.

Part of the sulphur being adsorbed by the solid, it is easy to see that the extraction will be more difficult than if it were merely mixed or dissolved, and the results of previous investigators, which apparently justified Ostwald's statement that the sulphur could never be completely removed in this way, are explained.

The problem of devulcanisation is discussed more fully in Chapter V., where it will be seen that there is great difficulty in believing that the simple reversal of vulcanisation has ever been performed. Nevertheless Bary and Weidert claim to have diminished the combined sulphur in vulcanised rubber by extracting the free element with acetone and reheating the extracted material.

The balance of evidence is nevertheless strongly against the reversibility of vulcanisation, and to meet this fact it has been asserted that adsorption itself may be irreversible. The dye methyl violet, a hydrochloride, is said to be adsorbed by charcoal and to be incapable of extraction from the charcoal by water. It is more probable that the base only of the dye is adsorbed. Pure water of course fails to remove it.[176]

Wo. Ostwald [115] is still of opinion that the results of Spence and others can be reconciled with the adsorption theory, but in two vital points this theory is opposed to the facts:—There is no evidence that vulcanisation can be reversed, and there is a limit to the addition of sulphur.

The chemical theory is therefore, in the opinion of the present writer, much the more probable of the two. The effect of small percentages of sulphur in rendering the whole material totally insoluble, which may be urged as an objection against it, is probably a consequence of the colloidal nature of the material. If the results of Spence can be confirmed, there will be no doubt about the matter. A combination which is irreversible, is limited by a stoichiometric relation, and is accompanied by the striking changes which vulcanisation causes, can hardly be other than a chemical reaction.

# SECTION V.

## WASTE RUBBER AND ITS UTILISATION.

FOR success in any industry it is essential to make as little waste and bye-product as possible and employ such as is unavoidable to the best advantage. This applies to the rubber industry, and a glance at patent records shews that attention has for years been focussed on this point. "Reclaiming" at the present time is an industry by itself, several large works being exclusively engaged on this work.

Waste rubber can be divided broadly into two classes—

(*a*) Unvulcanised,
(*b*) Vulcanised.

Between the two classes there is an enormous difference in that the former is soluble in solvents, and is soft and plastic, while the latter cannot be obtained in solution without treatment entailing molecular destruction.

Unvulcanised waste consists mostly of trimmings from shoes, football bladder sheet, and other material. It contains no fabric and rarely comes on the market, and is used in the factory without treatment.

In the case of waste from diving dress, water bottles, motor-tyre duck, etc., it is necessary to remove the fabric before the "proofing" becomes available for use. This is effected by treatment with naphtha, wringing, and subsequent evaporation of the solvent.

When we come to vulcanised rubber it is as well to point out the probable constituents which will be encountered, so that the nature of the problem may be fully realised.

(*a*) Vulcanised rubber — insoluble in all solvents. May range from soft pure gum to semi-hard and ebonite, and may be hard and perished.
(*b*) Inorganic filling agents, amongst the most common being whiting, zinc oxide, lithopone, barytes, litharge, magnesia, French chalk, antimony sulphide, etc.
(*c*) Free sulphur.
(*d*) Organic matter—brown and white substitutes, oil, vaseline, pitch, etc.
(*e*) Foreign material, such as cotton, wool, wire, dirt, etc.

The material is, in addition, non-plastic, will not mill on the mixing rolls, and as it is already compounded, the nature and colour of the fillings limit its use to a particular class of goods.

It has, therefore, been the aim of every inventor working in this field to remove all the combined sulphur and fillings and obtain the rubber portion in its original plastic soluble form.

We may begin by saying that notwithstanding all statements to the contrary in patents, *such a result has never been obtained,* nor does there appear at present much likelihood of success. We will discuss the facts on which this view is based, concluding with a *résumé* of the methods at present in use for rendering this waste of some service in manufacturing work.

### Removal of Combined Sulphur.

It has been already mentioned that the combined sulphur in soft rubber goods falls far short of that required for $(C_{10}H_{16})S_2$, and that consequently one might expect the solution of a portion on treatment with a suitable solvent. Such, however, is not the case, and, moreover, the combined sulphur is retained extremely tenaciously. Numerous patents have been taken out to effect the removal of sulphur; for instance, sodium sulphite,[148] lime,[46] sodium sulphide,[147] cyanides,[147] and metallic oxides[9] have all been recommended.

From the fact that the majority have been allowed to lapse and that no sulphur-free "reclaimed" is on the market, we must conclude that they are impracticable. The widely used "Alkali Process," using caustic soda solution, first suggested by Brooman[32] in 1855 and elaborated by Marks,[106] never effects more than the removal of free sulphur and saponifiable matter.

Bary and Weidert[10] state that it is possible to remove the combined sulphur from vulcanised rubber. Hinrichsen and Kindscher, who examined the action of alcoholic soda and metallic powders on both cold and hot vulcanised rubber, came to the same conclusion.

This work has been severely criticised by Alexander,[2] who points out that there is no proof that the sulphur removed was chemically combined, and not free sulphur unextracted by the preliminary treatment with acetone. There can be no dispute that it is extremely difficult to remove entirely the free sulphur (probably present in the insoluble form), and, for complete extraction, prolonged treatment with hot acetone is necessary.[140]

Spence was unable to remove any combined sulphur by treatment with alkalis. The present writer found that the combined sulphur in vulcanised rubber was not removed by treatment with carbon tetrachloride and zinc, copper or iron dust at 100° for three weeks; in no case did any portion of the material go into solution.

The tendency of metallic sulphide to remain in colloidal solution under similar conditions may also be a disturbing factor.[102]

Hinrichsen and Kindscher adhere to their conclusions, but it is probable that they, in reality, did no more than is commercially effected every day by the "alkali" process.[3]

## Removal of Foreign Matter.

The majority of organic impurities may be removed by treatment in a finely ground condition with solvents, or alkali, whilst treatment with acid will remove a proportion of the mineral matter; but for the numerous instances where barytes, litharge, French chalk, and other indifferent fillings have been used, the methods mentioned fail.

Even were the material unvulcanised and soluble, the viscosity of the solution would render filtration impracticable. Alexander[4] has patented the production of an emulsion of rubber in water, which can be filtered free from mineral matter; but as his patents have been allowed to lapse, one may draw the inference that the process is unworkable.

### Technical Methods of Reclaiming.

From consideration of the above it will be understood that all the processes in use for reclaiming rubber have as object alteration in its physical condition with removal of fabric and coarser impurity, and in no instance is anything resembling the original rubber obtained.

The vulcanised material as received by the reclaimer may be divided into the following classes:—

(*a*) **Hard and Semi-hard Waste**—such as ebonite. Such material is ground up fine and so used in mixings. It is termed "crumb" or "dust."

(*b*) **Pure Waste**—such as elastic thread, golf-ball tape. This is usually milled up with a proportion of rosin and mineral oil and subjected to the action of steam under pressure for several hours. The resultant product is plastic and, except for solubility, can be treated in the same way as crude rubber.

(*c*) **Compounded Waste**, which may be pure or contain fabric, wire, steel studs, etc., as illustrated by articles like hose, rubber boots, insertion sheet, motor tyres, etc.

This compounded waste may be treated in several ways. Should it be fairly free from fabric it is often ground very fine and sieved. In this condition it is termed "crumb," and is used in mixings as a filling agent.

A very interesting modification, known as the "Gare Process," must be mentioned in this connection. It is found that "crumb" under high pressure and temperature tends to soften and coalesce.[63, 97] By such means moulded articles, closely resembling new goods, can be manufactured entirely from waste.

However, should it be desired to render the waste plastic and suitable for use in place of rubber in cheaper mixings a different process is adopted, resulting in the material being left in a soft and plastic condition.

To effect removal of fabric, three methods may be adopted: the "Mechanical," "Acid," or "Alkali" process.

**The Mechanical Process.**—The mechanical process, now little used except for material used for insulation purposes, consists in removing the fluff from the finely ground waste by means of a blast of air. Naturally the separation is incomplete and the process an extremely dirty one.

**The Acid Process.**—The chemical methods are much more largely used, the acid process being the older and more extensively employed. The waste is first of all finely ground and thoroughly washed to free from dirt, pieces of metal, and soluble matter. It is then run into steam-heated tanks containing dilute sulphuric acid, and allowed to soak until all the fibre is destroyed. The liquor is then drained off and the waste again washed until fairly free from acid. The resulting product, and also that from the mechanical process, now has to undergo a softening process, by being heated *in contact* with steam at about 300° F. for several hours. The resultant softened material is dried. It is then sheeted on mills, and is ready for use in the factory.

An ingenious modification of the process consists in the substitution of magnesium or zinc chloride for the sulphuric acid. Either of these supply sufficient acid by hydrolysis.[146]

**The Alkali Process.**—The "alkali" process remains to be considered. It undoubtedly yields the finest product—the sole disadvantage being the impossibility of complete removal of the alkali, however long the material is washed. The residual trace of alkali acts as an uncontrolled accelerator in vulcanisation. The process is a simple one, the waste being ground fairly fine, washed over riffles to remove dirt, centrifuged, and then heated at 344° F. for about twenty hours under a steam pressure of 125 lbs. per square inch with a 3 per cent. solution of caustic soda.[106] The liquor is then run off and strengthened up for further use, while the waste, after thorough washing, is dried and sheeted. In this process the removal of the fabric and the softening have been carried out in one stage. It has been suggested that the two chemical processes should be combined, the fibre and soluble mineral filler being first got rid of by acid, and the removal of saponifiable matter and softening effected by the alkali process.[49]

To estimate the consumption of reclaimed rubber is next to impossible, but it is probably equal to the world's production of raw rubber. One of the most important of our waste products, its use admits of the manufacture of serviceable articles where physical strength is non-essential, at prices far below those possible with crude rubber.*

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* For fuller information on Reclaiming, the reader is referred to Alexander, *I.R.J.* (1910), ii. pp. 421, 532, 573, 651; De Fleury, *Le Caout. et la Gutta Percha* (1912), p. 6530 *et seq.*

# SECTION VI.

## SYNTHETIC CAOUTCHOUC.

THE earliest chemical work on rubber was concerned with the products yielded by destructive distillation, and the synthesis of caoutchouc owes its inception to observations made during these researches. During a careful examination of these substances, Greville Williams[164] isolated from the lower-boiling fractions a product which he named "Isoprene," and on analysis this yielded figures agreeing with the composition $C_5H_8$.

This substance when kept for some months was observed to have lost its fluidity and to have absorbed oxygen, and Williams found that on distillation some unaltered isoprene passed over and a white spongy residue was left containing carbon, hydrogen, and oxygen. He says: "When burnt, it exhales a peculiar odour hitherto considered to be characteristic of caoutchouc itself." There can be little doubt that he was dealing with an impure sample of caoutchouc.

The properties of isoprene were examined more fully in 1875 by Bouchardat,[31] who observed that on heating it yielded a liquid polymer, $C_{10}H_{16}$, di-isoprene, and other indefinite bodies; later[30] he suggested the identity of this di-isoprene with turpentine (dipentene). While preparing the hydrochloride of isoprene by treatment with a concentrated solution of hydrochloric acid in the cold, and subsequent distillation, a solid residue was obtained. This was found to possess "the elasticity and other properties of rubber itself. It is insoluble in alcohol, it swells up in ether, also in carbon disulphide, in which it dissolves after the fashion of natural rubber." On dry distillation the same products were obtained as from the natural material, and he concludes: "All these properties seem to identify this polymer of isoprene with the source of isoprene, namely rubber."

This may, therefore, be said to constitute the first synthesis of caoutchouc, though the isoprene used had itself been prepared from rubber, and it was requisite that the isoprene should be obtained from other sources to render the work complete.

A few years later Tilden[151] was able to confirm Bouchardat's production of an elastic polymer on treatment with concentrated hydrochloric acid; he adds the following significant comment: "If it were possible to obtain this hydrocarbon from some other and more accessible source the synthetical production of India Rubber could be accomplished." At the same time he put forward the suggestion that isoprene had the constitution $CH_2 : C(CH_3) . CH : CH_2$, a view which was later confirmed by Euler's syntheses.

In 1884 Tilden[152] obtained a small yield of isoprene from the destructive distillation of turpentine, and again confirmed the previous results, noting in addition that its polymerisation took place most readily after a preliminary heating which yielded an oily body. This was recently the subject of a patent by Lilley.[103]

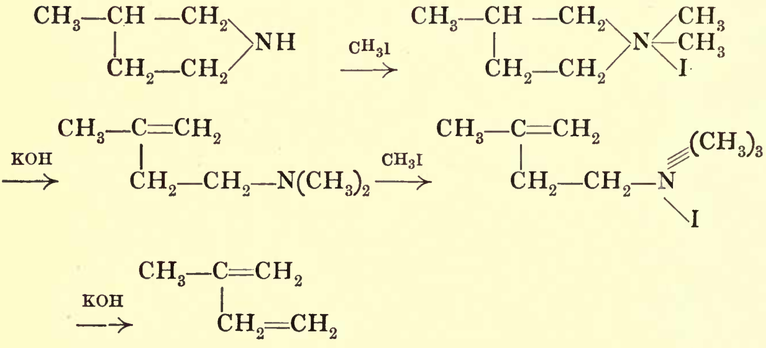
Tilden also here makes the suggestion that the homologues of isoprene might behave in a similar manner—an idea which in recent years has been a fruitful source of patents in the hands of the Bayer and Badische companies.

A complete investigation into the properties of isoprene by O. Wallach [163] resulted in the observation in 1887 that isoprene polymerised to a rubber-like substance when exposed to light, thereby anticipating Tilden's independent observation of the same phenomenon five years later.[153] The latter, however, vulcanised the material so obtained with sulphur, and was, therefore, the first to shew that the synthetic material possessed this property. It is somewhat interesting that patents have been taken out by the Badische and Bayer companies for vulcanisation of caoutchouc-like bodies obtained from isoprene, etc., on the ground that it is a property which could not be predicted.[170]

In 1906 Tilden exhibited a sample of synthetic caoutchouc at the British Association Meeting at York. Tilden and Bouchardat's work was confirmed by Weber,[159] who obtained 211 grms. of caoutchouc from 300 grms. of isoprene after keeping for a period of nine months, and subsequently by Pickles,[124] so that the scepticism expressed by Klages at Heidelberg, and later by Harries,[77, 79] both as to the possibility of the conversion of isoprene into caoutchouc by the methods employed by Tilden and as to identity of the product with caoutchouc, is somewhat remarkable. Harries went so far as to state, when reporting on samples of rubber prepared by a process devised by Dr Fritz Hofmann, submitted to him in 1909 by the Bayer Co.: "I could prove beyond a shadow of doubt that these samples were real caoutchouc, and therefore the substance was the first synthetic caoutchouc ever obtained." There can be little doubt, however, that the credit belongs to Bouchardat and Tilden, and that the failure of other investigators to reproduce their results is due to the uncertain methods employed and the use of products of varying degree of purity.

These early investigators had, however, obtained their isoprene from natural sources, and it remained for Euler[53] in 1897 to add the last link by his synthesis of this body.

As already stated, its structure had been suggested by Tilden; this was partially confirmed by Gadziatsky and Kondakow, and finally settled by the synthesis of Ipatiew[175] and Euler[53] working independently by different methods. Euler's method was based on the previous work of Ciamician and Magnaghi on divinyl in 1885, and Hofmann in 1881 on piperylene, and started from β-methyl-pyrrolidine—



The early work may therefore be summarised as follows:—

| | | |
|---|---|---|
| 1860. | Greville Williams. | Isoprene and dipentene from rubber. |
| 1875-1879. | Bouchardat. | Caoutchouc and dipentene from isoprene. |
| 1884. | Tilden. | Caoutchouc and dipentene from turpentine. |
| 1887. | Wallach. | Caoutchouc from isoprene. |
| 1898. | Euler. | Isoprene from β-methyl-pyrrolidine. |

It is evident that the problem of the synthesis of caoutchouc comes under two headings—

(1) The production of isoprene or its homologues;
(2) The polymerisation of these into substances having properties similar to those of natural rubber.

In order that it may be a commercial success, it is necessary to consider the requirements of the manufacturer and consumer of rubber goods, the essentials being (*a*) Physical and chemical properties; (*b*) Cost.

So far as the consumer is concerned, the constitution of a body is of secondary importance, so long as these points are satisfied, so that in effect the problem before the chemist is that of manufacturing a synthetic product, not necessarily true rubber, but of similar physical qualities, at a price equal to or below that of the natural product.

Should the synthetic product be inferior in physical strength in resistance to oxidation or in other ways, it will be largely a question of price whether it will prove interesting to the commercial world, for, owing to the many and varied applications of rubber goods, the use of the highest quality raw material is not always an essential.

It has already been mentioned that Tilden in 1884 suggested the polymerisation of analogues of isoprene, and a considerable number of observations have been made on such bodies. They yield products varying from sticky resin to brittle solids.

Piperylene has been found to polymerise on heating or if kept for some time.[95, 150]

A similar change takes place when dimethylisopropenyl-carbinol $(CH_3)_2C.OH.C(CH_3):CH_2$ is treated with dilute acids, when an oily polymer is obtained.[105] This probably depends on the formation of di-isopropenyl (dipropylene), $CH_2:C(CH_3).C(CH_3):CH_2$, as an intermediate stage. This last body has been studied by Couturier,[44] who found that it was readily polymerised by heat, but apparently did not do more with the resultant product than note its physical properties. Kondakow[98] made it the subject of an extended investigation, preparing it from pinacone bromide by the action of alcoholic potash—

$$CH_3.C(CH_3)Br.C(CH_3)Br.CH_3 \longrightarrow CH_2:C(CH_3).C(CH_3):CH_2 + 2HBr$$

On treatment of the dipropylene at 150° C. with alcoholic potash a portion was polymerised to a white elastic mass, and the same result was reached on keeping, or on exposing it to the action of light.[99]

Similar observations have been recorded by workers on dihydrotoluene,[69] phenylbutadiene,[100] *cyclo*pentadiene,[101] and other compounds which are characterised by containing a conjugated double linkage.

Most of these substances are unsaturated derivatives of butane, and are termed *butadienes,* the position of the double linkage and substituent groups being indicated by lettering or numbering thus:—

$$\begin{array}{ccccccc} C & = & C & - & C & = & C \\ 1 \text{ or } \alpha & & 2 \text{ or } \beta & & 3 \text{ or } \gamma & & 4 \text{ or } \delta \end{array}$$

The members of the series most interesting in connection with synthetic caoutchouc are as follows:—

Erythrene, divinyl, or buta-1, 3-diene $CH_2 : CH . CH : CH_2$

Isoprene or 2-methyl-buta-1, 3-diene $CH_2 : C(CH_3) . CH : CH_2$

Piperylene or 1-methyl-buta-1, 3-diene $CH(CH_3) : CH . CH : CH_2$

Di-isopropenyl, dipropylene, or 2, 3-dimethyl-buta-1, 3-diene $CH_2 : C(CH_3) . C(CH_3) : CH_2$

1 : 1, 4 : 4 Tetra-methyl-buta-1, 3-diene $C(CH_3)_2 : CH . CH : C(CH_3)_2$

Of these the first two are the most important, and we shall consider a few of the methods which have been proposed for their preparation and subsequent polymerisation into caoutchouc-like substances.

### Preparation of Isoprene.

The work in this field has, in the main, been carried out by the following: the Bayer Co., the

Badische Anilin und Soda Fabrik, and the Synthetic Products Co.

In connection with the Bayer Co. the names of Drs Duisberg, Hofmann, Coutelles, and probably Professor C. Harries, call for mention; whilst the British firm is assisted by Professor W. H. Perkin, Drs Strange, Matthews, Weizmann, and others.

**From Turpentine.**—As already mentioned, the early work on the production of isoprene had turpentine and similar natural products as a starting-point, and many efforts were made to obtain some improvement on the 5 per cent. yield obtained by Tilden. In this connection we may note the work of Lilley [103] and of Silberrad,[132] on the decomposition of turpentine under reduced pressure; of Matthews and Strange,[109] on distillation of rubber resins; and of Harries and Gottlob,[80] who obtained a much increased yield by passing dipentene or limonene over hot platinum spirals.*

**From Other Materials.**—It soon became obvious, however, that turpentine was unpromising as a raw material, owing to its limited supply and frequent fluctuations in price, and attention was turned to other cheap organic substances from which it might be possible to produce caoutchouc synthetically under 1s. 6d. per lb.

The only substances fulfilling these conditions seem to be wood, starch, sugar, petroleum, coal, and acetylene.

The original method of Euler has already been mentioned, together with that of Ipatiew; both give

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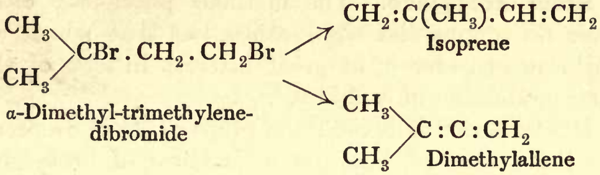
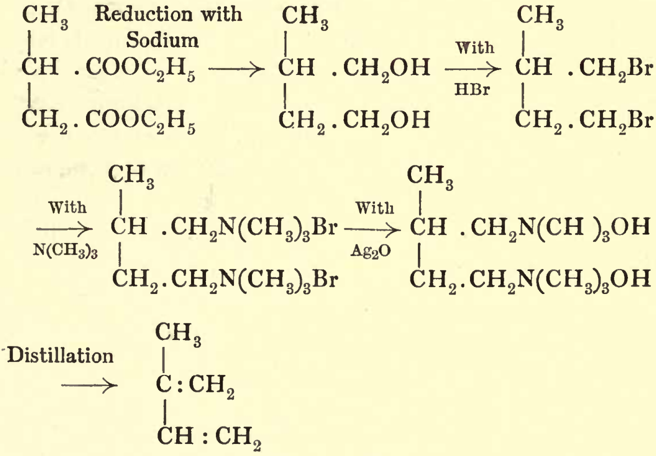
* A full investigation into such processes has been carried out by Staudinger and Klever.[143]

insignificant yields, and in addition the latter yields an impure product.



Blaise and Courtot[28] obtained isoprene from *αα*-dimethyl-*βγ*-dibrombutyric acid by distillation, and treatment of the product with quinoline.

A still better laboratory method is that of Neresheimer,[112] which gives fairly good yields of a very pure product. The starting-point is the diethyl ester of pyrotartaric acid.



$$\begin{array}{l} CH_3 \\ | \\ CH\ .COOC_2H_5 \\ | \\ CH_2.COOC_2H_5 \end{array} \xrightarrow{\text{Reduction with Sodium}} \begin{array}{l} CH_3 \\ | \\ CH\ .CH_2OH \\ | \\ CH_2.CH_2OH \end{array} \xrightarrow[\text{HBr}]{\text{With}} \begin{array}{l} CH_3 \\ | \\ CH\ .CH_2Br \\ | \\ CH_2.CH_2Br \end{array}$$

$$\xrightarrow[N(CH_3)_3]{\text{With}} \begin{array}{l} CH_3 \\ | \\ CH\ .CH_2N(CH_3)_3Br \\ | \\ CH_2.CH_2N(CH_3)_3Br \end{array} \xrightarrow[Ag_2O]{\text{With}} \begin{array}{l} CH_3 \\ | \\ CH\ .CH_2N(CH\ )_3OH \\ | \\ CH_2.CH_2N(CH_3)_3OH \end{array}$$

$$\xrightarrow{\text{Distillation}} \begin{array}{l} CH_3 \\ | \\ C:CH_2 \\ | \\ CH:CH_2 \end{array}$$

It will be observed that this method gets over the difficulty experienced in the previous synthesis of

Ipatiew, the formation of dimethylallene being impossible.

**From Acetylene.**—The methods previously cited have no commercial significance, but that which we will now consider is of great interest in view of the easy production of carbides.

Heinemann[81] proposed the preparation of isoprene by the action of heat on a mixture of acetylene, ethylene, and methyl chloride—

$$C_2H_4 + C_2H_2 + CH_3Cl = H_2C : C(CH_3) . CH : CH_2 + HCl$$

This excited much attention until shewn to be unworkable. In view of the work of Berthelot and others[111] on the pyrogenic condensation of acetylene the possibilities of this field cannot be said to be exhausted, and recently Dubosc[50] has proposed the preparation of acetaldehyde by passing acetylene into a solution of mercuric chloride. A precipitate is formed, and this yields acetaldehyde on treatment with acid and boiling, and is stated to constitute a starting-point for the cheap production of acetone and dipropylene.

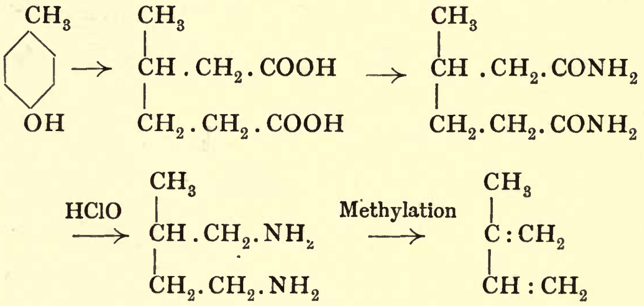
**From Petroleum.**—Attention has also been paid to the isopentane $(CH_3)_2CH . CH_2 . CH_3$ present in the low-boiling fractions of American petroleum.

In this connection we may notice two patents. The first[107] claims the conversion of isopentane into a dihalogen compound by the usual means and the removal of halogen acid with the formation of isoprene. The second[6] is more elaborate. The monohalogen derivative is first produced and, on treatment with lime to remove the halogen, yields trimethylethylene, $(CH_3)_2 : C : CH . (CH_3)$. This is then converted to the dihalogen derivative

$$(CH_3)_2 : CBr . CHBr . CH_3$$

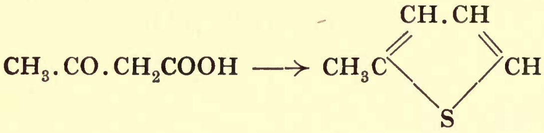
and passed, under reduced pressure at 350°, over a catalytic substance, such as alumina or barium chloride. The product is said to consist of pure isoprene free from dimethylallene.

**From Coal Tar.**—The next process is interesting in starting from a coal-tar product, and having been used successfully by the Bayer Co. for the production of isoprene on more than a laboratory scale. Here the starting-point is *p*-cresol, which is reduced by the Sabatier method. The resultant product is oxidised, thereby splitting the ring.[12] The $\beta$-methyladipic acid formed is after-treated as follows:—



Passing over several other processes for which the reader is referred elsewhere,[179] we come to those starting from starch and cellulose.

**From Starch and Cellulose.**—Heinemann[82] has proposed the preparation of methylthiophene, by hydrolysis of starch, oxidation, and subsequent treatment with phosphorus trisulphide.



Laevulinic acid Methylthiophene

This yields isoprene on reduction by Sabatier's method. Though a yield of 225 grms. of rubber is stated to have been obtained from 2 kilos of starch, the value of this process is somewhat doubtful, and the formation of piperylene rather than isoprene would seem more probable.

Alcohol is the basis of another process devised by Harries[75]—

$$C_2H_5OH \longrightarrow CH_3COOH \longrightarrow CH_3COCH_3 \longrightarrow \underset{\text{Dimethyl-ethyl-carbinol}}{(CH_3)_2C(C_2H_5)OH}$$

$$\longrightarrow \underset{\text{Trimethylethylene}}{(CH_3).CH:C:(CH_3)_2} \longrightarrow CH_3.CHBr.CBr(CH_3)_2$$

The resulting dibromide is passed over hot soda-lime which has previously been saturated with carbon dioxide at 600° C. By this method, which is shorter than that of Ipatiew, a 60 to 75 per cent. yield of isoprene is said to result. It will be remembered that this dibromide has been mentioned earlier in connection with *iso*-pentane, when a somewhat different method was used.

The greater portion of the work on these lines, however, has been carried out by the Synthetic Products Co. One complicated method[122] starts from lactic acid, obtainable from carbohydrates by fermentation, at less than 3d. per lb. The method depends on the treatment of an $\alpha$-halogen derivative of a fatty ester with a ketone in the presence of zinc; the resultant product is treated with bromine, then hydrolysed with the removal of two molecules of hydrobromic acid, and finally heated, with the elimination of carbon dioxide and the formation of isoprene.[120]

It is doubtful if such a complicated synthesis could have any technical importance, and, moreover, the final product is not pure, dimethylallene being formed at the same time.

These workers[108] then turned their attention to the *iso*-amyl alcohols present in fusel oil, particularly the fraction distilling at 128° to 131°. This consists of *iso*-amyl alcohol, $(CH_3)_2 : CH . CH_2 . CH_2OH$, and active amyl alcohol, $CH_3 . CH_2 . CH(CH_3) . CH_2OH$. These are converted to the monochlorides with hydrochloric acid, and then carefully chlorinated, so that dichlorides only result, the following predominating:—

*Iso*propyl-ethylene-dichloride $(CH_3)_2CH . CHCl . CH_2Cl$
Dimethyl-trimethylene-dichloride $(CH_3)_2CCl . CH_2 . CH_2Cl$
$\beta$-Methyl-tetramethylene-dichloride

$$\begin{matrix} CH_2Cl \\ CH_3 \end{matrix} \!\!> CH . CH_2 . CH_2Cl$$

On passing these over soda-lime at 470° and fractionating the product, a 40 per cent. yield of isoprene is obtained.

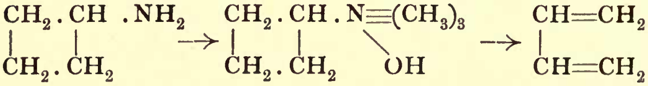
It has also been suggested that this result might be arrived at by dehydration and formation of unsaturated amylenes.[121] The dihalogen derivative could then be prepared by treatment with halogen, and isoprene eventually obtained, as in the previous instance.

### Preparation of Butadiene.

We will now consider the methods suggested for the preparation of butadiene, and it will be found that they closely follow those already mentioned for isoprene.

Ciamician and Magnaghi[42] started with pyrrolidine, using the method which was afterwards adopted by Euler for the preparation of isoprene. Its formation from acetylene and ethylene was early noted by Berthelot,[26] while Caventon[38] obtained a small yield by passing *n*-amyl alcohol through a hot tube, this latter being confirmed by Thiele.[149]

Another synthesis started from amino*cyclo*butane.[166]



A good laboratory method for the preparation of erythrene has been worked out by Harries; he first prepares *sec*-butyl alcohol either by the reduction of ethylmethylketone or from acetaldehyde and ethyl bromide by the Grignard reaction, and then dehydrates this with phosphorus pentoxide—

$$CH_3.CH(OH).CH_2.CH_3 \longrightarrow CH_3.CH:CH.CH_3$$

The dibromide yields butadiene by the soda-lime process (see p. 78).

The use of cresol for the preparation of isoprene has already been noticed, and it has been found that phenol can similarly be converted into adipic acid, and from that to erythrene.[18]

Another method of preparing butadiene is to heat *cyclo*hexanol (hexahydrophenol) to temperatures above 600° C. with or without the presence of catalysts,[19] when a good yield is said to result. A similar result is obtained when *cyclo*hexane comes in contact with an electrically heated aluminium silicate spiral,[21] and as the naphthenes present in Caucasian petroleum are of this type the method has been applied to them.[20]

**Butadiene from Carbohydrates.**—The process depending on carbohydrates as raw materials now remains to be considered.

Fusel oil is a bye-product produced only in small amount during ordinary alcoholic fermentation, and investigations were made to see if some improvement could not be effected in the yields obtained.

It had been noted by Ehrlich in 1905 and by other workers that the presence of amino-acids, such as leucine, greatly increased the production of higher alcohols during fermentation. Working on these lines, Fernbach and Strange[54] have devised processes for the cheap production of butyl alcohol and acetone, the fermentation of starch by the *butylic bacillus* of Fitz being accelerated by the products resulting from the action of the *Tyrothrix tenuis bacillus* on the nitrogenous matter present in yeast.

The butyl alcohol so obtained is converted to butylchloride, and then by chlorination, under carefully adjusted conditions, to the dichlorides—

$$CH_3.CH_2.CHCl.CH_2Cl$$
$$CH_3.CHCl.CH_2.CH_2Cl$$
$$CH_2Cl.CH_2.CH_2.CH_2Cl$$

These on passing over heated soda-lime yield butadiene in every case.

A process which seems promising in view of its simplicity has been worked out by the Synthetic Products Co., and depends on the conversion of aldehyde into aldol. This on reduction yields 1, 3-butylene-glycol, the dichloride of which yields butadiene on treatment with soda-lime.

$$CH_3CH(OH).CH_2.CHO \rightarrow CH_3.CH(OH).CH_2.CH_2OH$$

Before discussing the methods of polymerisation, the production of 2, 3-dimethyl-buta-1, 3-diene, or dipropylene, deserves mention, both on account of its preparation from acetone and the quality of the polymer. Pinacone is prepared by the method of Holleman,[96] acetone being condensed by means of magnesium amalgam—

$$2CH_3COCH_3 \rightarrow CH_3.C(CH_3)OH.C(CH_3)OH.CH_3$$

This is then dehydrated by distilling over sodium bisulphate,[14] giving dipropylene in satisfactory quantity. Another method said to give a 70 per cent. yield consists in passing the pinacone over alumina at 400°.[174]

## Preparation of Rubber from Isoprene and its Homologues.

It now remains to consider the methods which have been proposed to effect the polymerisation of isoprene and its homologues. Some have already been mentioned — for example, treatment with acid, auto-polymerisation, and the action of light, but these were in every case uncertain and too slow to possess any technical importance.

In 1909 the Bayer Co. found that polymerisation took place when isoprene was heated in a sealed tube, and the next year Harries found the presence of acetic acid under such conditions accelerated the change. The function of the acetic acid is probably that of a diluent, as other solvents appear to act in this manner.[13] The use of numerous other substances and methods has been suggested for the purpose, and amongst these may be instanced alkalis,[7] amides and nitrides, alkaline earths,[15] urea, blood fibrin, etc.[16]; heating followed by acid treatment, oxygen or ozone, ultra-violet light or Röntgen rays, anhydrides of organic acids and organic, inorganic acids or sulphur in traces.[8]

The products yielded by these methods will respond to the tests postulated by Harries[77] for a true caoutchouc; for this reason these bodies are termed "normal" caoutchoucs.

We now come to a discovery made almost simultaneously in Germany by Harries,[75] and in England by Matthews,[110] the formation of caoutchouc by treating isoprene or its analogues with a small quantity of sodium or metallic amalgam, either in the cold or with the application of moderate heat.

The great importance of this is that the reaction is practically quantitative, and takes place quickly at a low temperature. In addition, the presence of impurities seems to have less effect generally than in the other processes, in which successful polymerisation is somewhat uncertain.

The products prepared by the sodium process react less readily with ozone and yield ozonides different in character to those derived from the corresponding "normal" caoutchoucs. The following information is given by Harries[75, 77] regarding the properties of these bodies.

**"Normal" Isoprene-Caoutchouc**, prepared either by heating, auto-polymerisation, or the acetic-acid process, requires to be kept in carbon dioxide in the dark, as it readily oxidises, particularly when prepared at a high temperature. A proportion of a terpene is formed as a bye-product during polymerisation. The material prepared by auto-polymerisation gives the best product on vulcanisation.

**"Normal" Butadiene - Caoutchouc** has similar physical properties, and is also obtained admixed with a terpene bye-product.

**"Normal" Dimethyl Butadiene-Caoutchouc** is obtained in the same way, but more slowly. Its physical qualities are good, and it can be easily cold cured. As 50 grms. are stated to yield 16 grms. of caoutchouc after heating for twenty-three days at 100° C., the yield cannot be said to be very satisfactory. Its derivatives closely resemble those of the isoprene product.

**The "Sodium" Butadiene-Caoutchouc** is formed almost quantitatively after three hours' heating at 40° to 50°, and somewhat more slowly at ordinary temperature. After purification it is yellow in colour and transparent, and when newly prepared is soluble in ether, chloroform, and benzene, yielding a viscous solution, but it becomes insoluble on keeping. It can readily be vulcanised either by the cold or hot process, and is exceedingly strong and "nervy."

It forms a bromide and nitrosite, but reacts with ozone less readily than does the "normal" rubber, and it seems probable that the constitution of these bodies is different. This view is supported by the fact that the products of hydrolysis of the ozonides are completely different.

**"Sodium" Isoprene-Caoutchouc.**—The polymerisation of isoprene by the "sodium" process is much slower than in the previous instance, and is more dependent on the purity of the raw material, though under suitable conditions it is practically quantitative. The resultant product is tough and readily vulcanised, and appears to be of technical importance. It is soluble in the customary solvents, and forms the usual derivatives, but the ozonide again indicates that this body differs in constitution from the natural and "normal" products.

**"Sodium" Dimethyl Butadiene-Caoutchouc** is less readily formed, several days' heating at 60° C. being necessary. The product is brown in colour and appears to consist of two different bodies, one soluble and one insoluble in ether.

## Miscellaneous Methods.

It is interesting to notice that the use of enzymes has suggested itself to several inventors, possibly with a view to imitating the conditions of formation of rubber in the plant itself. The earliest application on these lines was that of Gottschalk in 1907, dealing with the action of bacteria on hydrocarbons.

Patents have been obtained for the production of rubber from peat,[29] tar,[37],[66] and "terpene material" by means of various enzymes.[162]

At various times paragraphs have appeared in the papers announcing successful syntheses from such unpromising materials as fish[168] and seaweed,[169] and though the writer has had the privilege of examining samples purporting to be manufactured by such processes, he has seen no ground to modify his previous opinions as to their value.

### Prospects of Synthetic Rubber.

It therefore appears that the "normal" caoutchouc from dimethyl butadiene and the "sodium" caoutchoucs from butadiene and isoprene at present hold out the most prospects of commercial success.

During the last two years rapid strides have undoubtedly been made, but it cannot be said that a successful issue has yet been reached, nor for that matter does it appear probable in the immediate future.[177]

The Bayer Co. certainly have exhibited articles manufactured from the synthetic product, but their chief chemist, Dr Duisberg, recently stated, "The difficulties which have been overcome were great indeed, but those which still remain to be surmounted are still greater."

Apart altogether from the important question of cost, it appears doubtful if any artificial rubber has been prepared which will answer the manufacturer's requirements in regard to strength, stability, and vulcanisation qualities.

Meanwhile, due credit must be given to the splendid work and results already achieved, and every chemist must hope that success will ultimately attend the efforts of workers in this difficult field.

For fuller information on Synthetic Caoutchouc, reference may be made to the following :—

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