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REPORT OF THE CHIEF OF THE BUREAU OF  
CHEMISTRY AND SOILS, 1935



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UNITED STATES DEPARTMENT OF AGRICULTURE,  
BUREAU OF CHEMISTRY AND SOILS,  
Washington, D. C., August 31, 1935.

HON. HENRY A. WALLACE,  
*Secretary of Agriculture.*

DEAR MR. SECRETARY: I present herewith the report of the Bureau of Chemistry and Soils for the fiscal year ended June 30, 1935.

Sincerely yours,

HENRY G. KNIGHT, *Chief.*

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### INTRODUCTION

The function of the Bureau of Chemistry and Soils is to apply chemistry and other natural sciences to the solution of problems connected with the production and profitable utilization of agricultural commodities. The solution of these problems benefits agriculture primarily, but also benefits the entire Nation, indirectly, since the products of the soil are used for food, clothing, and shelter, the three prime necessities of human life for which man must labor. The work is directed toward the conservation and profitable utilization of the soil, the acquisition and dissemination of knowledge concerning the distribution of soils of different types and the suitability of various soils for particular uses, a study of the fundamental factors concerned with the maintenance of soil productivity, the prevention of deterioration and loss of agricultural products and property, and the economic utilization of agricultural products and byproducts, by the application of the natural sciences to the technology of their preservation and conservation.

Most of the work is of research character with definite objectives intended to solve or assist in solving specific and urgent problems relating to soils, and the utilization of soil products, which have a direct bearing on the stabilization and prosperity of American agriculture. The activities for each year are definitely planned in advance and are divided into projects and subprojects for which funds are allotted from the annual appropriation for their support.

During the past year the Bureau's research work included investigations along the following lines: Soils and peats; nitrogen, potash, and phosphate fertilizer materials and their sources; concentrated mixed fertilizers; nitrogen fixation by living organisms; composition of foods; microbiology of foods; food deterioration and spoilage; food preservation and utilization; toxic effects of possible food contaminants; plant pigments; the nature of enzyme action; chemistry and nutritional value of proteins and vitamins; microbiology, preservation and utilization of hides and skins; sources of tanning materials; composition and properties of vegetable oils; chemistry of lignin; fermentation methods for the production of lactic and gluconic acids from sugars; utilization of wastes from crops and industries using farm products; prevention of farm fires and dust explosions; composition and properties of turpentine, rosins, and pine gum; and improvements in the technic of producing fertilizers, feeds, sugars, starches, sirups, proteins, tanning materials, turpentine, rosin, and fruit products.

In large measure the work of the Bureau requires the practical application of scientific knowledge, particularly a knowledge of chemistry in its broadest



sense, and other sciences involved in the study of soils, fertilizers, and agricultural materials. When there is a lack of fundamental knowledge needed to attack a specific problem, such knowledge must first be acquired through research in pure science. The results of such research contribute to the advancement of science in general and may have applications in fields other than agriculture.

Obviously scientific facts and principles already known should be put to useful purposes in farming, in utilizing the products of the farm, in the production of fertilizers, and in the industrial utilization of agricultural products. Usually the practical application of such knowledge comes many years after its development and dissemination. As needs arise, however, informed and progressive individuals in agriculture and in industries manufacturing fertilizers or using agricultural products may be depended on to make useful application of existing and available scientific knowledge and to pioneer in new or improved practices. The Bureau of Chemistry and Soils, therefore, is continually striving to give more of its attention to basic or fundamental research to develop new scientific facts and principles relating to soils, fertilizers, plant and animal nutrition, the elaboration of chemical substances by plants and animals, and the chemical composition and properties of agricultural products, which facts and principles may be applied by those engaged in agriculture or industries based on agriculture.

#### BASIC RESEARCH ON SOILS

Much of the investigational work in the chemistry and physics of soils, incidental to soil classification and the study of soil erosion, is of fundamental importance. During the past year it was found that certain soils contain, to varying degrees, selenium, arsenic, cobalt, nickel, zinc, copper, chromium, vanadium, and barium, and it appears that these trace elements may play an important role in soil behavior. Work on the detailed chemical composition of typically representative profiles of the great soil groups has shown that the composition of the active component of the soil, the colloid, is characteristic for each group. Soils and colloids of the semiarid areas were found to owe their characteristic differences primarily to the parent material. This is in sharp contradiction to the results previously found for humid soils. A study of the base-exchange capacity, neutralization curves, and the maximum acids shown by the colloids of the great soil groups is expected to yield a scientific explanation for the differences in the deterioration of soils by use. Studies are also under way on the effects of different climatic conditions on soils derived from the same parent material. An investigation of the causes of infertility in a group of soils derived from serpentine showed that in addition to having unfavorable physical characteristics, these soils contained large quantities of magnesium, chromium, and nickel, any or all of which may contribute to their low productivity.

#### BASIC RESEARCH ON FERTILIZERS

In the fertilizer investigations studies were made by physico-chemical methods of the factors which influence and determine the activities of catalysts in the various steps of processes for converting atmospheric nitrogen into nitrogenous fertilizer materials. In the synthesis of ammonia from nitrogen and hydrogen the two gases do not combine under any known conditions of temperature or pressure unless certain substances are present, which bring about chemical reaction on their surfaces. These substances are called catalysts. The success of the process depends upon effective and continuous functioning of the catalyst. A fundamental understanding of catalytic phenomena is useful in devising improved catalysts and catalytic procedures for the production of nitrogenous fertilizer materials. It will also be useful in other processes, not related to agriculture, where catalytic reactions are involved.

It was discovered during the past year that the isotherms of a number of gases near their boiling points bear a certain relationship to the amount of gas necessary to form a monomolecular layer on the catalyst surface. This fact furnishes an apparent means for estimating the surface area of synthetic ammonia catalysts. By decomposing ammonia on promoted iron catalysts it was found that the rate of reaction between nitrogen and hydrogen depends upon the partial pressures of ammonia and hydrogen and upon temperature. In measuring the heat of vaporization of electrons from catalytic surfaces



by the photoelectrical method it was discovered that activated adsorbed gases have a pronounced effect in lowering the energy of the escaping electrons, which indicates that in one form of adsorption the dissolved gas approaches an ionized state, and helps to substantiate recent theories of surface reactions.

Other research work of a fundamental character included the determination of the solubility of helium gas in water at various temperatures and at pressures ranging up to 1,000 atmospheres and the solubility of a 3:1 hydrogen-nitrogen mixture in water at 25°C. under pressures ranging from 50 to 1,000 atmospheres. Data were obtained which contribute toward a better understanding of the nature of the solution of gases in liquids.

Measurements were made of the vapor pressures of phosphorus pentoxide at temperatures ranging from 200° to 600° C. with specially constructed apparatus capable of measuring vapor pressures at temperatures up to 1,000°.

The crystallographic and optical constants of various acid phosphates and their hydrates, in pure form, were measured by X-ray diffraction analysis. An X-ray study of a number of oxalates, selected as representative organic compounds, showed a correlation of the shape and orientation of the oxalate group in the crystals with the optical properties of oxalates in general. The use of electron diffraction as a method of analysis disclosed that the phosphorus molecule in the gas phase at 200° C. is a regular tetrahedron.

In work upon the absorption of light by nitrogen trioxide gas a band spectrum due to nitrous acid was discovered, which furnishes a means for determining this substance in gaseous systems. The effect of pressure upon the absorption spectrum of nitric oxide was studied and a theoretical explanation was deduced. Infrared absorption coefficients were determined for more than 50 organic compounds containing the groups  $\text{NH}_2$ ,  $\text{NH}$ , and  $\text{OH}$ . The results are particularly important because they provide a method of quantitative analysis of these groups in molecules that are soluble in nonpolar solvents.

By use of the mass spectrograph it was found that the atomic weights of lithium, potassium, and rubidium can be determined with an accuracy far greater than by chemical means. Certain plant and animal tissues were found to have a pronounced ability to concentrate the heavier radioactive isotope of potassium. Studies will be made to determine the physiological significance of this preferential selection of one potassium isotope over another.

In a study of the production of nitrogenous compounds by the organism, *Azotobacter*, it was found that nitrogen fixation is probably a reduction rather than an oxidation process, and that the ammonia production reported by previous investigators must have been derived from cell nitrogen and not by direct synthesis from nitrogen gas as was supposed. Various intracellular enzymes, which may be instrumental in the production of nitrogen compounds by *Azotobacter*, were identified and a number of the intermediate compounds formed in ammonification were determined. It was found that the recently discovered accessory substance which is essential for the respiration and growth of certain species of organisms in legume nodules has many properties in common with pantothenic acid, but is not identical with it. Studies on leguminous plants indicated that the greater part of energy supply is not consumed in the chemical process of nitrogen fixation, as is commonly believed, but is utilized chiefly for the respiration and growth of the bacteria and host.

A nitrogenated compound was obtained by the reaction of active nitrogen with diphenyl acetylene. This is the first time that the possibility of such nitrogen reacting with organic substances has been demonstrated and the first case in which nitrogen has been fixed directly by an organic compound apart from living processes. The reaction has little practical significance but serves as a foundation for anticipating the introduction of nitrogen of a much lower energy content into organic compounds.

The use of modern physical and physicochemical research methods in the furtherance of fertilizer investigations constitutes pioneer work and will assist scientific investigators in the solution of numerous problems which depend upon a knowledge of the physical constants and ultimate structure of the elementary substances and compounds involved.

#### BASIC RESEARCH ON AGRICULTURAL PRODUCTS

Much of the research on the chemistry and technology of agricultural products is also fundamental. New knowledge gained from the study of the nature of enzyme action will be useful in many fields. Enzymes are organic substances of unknown chemical constitution contained within the living cell which are able to bring about chemical changes in plant and animal tissues



They are responsible for all the changes of ripening, curing, digestion, and decay, including food spoilage and fermentation. With an adequate knowledge of enzyme chemistry the course of chemical changes in plant and animal products may be predicted and possibly controlled. During the past year studies were made on the action of four different enzymes including the protein-digesting enzyme of wheat flour and the enzymes taking part in the spoilage of eggs, the darkening of fruits on drying, and the heating and decomposition of moist alfalfa hay. The wheat enzyme separated from bran was obtained for the first time in solution and was identified as belonging to the class of enzymes represented by papain.

Another research of fundamental character is that on plant pigments, which is a comparatively new field. Work outside of the Department showed a few years ago that some of the yellow plant pigments are the precursors or parent substances of vitamin A. It is likely that other plant pigments contribute toward the nutritional value of the foods in which they occur. Plant pigments are also important in that they affect the salability of fruits and vegetables, and food products prepared from them. The Bureau's work on plant pigments during the past year was concerned mostly with the coloring matters of apples and corn. The yellow pigment occurring in Grimes Golden and Jonathan apples was isolated and identified as a new and previously unreported galactoside of the flavonol, quercetin. Chrysanthemine chloride, an anthocyanin coloring matter, was isolated in pure form from purple-husked corn. Comparative studies on the pigments from brown-husked and purple-husked types of corn have indicated the possibility of a conversion in the plant of the flavonols (yellow pigments) to anthocyanidins (red pigments) by reduction of their corresponding homologous glucosides. Similar indications were observed in the study of red and yellow coloring matter in apples. This relationship, if definitely proved, constitutes a new and important discovery in connection with plant pigments. The work on corn pigments is of interest and value in connection with corn-breeding experiments.

Additional knowledge was gained during the year on the chemical components of the cuticle waxes of fruits. Oleic acid and the hydrocarbon, *n*-nonocosane, were found to be the predominant compounds of their respective classes in pear wax. Ursolic acid, previously found in apple and cranberry waxes, is also present in pear wax.

Studies on yeast proteins yielded more definite information concerning the actual quantity of proteins in yeast and the amino acid content of yeast proteins. An investigation on wheat containing the toxic element, selenium, showed that the selenium is present in an organic form intimately associated or combined with the protein. Most of the selenium could be concentrated in the leucine and tyrosine fractions of the hydrolysis products of the wheat gluten. An improved method was devised for determining the amino acids in wheat flour. A popular brand of commercial wheat flour was found to contain 0.31 percent cystine, 0.16 percent tryptophane, and 0.22 percent lysine, which shows that the protein of wheat flour compares more favorably with other proteins, as regards the nutritional value of its amino acids, than is generally appreciated.

Studies on the value of alpha- and beta-carotene as sources of vitamin A showed that alpha-carotene has about 56 percent of the potency of beta-carotene. The laboratory findings lend support to the view that gamma-carotene and cryptoxanthin, which also serve as sources of vitamin A, are only one-half as valuable as beta-carotene. These results have an important bearing on attempts to establish vitamin A potency of plant products by chemical and physical methods.

In the work on industrial fermentations a species of mold was found which will give high yields of dextro-lactic acid as a result of its action on glucose. This discovery is of fundamental significance because it is the first time that dextro-lactic acid, which differs in its properties from the usual kind of lactic acid, has been produced in appreciable quantity outside of a living animal body, where it exists as a constituent of muscular tissue. This form of lactic acid may prove to have industrial and medicinal uses.

Progress is being made in the research on lignin, one of the three principal constituents of plant materials. While the ultimate purpose of this investigation is to develop uses for the immense quantities of lignin annually going to waste with crop byproducts, the work on its chemical structure and derivatives, which is an essential prerequisite to the practical utilization of lignin in chemical industries, is of interest to science in general.



Fundamental studies are being made on the microbiology of hides and skins to develop knowledge required for the very practical purpose of preventing hide damages and serious losses in leathermaking from the action of microorganisms during cure, or temporary preservation, prior to tanning. During the past year further attention was given to the organism causing the flesh reddening of salted hides. The organism was isolated and tentatively identified. A stage of growth of this organism with which no well-defined stainable bacterial cells could be associated was observed for the first time, as was also its great variation in cell types, or appearance, depending on the nutrients upon which it grows. This observation helps to explain the origin of much confusion in this field of work which is of interest in connection with the salting of fish, meats, and other food products, as well as in the curing of hides and skins.

Another example of fundamental research with practical value to agriculture as the ultimate goal is the study of the chemical components of pine gum, rosin, and the various kinds of turpentine obtained from southern yellow pines. Work is in progress on the separation and identification of the chemical components of steam-distilled wood turpentine, which contains approximately 20 compounds, including terpene and aromatic hydrocarbons, aldehydes, secondary and tertiary alcohols, phenols, oxides, and phenol ethers. More complete knowledge regarding the minor constituents of various kinds of turpentine is useful in distinguishing one kind from another and also in connection with the development of new uses for turpentines and the suitability or adaptability of different turpentines for specific uses.

The examples cited show that the work of the Bureau of Chemistry and Soils, although designed to be of practical service to agriculture, nevertheless contributes materially to the advancement of science. More detailed information regarding the investigations mentioned is given in the body of this report, together with the results of other activities.

## CHEMICAL AND TECHNOLOGICAL RESEARCH

### CARBOHYDRATE INVESTIGATIONS

#### SUGARCANE

A proper evaluation of the new varieties of sugarcane, which have recently been developed, requires a knowledge of the "working quality" of the juices in the sugar factory, as well as information regarding cultural requirements and disease-resistance characteristics.

During the 1934 cane-harvesting season additional studies were made on the sulphur-lime and the tannin-lime methods of clarification when applied to juices from new varieties of cane. Particular attention was directed toward the effects of the clarification process upon the chemical composition of the juice, concentrated sirup, and crystallized sugar, upon certain physical characteristics of the sirup and sugar, and upon the yield of crystallizable sugar. Preliminary data were obtained on the volume and weight of "mud" separated by the different clarification methods.

Examination of the results of the clarification studies during the past 3 years is under way, and a comprehensive report will be made comparing the various modifications of the methods which have been used.

The studies pertaining to the effect of cultural conditions on the composition and workability of different varieties of sugarcane were continued at the Houma, La., station in cooperation with the Soil Fertility Division and the Division of Sugar Plant Investigations of the Bureau of Plant Industry. The samples of cane were from test plots, which represented various soil types and fertilizer treatments, located in different sections of the sugarcane belt. Particular attention was given to the two newly released varieties, C. P. 28/19 and C. P. 28/11. From the chemical standpoint the juices of these two varieties are strikingly different, for C. P. 28/19 is low in ash, being nearly on a par with the P. O. J. varieties, with which they were compared and which have previously been studied, while C. P. 28/11 is decidedly higher in ash than any variety thus far examined. This higher ash content is principally due to increased quantities of potash, phosphate, and sulphate. The high ash content of juice from C. P. 28/11 resulted in increased quantity of ash in the sugar, but in other respects the sugar quality was average. The sugars from C. P. 28/19 were lower in ash and of better color.



The effect of soils on juice and sirup composition was seen to be greatest when comparing the southwestern portion of the Louisiana sugar belt with the southeastern portion. There were marked contrasts both in the quantity of ash and its composition, and also in the color of the sirups and sugars. The juice of cane from the former section was low in ash, yet comparatively high in lime and silica; the reverse was true for the southeastern section. These differences are in some cases more marked than is the contrast of the effects of so-called "sandy" and "black land" soil.

The investigation on the deterioration of harvested sugarcane was continued in cooperation with the Division of Sugar Plant Investigations. The primary object of this work is to ascertain how harvested sugarcane may be stored for fairly long periods with a minimum of deterioration in order that cane mills may have sufficient supplies for continuous operation and not be forced to shut down during wet weather when it is impossible to haul cane from the fields.

It was found previously that deterioration could be retarded by occasionally sprinkling the piles of harvested cane with water. This practice has been adopted by a few of the sugarcane plantations and it is believed it will expand as additional detailed information becomes available from further investigational work by this Department and as the growers become familiar with the method and the advantages of its adoption.

During the 1934 season particular attention was given to some of the fundamental phases of the problem, such as the influence of temperature, humidity, maturity, and varietal differences on the rate of deterioration. The findings substantiated those of previous seasons in that storage under dry conditions was conducive to deterioration. The best temperature for storing cane under moist conditions was about 65° F. More deterioration took place at 45° than at any higher temperature studied, the highest temperature being 75°. Of the four varieties of cane studied Co. 281 was the most resistant to deterioration; the others in descending order were Co. 290, C. P. 807, and C. P. 28/19. Cane harvested late in the season deteriorated at a slower rate than less mature cane.

Some attention was also given to the deterioration characteristics of a number of the new varieties of sugarcane being developed by the Bureau of Plant Industry for the purpose of aiding in their evaluation for commercial planting. These canes, after harvesting and stripping as for milling, were stored in small piles under shelter and were also windrowed in unstripped condition in accordance with the usual practice. None of the varieties tested was as resistant toward deterioration as was Co. 281, which was used as a standard.

It was found that the invertase content of sugarcane increased with the time of storage and to a somewhat greater degree under dry than under moist storage conditions. It was also found that, roughly, the invertase content of the fresh cane was proportionate to the susceptibility of the different varieties of cane to deterioration. Although Co. 281 deteriorates very slowly, even under adverse storage conditions, it contains sufficient invertase to cause a very much higher degree of inversion than ever takes place. The factors which control the reaction between the invertase and the sucrose in the live plant are unknown. Analyses of the nodes and internodes for sucrose and reducing sugars revealed the fact that inversion takes place at approximately the same rate in both types of tissue in spite of the much higher concentration of invertase in the nodes.

#### SUGARCANE SIRUP

The greatest need of the farmers who produce sugarcane sirup as a cash crop continues to be an improvement in the quality and uniformity of their product in order to meet market requirements to the best advantage. The many requests for information on practical farm methods for the production of sirup of more uniform and higher quality have been met by the dissemination of circulars on the subject and by demonstration work in the field. In cooperation with the east-Texas branch of the Texas Agricultural Experiment Station, the sirup-making qualities of six of the newer varieties of sugarcane were compared by use of the Department's standard small-scale method of sirup making. Demonstrations of farm-scale sirup making, including the use of invertase to prevent crystallization, were given in Texas and Mississippi. During the past few years sirup makers in Mississippi have been growing increasing quantities of the newer varieties of sugarcane. These new canes are not only better tonnage producers and more resistant to disease, but are also richer in crystallizable sugar than are the older varieties. Sirup makers are rapidly learning that they



now need to use the invertase process, whereas a few years ago with the older varieties of cane the use of invertase was not so frequently necessary.

In cooperation with the Division of Sugar Plant Investigations, about 50 samples of table sirup were made from several of the newer varieties of sugarcane at the Houma, La., Experiment Station. This investigation of the sirup-making qualities of the new canes is of considerable commercial importance, and supplements the determination of cultural requirements, and tonnage and sirup yields, as a means for deciding what varieties are best for commercial cultivation.

#### SORGO SIRUP

Sorgo sirup as produced on many farms in the United States is decidedly nonuniform in quality. This defect has been a serious handicap to farmers in obtaining the fullest profit from this important cash crop. Investigations were continued for the purpose of devising means whereby sorgo sirup of more uniform and improved quality may be made directly on the farm. The new methods which have been previously reported were studied further in order to adapt them in the most practical and efficient manner to farm-scale operation. Considerable attention was also given to the effect of variety and cultural conditions on the quality of sirup produced by a standardized method.

One of the principal difficulties experienced by sorgo sirup producers is slow boiling, which often results in scorching the sirup. This trouble was found to be caused by the presence of starch in the juice, which in addition to retarding evaporation will, if present in large quantity, cause actual jellying of the sirup. The use of a high diastatic malt for hydrolyzing the starch is recommended to overcome this difficulty. It was found that the greatest benefit from the use of malt is obtained by applying it after the juice has been evaporated to a semisirup. The usefulness of the diastase method for preventing slow boiling, scorching, and jellying of sorgo sirup was demonstrated in cooperative work with the Arkansas Agricultural Experiment Station. The drought of 1934 apparently was responsible for the fact that it was practically impossible to produce sirup of satisfactory quality by the usual farm methods. By employing the newly developed improved method, sirup of excellent quality was produced from the same sorgo cane.

In a further study of the quality of sirups made from different portions of the stalk it was found that considerable improvement in the quality of sirup could be obtained by utilizing only certain portions of the stalk. Whether this will prove to be a practical aid has not yet been fully determined.

Demonstrations of the new methods for sirup making were made in Texas, Arkansas, and Mississippi at the request of the respective State directors of extension. Cooperative agreements between the Bureau of Chemistry and Soils and the State agricultural experiment stations at Starkville, Miss., and Fayetteville, Ark., were entered into for the purpose of conducting research on the suitability of different varieties of sorgo for sirup production, particularly when considered in relation to soil types, fertilizer treatment, and climatic conditions.

#### HONEY

Further work was done on a new method of processing extracted honey and a description of the method was published in a number of trade journals. The new method, as finally developed, is based upon the filtration of honey at its original density mixed with a small proportion of diatomaceous earth having rapid filtering quality, preceded by rapid heating and followed by rapid cooling. The resulting product is brilliantly clear, and there is no tendency to form surface foam or scum. The color, flavor, and aroma of the honey are not changed. Granulation is retarded, which is an important factor in the marketing of extracted honey. The development represents a decided improvement over existing methods of processing honey, which do not reduce turbidity to any appreciable extent, which cause an appreciable loss of aroma and flavor, and which are likely to result in the formation of scum on the surface and, usually, in some darkening of color due to long heat treatment.

In cooperation with a commercial firm about 1 ton of extracted honey was processed by the improved filtration method for the purpose of trying out the method thoroughly and to make available material for further large-scale and laboratory tests.

Laboratory tests on samples of honey processed by the improved filtration method showed that sensitive constituents, such as enzymes, were unaffected



by this method of processing. This is in contrast to results obtained by the usual methods of processing in which the diastase and other enzymes are greatly weakened in activity, and in some cases entirely destroyed. The mineral content of the honey was unchanged. Changes in density were in most cases too small to be measurable by the usual methods. Color and flavor were unchanged. The number of colonies of yeasts which could be developed from the filtered honey was only a fraction of the number which could be developed from the unprocessed honey. This characteristic may be important as a means of combating fermentation in honey without resort to drastic heat treatment, which usually results in injury to the color and flavor of the honey.

Work was continued on the development of a small processing plant suitable for the honey producer. Certain parts of the equipment were built and tested to insure proper working, and drawings of a small-plant design were made for publication.

#### SUGAR BEETS

Certain food industries in the areas of beet-sugar production have not been inclined to use beet sugar for all their sugar requirements because of nonuniformity in quality. This is a serious drawback to the economical distribution of this important agricultural product and materially reduces the price obtained by sugar-beet growers. As an aid in combating this situation investigations have been continued to determine the identity of those non-sugar constituents of the sugar beet which have an adverse effect upon the quality of sugar and means for reducing or eliminating these constituents. Further study was also made of the analytical methods employed in the examination of the samples of sugar and other products.

As a result of the research work by the Bureau of Chemistry and Soils, commercial beet sugar has become more uniform in character, and its quality has improved progressively during the past few years. The improvement in quality is indicated by the yearly average values for the ash content of beet sugars analyzed since 1929. In that year the average value for ash content was 0.043 percent. There has been a decrease in the average value for ash content each year, and in 1934 it was only 0.014 percent. Samples submitted by 18 of the 52 cooperating factories during the 1934 beet-sugar season showed an ash content of 0.01 percent or less, while in 1933 there were only 5 of 53 factories in this class. Complete analytical data on these sugars, including screening tests, in correlation with the factory operating data, are being prepared for publication.

#### UTILIZATION OF CULL SWEETPOTATOES FOR STARCH

The starch content of sweetpotatoes determines their intrinsic value from the standpoint of industrial utilization. A survey previously made by the Bureau showed that there is a potential market for root starches in the United States to replace imported potato and cassava starches. In previous reports it was shown that sweetpotato starch is suitable for the sizing of warp yarns, for finishing cotton fabrics, for laundry use, for conversion into dextrin to be used for adhesives, and for paper sizing.

As a step toward establishing a sweetpotato-starch industry in the United States, the Federal Emergency Relief Administration allocated funds to the Mississippi Emergency Relief Administration for the manufacture of starch and byproduct pulp by the process developed in the Bureau of Chemistry and Soils. The Bureau provided the technical, chemical, and engineering direction and supervision necessary for the purchase, installation, and operation of the equipment, conducted such plant research as was required to insure successful operation of the factory, and acted in a directing capacity in the disposal of the finished products and byproducts. The Mississippi Agricultural Experiment Station acquired the title of the factory equipment and properties and leased them to Sweet Potato Growers, Inc., a cooperative agency organized under the Mississippi State cooperative laws for operation of the plant.

During the summer and early fall of 1934 starchmaking equipment necessary for processing 60 tons of sweetpotatoes per 24 hours was selected and installed as well as a laboratory and experimental plant. The latter were put in operation about October 10, and the factory proper about November 10. During the operation of the plant detailed tests were conducted to determine the



capacity and efficiency of the various pieces of equipment. The plant ceased operations on December 29.

From the result of the first season's operation and further study of the project, a number of changes, both in the chemical treatment and mechanical equipment, are being made which should place the plant on a wholly satisfactory operating basis.

About 70 tons of starch were produced, most of which was purchased by a local cotton mill for use in sizing warp yarn. Feeding tests conducted by the Mississippi station, using sweetpotato pulp, a byproduct of the starch factory, showed it to be a highly satisfactory feed for milk cattle and for fattening beef cattle when used as a substitute for corn in certain mixed feeds. Dextrin prepared from sweetpotato starch produced in the Laurel plant was submitted to the Bureau of Engraving and Printing, which reported it to be suitable for postage-stamp adhesive.

#### CARBOHYDRATES IN DOMESTIC PLANTS

The investigation on the utilization of chicory roots as a source of inulin and of levulose sirup was continued.

There is a definite market for levulose sirup of good color and clarity and a high degree of sweetness, because it is noncrystallizable under ordinary conditions of use and promotes retention of moisture when used in food and other products. Levulose sirup from chicory gives promise of utilizing an agricultural crop which now is grown only to a limited extent, but could be easily expanded.

Particular attention was given to the production of a suitable grade of levulose sirup on a semicommercial scale and to overcoming some of the difficulties previously encountered. Several improvements of a chemical and mechanical nature were introduced, which resulted in the production of a very satisfactory sirup of light amber color and neutral flavor. Further study is being made for the purpose of lowering, if possible, the cost of producing levulose sirup from chicory and of finding means of utilizing profitably the extracted pulp.

Cooperative work on the value of inulin from a medical and dietetic standpoint was continued in cooperation with medical specialists, and a fundamental study on the hydrolysis of inulin was begun.

#### FOOD-RESEARCH INVESTIGATIONS

##### ENZYME STUDIES

A continuation of the study of trypsin in egg white has confirmed the opinion expressed in the last annual report that spoilage of eggs in storage is due to the activity of this enzyme. Such spoilage results in a loss of millions of dollars annually. Carefully controlled experiments have shown that the amount of active enzyme decreases as the hydrolysis of the thick white progresses, while at the same time the alkalinity rises to a maximum and then drops back. The same trend was shown by stored eggs treated by the vacuum oiling process developed in this Bureau and previously reported. Changes were in smaller degree, and the difference was so marked as to show very clearly that the oiling process slows down the proteolytic cleavage of the egg white which causes the spoilage.

Based on this work an improvement in the commercial manufacture of dried egg albumen has been devised. Trial runs demonstrated that by the use of the specified enzyme treatment the processing time can be reduced to 2 days as against the usual 7½ days; the quality is better, as shown by the usual trade laboratory tests; and the sanitary condition of the product is markedly improved, as evidenced by a bacterial count of about one-sixth of that to be expected from material treated by the usual commercial methods.

Owing to cost of production the domestic egg-drying industry has been unable to make much headway in competing with the imported product. It is hoped that the advantages of this new process, on which a patent dedicated to public use is being secured, will enable the industry to operate with profit to themselves which should be reflected back in profits of egg producers.

Work on the enzymes encountered in breadmaking showed that the protein-digesting enzymes of flour interfere with the production of high-quality com-



mercial bread. These undesirable enzymes were known to exist but had never been measured, isolated, or identified.

Coarser flours containing more of the outer tissues of the wheat were found to contain more of the enzymes. Wheat germ and bran are particularly rich sources. The enzyme was finally separated from the bran, obtained for the first time in solution, and identified as belonging to the class of enzymes represented by papain.

The effect of this enzyme solution upon the process of commercial bread-making was found to be very unfavorable. The beneficial effects due to bleaching or aging flour, or adding oxidizing agents such as persulphate to the dough, are mainly the results of the destruction of this proteinase.

The work on dried fruit darkening has been continued. It was found in the practical handling of evaporated apples that in order to obtain the best results in the prevention of discoloration care is necessary to prevent contamination with heavy metals. Nickel and copper are apparently worse than iron; hence stainless-steel equipment is preferable to monel metal in commercial drying plants.

A series of experiments on the decomposition of alfalfa in oxygen, in nitrogen, and in carbon dioxide was conducted. While the decomposition is due to enzymic change, the causative enzymes are found both in the plant itself and in the micro-organisms contaminating it. These two factors were not evaluated separately. The thermal effects, as was to be expected, were marked only in oxygen and air. Sugar decomposition occurred also in nitrogen, the aerobic decomposition apparently differing from the anaerobic, which is probably a type of fermentation. Carbon dioxide inhibited this fermentation, presumably by affording an overwhelming concentration of one of the reaction products. Moist alfalfa was kept in an atmosphere of carbon dioxide for periods as long as 5 weeks without spontaneous heating or visible signs of putrefaction, and with very little loss in sugar. Similar samples kept in oxygen or in nitrogen decayed badly.

#### PHYTOCHEMICAL INVESTIGATIONS

Work on the isolation and identification of component constituents of the cuticle waxes of various fruits, principally of the pear and grapefruit, has been continued during the past fiscal year. The predominant fatty acid isolated from pear wax was oleic, and the predominant hydrocarbon was *n*-nonacosane. Ursolic acid, previously reported in apple and cranberry waxes, was also present in pear wax. These waxy coatings, now studied in the apple, pear, cranberry, and grape, are important factors in the adherence of insecticidal dusts and sprays and their subsequent removal. Some of their chemical constituents offer promise of commercial use in protective coatings such as lacquers, or as emulsifiers in certain food products. The raw materials from which they may be obtained are available in large quantities in the cannery wastes which accumulate every year and constitute an acute problem in economic and sanitary disposal.

Investigations of the composition of grapefruit wax, which forms 7 to 8 percent of Florida grapefruit-peel oil obtained by pressing the peel between rolls, was begun during the past year. Although the work is not yet complete, the wax appears to be unlike any previous waxy coating investigated. From the standpoint of both the number and the nature of its constituents it appears to be quite complex.

#### PLANT PIGMENTS

The study of plant pigments has been continued, with particular emphasis on the coloring matters of apples and corn. The yellow pigment occurring in Grimes Golden and Jonathan apples has been completely identified as a new and previously unreported galactoside of the flavonol quercetin. The anthocyanin or red pigment occurring in Jonathan and Stayman Winesap apples has been isolated and identified as idaein, a galactoside of cyanidin which has previously been reported from other sources.

We have in the case of apples another instance where the anthocyanin corresponds to the flavonol in being its reduction product. A similar relation between the pigments of corn husks is the only other case where a correspondence has been shown between the glucoside of an anthocyanidin and of a flavonol. In view of the importance of color in apples to both grower and consumer it is a step forward to know definitely the exact value of the pigments involved.



Progress has previously been reported on the isolation and crystallization of the purple pigment of purple-husked maize, one of a series of color types whose heritable behavior has been determined by R. A. Emerson at Cornell University. One phase of the corn-pigment work has now been brought to a successful conclusion. Chrysanthemine chloride, an anthocyanin coloring matter, was isolated in pure form and identified as such from purple-husked maize. The pigments have now been isolated from the brown-husked and purple-husked types. The evidence obtained thus far favors the possibility of a conversion in the plant of the flavonols (yellow) to anthocyanidins (red) by reduction of their corresponding homologous glucosides.

This work, besides being of interest and value from the standpoint of corn-breeding experiments, may prove to be of considerable importance in connection with results published by R. A. Brink, who has recently pointed out that anthocyanin pigments may have an economic value not heretofore suspected, since certain of these coloring substances in corn appear to be correlated with yield of ears. Should such a relationship be substantiated, the Bureau's work on the nature of corn pigments would form the basis for further extensive research in order to determine and evaluate the exact relationship between pigment content and yield of ears.

#### THE TOXICITY OF FLUORINE COMPOUNDS

The toxic action of fluorine ion on various enzymes is well established, and it has been shown in this Bureau that an active preparation of bone phosphatase exhibits a diminished hydrolytic action on sodium glycerophosphate in the presence of fluorine ion. Such an action suggests the possibility that fluorides have an effect on carbohydrate metabolism which involves the hexose phosphates and phosphate ion. Making use of the micro-organism *Glaucoma piriformis* it has been shown in this Bureau that fluorine inhibits glycolysis. This result is in agreement with the observation of K. Lohmann that the addition of fluoride to a muscle extract leads to the formation of a difficultly hydrolysable hexose diphosphoric acid ester.

Because of the ability of fluorine ion to inhibit phosphatase activity in the living animal, experiments were carried out in vitro in an effort to obtain a quantitative idea of the ability of fluorine ion to inhibit the hydrolytic action of a bone phosphatase preparation on sodium glycerophosphate. It was found that a definite degree of inhibition was present when the concentration of sodium fluoride was as low as one two-hundredths molar. Attempts to reverse this action by dialyzing out the fluoride have failed, although the liberated phosphate ion is freely dialysable under the same conditions.

#### SPOILAGE IN SIRUPS AND BEVERAGES MADE FROM WHITE SUGAR

Results of surveys carried on during the past year indicate that continued improvement is being shown in the biological quality of commercial sugars, due to the elimination of yeast stimulants and the reduction in numbers of spores of thermophilic bacteria of the food-spoilage type in the processes of sugar making and sugar refining.

Especially unsatisfactory conditions had been found in sugars collected from various domestic factories in previous seasons, in that excessive numbers of spores of thermophilic bacteria of the food-spoilage type were present, which would render the sugars unsuitable for commercial canning purposes according to established trade standards. On this account a careful study was made and at the close of a 14-week survey, during which 379 samples of finished sugar from 20 factories were examined, only 1 factory was found that was unable regularly to produce sugar that was suitable for cannery uses when production was controlled by methods previously suggested by the Bureau.

#### EGGS AND EGG PRODUCTS

The possibilities in the commercial oil treating of shell eggs by the vacuum carbon dioxide method have been further enlarged by demonstrating that oil at ordinary room temperature (60°-80° F.) may be used without the application of heat. This oil is a commercial product, developed especially for oiling eggs at room temperature. After 7 months in commercial storage, eggs graded by Department experts showed that this new application of the vacuum carbon



dioxide process is far superior to other oil treatments, in that eggs so treated graded between 55 and 32 percent higher than control lots both oiled and unoiled. Use of an oil of this type brings the vacuum carbon dioxide oiling method within reach of the egg producer, and indicates the possibility of more general usage of vacuum oiling on the farms where eggs are produced. This should result in a larger percentage of storage eggs of high grade with increased profit to the farmer and greater satisfaction to the consumer.

#### STUDIES ON WINE MAKING

The experimental lot of champagne bottled in 1933 in cooperation with the New York State Agricultural Experiment Station and wineries in the Finger Lakes section of New York has been opened and compared with commercially prepared champagne, the aim of the experiment being to study the value of various fermentable sugars in promoting the secondary fermentation in the bottle, and the role of our stock yeast cultures in developing characteristic flavors.

Results seem to indicate that cane, beet, corn, and invert sugars of high purity may be used with results equal to those obtained with rock candy, which is in general use. Preliminary examination has shown that not all yeasts listed as champagne yeasts gave desirable results. On the other hand, some of the still-wine yeasts showed very desirable characteristics for champagne making. These studies are being continued.

Pasteurizing experiments carried out in the laboratory and in commercial wineries indicate that New York State wines, both sweet and dry, which are normally low in alcohol content but high in acid, may be safely pasteurized at lower temperatures than those in common use, a holding temperature of 130° F. for 20 minutes providing an ample margin of safety when applied under controlled conditions. Lower pasteurizing temperatures mean less change in flavor and therefore a more acceptable product.

#### ORANGE AND GRAPEFRUIT JUICE INVESTIGATIONS

Shipments of deaerated and flash-pasteurized orange juice in bulk under refrigeration have been made in cooperation with Florida firms and individuals interested in this method of distribution. The juice was considered of satisfactory quality in every respect upon arrival in northern markets. This type of product is readily adaptable to distribution by dairies, as is a newly developed beverage concentrate suitable for making orangeade. If properly handled in the retail market such products should provide a growing market for cull and surplus fruit of high juice quality but not salable as fresh fruit.

Deaeration and pasteurization experiments have been carried out in canneries, and several commercial installations of equipment designed by this Bureau were in use during the past season in different citrus-producing sections. It is expected that other installations will follow during the coming season.

Experiments on canning Texas grapefruit have been tried, but owing to the inherent tenderness of the fruit it is difficult to keep the segments intact during processing. On this account it is probable that Texas grapefruit not of satisfactory grade for the fresh-fruit market will find an outlet in juice and beverage products.

Methods of preserving the flavor of concentrated grapefruit juice have been studied and formulas for the preparation of beverage concentrates have been developed.

#### ALCOHOLIC CITRUS BEVERAGES

Wine of excellent quality has been made from oranges, tangerines, and grapefruit. Citrus wines on naturally aging develop a sherry flavor. Grapefruit wine has a tendency to be bitter, but by proper selection of fruit and treatment with activated charcoal much of the bitterness is eliminated.

Refrigeration is necessary in the warm climate of citrus-growing regions to obtain a desirable fermentation temperature (60° F.). Experiments with carbonated wines have not given a satisfactory product, mainly because the natural sherry flavor in citrus wines is not satisfactory under carbonation.

Brandy was made, utilizing the waste juice from canneries. Part of this brandy was used in the preparation of citrus cordials.



## CITRUS OILS

Quite satisfactory yields of orange- and grapefruit-peel oils were obtained by means of a continuous screw press of special design. This oil did not differ in physical constants from oil obtained by a roller-pressing process already in commercial use. Concentrated citrus oils were prepared by vacuum evaporation of 80 percent of the limonene from the oils.

A ready market takes the entire output of orange oil, but it is essential that outlets be found for grapefruit-cannery waste. This byproduct is available in increasing amounts and is a potential source for oil, pectin, and naringin, the glucoside that gives grapefruit its characteristic, bitter flavor. Limited amounts of the waste are now being utilized for feeding purposes and as fertilizer.

## CHEMICAL COMPOSITION OF THE LOQUAT

The loquat, or Japanese medlar, is closely related to the apple, quince, and pear. It has been grown in the United States for at least 40 years but has not attained a large production, possibly because it requires essentially the same type of land and cultural and climatic conditions as the citrus fruits. The loquat has a pleasant, subacid flavor and may be used for jellies, jams, and pies, although it is largely consumed as fresh fruit. It appears on the southern markets when there is little fresh fruit other than citrus, and there is a large local consumption but not much wide-spread distribution.

A careful study has been made of the composition of the fruit, about which little has been known. A comparison of the loquat with the apple indicates that the apple is higher in total and soluble solids and total sugars and lower in water, total ash, and alkalinity of the ash, the difference naturally varying somewhat with variety. This type of data is of material assistance to nutritionists and dietitians and can be used to good advantage in popularizing food plants introduced into this country by the Department's Division of Plant Exploration and Introduction.

## PASSION FRUIT PRODUCTS

Although the passion fruit, which superficially resembles a large purple plum, is native of the tropical or subtropical Americas, its cultivation in the United States on a commercial scale is quite recent. The flavor of the fresh fruit has been likened to a combination of pineapple, guava, mango, apricot, and strawberry, but on account of the large number of small seeds, the sale of fresh fruit is limited, in spite of its delightful flavor and odor. Means have therefore been sought for utilizing the fruit in manufactured products of various kinds. A machine has been devised for separating the juice from the shell and seeds, and methods have been developed for preserving the juice by freezing, pasteurizing, and concentrating, and for making carbonated drinks, jellies, and sirups. Both wine and brandy have been prepared from the juice and have a fine, highly characteristic aroma, but have not sufficiently aged as yet to indicate their full possibilities as to flavor.

## LOOSENING THE HULLS OF WALNUTS

Preliminary work cited in the last annual report indicated that the use of ethylene in loosening the hulls of sticktight walnuts resulted in a larger proportion of high-quality shelled nuts, but that several problems connected with its use were still unsolved.

In continuing this work, five locations in California were selected representing the different climatic conditions under which walnuts are grown. In the coast section, where there is a natural tendency for the nuts to "vein", heavily veined kernels are classed as "ambers" and are not included in the highest grade. Since the ethylene treatment seems to accentuate this condition its use in the districts affected is being discouraged for the present.

The proportion of green sticktights is high in the early part of the harvesting season. If allowed to remain on the trees until the nuts can be hulled without treatment, the proportion of dark kernels, or ambers, increases. The ethylene process will be most valuable to the growers in localities, especially in the interior sections, where hot weather at the time of maturity delays the cracking and loosening of the hulls. Our work has demonstrated that there



is a proper time to begin the harvest and to delay it beyond that time results in serious loss from the development of dark kernels. No difference has been detected in the flavor of treated and nontreated nuts, and the first year's storage tests show no greater decline of color quality in the treated than in the untreated samples.

As a result of the work this past year, a number of walnut growers are erecting new plants for the treatment of nuts. A survey shows that there were 77 growers in Los Angeles County alone who used the ethylene treatment in last year's harvest. In a few instances where cost figures were kept, returns were increased by \$50 to \$100 per ton.

#### LIGHT AND RANCIDITY

In studying the rancidity-delaying properties of well-known antioxidants it has been found that the absence of light (afforded by an opaque or green wrapper) is more efficient in delaying the rancidity of oil than any of the antioxidants tested, with the possible exception of pyrogallol, which cannot, of course, be used in products for either human or animal consumption.

Experiments have shown that when rancidity results from exposure to sunlight it is not necessarily dependent upon the actual peroxide formation.

Experiments conducted with filters, chosen according to their ability to transmit light within certain limits indicate that oil thus exposed to light becomes rancid in every case except under green filters delimited by 4900-5800 Angstrom units and filters transmitting mainly infrared light.

#### STUDIES ON SOYBEANS

Soybeans of the Mammoth Yellow variety were used. Beans of both high- and low-moisture content were stored in various types of containers at temperatures ranging from  $-10^{\circ}$  to approximately  $+30^{\circ}$  C. Our analyses showed that in general the lecithin content was greatest in beans of low-moisture content which had been stored at a low temperature and decreased as the temperature of storage and/or the moisture content increased. Such differences are important to growers of soybeans and manufacturers of lecithin and other soybean products. This work was done in collaboration with the Bureau of Plant Industry.

#### SPECIAL BREADS

A greater consumption of wheat flour in this country might result if well-risen, appetizing special breads with an appeal to those who now eat little or no bread were given greater prominence and publicity.

Well-risen, high-protein breads of good flavor have been made with combinations of gluten flour or gum gluten and soybean flour and with the further addition of inulin. Other special breads of very good quality have been made by using varying amounts of soybean flour in the usual baker's formulas for bread. A novelty bread is an entirely new type of yeastless bread raised by means of hydrogen peroxide of the grade known commercially as 100 volume or 30 percent. Since this peroxide bread, while of very good appearance, is lacking in flavor, the use of cheese or other highly flavored ingredients has been found to increase the appetite appeal.

Both yeast and peroxide breads were analyzed and it was found that while the percentage of fat, ash, and total nitrogen were the same, the peroxide bread contained approximately three times as much sugar, alcohol-soluble nitrogen, potassium-sulphate soluble nitrogen, salt-soluble nitrogen, and water-soluble nitrogen. This comparison of the composition of yeast-leavened bread with bread raised by means of hydrogen peroxide gives additional insight into the changes that take place when flour is converted into bread as the result of yeast fermentation.

#### STALING OF BAKERY PRODUCTS

The use of commercial canned pineapple juice in baking seems to retard staling to some extent, and baking tests with certain fat emulsions have also given results which appear quite encouraging.

Analyses of bread that had been stored at  $-10^{\circ}$  C. for 1 year showed that, in comparison with fresh bread from the same baking, the composition was practically the same except that the fresh bread contained four times as much



soluble starch as the stored bread. This corroborates the statement of J. R. Katz that the process of staling is accompanied by a decrease in the soluble-starch content of bread.

## INDUSTRIAL FARM PRODUCTS DIVISION

### HIDES AND SKINS

Better cured hides and skins are desired by all producers, packers, and tanners. They are worth more and bring the farmer greater returns because they yield more and better leather. First-quality leather can be made only from sound, well-preserved hides and skins.

Salt, which has been used so long and so extensively for curing hides and skins, is not a perfect preservative. Certain bacteria and molds can live and grow in its presence. A search is therefore being made for suitable chemicals that can be added in very small quantities to salt to prevent the growth of these micro-organisms. Three treatments have been found thus far to be exceptionally promising for preventing the growth of bacteria and molds and the stains and putrefaction caused by them. These are: (1) Salt plus 0.2 percent of its weight of sodium trichlorophenate; (2) salt plus 2 percent and 0.1 percent of its weight, respectively, of sodium silicofluoride and paranitrophenol; and (3) salt plus 2 percent and 0.1 percent of its weight, respectively, of sodium silicofluoride and sodium trichlorophenate.

Curing experiments on large enough scale to give significant tannery results were made with calfskins, using the first two of these treatments. The packs were in cure for 3 months under adverse conditions of a warm temperature and a minimum of salt. The control packs, with salt containing no special preservatives, showed gradual but pronounced spoilage after the first 3 weeks, and, when taken up after 90 days, were in poor condition, having general hair slip, a foul ammoniacal odor, and a dead, dirty appearance. The two test packs with salt containing special preservatives were in much better condition, being almost free from odor and having tight hair and bright appearance. Several tanners expressed the opinion that the skins cured with treated salt were in an excellent state of preservation. All the skins are being processed by a cooperating tanner to determine the influences, if any, of the treated salts upon the various operations of tanning and, especially, to grade the final leathers for quality, selection, and value.

The organism causing flesh reddening of salted hides, a serious damage of frequent occurrence that lowers the value of hides, has been tentatively identified as *Myxococcus rubescens*, Thaxter. A stage of growth of this organism with which no well-defined stainable bacterial cells could be associated was observed for the first time as was also the organism's great variation in cell types, or appearance, depending upon the nutrients on which it grows. When isolated from contaminated salt on a fish-broth agar the organism appears entirely different than when grown on the same agar plus peptone, gelatin, casein, or various carbohydrates. This observation is of both practical and fundamental importance in that it not only helps to isolate and identify the organisms which cause spoilage of hides and skins, but also explains the origin of much confusion in this field of work.

Processors of hides and skins are continually meeting with damages of unknown origin, and tanners spend much money and time trying to determine whether the cause is in their processing and consequently within their power to correct. From a study of authentic specimens of hides and skins from the Bureau of Animal Industry important contributions were made toward the identification of damages that occur on the hides and skins of living animals. These damages, as they appear in the hide or skin and in the leather made from it, were described and illustrated in three articles published in the journal of the American Leather Chemists Association. One article shows the consequences of ringworm infection of the hide of a living animal wherein numerous lesions are formed that partly destroy the structure of the hide and the leather made from it. Another illustrates an eczema, not of parasitic origin but arising from a systemic disorder, which decreases the value of the hide by at least 50 percent, because the numerous patches of destroyed grain permit the production of nothing but low-grade leather. The third article describes a damage to hides from an infection of cattle by a parasitic nematode or worm, *Stephanoflaria stilesi*, which during the last year was definitely identified among domestic hides for the first time. On cattle in the United States infection seems to be



confined to the belly region where deep lesions develop and spread over the hide. Leather made from the infected areas is worthless. Cattlemen and farmers should familiarize themselves with these damaging disorders and take effective steps to prevent their spread. Otherwise the hides from their cattle may bring less than they should or be entirely unsalable.

The cattle-killing program of the Federal Government, entered upon as a measure of drought relief and reduction of livestock, brought with it major problems in handling the hides and skins. In order to prevent disastrous glutting of the market, all hides and skins taken off after September 5, 1934, in connection with the cattle- and sheep-killing program, remained the property of the Government instead of being turned over to the packers as was previously done. This involved the handling and storage of some 6,000,000 cattle hides, calfskins, and sheepskins, worth about \$8,000,000. The killing program introduced the important economic question as to what should be done with the hides and skins. Various plans were considered by representatives of the Government and of the industries concerned. These included the orderly marketing of the hides and skins by the Government, long-time storage and gradual release according to market demands, contract tanning and manufacture of the leather into goods for relief purposes, and use of idle tanneries and labor for tanning and making leather goods for relief purposes. The Bureau of Chemistry and Soils acted in an advisory capacity on the technical points involved in these several programs in cooperation with the Agricultural Adjustment Administration, the Federal Surplus Relief Corporation, the Federal Emergency Relief Administration, the packers, the tanners, and members of the leather trade. The Bureau, from its extensive experience, was able to offer suggestions on the program and procedure for curing, storing, and taking up hides and skins to insure the least spoilage and orderly marketing and prepared detailed descriptive matter for Government contracts for curing sheepskins, shearlings, cattle hides, kip skins, and calfskins and for holding the same with and without cold storage, and similar material for Government contracts for tanning garment, glove, shearling, shoe upper, sole, and lining leathers.

#### TANNING MATERIALS

Chestnut wood, chestnut-oak bark, and eastern hemlock bark, the principal tanning materials of the United States, are nearing exhaustion. The Bureau, therefore, is giving close attention to the development of new sources of tannin in this country. One material of promise is the bark of the Pacific coast hemlock. This bark is rich in tannin and occurs from the vast lumbering operations and pulp production of the Northwest in great quantity as a byproduct, which is not put to any useful purpose except for a very minor portion sold as "hogged" fuel at about 75 cents per ton. It is estimated that in Washington and Oregon alone about 400,000 cords of this bark are removed annually from saw logs and pulpwood. This quantity has a potential value of some \$5,000,000 as a new commercial source of tannin for making leather. An investigation on the possibility of making satisfactory tanning extracts from this waste bark that can be delivered to the consuming markets in the East at competitive prices was actively continued and is approaching completion. In the course of this study it was found that the successful utilization of the bark on a large scale depends upon artificial drying, regardless of whether the bark comes from logging ponds or direct from the woods, because of its high moisture content, climatic and woods conditions unfavorable to natural drying, and the necessity of storing the bark for 6 months or more before extracting it. Drying experiments were made on a large scale on the Pacific coast with both fresh and wet hemlock bark. It was found that artificial drying is entirely feasible, at a cost of less than \$1 per cord and without material detriment to the bark or to the yield or quality of the extract made from it.

#### LEATHER

Further progress was made in the study of the "red rot" or acid rot of leather, which has been pursued intensively during recent years because of its promise of yielding results of both fundamental significance and practical value. The results of an elaborate investigation showed the superior resistance of chrome-tanned leathers to red rot, a damage to leathers resulting from absorption of acids from the air. The important practical feature involved is that most of the bookbinding and other leathers subjected in actual use to this



type of deterioration are now vegetable-tanned. If chrome-tanned leather can be substituted for vegetable-tanned leathers for uses involving long exposure to polluted atmosphere, rotting will be slowed down greatly and the useful life of the leather will be doubled or trebled. Aside from its practical value this discovery has a fundamental bearing on the theories of tanning. Chrome-tanned leathers are shown to have a much lower rate of pick-up of acid from the air, with the formation of but little soluble nitrogen accompanying their deterioration. In contrast to this, vegetable-tanned leathers are quite basic in character, acting as attractants for the acids in the air. As a result comparatively rapid rotting of the leather sets in with the formation of a high percentage of soluble nitrogen decomposition products.

It was also found that the nontannins occurring with the natural tannins in woods, barks, leaves, and fruits used as tanning materials help to protect leather against acid rot, which is in harmony with the finding of R. F. Innes, that nontannins have a protective influence. This discovery focuses attention on the nontannins rather than the tannins for making more resistant leathers. It also helps to explain why modern leathers, with their low content of natural nontannins, are not more resistant to acid rot.

The results of this research work are serving as a guide in a program in cooperation with tanners and the Government Printing Office to develop more durable leathers for use in binding books for the Government. Thus far, 4 special leathers have been secured, 2 full-chrome-tanned sheepskins and 2 combination vegetable-chrome-tanned sheepskins, for trial as substitutes for the type of sheepskin leather commonly used on law books, which is entirely vegetable-tanned and of poor serviceability. These special leathers are being put through the Government Printing Office bindery for observation of their behavior on wetting back, pasting, stamping, and other operations. Three volumes are being bound with each leather, two being for reference and the third for natural aging. Each leather is also being artificially rotted by gas-chamber exposure to determine its comparative life and resistance to decay. Some of the new leathers are promising, and doubling the life of the average leather binding appears entirely feasible. This would result in an estimated annual saving of at least \$75,000 for leather bindings in Government libraries alone.

#### CHEMISTRY OF NAVAL STORES (TURPENTINE AND ROSIN)

Research was continued on the composition of pine gum, turpentine, and rosin, separation of components, formation of derivatives, and determination of chemical and physical properties of raw materials and derived products to acquire fundamental knowledge regarding the chemistry of pine-tree products, which may also have a practical bearing upon the increased utilization of these products for industrial purposes.

As a result of the study of resin acids in pine gum, "special rosins" possessing physical and chemical properties different from those of ordinary rosins were prepared. These were highly transparent and some so nearly colorless as to be seven grades above X, the highest grade produced commercially in this country. These special rosins may offer advantages over ordinary rosin for certain purposes and thus extend the use of rosin in industry. Application was made for a public service patent to cover the process.

A study was made of means for extracting the neutral components of rosin, usually referred to as "resenes," in connection with collaborative work for the Association of Official Agricultural Chemists on the determination of unsaponifiable matter in rosin. As a result, a radical modification of the usual methods for extracting and determining the neutral components of rosin was proposed. This should prove useful not only in providing a more dependable means for determining the suitability of rosin for certain industrial purposes, but also in providing quantitative basic information regarding the composition of rosin.

Preliminary study has shown that available methods for evaluating the total saponifiable matter in rosin are subject to several errors. Since this property constitutes an important index in determining the suitability of various rosins for soapmaking and other industrial purposes, a study of this problem is being continued.

In connection with the work on turpentine-fractionating equipment, several improvements in accessory apparatus have been developed, including a novel



precision oil gage. Application has been made for a public-service patent covering this gage.

In continuation of the fundamental research on composition and properties of American turpentines, the general objective of which is to extend the use of turpentines in chemical industries, a systematic fractional distillation was made on a large sample of steam-distilled wood turpentine and study of the composition of individual fractions was begun. Methods suitable for detection and separation of the constituents, particularly those present in small amounts, required detailed study before being applied. While the bulk of refined wood turpentine consists of alpha pinene, there are about 20 constituents, including terpene and aromatic hydrocarbons, aldehydes, secondary and tertiary alcohols, phenols, oxides, and phenol ethers. Some of the aldehydes have been identified, and study of the hydrocarbon, alcohol, phenol, and other constituents is being continued.

In continuation of the investigation on the character of turpentine and rosin in fresh pine gum, on which there has been no adequate data, work was completed on the chemical and physical constants of 173 samples of rosin made from gum collected from individual longleaf and slash pine trees, and on 42 samples of commercial gum rosin. Incidentally it was necessary to make a critical study of the methods used for the several determinations. Noticeable differences were found to exist between the rosins from longleaf pine and slash pine as regards some of their chemical and physical constants as well as between commercial rosins and rosins made in the laboratory from fresh gum. The results show the need for improvements in the usual practices of handling pine gum, and the desirability, in producing rosin for special purposes, of collecting longleaf and slash pine gums separately.

In order to obtain additional data for converting volume to weight, or weight to volume, records were kept of the specific gravity of all turpentine produced with fire and steam stills at the Naval Stores Station and of turpentine obtained by laboratory distillation from gum collected in cup tests. Gum from the cup tests, all from longleaf pine, produced turpentine having an average specific gravity of 0.8680, while turpentine from the stills had an average specific gravity of 0.8672.

Investigations upon the changes that take place in turpentine during storage were continued to show the effect of dissolved and free water in turpentine in the presence of iron and zinc (the metals with which turpentine usually comes in contact during storage) with and without the addition of certain water-absorbing chemicals. During the first year when the containers were opened only at 3-month intervals no material change took place in specific gravity or optical rotation. There was decided change in color in some cases. Free water in turpentine containing no dehydrating agent caused severe corrosion of iron and red coloration of the turpentine. The presence of oxalic acid did not prevent corrosion of iron but did prevent coloration of the turpentine. Contact of crystalline oxalic acid with turpentine during 6 months did not change any of the usually determined physical properties of the turpentine. Turpentine saturated with dissolved water quickly corroded both iron and zinc. Turpentine dried over calcium chloride did not corrode or tarnish iron or zinc in 9 months. Calcium oxide was effective in preventing rusting of iron in turpentine saturated with water, but when free water was present the lime gradually slaked and lost its effect. A commercial dehydrating agent of the alumina type proved to be impractical because it caused the turpentine to become yellow and therefore unmerchantable. While not complete, these experiments indicate that in order to prevent discoloration or clouding which will lower commercial value, turpentine stored in iron or galvanized containers should be dehydrated thoroughly.

#### TECHNOLOGY OF NAVAL STORES

Studies on equipment for the collection and handling of pine gum and on equipment and methods for the production, handling, and storage of gum turpentine and rosin were continued at the Naval Stores Station near Lake City, Fla. The purpose of this work is to reduce waste and deterioration of pine gum and its products, to raise the yield and quality of products, and to reduce costs of operation by developing and introducing improved processes, equipment, and practices.

Construction of the office and laboratory building, from funds allotted in 1934 by the Public Works Administration, was completed. New equipment for



the station includes a gum-refining plant, an aluminum vacuum still with aluminum tubular condenser, and an aluminum vacuum filter for cold gum. The gum-refining plant has a capacity of about 100 barrels of gum per 8-hour day. In building this plant care was taken to select metals and alloys that are not corroded by the action of hot turpentine gum. The digesters are of stainless steel. The storage tanks, reflux condensers, filter units, and gum lines are of aluminum. The valves are made of a special bronze-nickel alloy.

Preliminary tests were made to obtain information for use in developing the best procedure for refining gum to be used for making cleaner, paler rosins. Two distinct operations are involved. The first is the removal of all solid foreign matter by pressure filtration of the hot gum through filter paper, cotton batting, and burlap. The second is the removal of water and any contaminating dissolved material by washing and settling. The washing is effected in the storage tanks with hot water, using eductors and injectors for circulation. Separation of the wash water and gum is effected by controlling the temperature and viscosity of the gum. Rosin made from gum cleaned in the preliminary experiments had a brightness about 10 percent greater than that of rosin made from uncleaned gum of the same grade. Such rosin is more desirable for certain purposes, such as varnish making, and will probably command a higher price.

Continued use of the turpentine dehydrator built in 1934 showed that common salt was the most satisfactory dehydrating agent tried thus far. Lime, calcium chloride, sodium hydroxide, and sodium bicarbonate were tried but, because they discolored the turpentine, had to be abandoned. Many dehydrators are being installed by producers who are finding that dehydrated turpentine gives less trouble than undehydrated turpentine from leaking barrels and discoloration in shipment and storage.

A combined turpentine separator and dehydrator made of sheet copper tinned on the inside was designed and introduced. Several are in use at turpentine stills. General use of the covered separator and of the dehydrator will save the industry at least \$100,000 a year.

Continued tests with turpentine gum cups made of various materials less breakable than clay showed that after long use none is quite equal to clay cups as regards the grades of rosin obtained. The best were zinc, aluminum, and lead-dipped galvanized iron, in the order named.

About 225 charges of gum were run through the fire still. Records were made of the yield of turpentine, the yield, grade, and brightness of rosin, weights and percentages of water and other waste materials, fuel consumption per charge, amount of condensing water required, and other data pertaining to the stilling process. The stilling data were compiled and summarized in order to give naval-stores producers the first available concise and accurate information on stilling and to serve as a guide in their own practices. Average yields with charges containing 90 percent longleaf pine gum were 19.7 percent of turpentine, 67.8 of rosin, 1.7 of batting dross, 0.4 of rock dross, 2.2 of chips, 7.9 of water, and 0.3 percent of other losses. Average yields with charges containing 90 percent of slash pine gum were 18.6 percent of turpentine, 68.7 of rosin, 1.6 of batting dross, 0.5 of rock dross, 3.3 of chips, 6.9 of water, and 0.4 percent of other losses. The ratio of 1 pound of turpentine to 3.43 pounds of rosin held in the case of essentially longleaf-gum charges, and 1 pound of turpentine to 3.69 opunds of rosin in the case of essentially slash-gum charges.

From its past year's work the Naval Stores Station finds that dross, chips, and water have averaged about 550 pounds per 10-barrel charge. On the average, 1 barrel in every charge is waste. Batting dross averaged about 72 pounds and strainer dross about 20 pounds. Chips and trash ranged from about 100 to 160 pounds, and water from about 350 to 315 pounds. The dross and chips contained 58 round barrels of rosin per 10-crops basis. One hundred pounds of chips per charge costs the producer \$1 per charge in lost rosin.

About 820 barrels of gum of various grades were distilled on the steam still. By the use of high-pressure steam for heating, each of the different grades of gum was stillled under complete control. As compared with the fire still, the steam still required about 60 percent less time for distillation to start and about 40 percent less time for it to be completed. The steam still can be used efficiently for uncleaned as well as for cleaned gum. It gives somewhat higher yields of turpentine than does the fire still. The grade of rosin obtained from a particular grade of gum is the same for both types of still.



Advice on the stilling problems of individual producers and on other matters relating to naval-stores production was given through correspondence to 152 persons, and orally to the operators and visitors at 23 stills visited by members of the station staff and to the 589 persons who visited the Naval Stores Station. Plans, blueprints, line prints, and pencil sketches, covering complete lay-out of turpentine plant, design of still building, fire-still setting, and various types of equipment were distributed to 109 operators.

#### COOPERATION WITH STATES IN NAVAL STORES WORK

Cooperative arrangements were continued with the States of Florida and Georgia for the introduction of improved processes and equipment for producing naval stores through the work of cooperative agents who are employed jointly by this Bureau and State agencies.

In Florida assistance was given on problems relating to naval-stores production through 293 personal contacts and 279 letters. The cooperative agent directed the erection of 33 turpentine fire stills according to the approved plans and recommendations of the Bureau of Chemistry and Soils and the installation of 14 recording still thermometers. Of those furnished information on the covered turpentine separator and the turpentine dehydrator approved by the Bureau, about 10 percent have installed dehydrators and 25 percent have installed covered separators. The Bureau method of stilling, using the chart, graduated receiver for condensate, and with or without recording thermometer, was demonstrated to 115 operators and stillers. The cooperative agent also collected data on the cost per crop of producing pine gum when 15, 60, and 120 cups per acre are worked, on returns to gum producers compared to leasing values, and on the cost of producing turpentine and rosin.

The naval-stores cooperative agent for Georgia is making progress in introducing in that State improved practices and equipment for producing turpentine and rosin. In 137 personal contacts with naval-stores operators assistance was given in the construction of stills, in the design of and preparation of plans and specifications for improved plants, in the operation of these plants, and in solving various problems related to the production of naval stores. Thirty-five fire-still settings, according to specifications of the Bureau of Chemistry and Soils, were built under the supervision or with the assistance of the cooperative agent. Eleven improved processing plants were constructed and 52 complete sets of turpentine separators and dehydrators were installed with the assistance of the cooperative agent.

#### INDUSTRIAL USE OF FARM PRODUCTS AND BYPRODUCTS

Work on the industrial utilization of agricultural products and byproducts was continued in the field station at Ames, Iowa, in collaboration with Iowa State College.

The construction of an agricultural products laboratory, with funds from the Public Works Administration, was completed. Office and laboratory equipment were moved into the new building so far as available funds permitted. The time of the administrative and engineering staffs was largely occupied with the supervision of erection and accounting connected with the building project.

Destructive-distillation studies with continuous-process retorts were limited to experimental runs on black walnut shells and tobacco stems in the Cline retort. The walnut shells gave a yield of acetic acid of 125 pounds per ton, which compares favorably with the production of acetic acid from wood. A yield of 575 pounds of carbon per ton of walnut shells was obtained. It was found that remodeling of the internal heating element was necessary before the machine could function commercially. The Cline apparatus was taken down and reerected in the new laboratory building. On dismantling, it was found that failure of internal portions of the retort structure necessitated purchase of new parts. The lay-out for the apparatus in rebuilt form is being considerably extended.

A series of pot-still runs was made to determine the factors influencing the yield of destructive-distillation products from farm wastes and the results were prepared for publication. It was found that there is a definite relationship between the temperature of distillation and the character and yield of resulting products. Further work was done on analytical methods for deter-



mining formic acid and methoxyl in pyroligneous liquors and the results were incorporated with those of previous work for publication.

The insecticidal value of destructive-distillation oils from tobacco stems, reported last year, was confirmed by reports from the Bureau of Entomology and Plant Quarantine. Laboratory experiments were made to increase the yield of oil from tars previously obtained from plant wastes. All the tars produced in previous experimental work were distilled for the preparation of tar oils for future experimental work.

Further studies were made on the production of fuel briquettes and pressed masses from farm wastes, using various binders. Considerable work was done on the design of a briquetting machine suitable for farm-waste materials. If briquetting proves successful, crop wastes may have extensive use as fuel in regions where coal is not readily available.

In the investigation of microbial decomposition of cellulosic wastes to form fuel gas, and other useful products, experiments were made to determine the rate of break-down of cornstalks under aerobic conditions and under anaerobic conditions at moderate and comparatively high temperatures. Under aerobic conditions, the rate of break-down was practically uniform for cellulose, pentosan, and lignin. It appeared that lignin became soluble but was not destroyed. At moderate temperature under anaerobic conditions the pentosan was decomposed fairly rapidly from the start. Cellulose was decomposed more slowly at the start, but the rate of break-down gradually increased. Lignin was not appreciably attacked. At higher temperature the pentosan break-down was more rapid and that of cellulose slower, the time of fermentation being decreased 50 percent.

Experiments on the effect of added lignin upon gas production by microbial decomposition of farm wastes showed that beyond a certain point additions of lignin did not increasingly inhibit the fermentation.

In the cooperative study of a farm-unit fermentation plant for producing fuel gas from farm waste and house sewage, it was found that ordinary house sewage is usually diluted too much with water to be useful. When barnyard sewage was used, better results were obtained. Since very little livestock was available where the plant was located it was decided to repeat the experiments on another farm where conditions were more favorable, and possibly in duplicate to compare the effects of indoor and outdoor temperatures. When suitable equipment and operating conditions are worked out, farmers and small communities may be able to obtain gas for cooking and lighting from crop wastes and barnyard sewage, and to use the spent residue as fertilizer.

A study was made of the utilization of waste glucose, gluten, and other by-products of the corn-products industry in the production of butyl and isopropyl alcohols by fermentation. Glucose in 4 percent solution was completely fermented by *Clostridium butylicum* with the production of 27 percent butyl alcohol and 4 to 10 percent of isopropyl alcohol, based on the weight of sugar fermented. Corn-steep water and malt sprouts were used as sources of nitrogen. A theoretical study was made on the chemical mechanism of the fermentation.

Preliminary experiments on the preparation of alpha cellulose from cornstalks by the improved nitric acid process indicated that the process may be applicable to farm wastes other than bagasse. Good results were obtained with shredded cornstalks from which the pith had been removed. The product obtained from the pith did not appear to have commercial value.

Contact was maintained with a commercial firm which has developed equipment for the production of paper pulp from straw by a continuous cooking process. Experiments were made in the laboratory to ascertain the possibilities of continuous cooking at atmospheric pressure in apparatus other than that of the patented design. Considerable time was spent in the perfection of analytical methods suitable to waste liquors obtained in the pulping of agricultural byproducts.

#### FARM FABRICS

During the past year, through cooperative work with a commercial firm, the weather-resistant fireproofing treatment developed by this Bureau for use on cotton fabrics was converted from a laboratory treatment to a plant process. Special equipment was manufactured and assembled and subsequently modified in design. The product obtained was practically as fire-resistant as fabric treated in the laboratory. About 700 yards of fabric were treated during the course of the work. In weather-exposure tests it was



found that the fabric treated in the plant was about equal to that treated in the laboratory as regards resistance to deterioration. The results show that the treatment can be applied successfully by cotton-converting plants. If the cost can be sufficiently reduced, the treatment will be of great value in reducing fire risks where canvas is used for protective covers, tents, and awnings.

#### PAPER

An investigation on the effect of atmospheric sulphur acids on paper as indicated by gas-chamber tests was completed and the results were prepared for publication. High- and low-grade current types of book and writing papers were tightly bound in book form and exposed for 330 days in a chamber heated to a temperature of 50° C. and containing the total gaseous sulphur products of combustion produced by a small constantly burning jet of illuminating gas. Comparative chemical and physical tests were made on different sections of the leaves at the end of 90, 180, and 330 days of exposure. At the end of 330 days all the papers showed decided deterioration near the edges of the leaves. The polluted air had the least injurious effect on the rag-ledger and the highly purified wood-bond papers. They were hard-finished papers containing relatively high percentages of glue, and were among those absorbing the least acid. There was a progressive decrease in acidity and in degree of deterioration, measured by folding endurance, as the distance from the edge of the leaves increased. The center sections of the leaves absorbed little or no acid. The results show the manner in which the paper of books deteriorates when such books are exposed to atmospheres polluted with sulphur gases, as is usually the case in cities, and emphasize the importance of purifying the air of libraries and of adding to the paper at the time of manufacture a material that will neutralize or counteract acidic sulphur compounds as they are absorbed by the paper.

#### OIL, FAT, AND WAX INVESTIGATIONS

The oil, fat, and wax investigations of the Bureau relate to the composition and characteristics of agricultural fats and oils with reference to commercial requirements in order to make possible their more profitable production and utilization. Oil-bearing farm products now wasted or inadequately used are studied for the purpose of finding profitable market outlets.

#### TUNG OIL

Owing to its unique property of drying, both by absorption of oxygen and by polymerization in light, tung oil has exceptional value for the manufacture of varnishes, paints, and paint driers. The increasing demand for tung oil, fully 100,000,000 pounds of which are imported annually from China, has recently stimulated the planting and cultivation of tung trees in Florida.

In connection with this young tung-orchard industry, an investigation was made by the Bureau during the past year with reference to the composition of tung oil, using a sample expressed from Florida tung nuts. It was shown that the oil contained over 90 percent of elaeostearic acid, instead of about 73 percent as previously reported by other investigators. The remarkable drying powers and unique properties of this oil are due entirely to the large quantity of elaeostearic acid present as glyceride.

#### BAGILUMBANG (BANUCALAG) OIL

Bagilumbang or banucalag oil is obtained from the nuts or seeds of the tropical tree *Aleurites trisperma*, which is closely related botanically to the semitropical tung trees. During the past year an investigation was made by the Bureau of the oil from the seeds of a bagilumbang tree growing in calcareous soil near Homestead, Fla. It was discovered that the oil contained 67 percent of elaeostearic acid glycerides. Previously, it was believed that the oil was similar to lumbang or candlenut oil from the *A. moluccana* but this oil contains no elaeostearic acid and has notably less drying powers. Although paints and varnishes made with bagilumbang oil appear to produce waterproof films as do those made with tung oil, the former oil, as would be expected from the smaller quantity of elaeostearic acid glycerides present, does not possess such strong drying powers. In view of the composition of this oil and



the fact that the tree producing it appears to thrive on calcareous soils, cultivation experiments are planned in southern Florida and other regions having a suitable climate, but in which tung trees cannot be grown, as soon as an adequate supply of seed can be obtained.

#### SOYBEANS AND OIL

During the past year, the seed of about 50 new varieties of soybeans introduced from the Orient by the Division of Forage Crops and Diseases of the Bureau of Plant Industry were examined. As previously mentioned the chief object of this study is to find varieties, the beans of which contain oils having stronger drying powers than our domestic product, and which would be of special value to the paint, varnish, lacquer, and linoleum industries. As a result of the present investigation, two varieties of beans were found which contained oils that possessed somewhat stronger drying powers than that on our market. Cultural experiments are planned to ascertain whether these two varieties are adapted for cultivation on a commercial scale in this country.

### PROTEIN AND NUTRITION INVESTIGATIONS

#### STUDIES ON YEAST PROTEINS

The investigation on the proteins of yeast has been continued. This work was undertaken because yeast is assuming an increasing economic and scientific importance. Yeast is being irradiated by ultraviolet light, and the product fed to dairy cows in order to increase the quantity of vitamin D in the milk. Yeast is also being increasingly used for human consumption. It is an excellent source of vitamin G ( $B_2$ ), the antipellagric factor. Large quantities have been distributed in the Southern States by relief agencies for the cure and prevention of pellagra. Yeast is also used to some extent in human consumption to supply vitamin B.

Vitamin B in basal rations used for experimental feeding studies is usually incorporated by addition of yeast. A knowledge of the amino acid content of the yeast added is important in order to evaluate the results obtained when the rate of growth is used as a criterion for the amount of the unknown substance which is being assayed. The proteins and amino acids of unknown character and quantity thus incorporated with the yeast into the experimental rations introduce complicating factors which may lead to erroneous conclusions.

When this investigation was started there was very little data or information about the actual quantity of protein in yeast or about its amino acid content. Consequently, there was no basis for making corrections to errors in feeding experiments arising from the introduction of the proteins in the yeast added.

A method was used for the extraction of the protein from yeast which enabled the separation of a much greater proportion of the protein than had been heretofore accomplished. This method involves a preliminary treatment of the fresh yeast with ether before making the extractions with the usual protein extractants. Without this preliminary treatment with ether only about 40 to 50 percent of the total nitrogen could be extracted, whereas after the ether treatment, 91 percent of the yeast nitrogen was removed.

Different fractions of proteins isolated from yeast varied greatly in their composition, particularly with respect to phosphorus, the content ranging from about 0.3 to about 3 percent. This information is important in connection with the use of yeast for preparing basal diets in vitamin determinations, particularly of vitamin D. The nutritionally essential amino acids are well represented in the yeast proteins. Not much difference was found in the amino acid contents of bakers' and brewers' yeast.

Methods developed for the determination of certain amino acids in the whole yeast showed bakers' yeast to contain 0.27 percent of cystine, 1.32 percent of arginine, and 2.15 percent of lysine. The corresponding values for brewers' yeast were similar, namely, cystine, 0.3; arginine, 1.37; and lysine, 2.61 percent. Analyses made on the isolated proteins showed them to be good sources also of histidine and tryptophane. These amino acids are indispensable for the nutrition and normal growth of animals.

The high percentages of the nutritionally essential amino acids in yeast proteins emphasize the importance of giving consideration to them in feeding experiments conducted for the purpose of studying the nutritive value for proteins when yeast is used in the ration to supply vitamins.



## STUDIES ON THE DIGESTIBILITY OF PROTEINS

Studies have been continued which were inaugurated last year on digestibility of proteins *in vitro*, with special reference to the rate of liberation of cystine from casein when the latter is subjected to tryptic digestion. It was previously shown in this Division that when casein is digested with pepsin the digestion proceeds only to the point where the protein is broken down into large fragments of the molecule, such as peptides, peptones, and proteoses. No free amino acids were found to be liberated. With trypsin, however, it was found that the digestion goes much further than with pepsin, and that cystine is liberated at an early stage of the digestion. Tryptic digestion usually proceeds most rapidly in alkaline media (pH 8 to 9). At this alkalinity, however, cystine is decomposed, so that a quantitative estimation of the amount liberated within a given time could not be determined. By conducting the digestion a little on the acid side of neutrality (pH 6.8) the cystine was gradually liberated to completion, amounting to 0.34 percent of the casein.

It has been shown elsewhere that when heated to 150° C., the biological value of casein is lowered, and that this deterioration can be compensated for by addition of lysine to the experimental diet. This observation may be explained by assuming either that the heating destroys the amino acid lysine or that the protein is so changed that a part of the lysine can no longer be used effectively by the animal for its nutritional requirements. That the latter is the true explanation, which doubtless represents a certain type or form of indigestibility, was demonstrated by determining quantitatively the amount of lysine in the raw casein and in the heated casein. In both cases identically the same quantity of lysine was isolated. It is not unlikely that a molecular rearrangement is brought about so that a part of the lysine precursors become resistant to enzymic digestion, and that this resistance explains in part the lowered nutritive value of the heated protein.

## CHEMICAL INVESTIGATIONS ON TOXIC WHEAT

Feeding experiments conducted in this Division with white rats have demonstrated that selenium in wheat cannot be removed by extraction of the wheat in the cold with water, alcohol, or ether; that it is fairly uniformly distributed in the different milling parts of the kernel, namely, the flour, bran, and middlings. Gluten prepared from toxic flour by washing out the starch was found to retain all the toxicity of the flour from which it was prepared. The two proteins, gliadin and glutenin, which comprise wheat gluten, were prepared. These proteins were found to be as toxic as the gluten. Complete hydrolysis of the toxic gluten with sulphuric acid did not destroy the toxicity. The products of hydrolysis were found to be as toxic as the unhydrolyzed gluten. The results of the feeding experiments indicate quite definitely that the selenium in the toxic wheat is present in an organic form intimately associated with or combined with the protein.

The feeding experiments have been followed by chemical investigations with the object of isolating and identifying the form in which the selenium is present in the hydrolysate after toxic gluten has been completely hydrolyzed. By applying methods of fractionation and analyses generally applied to proteins, certain fractions of amino acids have been separated which contain nearly all of the selenium in the hydrolysate. Although small fractions have been isolated that had a high concentration of selenium, they still contained too large a proportion of amino acids to enable any definite characterization of the selenium compound. The results of these studies, however, have yielded considerable information regarding the properties and nature of the selenium compound in the hydrolysate of the toxic wheat gluten.

The organic selenium compound is quite stable. There are no indications of decomposition when it is heated to boiling with 35-percent sulphuric acid or 20-percent sodium hydroxide. It is apparently an organic hydrolytic product of the protein much in the same manner as the amino acids. Like the amino acids, the selenium cannot be removed from the unhydrolyzed gluten by water, but after hydrolysis it is readily soluble in water, dilute acids, and alkalis. It is insoluble in the common organic solvents such as ether, chloroform, carbon disulphide, ethyl acetate, benzene, alcohol, and acetone. Addition of hydroxyl amine or sodium sulphite to aqueous solutions of the selenium-containing fractions does not throw out selenium, as happens in the case of many inorganic selenium salts. In general, its properties are very similar to those of the amino



acids. It is precipitated along with amino acids when they are thrown down from their solutions as salts of certain metals commonly used for the precipitation of amino acids. By systematic fractional crystallization of the hydrolytic products of toxic wheat gluten, most of the selenium is concentrated in those amino acid fractions which may be referred to as the leucine and tyrosine fractions.

#### AMINO ACID CONTENT OF WHEAT

The proteins of wheat flour consist chiefly of gliadin and glutenin. There are other proteins occurring in smaller quantities. Gliadin and glutenin occur in approximately the same proportions, although varying to some extent with the type and variety of wheat and environmental conditions. The amino acid content of gliadin and glutenin is fairly well known, but the composition of the other proteins in flour is not known. Supplementation of one food material with others in order to provide a protein mixture which will contain enough of those amino acids essential for the satisfactory nutrition of animals is a problem that not only frequently confronts investigators in nutritional work, but is of importance in the practical feeding of farm animals and in human nutrition. Knowledge of the amino acid composition of the 1 or 2 chief proteins of food materials will not suffice because of the amino acids present in the other proteins in quantities concerning which there is little or no information. Furthermore, many naturally occurring foods contain free amino acids that are not combined with any protein. Using wheat or wheat flour as an illustration, the total amount of lysine, cystine, or any other amino acid in a pound thereof is not known. If it were desired to add to the wheat some other cereal or nitrogenous product so as to bring the mixture up to a certain definitely desired amino acid content, it would obviously be necessary to know the percentages of the amino acids in the total materials which were mixed.

Methods for the determination of amino acids in isolated and purified proteins are available, but no satisfactory method has been worked out for determining the total amino acids in staple foods, such as cereals, flour, nuts, meat, eggs, milk, etc.

Direct hydrolysis in the manner generally applied to purified proteins in amino acid determination is not applicable to food material such as flour, meals, seeds, etc., because hydrolysis in the presence of starch and other nonprotein substances results in the decomposition of cystine and histidine, two of the amino acids essential for the growth and nutrition of animals. In studies carried on to ascertain the quantity of certain nutritionally essential amino acids in wheat flour, this difficulty has been largely overcome by hydrolyzing extracts obtained by treating the flour with suitable solvents which removed the nitrogenous compounds practically quantitatively.

Working with a popular brand of commercial wheat flour, it was found that it contains 0.31 percent cystine, 0.16 tryptophane, and 0.22 percent lysine. When one considers that only about 12 percent of the flour represents protein material these figures place the total flour protein in a more favorable light with respect to the above-named amino acids than is generally appreciated, and it does not compare unfavorably with purified casein (cystine, 0.31 percent; tryptophane, 2.09 percent; lysine, 7.6 percent).

#### BIOLOGICAL STUDIES ON COTTONSEED OIL

Refined cottonseed oil, a uniformly hydrogenated cottonseed-oil shortening, and a cottonseed-oil shortening made by mixing the oil and a highly hydrogenated oil were all found to be excellent media for carrying carotene. There was no measurable loss of carotene either biologically or spectrophotometrically following 6 months' storage at room temperature. This fact is important because it shows that these oils may be used advantageously and safely, within the time mentioned, as diluents and carriers for carotene, which is used internationally as a standard for vitamin A.

#### ALPHA- AND BETA-CAROTENE AS SOURCES OF VITAMIN A

The studies on the value of alpha- and beta-carotene as sources of vitamin A have been completed. It was shown that there is a distinct difference in the biological value of these two substances. The international standard for



vitamin A was used as a basis for comparing the potency of the two preparations. The alpha-carotene had about 85 percent of the vitamin A value of the international standard and the beta-carotene was about 50 percent more potent than the international standard. In other words, alpha-carotene was found to have about 56 percent of the potency of beta-carotene. There is a theoretical basis and some experimental work to support the view that a molecule of alpha-carotene will form only one molecule of vitamin A while a molecule of beta-carotene will form two molecules of vitamin A. This Bureau's findings lend support to the view that gamma-carotene and cryptoxanthin, which also serve as sources of vitamin A, are only one-half as valuable as beta-carotene. These results have an important bearing on attempts to establish vitamin A potency of plant products by chemical and physical methods. The results were also used in defining the international unit for vitamin A in terms of beta-carotene.

#### INTERNATIONAL VITAMIN CONFERENCE

At the International Vitamin Conference attended by a member of this Bureau new standards were adopted for vitamins A and C. Due to some technical difficulties in using the first standard for vitamin A and also to the fact that much information concerning carotene had been developed since the first conference, it was deemed advisable to adopt beta-carotene dissolved in vegetable oil as a standard for vitamin A. The chemical nature of vitamin C has been definitely established and the pure vitamin called ascorbic acid is now available. Since this substance is sufficiently stable to permit its distribution and use for biological studies, it was adopted as a standard for vitamin C.

#### COLOR AND FARM-WASTE INVESTIGATIONS

##### FAST DYES FOR AGRICULTURAL FIBERS

The work of the Bureau in color and farm-waste research has resulted in the establishment of several industries which have directly stimulated utilization of domestic farm products and have created new market outlets. The American vat-dye industry, made possible by the method developed by the Bureau for the production of phthalic anhydride, has not only broken foreign monopoly but has effected drastic economies in vat-dye manufacture. By use of vat-dye colors it is possible to obtain attractive effects more cheaply with domestic cotton, wool, and synthetic fibers, thereby widening the market for these agricultural materials. The result has been the expansion of the use of American textiles and decreased use of textiles of foreign origin.

During the past year the Bureau has discovered a new process for doubling the yields of a whole series of ketones which are valuable in the manufacture of intermediates for dyestuffs and medicinals. It has also set forth the important theoretical considerations which underlie the reactions employed. These discoveries and reports are not only of fundamental importance in revealing the mechanism of the Friedel and Crafts reactions in organic syntheses but also make possible great monetary savings to industry through more efficient synthetic processes.

##### BIOLOGICAL STAINS

The Bureau continues its work in cooperation with the commission on standardization of biological stains by establishing and maintaining a satisfactory source of stains for the use of the biological scientists of this country. Research of the past year on biological applications of dyes resulted in the discovery of benzoyl auramine G, a new indicator suitable for use in routine Kjeldahl determinations, and requests for small amounts of this indicator have been received.

##### BAGASSE CELLULOSE

The experimental work on utilization of sugarcane bagasse is assuming increased importance. Tests made by the Bureau have shown that an excellent grade of alpha-cellulose can be produced from sugarcane bagasse, thus opening a promising market for the 500,000 tons of waste sugarcane fiber available annually in the continental United States. Industrial experiments based on these results, in which the Bureau has cooperated in an advisory capacity, have indicated that there should be no difficulty in making use of sugarcane fiber to supply needs arising from a shortage of cotton linters. As a result of an



experiment in collaboration with this Bureau, a commercial company at Maui, Hawaii, has recently built and is operating a pilot plant producing 2,000 pounds of high-grade cellulose daily. Under the direction of a specialist from the Bureau, a cellulose was produced at an estimated cost of about \$50 a ton which compared favorably with the best commercial material obtainable.

#### INDUSTRIAL FERMENTATIONS

The chemical action of micro-organisms is receiving attention both from a fundamental and a practical standpoint. Since work was started in the Bureau on industrial fermentations a few years ago, the Bureau has become recognized as a leading authority on the subject.

A new technic, involving the use of aluminum rotary drum fermenters, has been devised by the Bureau for carrying out oxidative fermentations under increased air pressures. This procedure makes possible the use of submerged mold growths in industrial processes and will greatly reduce the cost of certain fermentation products, such as calcium gluconate.

A species of mold has been found that will give high yields of dextro-lactic acid (sarco-lactic acid) as a result of its action on glucose. Dextro-lactic acid, a new product expected to have technical uses, may be produced in the solid form, which will make it more convenient for handling and shipping than is the ordinary liquid lactic acid. New applications may also be found for some of its derivatives, notably the calcium salt. Dextro-lactic acid has not been produced in appreciable quantity heretofore outside of a living animal body, where it exists as a constituent of muscular tissue.

#### LIGNIN

The profitable utilization of lignin, which represents about 30 percent of the dry material in all vegetation and one of the greatest farm wastes, continues to be the object of continuous research by the Bureau. During the past year fundamental studies on the chemistry of lignin were continued; also work on the ammoniation of waste sulphite lignin, with a view to utilizing the ammoniated product as a nitrogenous fertilizer. In the experiments on ammoniation of lignin it was possible to obtain a product containing over 11 percent nitrogen, and greenhouse experiments during the past year indicate that this material may become a successful carrier of nitrogen for the plant.

Studies on the decomposition of lignin and other plant components in alfalfa hay by thermophilic bacteria indicate that, in general, lignin is the most resistant to microbial attack of all the major plant constituents. As a result of microbial activity there is an accumulation of lignin in the residue, which it appears from studies of the past year, plays an important part in the spontaneous ignition of hay and similar agricultural materials.

#### DUST-EXPLOSION INVESTIGATIONS

The Bureau of Chemistry and Soils is the only governmental agency studying dust explosions in agricultural operations and in industrial plants. It is looked to, both in the United States and in foreign countries, for technical information on the subject. The investigations relate directly to the development of methods and appliances for the saving of life, property, and foodstuffs.

Eight dust explosions were investigated by the Bureau during the past year. These explosions resulted in the destruction of property valued at \$1,150,000 and in the death of 11 persons and injury to 16 others.

The two explosions which caused the heaviest loss during the year were those at Newport News, Va., on November 8, and at Omaha, Nebr., on November 23.

The elevator at Newport News was a wood-frame metal-clad structure, and the fire that followed the explosion completely destroyed the building and the grain it contained. The explosion occurred while grain was being turned and in connection with this operation fumigation or treatment of the grain to kill weevils was in progress or had just been completed. The men engaged in this operation were killed. In view of the fact that the use of a fumigant may have been associated with this explosion, it has been suggested that studies be made to determine whether fumigants, presumably safe based on laboratory tests, are safe at all times during or after application as practiced in industrial plants.

The explosion at Omaha occurred in a new type of elevator, radically different from the usual type of grain storage plant, and the method by which the ex-



plosion in this house vented itself through the roof indicated the value of light construction for the release of explosion pressures. In the opinion of the investigators a much more severe explosion with greater life and property loss would have occurred if the plant had been of heavier construction.

#### ARLINGTON TESTS ON DETERMINATION OF RATIO OF EXPLOSION PRESSURES TO VENTING AREA

The testing work now under way is designed to show the venting area necessary to release explosion pressures produced by ignition of dust clouds of different particle size. Tests have indicated the particle size of grain dust necessary to propagate flame and the size required to produce explosive pressures. The venting area necessary to release these pressures without structural damage has been determined for grain dust, and it is planned to continue the work with other kinds of dust.

A considerable amount of testing was done during the year in order to determine the comparative value of top and side vents for releasing dust-explosion pressures in tall towers, tanks, or bins.

A series of tests was included in the above program to determine the maximum permissible length of a venting duct designed to carry explosion pressures from a bin, elevator leg, or enclosure within a building to the outside.

Some preliminary work was carried on to determine the possibility of using preaction vents designed to open under a temperature rise or a slight increase in pressure, and thus be in position to release an explosion should one occur. This work indicated the possibility of using the initial pressure wave of an explosion to operate some equipment or stop some mechanism in another section of a plant, but further work will be necessary to determine how effective such apparatus will prove to be.

Further tests were made during the year with different types of glass scoring designed to weaken windowpanes, and thus permit the release of explosions at lower pressures.

A number of demonstrations were given during the year at the Arlington station to show how dust-explosion pressures could be released through properly proportioned and properly located vents without damage to the structure. Visitors to the station to witness demonstrations included grain-elevator officials and operators, railroad fire-protection engineers, manufacturers, students, and members of 4-H clubs.

#### EXPLOSIBILITY AND IGNITION TEMPERATURES OF VARIOUS DUSTS

The lower limits of concentration for explosion of wood dust from 7 conifers, 6 broadleaf woods, and 4 barks were determined by the Bureau during the past year. In addition tests were made to determine the maximum pressure, and maximum and average rates of pressure rise at concentrations of 10, 25, 50, 100, 250, 500, 750, and 1,000 mg per liter for the 17 dusts. In some instances, due to the low density of the dust, the capacity of the apparatus was not great enough to hold the amounts required for the higher concentrations, which prevented the making of tests at those concentrations. These tests give a complete story on the explosibility of these wood and bark dusts.

The lower limit of concentration for explosion of ground malt and barley and malt elevator dusts and the maximum pressure and maximum and average rates of pressure rise were determined over a wide range of concentrations.

The ignition temperatures of barley and malt elevator dusts are 247° and 252° C., respectively. These are lower than those previously reported for wheat and corn elevator dusts, which were 265° and 267°. The ignition temperature of ground malt is 319°, which compares favorably with cornstarch and hard wheat flour.

#### SCHOOLS OF INSTRUCTION FOR FIREMEN

The Bureau cooperated actively with the various States in presenting the dust-explosion prevention work at schools of instruction for firemen. Addresses and dust-explosion demonstrations were presented at the following meetings: Lancaster County Firemen's School, Lancaster, Pa. (Millersville State Teachers' College); International Fire-Fighters' Convention, Cedar Point, Ohio; International Association of Fire Chiefs' Convention, Milwaukee, Wis.; Pennsylvania State Firemen's Association Convention, Sunbury, Pa.; Illinois State Firemen's Association Convention, Granite City, Ill.; Iowa State Fire College, Ames, Iowa; and Training Institute for Fire Chief, Syracuse, N. Y.



## SPECIAL MEETINGS

The dust-explosion-prevention work was presented at a large number of special meetings in various sections of the country throughout the year. Among the more important meetings were the following: National Fire Protection Association meetings at Atlanta, Ga., Atlantic City, N. J., and Boston, Mass.; annual meeting of Grain Elevator Superintendents, Chicago; annual meeting of Operative Millers' Association, St. Louis, Mo.; conference with railroad officials, Philadelphia; and meeting of committee on static electricity, National Fire Protective Association, New York.

During the year a number of conferences were held with representatives of industrial companies and trade associations to discuss various dust-explosion-prevention problems.

## FARM FIRES

## LARGE-SCALE EXPERIMENTS ON SPONTANEOUS IGNITION OF HAY

Recognizing the need for extending research into the field, the Bureau has been conducting for several haying seasons at the Experiment Farm, Beltsville, Md., large-scale experiments on the spontaneous heating and ignition of hay. The purpose of these experiments was to study some of the causes and the effects of the self-heating and ignition of long hay in storage and of developing practicable methods of prevention and control.

The tenth experiment of this series, designed primarily for studying the efficacy of salt as a retardant or preventive of spontaneous heating and ignition, was carried on during the summer of 1934.

As a general observation, this experiment indicates that 1½ percent by weight of salt added to 12½-ton lots of long alfalfa hay averaging 35-percent moisture content has no appreciable effect as a preventive or retardant of spontaneous heating.

One phase of the investigation of the causes and effects of the spontaneous heating of hay in large-scale experiments was a study of the gases formed during the heating. Closely related to this study was a laboratory investigation of the oxidation of hay under the influence of heat supplied from external sources. As a result of the consideration of the results of these two lines of investigation, it has been possible to form some important conclusions regarding the nature of the oxidation occurring in the mow undergoing spontaneous heating. The results indicate that along with the respiration processes of the living plant cell and the activity of micro-organisms, chemical oxidations also occur throughout the whole range of temperature usually ascribed to biological agencies. The results further lend support to the view that in spontaneous heating of hay unsaturated, easily oxidizable chemical substances are formed, which would at least partially account for the ready consumption of oxygen. The results of this phase of the investigation are embodied in a manuscript entitled, "Oxidation and gas formation in the spontaneous heating of hay", which has been submitted and approved for publication.

Another line of investigation connected with the large-scale experiments and which was continued in the experiment ended in the present fiscal year was that of the losses of hay substance resulting from the excessive fermentation of improperly cured hay as stored in these experiments. It is proposed to present the results of this investigation for publication, and to this end considerable progress has been made in preparing the manuscript. The results of this work confirm previous opinions of the great seriousness of the losses from the spoilage or complete destruction of farm produce incident to excessive spontaneous heating which may occur and often does occur without reaching the temperature limit at which ignition occurs.

An investigation related to the general problem of spontaneous heating is that of the individual constituents of hay which may be attacked during spontaneous heating. Progress has been made in the separation and examination of the constituents which are soluble in organic solvents.

## SOIL INVESTIGATIONS

The importance of fundamental knowledge of the soils of the United States has never been greater than at present or more generally appreciated. The fundamental fact of agriculture is the relationship between the plant root and the soil in which it grows. Each plant has specific requirements and each



type of soil certain capabilities under methods of management which man may employ. More than upon anything else, successful agriculture is predicated upon a successful adjustment of plant and soil. Crops and farmers fail on soils which are better suited to grazing and forests than to farming, soil erodes when wrongly used, and taxes become delinquent in those areas where the land is unsuitable for intensive use. To the extent that the individuals or governments affected by these problems cope with them through the adoption of rational policies of land use, such programs must be based on a fundamental understanding of the soil and its capabilities.

#### SOIL SURVEY

During the past fiscal year 23,590 square miles of rural lands in 28 States and Puerto Rico were mapped by the Division of Soil Survey. This brings the total area covered by the Soil Survey to somewhat more than one-half the arable lands of the Nation. Essentially all of this work is accomplished in direct cooperation with local State agencies, especially the State agricultural experiment stations. In this way the broader perspective of the Federal organization and the more detailed local knowledge of the State agency can both be utilized, each supplementing the other.

These maps furnish the fundamental groundwork for planning a land policy by individuals and by various governmental agencies, both local and national. The soil maps, together with the accompanying reports giving descriptions of the soils and their uses, provide farmers and local officials with a practical working handbook of the soil.

The extended use of these maps whenever they are available for determining land-use policies testifies to their accuracy and value. In 1931 a detailed soil survey was initiated in North Dakota at the request of the local people as a basis for the classification of lands for the purpose of appraisal for taxation. This work has been continued in additional areas during the past year. An explanation of the logic and procedure of the method currently used to classify land for purposes of tax assessments was published recently by the Bureau as Technical Bulletin 469, *A Method of Rural Land Classification*.

During the past year this Bureau, in conjunction with the Washington State Agricultural Experiment Station began a somewhat similar survey in western Washington. The Federal Soil Survey is cooperating with the seven experiment stations concerned with the agricultural program in the Tennessee Valley for a detailed survey of that area.

For the purpose of carrying out the Department's policy of removing land from the production of surplus crops, especially where these crops are produced only at a low labor income for the operator, the Division of Soil Survey furnishes the necessary information required to readjust the use of these areas for other crops, grazing, or forestry.

In the Western States the soil survey is proving of incalculable value in the extension of the acreage of certain special crops and at the same time serves to point out the areas where the accumulation of salts and the development of alkali would be a menace to irrigation projects. The selection of those soils suitable for the production of cotton and those best adapted to other crops in southern areas infested with the bollweevil has been greatly expedited by the use of the soil maps. Land suitable for the production of high-quality tobacco is selected through the use of soil maps where they are obtainable.

Interpretation of experimental work in the use of lime, fertilizers, and other farm-management practices depends on the soil survey. Experimental results on one soil type may be applied to other areas of that same soil. Because of the exact descriptions and classification of soils contributed by the Soil Survey, it has become more and more the policy of experiment station workers and county agricultural agents to make their recommendations regarding agricultural practices by soil type. The work of experiment stations finds its application through the Soil Survey.

Tables 1 and 2 show the details of the work done during the fiscal year 1935, the areas covered, and their distribution.



TABLE 1.—Individual areas surveyed and mapped during the fiscal year ended June 30, 1935

State or Territory	Area	Area surveyed	
		Square miles	Acres
Alabama	Elmore County	24	15,360
	Hale County	<sup>1</sup> 148	94,720
	Marion County	<sup>1</sup> 85	54,400
Arizona	Sumter County	<sup>1</sup> 374	239,360
	Casa Grande area	<sup>1</sup> 346	221,440
California	Pixley area	<sup>1</sup> 216	778,240
	Visalia area	<sup>1</sup> 42	26,880
	Sacramento-San Joaquin Delta area	500	320,000
Georgia	Toombs County	<sup>1</sup> 240	153,600
Idaho	Bingham County	39	24,960
	Bonner County	<sup>1</sup> 174	111,360
Indiana	La Porte County	<sup>1</sup> 153	97,920
	Cerro Gordo County	165	105,600
	Decatur County	<sup>1</sup> 375	240,000
Iowa	Jackson County	237	151,680
	Osceola County	<sup>1</sup> 112	71,680
	Story County	186	119,040
Kansas	Allen County	<sup>1</sup> 145	92,800
	Cheboygan County	<sup>1</sup> 103	65,920
Michigan	Clinton County	159	101,760
	Mason County	53	33,920
Minnesota	Pine County	<sup>1</sup> 340	217,600
	Frontier County	376	240,640
	Garfield County	218	139,520
Nebraska	Gosper County	464	296,960
	Hayes County	722	462,080
	Lancaster County	118	75,520
New Hampshire	Loup County	576	368,640
	Grafton County	178	113,920
	Albany-Schenectady Counties	<sup>1</sup> 209	133,760
New York	Cattaraugus County	<sup>1</sup> 305	195,200
	Niagara County	85	54,400
	Onondaga County	<sup>1</sup> 328	209,920
	Otsego County	<sup>1</sup> 352	225,280
	Ulster County	<sup>1</sup> 574	367,360
North Carolina	Cartaret County	<sup>1</sup> 402	257,280
	Clay County	<sup>1</sup> 41	26,240
	Stokes County	<sup>1</sup> 180	115,200
North Dakota	Warren County	145	92,800
	Billings County	<sup>1</sup> 602	385,280
Ohio	Morton County	<sup>1</sup> 254	162,560
	Tuscarawas County	106	67,840
	Garfield County	<sup>1</sup> 464	296,960
Oklahoma	Major County	<sup>1</sup> 484	309,760
	Murray County	<sup>1</sup> 271	173,440
	Pontotoc County	<sup>1</sup> 173	110,720
Oregon	Tulsa County	<sup>1</sup> 172	110,080
	Washita County	<sup>1</sup> 306	195,840
	Umatilla County	<sup>1</sup> 22	14,080
Pennsylvania	Bucks County	<sup>1</sup> 246	157,440
Puerto Rico	Huntingdon County	<sup>1</sup> 196	125,440
Rhode Island	Island	<sup>1</sup> 666	426,240
	Kent and Washington Counties	<sup>1</sup> 61	39,040
South Carolina	Edgefield County	<sup>1</sup> 32	20,480
	Pickens County	142	26,880
Tennessee	Sumter County	<sup>1</sup> 234	149,760
	Jefferson County	262	167,680
	Fannin County	<sup>1</sup> 162	103,680
Texas	Kaufman County	366	234,240
	Maverick County	<sup>1</sup> 424	271,360
	Williamson County	<sup>1</sup> 84	53,760
Utah	Virgin River area	195	124,800
	Salt Lake Valley area	223	142,720
	Albemarle County	<sup>1</sup> 302	193,280
Virginia	Halifax County	<sup>1</sup> 198	126,720
	Isle of Wight County	143	91,520
	Mecklenburg County	79	50,560
Washington	Washington County	31	19,840
	Kitsap County	371	237,440
	Kittitas County	55	35,200
Wyoming	Snohomish County	435	278,400
	Yakima County	482	308,480
	Fremont County	862	551,680
	Uinta County	<sup>1</sup> 1,536	983,040
Total		21,030	13,459,200

<sup>1</sup> These figures do not include portions of these areas surveyed in preceding years.



TABLE 2.—Areas surveyed and mapped in the several States during the fiscal year ended June 30, 1935, and the areas previously reported

## DETAILED

State or Territory	Work during 1935	Work previously reported	Total	
	Square miles	Square miles	Square miles	Acres
Alabama.....	631	58,886	59,517	38,090,880
Arizona.....	346	4,136	4,482	2,868,480
Arkansas.....		15,547	15,547	9,950,080
California.....	1,758	35,632	37,390	23,929,600
Colorado.....		5,865	5,865	3,753,600
Connecticut.....		1,704	1,704	1,090,560
Delaware.....		2,276	2,276	1,456,640
Florida.....		15,160	15,160	9,702,400
Georgia.....	240	35,947	36,187	23,159,680
Idaho.....	213	12,312	12,525	8,016,000
Illinois.....		6,770	6,770	4,332,800
Indiana.....	153	21,039	21,192	13,562,880
Iowa.....	1,075	49,334	50,409	32,261,760
Kansas.....	145	16,641	16,786	10,743,040
Kentucky.....		5,542	5,542	3,546,880
Louisiana.....		17,431	17,431	11,155,840
Maine.....		2,197	2,197	1,406,080
Maryland.....		13,959	13,959	8,933,760
Massachusetts.....		8,811	8,811	5,639,040
Michigan.....	315	32,069	32,384	20,725,760
Minnesota.....	340	12,241	12,581	8,051,840
Mississippi.....		30,740	30,740	19,673,600
Missouri.....		37,177	37,177	23,793,280
Montana.....		3,287	3,287	2,103,680
Nebraska.....	2,474	65,418	67,892	43,450,880
Nevada.....		652	652	417,280
New Hampshire.....	178	1,411	1,589	1,016,960
New Jersey.....		9,895	9,895	6,332,800
New Mexico.....		2,565	2,565	1,641,600
New York.....	1,853	34,431	36,284	23,221,760
North Carolina.....	768	47,332	48,100	30,784,000
North Dakota.....	856	20,947	21,803	13,953,920
Ohio.....	106	18,407	18,513	11,848,320
Oklahoma.....	1,870	22,300	24,170	15,468,800
Oregon.....	22	15,799	15,821	10,125,440
Pennsylvania.....	442	22,033	22,475	14,384,000
Puerto Rico.....	666	2,100	2,766	1,770,240
Rhode Island.....	61	1,523	1,584	1,013,760
South Carolina.....	308	26,525	26,833	17,173,120
South Dakota.....		8,286	8,286	5,308,040
Tennessee.....	262	11,198	11,460	7,334,400
Texas.....	1,036	64,258	65,294	41,788,160
Utah.....	418	2,497	2,915	1,865,600
Vermont.....		1,175	1,175	752,000
Virginia.....	753	14,073	14,826	9,488,640
Washington.....	1,343	10,752	12,095	7,740,800
West Virginia.....		23,683	23,683	15,157,120
Wisconsin.....		26,659	26,659	17,061,760
Wyoming.....	2,398	9,929	12,327	7,889,280
Total.....	21,030	908,551	929,581	594,931,840

## RECONNAISSANCE

Alaska.....		31,915	31,915	20,425,600
Arkansas-Missouri.....		58,000	58,000	37,120,000
California.....		32,135	32,135	20,566,400
Kansas.....		39,960	39,960	25,574,400
Michigan.....		1,322	1,322	846,080
Minnesota.....	562	11,074	11,636	7,447,040
Montana.....	2,098	49,685	51,783	33,141,120
Nebraska.....		53,064	53,064	33,960,960
North Dakota.....		39,240	39,240	25,113,600
Ohio.....		41,420	41,420	26,508,800
Pennsylvania.....		41,405	41,405	26,499,200
South Dakota.....		41,400	41,400	26,496,000
Texas.....		152,855	152,855	97,827,200
Vermont.....		9,124	9,124	5,839,360
Washington.....		16,540	16,540	10,585,600
Wisconsin.....		14,425	14,425	9,232,000
Total.....	2,660	633,564	636,224	407,183,360



## SPECIAL WORK OF THE SOIL SURVEY

In addition to the publication of 28 soil-survey maps and reports and other bulletins reporting results of regular projects, members of the staff have given a great deal of time to special problems in connection with the various activities relating to land use of the Federal Government and of cooperating State agencies.

As the soil-survey data are necessary and basic for almost all kinds of agricultural activity, thousands of private individuals and organizations seek the advice and assistance of the soil scientists of the Bureau, both as to the location of actual soil types and the interpretation of soil-survey data in terms of practical agriculture. Typical of these special services the following may be mentioned:

## SUBSISTENCE HOMESTEADS

During the past fiscal year the Division of Subsistence Homesteads has called on the Division of Soil Survey for continued assistance. Scientists in the Division have made detailed soil maps of several tracts of land to determine the suitability of the soils for the production of garden vegetables. About 18 such projects were examined and reported,

## SHELTERBELTS

In order to plan the development of shelterbelts in the Great Plains, detailed information is required regarding the nature and distribution of the various types of soil. The general area includes many soil types, varying widely in their capability to produce trees. Certain soils are best suited to particular species of trees; some cannot be expected to support any sort of tree growth. Several soil scientists from the Soil Survey have been securing the data necessary for planning these plantings.

## SOIL EROSION

Serious injury to soils through erosion generally occurs when they are wrongly used. The fundamental nature of the soil type determines its erosivity. The published soil maps serve as a basis for erosion surveys and erosion-control projects. In many cases where these maps have been unavailable, scientists in the Soil Survey have made special studies and maps for the use of Federal and State agencies charged with the responsibilities for erosion control.

## FARM CREDIT

Not only have the land appraisers of the Farm Credit Administration made wide use of the soil-survey maps and reports now available but have also called upon several scientists of the Soil Survey staff to assist them in conducting schools for land appraisers in order that they may recognize the individual soil types and understand their capabilities for agricultural use.

## PEAT

During the past fiscal year the work in peat investigation continued along the following lines:

(1) Inventory of the acreage, location, and geographic distribution of peat and muck resources.

(2) Improvements of technic of peat-profile morphology, identification of organic materials, and classification of peat land on a national and international basis.

(3) Collecting basic information relating to the selection and use of peat deposits for domestic grades of peat in place of imported peat products—for improving the physical condition of arable mineral soils, and for supplying raw material to a future chemical industry.

(4) Cooperation with Federal and State agencies in research and in planning the use of submarginal peat areas to alleviate the menace of floods, erosion, and silting, and the retention of unprofitable types of peat land for waterfowl, fur bearers, and wildlife.



## SELENIUM

During the past fiscal year the Division of Soil Survey detailed two specialists for a part of their time to assist in the selenium investigations being carried on by the Bureau. Examinations were made of the shales, soils, and vegetation in several States, and the results are incorporated in the report of the Division of Soil Chemistry and Physics contained in this publication.

## SOIL SURVEY OF PUERTO RICO AND HAWAII

Under an allotment of funds from the sugar-processing tax of the Agricultural Adjustment Administration, the Soil Survey has undertaken the detailed survey of the soils of Puerto Rico and Hawaii. The work in Puerto Rico will be completed during the coming fiscal year, and that in Hawaii will require a few months longer. These soil maps will furnish the basis for planning the necessary agricultural adjustments.

## SOIL CHEMISTRY AND PHYSICS

The work of the Division of Soil Chemistry and Physics during the past year has centered around four major problems. These are the physical and chemical study of the soils from the erosion experiment stations; the study of soils and colloids with reference to soil classification; study of the occurrence and distribution of selenium in agricultural areas; and the service work of the Division.

Besides these, work is being conducted along other lines which include the moisture relations and chemical constitution of peat; the relation between soil composition and the toxic effect of arsenic upon vegetation; and the study of the causes of infertility of certain soils.

## STUDIES ON SOILS FROM THE EROSION STATIONS

Continuing the investigation of the soils from the erosion stations a very complete study of the exchangeable bases and acids of the colloids has been made and the results published in Technical Bulletin 461. These investigations have shown, through the wide differences in the base-exchange relation, the necessity for different soil treatments in the handling of the divergent soil types. A new investigation of great interest is under way in connection with the trace elements which appear in these soils. It has been demonstrated that all of them contain, to varying degrees, selenium, arsenic, cobalt, nickel, zinc, copper, chromium, vanadium, and barium. It becomes increasingly apparent that these trace elements play an important role in soil behavior, and this investigation, together with those undertaken elsewhere, appears to make imperative a broad study of these relationships.

## SOIL AND COLLOID COMPOSITION

During the year two investigations have been completed in the field of soil and colloid composition. One of these concerns the detailed chemical composition of typically representative profiles of the great soil groups. This work has been reported in a technical bulletin now in press. The work clearly demonstrates that in the great morphological groups the chemical composition of the active component of the soil, the colloid, is characteristic for each group, and that for proper and intelligent control of the soil the treatment must be adapted to the particular characteristics shown. In addition, an indication is found which points to a method of simplification of soil classification which will assist materially in the solution of land-use problems.

A second investigation which has been completed involves a study of the chemical composition of the soils of the semiarid areas. This work is reported in a bulletin that has been submitted for publication. This research has shown that soils and colloids of the semiarid areas owe their characteristic differences primarily to the parent material, which is in sharp contradiction to the results previously found for humid soils. One of the important inferences to be drawn from this study is the necessity for studies of inherent productive capacity of virgin soils.

A third study, nearing completion, is concerned with the base-exchange capacity, neutralization curves, and the maximum acids shown by the colloids



of the great soil groups. This study, when completed, will give the scientific explanation for the differences which reveal themselves in the great deterioration of such soils by use, and will make for more satisfactory recommendations in connection with soil control.

In various parts of the United States closely related soil series are derived from the same parent material under the same climatic conditions. A very intensive study of one of these groups is being undertaken in order to determine what the differences are, and, if possible, their causes.

A fifth investigation which is begun concerns itself with the soil differences manifested under widely different climatic conditions when the parent material is as nearly as possible the same. It is hoped that this study may produce results of value in relation to the soil morphology of the soils of the Atlantic coast.

A sixth investigation concerns itself with the study of the soil composition of limestone soils developed under different climatic conditions, together with a study of the parent material. It is to be expected that this investigation will reveal the causes of the variation in character manifested by these soils.

#### SELENIUM INVESTIGATIONS

During the past year the investigations of the distribution of selenium have continued, and the first detailed report will appear in a technical bulletin now in press. This report presents a synopsis of the data accumulated previous to January 1, 1935. The presence of selenium in quantities which appear to call for serious consideration has been shown in soils and vegetation in seven States. The study has shown that the problem is an exceedingly complex one, in that the selenium in vegetation depends not only upon the quantity of selenium present in the soil, but upon its distribution within the profile and upon the kind of plant, and apparently upon its degree of maturity. The work was continued with support of emergency funds until the end of the fiscal year 1935, and is now being continued under the usual conditions of scientific research.

A number of areas are under investigation and it has been shown that at least two irrigation areas have a serious selenium problem, though it begins to appear that in such areas remedial measures are available. A number of new areas of seleniferous soils have been discovered, and a study of these soils and their vegetation is proceeding. In addition, advantage is being taken of the wide difference between the rainfall of the present year, as compared with previous years, in an endeavor to gain information on the effect of rainfall upon the intake of selenium by plants. Supplementary investigation in connection with selenium in soils, vegetation, and animal organisms has been started at a number of the universities and by private organizations as a consequence of the discoveries so far made.

#### SERVICE WORK

The Division is called upon to make routine measurements, both physical and chemical, on soils and soil materials for numerous governmental agencies, particularly the Division of Soil Survey. In addition, queries are frequently received from officials of the Government and from individuals which require minor tests for proper reply. The tests most frequently required are mechanical analyses to determine soil specifications in connection with contracts, hydrogen concentration, soluble-salts content, and identification. During the course of the year several thousand of such determinations have been made.

#### MISCELLANEOUS INVESTIGATIONS

An investigation has been completed dealing with the effect of soil colloids of varying composition upon the availability of arsenic as affecting plant growth. The results have been prepared for publication. They show that while arsenic administered in quantities comparable with those sometimes employed will produce serious inhibition of yields, at least in the case of the control plant employed, the degree of inhibition varies widely with the soil type. The results point clearly to the necessity of careful consideration of the quantities of arsenic which may safely be used in insecticidal control.



The studies of infertile soils which have been continued for several years have been completed, so far as they concern a group of soils derived from serpentine, and which cover wide areas in the United States and elsewhere. The results of these studies have been published in Technical Bulletin 471. They show that in addition to the unfavorable physical characteristics shown by these soils, they contain abnormally large quantities of magnesium, chromium, and nickel, any or all of which may contribute to the low productivity. Studies along this line are being continued in an effort to determine the relation of barium, which occurs widely distributed in soils, upon the productivity of the soil.

The studies upon peat were continued. It has been demonstrated that the different varieties of peat show apparently characteristic different decomposition products. This study is extremely difficult and the interpretation of the results obtained is not as yet possible.

A study of the powers of water retention by peat is in progress and so far as it has gone seems to promise extremely important results as affecting the use of peat as a soil amendment.

## FERTILIZER INVESTIGATIONS

The fertilizer work of the Bureau of Chemistry and Soils had a twofold origin. Explorations in search of natural deposits of phosphates, nitrates, and potash-bearing minerals and brines, surveys of known and newly discovered occurrences of these, of the potash-containing kelp beds of our Pacific coast, and of organic wastes, and investigations of methods for the utilization of all these for fertilizer purposes were conducted in the former Bureau of Soils. The problems involved in devising methods and apparatus for the economic fixation of atmospheric nitrogen and studies of related projects, occupied the attention of the Fixed Nitrogen Research Laboratory, originally in the War Department but transferred in 1921 to the Department of Agriculture.

The work has for its purpose making the best use of our many resources—air, minerals, and byproducts—to give the farmer the greatest value for the money he invests in plant food. The solution is complicated, involving national and international commerce and transportation, as well as intricate chemical manufacture. In the past, the United States has been dependent on imports for both nitrogen and potash; fertilizers diluted with inert materials and therefore unnecessarily low in plant food have been too generally accepted with the incident high costs for bagging, handling, and freight; too little care has been exercised in securing uniform mixtures and uniform and properly placed distribution in the field. The trend has been toward correction of these faults, and cheaper and better fertilizers are available as a result.

## NITROGEN

### CATALYSTS IN NITROGEN FERTILIZER INVESTIGATIONS

The development by this Bureau of efficient ammonia catalysts, high-pressure catalytic technic and apparatus, and hydrogen-purification catalysts, made possible this country's general employment of the direct synthetic ammonia process with resultant low fixed-nitrogen prices and self-sufficiency for peace-time industries and national defense. The work was originally mostly empirical in nature and found application also in allied industrial processes.

The investigations have as their purpose the gaining of a fundamental understanding of catalytic phenomena so that the information gained may be applied to the devising of improved catalysts and catalytic procedures for use in the production of fertilizer materials.

Two types of work relating to the kinetics of ammonia synthesis have been in progress during the past year. The dependence of rate of reaction upon the partial pressures of ammonia and hydrogen and upon temperature was determined in the reverse reaction of the decomposition of ammonia on promoted iron catalysts. Also an apparent means for estimating the surface areas of synthetic ammonia catalysts was found as a result of the discovery that the isotherms of a number of different gases at only a few degrees from their boiling points bear a certain relationship to the amount of gas necessary to form a monomolecular layer on the catalyst surface.

Work on the kinetics of the conversion of ortho- to para-hydrogen, mentioned last year, has been completed. In the course of this work it was shown that the adsorption and activation of hydrogen is not the rate-determining step in



ammonia synthesis, that at least two types of activated adsorption of hydrogen occur on iron synthetic ammonia catalysts, in addition to the usual physical adsorption, and that the observed dependence of the rate of the para- to ortho-hydrogen transformations over iron catalysts on temperature and pressure is explainable in terms of the effect of these two factors on the adsorption of hydrogen by the catalysts.

A preliminary study of a method of producing hydrogen for ammonia synthesis by oxidizing phosphorus vapor with carbon dioxide to form phosphorus pentoxide and carbon monoxide, and then converting the carbon monoxide with steam into hydrogen and carbon dioxide, definitely showed the possibility of carrying out the first step of the procedure and that this reaction involves an equilibrium in the temperature range 800° to 1,000° C.

In the study of the "work function", that is a measure of the heat of vaporization of electrons from catalytic surfaces by the photoelectrical method, it was discovered that activated, adsorbed gases have a pronounced effect in lowering the energy of the escaping electrons. These experimental results fit in very well with recent theories of surfaces and indicate that in one form of adsorption the dissolved gas approaches an ionized state.

#### PHYSICAL CONSTANTS OF GASES AND FERTILIZER SALTS

Although concerned largely with fundamental studies of the reactions involved in nitrogen-fixation processes and the formation of fertilizer compounds, the Division of Physics and Physical Chemistry meets a constant demand for cooperative work from other divisions of the Bureau as well as from other bureaus of the Department of Agriculture by assisting them with X-ray, crystallographic, spectroanalytical, photochemical, high temperature and pressure, mathematical, and statistical problems. The solution of numerous problems confronting scientific investigators depends on a knowledge of the physical constants and ultimate structure of the elementary substances and compounds involved. The use of modern physical and physicochemical research methods in the furtherance of fertilizer and other agricultural investigations constitutes pioneer work in a field filled with incalculable possibilities.

In studying the vapor contents of compressed gases that are in contact with liquids, composition and compressibility measurements on both the liquid and gaseous phases of ammonia-hydrogen mixtures were made during the year at 100° under total pressures up to 800 atmospheres. The work on the solubility of hydrogen in liquid ammonia reported last year has been extended to the determination of the solubility of helium in water at 0°, 25°, and 50° under pressures up to 1,000 atmospheres, in order to obtain a better understanding of the nature of the solubility of gases in liquids. In addition, measurements were made of the solubility of a 3:1 hydrogen-nitrogen mixture in water at 25° under pressures ranging from 50 to 1,000 atmospheres. A closely additive relationship was found.

To further our knowledge of the thermal properties at high temperatures of substances important in fertilizer production, an apparatus has been constructed capable of measuring vapor pressures at temperatures up to 1,000°, and measurements have been made therewith of the vapor pressures of phosphorus pentoxide at 200° to 600° over three solid phases, the metastable, glassy, and crystalline, and over the liquid phase.

In continuation of the work on the physical examination of fertilizer materials by X-ray diffraction analysis reported last year, the various acid phosphates and their hydrates have been prepared in pure form and their crystallographic and optical constants measured. Partial isomorphism was found to exist between gypsum and dicalcium phosphate dihydrate. Routine examinations were also carried out on soil colloids, fertilizer mixtures, and products obtained in experimental work. In addition an extensive study was conducted on a number of oxalates, selected as representative organic compounds, to show the correlation between crystal optics and crystal structure. This work showed that the oxalate group is invariant in shape and that the high optical anisotropy of oxalates is completely explained by the orientation of the group in the crystals. The use of electron diffraction as a method of analysis disclosed that the phosphorus molecule in the gas phase at 200° is a regular tetrahedron.

The Bureau's recent work upon the absorption spectra of ozone and the nitrogen oxides has suggested the probable importance to agriculture of



chemically active trace constituents of the atmosphere, a field which merits careful study. During this year's work upon the absorption of light by nitrogen trioxide there was discovered a band spectrum due to nitrous acid, which furnished a means for determining this substance in gaseous systems. Having this spectrum, an almost complete control is afforded for the complicated and economically important system, consisting of nitric oxide, nitrogen dioxide, water, nitrous acid, and nitric acid, involved in the production of nitric acid. A study was also made of the effect of pressure upon the absorption spectrum of nitric oxide and a theoretical explanation of the cause of this phenomenon has been deduced. Infrared absorption coefficients were determined for more than 50 organic compounds containing the groups  $\text{NH}_2$ ,  $\text{NH}$ , and  $\text{OH}$ , the results being particularly important because they provide a method of quantitative analysis for these groups in molecules that are soluble in nonpolar solvents.

By use of the mass spectograph mentioned in last year's report, it was found that the atomic weights of lithium, potassium, and rubidium can be determined with an accuracy far greater than by chemical means. The isotope ratios of potassium have been measured for a large number of mineral, plant, and animal sources, and found fairly constant in minerals but not at all so in plants and animals, kelp and bone marrow, for example, having a pronounced ability to concentrate the heavier radioactive isotope. The investigation is being extended to determine the physiological significance of this preferential selection by certain plants and animal organs of one potassium isotope over another.

#### NITROGENOUS FERTILIZER MATERIALS

Although the development of the nitrogen-fixation processes with the resultant abundance of nitrogen compounds, as well as increased consumption of organic ammoniates in animal feeds, have caused considerable displacement of the use of these ammoniates for fertilizers, demand for them still remains strong despite a price per unit of nitrogen greatly exceeding that of inorganic materials, because of their resistance to leaching, action as conditioners in mixed fertilizers, slight tendency to increase soil acidity, and slow rate of availability. Among the products obtained by the Bureau in an endeavor to produce from organic materials of little or no value a cheap fertilizer material that possesses these desirable properties, those obtained by the ammoniation of peat give most promise of serving as substitutes for the expensive organic ammoniates.

Continuing the previously reported work on the ammoniation of peat, a study was made to determine differences in the products obtained as a result of changes in temperature, pressure, moisture present, and ratio of ammonia to peat in the ammoniation process. Increasing the ratio of ammonia, pressure, and moisture produces a material of better quality but increasing the temperature raises the proportion of inactive nitrogen in the product. The value of the products has been judged from pot and nitrification tests and from permanganate methods for determining activity. The results obtained have not all been favorable but indicate that under certain conditions of preparation or use the ammoniated material is a suitable fertilizer material. Treatment of peat with alkalies, acids, and steam has been carried out prior to ammoniation with a view to obtaining products in which the insoluble nitrogen was highly active. The results obtained have not been very uniform although some improvement in activity has been achieved, but marked improvement has been noted in some cases in which the ammoniated product has been thus treated. Activities of the insoluble nitrogen have been raised in instances from about 50 to more than 90 percent as indicated by the neutral potassium permanganate test. Verification of the value of the nitrogen for plant growth remains to be tested by nitrification and vegetative tests.

A comprehensive study of the mechanism of the formation of the water-soluble nitrogenous constituents of the ammoniated peat has been made. The data obtained show that the organic acids of the peat combine with the ammonia to form ammonium salts which, upon continuation of the ammoniating process, are transformed into urea and into other amides. The desirability of increasing the potential organic acid content of peat to a maximum before ammoniation is thus indicated.

Among several double salts of urea that have been prepared during the past year, one of promising fertilizing utility is a combination of urea with magnesium sulphate. The properties of this compound are being investigated. Difficulties encountered in determining accurately the urea content of such



salts during the course of the work have led to the development of an improved analytical procedure for this purpose. Although a number of double compounds of ammonia have been formed by treatment of inorganic nitrogen carriers and compounds with liquid ammonia, none of these was found to be suited for fertilizer use because of the high vapor pressure of the ammonia contained in them. The possibility of producing more stable compounds of this type is still under investigation.

#### BIOCHEMICAL AND ORGANIC NITROGEN INVESTIGATIONS

Our investigations during the year have shown that *Azotobacter* is able to produce ammonia from a large number of nitrogenous compounds, including proteins, amino acids, nucleic acids, and simple and substituted amides, and also from its own cell nitrogen and that the ammonification takes place under aerobic and anaerobic conditions though to a smaller extent in the latter case. Various intracellular enzymes have been identified, including urease, arginase, adenase, and guanase, and a number of the intermediate compounds formed in ammonification have been determined in certain important cases. The influence of various factors such as added carbohydrate, toluene, cyanide, hydrogen-ion concentration, and gas phase have been studied. As a result of these studies it may be concluded that the ammonia production reported by previous investigators was derived from cell nitrogen and not by direct synthesis from nitrogen gas as they had supposed.

The influence of high temperatures upon the growth of *Azotobacter* in free nitrogen and on various fixed-nitrogen compounds was also studied and the growth velocities at both suboptimal and optimal temperatures found to occur in the increasing order: nitrite, nitrate, free nitrogen, ammonia, urea, and glutamate. At temperatures above optimum, the relations are somewhat altered. In general the cultures in free nitrogen behave, over the entire temperature range, more nearly like those using reduced nitrogen compounds such as urea and ammonia than like those supplied with oxidized compounds like nitrite or nitrate. These results indicate strongly that nitrogen fixation is a reduction and not an oxidation process. Other data obtained, dealing with the catalytic effect of molybdenum on the fixation process, indicate that an amide compound may occur as an intermediate in nitrogen fixation.

During the year work was started on a study of cell oxidation as it occurs in legume nodule bacteria as a continuation of the research which recently resulted in the discovery of an accessory substance essential for the respiration and growth of certain species of these organisms. Preparations of the growth substance, considerably more concentrated than those obtained previously from sugar and molasses, have been obtained by taking advantage of the fact that it is synthesized by *Azotobacter*. Fractional electrolysis experiments showed that the growth factor has many properties in common with pantothenic acid, a constituent of the "bios" complex, but is not identical with it.

The Bureau's studies dealing with leguminous plants serve to emphasize the importance of carbohydrate supply in nodulation and nitrogen fixation and in the maintenance of a healthy condition. The harmful effects of high concentrations of fixed nitrogen on nodule development can be overcome partially by increasing the rate of photosynthesis. Contrary to the view of many research workers, it is now fairly certain that the bulk of the energy supply is not consumed in the chemical process of nitrogen fixation but is utilized chiefly for the respiration and growth of the bacteria and host. Results that were obtained in work on the effect of older plants on the production of nodules on young seedlings indicate that the favorable effect of such older plants is of negligible benefit to the farmer.

Considerable work was done during the year in an effort to determine the life cycle of a nitrogen-fixing blue-green alga that has been isolated from the soil. It has been shown to be probably a species of *Nostoc* although having many characteristics in common with *Anabaena*. Studies of the various stages of its growth indicate that much of the soluble nitrogen which it often liberates into the medium represents portions of the original cells liberated in the normal growth of the organism. This liberation of available nitrogen is undoubtedly a factor of considerable economic importance in nature.

In a study of the behavior of active nitrogen with organic compounds a comprehensive investigation was made of its reaction with diphenylacetylene. Excellent yields of a nitrogenated organic material, having the approximate empirical formula  $(C_{24}H_{17}N_3)_x$ , were obtained when optimum conditions were



approached. The general mechanism of the reaction has been determined and it has been shown that the fixation is produced by excited molecular nitrogen. This work of the Bureau clearly demonstrates for the first time that such nitrogen will react with organic substances, and it is the first case in which nitrogen has been fixed directly by an organic compound apart from living processes. Although this reaction has little practical significance it is of importance theoretically since it serves as a foundation for anticipating the introduction of nitrogen of a much lower energy content into organic compounds.

When *Azotobacter vinelandii* was grown in a medium containing urea as a source of nitrogen, progressive morphological changes occurred, and the sucrose, which was used as a source of energy, was extensively hydrolyzed, a strikingly different behavior than that exhibited by the bacteria when grown in media in which atmospheric nitrogen was the only source of nitrogen. A sugar-hydrolyzing enzyme isolated from the bacteria under both conditions was found to be quite similar, hydrolyzing not only sucrose but also maltose, raffinose, and alpha-methylglucoside, but not melizitose. Optimum hydrolyzing power was exhibited at a lower hydrogen-ion concentration than for yeast invertase (pH about 6.8 compared with 4.7). When the *Azotobacter* was grown on fructose instead of sucrose, none of the enzyme was manufactured by the bacteria.

#### POTASH

The termination last year of the potash-phosphate blast-furnace project of the Bureau, left behind collateral projects of fundamental importance such as the most feasible utilization, chemically and economically, of the products potassium chloride and phosphoric acid. Their combination to produce potassium metaphosphate with byproduct hydrochloric acid appeared to be of first importance.

A study of processes for the production of potassium metaphosphate, a compound of 100-percent plant-food content, from potassium chloride and phosphoric acid showed that a two-stage procedure, the first conducted at 200° C. with the introduction of steam and the second at 540° without the use of steam, gives a product which when ammoniated can be used directly as a concentrated fertilizer.

Recent developments in the cement industry, based on earlier investigations of the Bureau, have made possible the large-scale production of byproduct potash as fume from cement kilns. This is separated from the dust by means of multiclones, then humidified, and finally subjected to electrical precipitation. The Bureau's work has shown that the product may be subjected to various treatments such as simple extraction with water, neutralization with oxides of nitrogen or extraction with ammonia and carbon dioxide in aqueous solution to yield higher grade fertilizer materials.

Since hydrochloric acid is a byproduct of many processes for the conversion of potassium chloride into other potash salts, such as potassium nitrate, sulphate, and metaphosphate, studies have been conducted of methods for its utilization. When used for the treatment of phosphate rock, it was found that the major portion thereof can be recovered for re-use and that a hitherto unknown salt, calcium phosphate-chloride can be formed. The properties of this new compound indicate that it is a suitable fertilizer material in itself. It may also be used for the preparation of dicalcium phosphate and calcium pyrophosphate.

In a continuation of the study of the extraction of potash from silicates by hydrochloric acid an improved procedure was designed wherein the dissolved salts obtained are precipitated with gaseous hydrochloric acid instead of by vaporization, the precipitated salts being then selectively hydrolyzed for the separation of the potash and alumina as high-grade products. The past year has seen the completion of the work on the solubility of alunite in various commercial solvents. The data obtained indicate the possibility of the use of either potassium or sodium hydroxide to extract both the potash and the alumina from previously roasted alunite.

The drastic reduction in the prices of fertilizer-potash salts that has occurred within the year has altered the economic prospects of chemical processes developed or under development for the extraction of potash from the potassium aluminum silicates long regarded as potential sources of potash. In consequence, future research aiming at the utilization of the potash silicates



must necessarily be restricted to processes yielding the potash either as a by-product or as a constituent of fertilizer materials that also contain one or both of the other fertilizer essentials, nitrogen and phosphoric acid.

### PHOSPHATES

Further work on the process for preparing phosphate fertilizer by calcining silica-bearing phosphate rock at 1,400° C. in the presence of water vapor has shown that Tennessee brown-rock phosphate is somewhat better adapted to the manufacture of calcined phosphate than are the other types of domestic phosphate rock; that for the best results the silica should be present in a comparatively fine state of division and should be thoroughly dispersed throughout the phosphate particles; and that phosphate rock that has been concentrated by flotation methods can be used directly (without further crushing or grinding) in the manufacture of calcined phosphate. Vegetative pot tests, in cooperation with the Bureau of Plant Industry and the Alabama, Arkansas, and West Virginia Agricultural Experiment Stations showed that properly prepared calcined phosphate is as good (frequently better) a source of phosphorus for plant growth as is either superphosphate or dicalcium phosphate. The reactions involved in the preparation of calcined phosphate constitute an entirely new field of phosphate chemistry which it is believed will have far-reaching effect on the future phosphate fertilizer industry and practice in this country. The process has attracted wide-spread interest in the fertilizer and phosphate-rock industries.

During the year considerable work has been done on the composition, chemistry, and properties of ordinary superphosphate and double or triple superphosphate. In this connection, studies were made of (1) the nature and interrelationships of the free acids in fresh and in cured superphosphates, (2) the solubilities of the superphosphate components in water and in neutral ammonium-citrate solution, with special reference to the changes occurring during the aging of superphosphate, and (3) the occurrence and identification in superphosphate of dicalcium phosphate, hydrated and anhydrous monocalcium phosphate, and the different hydrates of calcium sulphate. The information obtained in these studies is of primary importance in the preparation of superphosphates and complete fertilizer mixtures having good mechanical condition and satisfactory storing and drilling qualities. The crop-producing efficiency of a given fertilizer depends to a considerable extent on the mechanical condition and the uniformity with which the fertilizer can be distributed in the field.

Waste sulphuric acid from the refining of petroleum is available in considerable quantity in certain sections of the country, and under certain conditions it can be used economically in the manufacture of superphosphate. With these facts in view an investigation has been started to determine whether superphosphate prepared with waste sulphuric acid from the refining of petroleum, contains substances harmful to plants and to the nitrifying organisms of the soil.

Studies have been made on the preparation of tetracalcium phosphate and on the behavior of tricalcium phosphate and hydroxyapatite at high temperatures in the presence and absence of silica and in both dry and moist furnace atmospheres. All these compounds are involved in the reactions occurring in the preparation of phosphate fertilizers by heating silica-bearing phosphate rock in the presence of water vapor.

Important findings by the Bureau in regard to the toxic effects of selenium in certain soils have led to a study of the selenium content of domestic phosphate rock. This study showed that the largest quantities of selenium (up to 55 parts per million) occur in phosphate rock from certain deposits in the West. The Florida and Tennessee phosphates were found to contain little or no selenium.

A comprehensive report, which will give a detailed account of the recently concluded experimental work of the Bureau on blast-furnace smelting methods as applied to phosphate and potash rocks, is now in course of preparation.

### MIXED FERTILIZER TECHNOLOGY

A study of the effects of particle size on the drillability and efficiency of fertilizers has been completed. The results indicate that finer than 80-mesh particles of superphosphate are more efficient for growing cotton in the soils



used than are coarser particles. On the contrary, large particles of readily soluble nitrogenous materials are better than fine powders of the same materials. Grained mixed fertilizers were most efficient when of 80- to 150-mesh particle size. Drillability tests showed that caking takes place more readily in fertilizers consisting of fine-sized particles and that segregation in mixed fertilizers is due largely to differences in particle size of the different components. A segregating mixture can often be rendered nonsegregating by regrinding the entire mixture a little finer. Nitrogen, potash, and total soluble salts were found to be removed by natural agencies from the placement area in the soil, and thus out of reach of the roots of the plants, in greater proportion as the size of the particles diminished, the nitrogen disappearing relatively much more rapidly. Decrease in size of superphosphate particles was accompanied by greater reversion of phosphoric acid to insoluble forms.

An investigation of the effect of urea and other admixed salts on the hygroscopicity of calcined phosphate disclosed that the mixtures were in every case less hygroscopic than corresponding mixtures containing ordinary superphosphate. Such fertilizer mixtures will, therefore, be less likely to absorb moisture and become damp and to lump and cake than the corresponding mixtures containing ordinary superphosphates.

The effect of the increased temperatures produced when superphosphate mixtures are ammoniated with urea-ammonia solution on the decomposition of the urea has been studied further. In the course of the investigation the hydrolysis products of pure urea, urea phosphate, and mixtures of urea with the various components of ordinary and double superphosphates were determined, and it was found that in many cases the urea was destroyed with a loss of ammonia while the orthophosphates present were reduced to pyrophosphates or metaphosphates.

In a study of the reactions of diammonium phosphate with limestone and with dolomite, it was found that all proportions of the materials in mixtures of this kind cause loss of ammonia. Neither limestone nor dolomite should be added to an ammoniated double superphosphate in sufficient quantity to give a physiologically neutral mixture when the ammonia in the ammoniated phosphate exceeds 10 percent. Charts have been drawn from the experimental data that show the maximum quantities of limestone that may be included in various mixtures of ammonium sulphate and ammoniated double superphosphates without causing loss of plant-food value. A study of the use of calcined phosphate in fertilizer mixtures showed that it causes loss of ammonia from ammonium sulphate. This loss of ammonia may be prevented by adding to the mixture one part of superphosphate per part of calcined phosphate present.

As a result of the frequent claims made by fertilizer chemists that the official method gives low results for water-soluble potash in mixed fertilizers, an investigation was undertaken of the cause of these low results and of the extent to which a loss of potash takes place. It was shown that the low results are limited to mixtures containing superphosphate and that they are due to occlusion or adsorption of a small portion of the potash in the basic iron and aluminum phosphates formed in the extraction of the sample. The loss varies with the iron and aluminum content of the phosphatic materials used in the manufacture of the superphosphate and is greater in mixtures of superphosphate with potassium sulphate than in the corresponding mixtures with potassium chloride. The loss increases within limits with the age of the mixture, and it is greater when the potash salt is mixed with a cured superphosphate than when mixed with a fresh superphosphate. It was also found that the loss in the average mixed fertilizer amounts to about 1.5 percent of the total potash present.

The collaborative study of methods for the determination of free acids in superphosphates, mentioned in last years' report, disclosed (1) that the free acid in a sample of monocalcium phosphate may or may not be increased by the addition of moisture, depending on the proportion of free acid to monocalcium phosphate initially present; (2) that the variations in results with the different methods in the analysis of samples having a low ratio of free acid to moisture are greater than in the analysis of samples in which this relationship is reversed; (3) that more concordant results are obtained with the acetone method than with any other method, and that this method gives the closest agreement with the theoretical values; (4) that when the water-extraction method is used to determine free acid in a monocalcium phosphate sample containing dicalcium phosphate as well as free phosphoric acid, the results obtained will be correct,



too high, or too low, depending on whether the solid dicalcium phosphate is unchanged, increased, or decreased in the process of extraction; and (5) that an extraction method cannot be used as a measure of the physiological acidity arising from the free acid in a superphosphate.

The results of the work done on the use of filler in fertilizer mixtures and showing the changes in composition and physiological acidity of fertilizers from 1880 to 1932, also mentioned in last year's report, elicited wide-spread interest. The National Fertilizer Association offered to cooperate in making a further study of statistics for the fiscal year ended June 30, 1934. This offer was accepted, and a large amount of information is being collected on the number of grades and kinds of fertilizer consumed in each State. When finished this work will show what progress has been made since 1932 in eliminating filler from mixed fertilizers and how many unnecessary grades of fertilizer are being manufactured. Neither filler nor large numbers of similar grades add anything of value to our economic scheme but increase the cost of fertilizer to the consumer.

The economy in the use of higher analysis fertilizers and the elimination of filler has been worked out from the price schedules submitted by fertilizer manufacturers to the code authority. This work shows that the use of double-strength mixtures at the prices actually being quoted will save the farmer about 20 percent of his fertilizer bill. Cutting the wholesale prices of nitrogen, phosphoric acid, and potash in half would not save as much money for the farmer as would result from simply leaving out the sand and other useless filler now being used in certain sections of the country in the preparation of mixed fertilizers.

### INFORMATIONAL AND EDITORIAL SERVICE

The 54 new departmental publications from this Bureau printed in the past fiscal year include 26 soil-survey reports, 7 technical bulletins, 3 circulars, 3 miscellaneous publications, 5 articles in the *Journal of Agricultural Research*, and 10 articles in the 1935 *Yearbook of Agriculture*.

Final editing of the page proofs of *Soils of the United States*, part 3 of the Department's *Atlas of American Agriculture*, prepared by Curtis F. Marbut, Chief of the Division of Soil Survey, was completed during the fiscal year, and advance copies came off the press in July 1935. The map and description of the soils of this country contained in this publication furnish the first complete inventory of the basic agricultural resources of an entire nation ever printed. Over 6,000 soil types which have been recognized and mapped in all parts of the United States by the Division of Soil Survey have been combined in this atlas into the 250 important groups of soils which form the first detailed map of a great continental area. The publication contains more than a hundred chemical and mechanical analyses of important soil types which are of great value in determining the agricultural values and potentialities of typical soils in the basic regional areas of agriculture. The description of the genesis and the classification and mapping of such great regional soil groups as the Podzols, Chernozems, Prairie soils, Red and Yellow soils, and the Gray-Brown Podzolics, contained in this volume, are of special interest to soil scientists and have great practical value for regional planning of agriculture.

In addition to the official publications listed below, more than 140 articles on various phases of the Bureau's work have been published in journals and periodicals during the past fiscal year. These articles have, for the most part, supplied technical information of value to scientists and, in other cases, have interpreted to farmers and the general public important phases of the Bureau's work. In cooperation with the Press Service of the Department, the Bureau has furnished newspapers with timely information on practical problems of agriculture and utilization of farm products.



**PUBLICATIONS OF THE BUREAU OF CHEMISTRY AND SOILS ISSUED  
DURING THE YEAR JULY 1, 1934, TO JUNE 30, 1935**

**TECHNICAL BULLETINS**

- No. 426. Relation of Fertilizers to the Control of Cotton Root Rot in Texas.  
 No. 430. Further Studies of the Physical and Chemical Characteristics of the Soils from the Erosion Experiment Stations—Second Report.  
 No. 449. Storage of Mill Cane. (Joint publication with the Bureau of Plant Industry.)  
 No. 452. Experiments with Nitrogen Fertilizers on Cotton Soils.  
 No. 461. Base Exchange and Related Properties of the Colloids of Soils from the Erosion Experiment Stations.  
 No. 469. A Method of Rural Land Classification.  
 No. 471. Chemical Studies of Infertile Soils Derived from Rocks High in Magnesium and Generally High in Chromium and Nickel.

**CIRCULARS**

- No. 319. Fertilizer Studies with Sugar Beets in the Arkansas Valley Area, Colo. 1921-28. (Joint publication with the Bureau of Plant Industry.)  
 No. 320. Report on a Preliminary Field Survey of the So-called "Alkali Disease" of Livestock. (Joint publication with the Bureau of Plant Industry.)  
 No. 329. Manufacture, Composition, and Utilization of Dairy Byproducts for Feed.

**MISCELLANEOUS PUBLICATIONS**

- No. 192. A Review of the Patents and Literature on the Manufacture of Potassium Nitrate with Notes on Its Occurrence and Uses.  
 No. 206. The Naval Stores Station of the Bureau of Chemistry and Soils.  
 No. 221. Soil Blowing and Dust Storms.

**JOURNAL OF AGRICULTURAL  
RESEARCH ARTICLES**

- The Occurrence of Ferrous Iron in Phosphate Rock.  
 The Cystine, Tryptophane and Tyrosine Content of the Soybean.  
 Oil Retention, Oil-Emulsifier Ratio and Oil-Water Ratio as Affecting the Insecticidal Efficiency of Emulsions. (Joint publication with the Bureau of Entomology and Plant Quarantine.)

Nitrogen Fixation Studies with Fungi and Actinomyces.  
 The Thermophilic Fermentation of Beet Pulp.

**SOIL SURVEYS**

- Hennepin County, Minn.  
 Reconnaissance of the Trans-Pecos Area, Tex.  
 Vermillion County, Ind.  
 Poweshiek County, Iowa.  
 Collin County, Tex.  
 Houston County, Minn.  
 Tioga County, Pa.  
 Potter County, Tex.  
 Benewah County, Idaho.  
 Tillman County, Olla.  
 Sherman County, Nebr.  
 Jefferson County, Ga.  
 Mercer County, Ky.  
 St. Clair County, Mich.  
 Frio County, Tex.  
 Furnas County, Nebr.  
 Reconnaissance of the Columbia Basin Area, Wash.  
 Galveston County, Tex.  
 Alger County, Mich.  
 Rockbridge County, Va.  
 Wyoming County, Pa.  
 Washtenaw County, Mich.  
 Bay County, Mich.  
 Columbia County, Oreg.  
 Knox County, Nebr.  
 Dixon Area, Calif.

**YEARBOOK ARTICLES**

- Citrus Byproduct Uses May Greatly Influence Fresh-Fruit Market.  
 Composts Are Good Means of Improving Soil of Small Farms.  
 Fruit Darkening Can Be Prevented by New Process.  
 Nitrogen Balance Sheet Shows Annual Deficit Requiring Replacement.  
 Phosphate Blast Furnace Is Nucleus for Balanced Fertilizer Trade in West.  
 Phosphate Fertilizer Prepared by Treating Phosphate Rock with Steam at High Temperatures.  
 Sirup Buying from Farms by Relief Agency Shows Need for Better Quality.  
 Soil Erosion Studies Develop Information of High Practical Value.  
 Soil Survey Provides Data for Classifying Land; Planning Uses.  
 Starch Making from Cull Sweetpotatoes Is Placed on Commercial Basis.







