

**SUGAR AND
SUGAR BY-PRODUCTS**
in the
PLASTICS INDUSTRY

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Foreword

This revised edition of our original Scientific Report No. 1 is being issued in the subsequently initiated Technological Report Series, in which it properly belongs, as Technological Report No. 5. Previous issues in both series are tabulated on the inside back cover.

Dr. Long has brought this report up to date by including further uses of sugar and sugar derivatives in the plastics industry, which have appeared in the chemical literature since the original survey was issued nearly five years ago. It is hoped that it will continue to serve as a stimulus in suggesting and making easier the development of new uses and new ideas for the utilization of sugar, the only pure organic chemical which has a tonnage production in the United States in excess of 14,000,000,000 lbs. annually.

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SUGAR RESEARCH FOUNDATION, INC.

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SUMMARY

The interest of manufacturers in the use of sugar or its by-products as raw materials for plastic substances was evidenced as early as 1929, and many attempts have since been made to utilize this abundant natural product. The advantages of sucrose as a plastic raw material are due to its almost unlimited supply as an inexpensive, very pure organic compound. Chemically, it has a number of reactive centers, enabling it to polymerize readily or react with other substances to form compounds which can be polymerized. To date, however, results have been of only theoretical interest because of the sensitivity of the molecule to heat and chemical treatment, causing it to discolor readily, and because of the difficulty of controlling the polymerization to produce desirable physical properties in the finished product. On the other hand, a certain degree of success has recently been attained in the formation of a plastic molding compound from bagasse, a waste product from sugar factories, and commercial production has begun on a small scale in Louisiana.

The attraction of the plastics industry as an outlet for excess sugar production and by-product utilization is obvious from a glance at its phenomenal rate of growth and at the large quantities of raw materials used in its manufacturing processes. During the sixteen years from 1931 to 1947, the annual total production⁽¹⁾ of all types of plastics in the United States rose from 35,000,000 pounds to 851,379,583 pounds⁽²⁾, an increase of 2400 per cent.

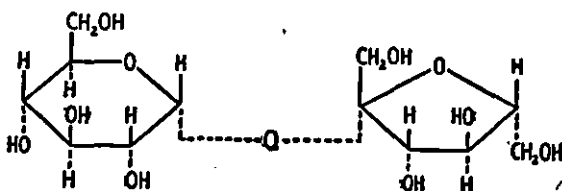
Sucrose, and its hydrolysis products glucose and fructose, are potential raw materials for the formation of both colored and colorless plastics of either the phenolic or the alkyd type, the two resins produced in the largest quantity in this country. Sorbitol and mannitol, reduction products of glucose and fructose, should find application

as polyhydric alcohols for alkyd resins. Bagasse molding powders are useful in the thermosetting phenolic plastic field.

The potential consumption of sugar or molasses for the production of lactic and citric acids to be used in the manufacture of plastic materials is already clearly outlined, and their actual consumption should increase rapidly in the near future. The application of the other acids under consideration—aconitic, levulinic, citraconic, and itaconic—in the plastic field is not yet as well defined. The cheapest of these, levulinic acid, is available on a small scale in commercial quantities at a price which is low enough to make it an attractive plastic raw material, but it is evident that further research is needed to determine its most effective use. The recently announced improvement in the method of preparation of itaconic acid should give a strong stimulus to investigations leading to its application as a plastic ingredient. The demand for esters of aconitic acid for use as plasticizers is established, and, if additional experimentation can make it more readily available, its utilization in the plastic field may become an important source of profit to the sugar industry. On the other hand, it is not expected that citraconic acid will find an extended usage as a plastic material, due to the fact that itaconic acid can replace it in almost every instance. From the foregoing, it is evident that, in the not too distant future, this group of hitherto less common organic acids may form a substantial market for a large volume of sugar and some of its by-products.

In view of the potential importance of plastics to the sugar industry, a survey of the patent and periodical literature has been made covering the applications of sugar and sugar by-products in the plastics industry reported to date.

SUGAR



Several moderately successful attempts have been noted in the literature to form a commercially useful plastic material from pure sugar. In 1929, a patent⁽³⁾ was issued in Germany covering the preparation of hard, insoluble, and infusible products by heating sugar with a persulfate, such as ammonium persulfate. It was stated that the physical properties of the products could be modified by including in the reaction mixture small quantities of oils, natural or synthetic resins, or inert salt solutions, and that fillers might also be added. It was claimed that the products could be used for making molded articles. This appears to be the first mention of the use of sugar for plastic formation.

Sugar was mentioned as a condensing and dehydrating agent⁽⁴⁾ in the preparation of plastic materials from formaldehyde and urea in the presence of ammonia in a French patent, granted to the inventors in 1930. In another French patent⁽⁵⁾, granted in 1931, it was claimed that condensation products which are soluble in organic solvents and (or) water were prepared by condensing, in the presence of acid catalysts, polyhydric alcohols containing at least six carbon atoms with cyclic ketones. Sugar was referred to as one of the polyhydric alcohols.

"Sakaloid," a new sugar plastic, was announced in the United States in 1931, and the inventor obtained three patents⁽⁶⁻⁸⁾ to cover its manufacture. In the first, it was stated that a plastic substance could be made by reacting together a disaccharide, an aldehyde, and urea. Phthalic anhydride was substituted for urea in the second, and an aliphatic carboxylic acid in the third. The inventor described his product in a current trade journal⁽⁹⁾ in terms, which are here reproduced as an example of what an ideal sugar plastic should be. It was said to be of an absolute water white clarity. He stated that a block of "Sakaloid," ten or more inches thick, could be placed over the smallest type, and that the latter could be read through the mass as well as if uncovered. The polymerization could be inter-

rupted to produce a product called "Rubba-glas," which was claimed to have all of the properties implied in its name. In the next stage, the hardened form, a brilliantly clear quartz-like product was said to be produced. It was reported to have a refractive index approaching quartz, a transparency to ultra-violet and infra-red rays, and in addition, it could be drawn, machined, or drilled. A molding powder made from this material could be pressure molded with heat in an irreversible manner. "Sak-a-tex" was the name given to the material when applied to paper or textiles; "Sak-a-lac," when used for varnishes and lacquers; and "Sak-a-tine" when extruded into filaments for spinning and weaving. A photograph of the new sugar plastics was displayed in which were included elastic, rubbery masses, completely hardened forms, some tinted and others water white, some molded from powder and some cast. However, no further mention of the manufacture of "Sakaloid" could be found in the literature, and it is believed to have met with little success.

In a patent⁽¹⁰⁾ issued during the following year, another inventor claimed to have prepared resins to serve as substitutes for shellac by heating together cane sugar, water, and crystalline phenol in the presence of a small amount of hydrochloric acid. In this case, the final product was a dark-colored hard resin.

Also in 1932⁽¹¹⁾, a patent disclosure was made describing the formation of a resin by the reaction of a carbohydrate such as sugar with a non-substituted ether-forming oxide, such as ethylene or propylene oxide, in the presence of aqueous alkali.

An interesting report of a plastic with the trade name of "Sucro-lite" was published in a British journal⁽¹²⁾ in 1935. It is described as a cheaper form of Bakelite in which sucrose has been substituted for formaldehyde, the most expensive of the raw materials involved in the Bakelite phenol-formaldehyde condensation process. An "A" resin is first produced by heating a mixture of phenol, sulfuric acid, and sucrose under suitable conditions. It is described as a black, brittle, shiny, lustrous, but not porous material. To increase its strength for molding purposes, the "A" resin is mixed with a filler, such as wood pulp, and a hardening agent. The composition of the finished product is about 25 per cent sucrose, 50 per cent filler, and 25 per cent phenol. Among the possible applications of the plastic are mentioned usage in the varnish and lacquer industry, as a material for table tops, in the radio and electrical industries, and as floor and wall tiles in the building industry.

A plastic made from sucrose and aniline in a similar manner and

with like properties is also described. However, due to the use of aniline, the manufacturing cost is higher.

A third plastic is mentioned, made from sucrose, formaldehyde, and urea. This plastic is said to have the same properties as glass, and to be convertible into any color. To obtain a satisfactory finished product, however, great care is required in its manufacture.

In a review of the progress made in this field, published in England in 1943⁽¹³⁾, it is stated that thus far these sugar plastics have been manufactured only on a laboratory or semi-industrial scale.

In 1937, a British patent⁽¹⁴⁾ granted to the German I. G. Farbenindustrie described the reaction of acetylene with carbohydrates at an elevated temperature, in the presence of a strongly alkaline acting substance as a catalyst. Carbohydrate derivatives which still contain at least one reactive hydroxyl group and are stable in the presence of basic substances above 100°C. may also be used. As examples of such substances are mentioned tetramethyl glucose or preferably carbohydrate derivatives that are acetalized to a considerable extent, such as β -diacetone fructose, mono-acetone glucose, or the mixture of these formed by treating sucrose with acetone and sulfuric acid. The products may be used as softening agents for lacquers and plastic masses, or may be polymerized. The polymerization products may be used, alone or mixed with other substances, for the preparation of lacquers, films, or foils.

A patent⁽¹⁵⁾ for the polymerization of a sugar, such as glucose or sucrose, was issued in 1937. The polymerization was effected by heating the sugar at about its boiling point in the presence of an aqueous solution of an inorganic acid, such as 20 per cent hydrochloric acid. The resin so formed is soluble in acetone, and is compatible with cellulose acetate and nitrate.

Insoluble resins suitable for use in the treatment of water by anion exchange are prepared by condensing *m*-phenylene diamine with a mono- or disaccharide in the presence or absence of a non-sugar aldehyde. The diamine is used as its salt. As an example, the hydrochloride of *m*-phenylene diamine is condensed with sucrose, and then with formaldehyde. This disclosure was made in a British patent⁽¹⁶⁾ issued in 1937.

An Italian chemist in 1943 reported a reaction between sucrose and aldehydes leading to the formation of a plastic material⁽¹⁷⁾. By condensation of sucrose with formaldehyde at 80°C.-120°C., there

is formed a solid polymerized compound which is transparent, slightly yellow, and insoluble in water and organic solvents. It was postulated that, in the intermediate reactions, hemiacetals are formed, which are transformed into acetals with two methylene bridges between two molecules of hexose.

Another interesting series of patents⁽¹⁸⁻²⁵⁾ describes the production of a polysaccharide from sucrose, called dextran⁽²⁶⁾, by a microbiological process. Dextran is said to form plastic amorphous masses when caused to react with an alkyl or aralkyl halide and sodium hydroxide. These plastics are either water-soluble, or insoluble, depending upon the reaction conditions, and the particular halide involved.

A plastic resin, useful as a resistant, protective, and decorative coating, has been prepared at the Eastern Regional Research Laboratory of the United States Department of Agriculture by treating sucrose with allyl bromide, or allyl chloride, and then polymerizing the allyl sucrose monomer^(27, 28). It also has potential uses as an adhesive, and as an impregnant for wood, paper, and similar materials. This coating appears to have some very desirable properties. It is shatterproof on impact, insoluble in almost all solvents, and has a smooth, shiny appearance superior to most varnishes. It should be relatively simple to produce commercially, and, if made industrially, should become available at a moderate cost. This work is still at the stage of laboratory experimentation, but seems to offer possibilities for industrial consumption of sugar on a large scale.

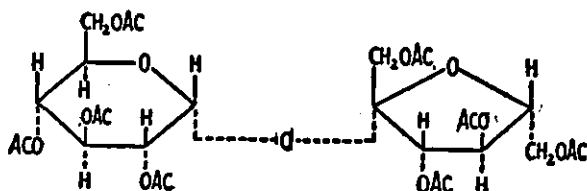
Following their study of the properties of various allyl ethers of sucrose and related polyhydric alcohols, the chemists at the Eastern Regional Research Laboratory have investigated the corresponding methallyl ethers⁽²⁹⁾. The latter were found to require more oxygen to reach the gelation point and to gel more slowly than the allyl ethers, but otherwise had similar properties. The β -chlorallyl ether of sucrose has also been prepared⁽²⁸⁾. Both the β -methallyl and the β -chlorallyl ethers behave essentially in the same manner as allyl sucrose, but apparently have no advantage over it.

In addition to its application as a raw material for the formation of plastics, sucrose has been used as a modifier in some plastics to reduce brittleness and to increase transparency⁽³⁰⁾.

A British patent⁽³¹⁾ issued in 1947 described certain improvements in the polymerization of mono- and disaccharides. The polymerization is carried out by heating the sugar in the molten state

in the presence of a suitable catalyst. The sugar and catalyst are in an anhydrous condition, since water tends to produce depolymerization of the polymers as they are formed. One per cent by weight of magnesium sulfate was used as a catalyst, and the mixture was heated at 150°C. for five hours.

SUCROSE OCTAACETATE

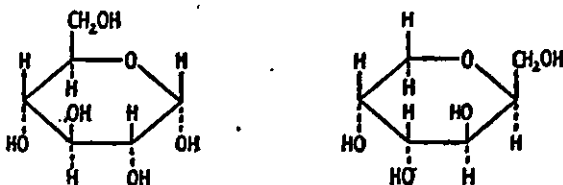


Although the esters of sucrose are not used to form plastics, they are of some importance in the plastics industry as plasticizers and solvents. Up to 1932, sucrose octaacetate had been used as a gum constituent of lacquers, a plasticizer in anhydrous adhesives, and in the treatment of paper⁽³²⁾. In 1933, G. J. Cox of the Mellon Institute for Industrial Research described⁽³³⁾ the semi-plant preparation of the octaacetate, octapropionate, and octabutyrate esters of sucrose. These compounds were made using acetic anhydride and sodium acetate. The work was done under a Multiple Fellowship of the Sugar Institute, Inc.

Another method^(34, 35) for the preparation of the octaacetate of sucrose is that utilizing pyridine instead of sodium acetate in conjunction with acetic anhydride. It is claimed that better yields are so obtained.

In 1943, British Celanese, Ltd. patented⁽³⁶⁾ a process to prepare sucrose octaacetate in a yield of 80 per cent of the theoretical, and, in 1945, an additional patent⁽³⁷⁾ was taken out in Canada covering a similar process.

GLUCOSE and FRUCTOSE



Several references to the use of glucose and fructose in the for-

mation of plastic materials have already been made under the discussion of sucrose plastics. Fructose and glucose were included as compounds useful for the preparation of water-insoluble resins⁽¹⁶⁾ suitable for use in the treatment of water by anion exchange. β -diacetone fructose and tetramethyl glucose were mentioned as two of the compounds available for reaction with acetylene⁽¹⁴⁾, to be followed by polymerization of the vinyl ether so formed.

In 1929, glucose was referred to in several patents as a condensing agent in the preparation of plastic materials from urea and formaldehyde. In one patent⁽³⁸⁾, it was used in the presence of a metallic oxide, preferably zinc oxide, whereas in another⁽³⁹⁾, ammonia, or an ammonium salt was used in conjunction with it.

A number of additional processes for the polymerization of glucose have been recorded. J. V. Meigs made numerous patent disclosures concerning synthetic resins from glucose during the period from 1931 to 1933 inclusive. The various methods included the use of mixtures with glucose of aniline and phenol⁽⁴⁰⁾; aniline and hydrochloric acid⁽⁴¹⁾; phenol, furfural and hexamethylenetetramine⁽⁴²⁾; phenol, china wood oil and hexamethylenetetramine⁽⁴³⁾; hexamethylenetetramine and calcium hydroxide⁽⁴⁴⁾; and glycerol and sulfuric acid⁽⁴⁵⁾. Also in 1933, a patent⁽⁴⁶⁾ was assigned to Weiss and Downs, Inc., covering the use of a hexose with the anhydride of a dicarboxylic organic acid at a temperature not exceeding 170°C.

The firm of Holzhydrolyse A-G in 1934 and 1935 patented a number of processes⁽⁴⁷⁻⁵⁰⁾ for polymerizing carbohydrates. Some of the methods included treating the solution of a monomeric aldohexose with a small amount of hydrochloric acid, evaporating to dryness, and then heating with a current of hot air. Another patent described treating finely powdered carbohydrates with a small excess of acetic anhydride in the presence of an acid condensing agent, and using the product as the starting material for a polymer.

In 1936, a patent⁽⁵¹⁾ described melting a monose with about one-hundredth of its weight of sulfuric acid, and heating to remove water at 120-180°C.

The Celanese Corporation⁽¹⁵⁾, in 1937, found that the resinous product formed by the polymerization of glucose in the presence of an aqueous mineral acid is compatible with cellulose acetate.

An animal or vegetable glue, water, and the reaction product of

glucose and an alkaline earth bisulfite was patented⁽⁵²⁾ in 1943 for use as an adhesive in laminating papers.

Glucose is among the substances described to form useful products when esterified with *α*-chloroacrylic acid and polymerized, in a patent⁽⁵³⁾ assigned to the Pittsburgh Plate Glass Company in 1944. The esters may be polymerized to form either insoluble infusible, insoluble fusible, or soluble fusible plastics. Numerous uses of the products include the preparation of lacquers and molded materials, and the manufacture of safety glass.

An interesting article⁽⁵⁴⁾ has been published by chemists at the Eastern Regional Research Laboratory of the United States Department of Agriculture. The paper describes the preparation and polymerization of tetra-allyl-*α*-methyl glucoside: Under the influence of oxygen and heat, the allylated glucoside gradually polymerizes, first to a viscous liquid and finally to a colorless transparent resin. The gradual increase in viscosity, followed by a marked increase to the point of gelation, along with the insoluble and infusible nature of the final product, is characteristic of the formation of a three dimensional net work. The yield of tetra-allyl-*α*-methyl glucoside from *α*-methyl glucoside is only about 40 per cent, which appears to be too low for any immediate significance.

In a later communication⁽⁵⁵⁾, in June of 1945, the preparation and polymerization of glucose pentamethacrylate was similarly described. Methacrylic anhydride, which had only recently become available for research purposes, was used for the esterification. It was suggested that besides the addition polymerization, catalyzed by benzoyl peroxide or cobalt naphthenate, polymerization accompanied by oxidation took place.

The use of fructose as a component of a thermosetting resin has been disclosed in a British patent⁽⁵⁶⁾ granted in December, 1946. A nearly quantitative yield of diphenyl furyl methane was obtained when one mole of finely powdered fructose was added slowly with stirring to a solution of four moles of resorcinol in 25 per cent hydrochloride acid, after heating the mixture to 50°C. The resin was formed by condensating the diphenyl furyl methane with formaldehyde.

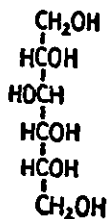
Glucose was revealed in a patent⁽⁵⁷⁾ taken out by the Monsanto Chemical Company in 1946, as an example of a polyhydric alcohol which could be used as a plasticizer for polyvinyl acetal resins when it is partially esterified with a saturated fatty acid containing at least

ten carbon atoms. Such plasticizers were stated to provide plasticized polyvinyl acetal resins with a high degree of retention of plasticizer over long periods of time and at elevated temperatures. Other advantages included the extremely high proportion of plasticizer that could be employed without making the resin unduly tacky or subject to exudation on standing, and the large amount of inexpensive filler, such as carbon black, which could be incorporated into the plastic while maintaining a high degree of durability. It was stated that these compositions may be formed into sheets or may be used for coating cloth, paper, wood, metal, or concrete.

The Corn Products Refining Company has taken out a series of patents in the last few years⁽⁵⁸⁻⁶¹⁾ describing the polymerization of glucose in the solid state by heating it in the presence of a catalyst, such as boric anhydride or boric acid. Traces of acidic compounds, such as sulfur dioxide or hydrochloric acid may serve as secondary catalysts. The products are light in color and have a high, but wide range of degree of polymerization. The glucose and catalysts are intimately mixed and heated to a temperature slightly below the melting point where the polymerization proceeds, causing the melting point to rise, and the reaction is then completed at a higher temperature. The total yield of polymeric material is between 70 and 80 per cent.

As oxidation products of glucose seemed to offer an opportunity of a better utilization of the glucose obtained from bagasse by hydrolysis, R. F. Garcia and I. A. Colon⁽⁶²⁾ attempted to form useful polymers of a mixture of 4- and 3, 6-glucosaccharolactones. The latter compounds were formed from the potassium salt of glucosaccharic acid by heating it in alcoholic hydrogen chloride. The glucosaccharic acid was prepared by the nitric acid oxidation of glucose. By reacting equal quantities of the lactone mixture and ethylenediamine, a decamer was obtained with a fundamental unit of one mole of glucosaccharic acid combined with one mole of ethylenediamine.

MANNITOL and SORBITOL



Haworth, Heath, and Wiggins⁽⁶³⁾ have described an attempt diamino-2, 3, 4, 5-dimethylene mannitol and adipic acid. They to prepare a Nylon type polymer from the condensation of 1, 6-obtained a hard mass which had a dark red-brown color. It could be drawn into fibers before cooling, but the fibers were brittle and therefore unsatisfactory.

Haworth and Wiggins also prepared⁽⁶⁴⁾ 2, 4, 3, 5-dimethylene mannitol from mannitol by first making the 1,6-dibenzoyl mannitol, methylenating it, and then removing the benzoyl groups. Although it was not possible to form polyester type polymers with dibasic acids of any value, this approach was considered worthy of further work⁽⁶⁵⁾.

Sorbitol is frequently used as the polyhydric alcohol component in alkyd and phenol-aldehyde resins. Application of the dilaurate, dioleate, and distearate esters of sorbitol as plasticizers has also been reported⁽³⁰⁾.

In 1925, the German I. G. patented⁽⁶⁶⁾ a synthetic resin made from sorbitol and a polybasic acid or its anhydride, using boric acid as a catalyst. In 1929, the same firm disclosed⁽⁶⁷⁾ the use of this compound for the esterification of monobasic acids containing at least ten carbon atoms, such as ricinoleic acid, china wood oil, etc. The products could be polymerized with sulfur, oxygen, or air.

In the same year, E. I. du Pont de Nemours and Company were granted a patent⁽⁶⁸⁾ describing a plastic composition containing a polymerized vinyl ester and, as a suppling agent, an ether of a polyhydric alcohol in which the ratio of the ether groups to the hydroxyl groups is at least two to one. One of the polyhydric alcohols mentioned was sorbitol.

The Atlas Powder Company reports in a patent⁽⁶⁹⁾ issued in 1938 that cast products can be formed of a urea-formaldehyde type synthetic resin containing sorbitol, which serves to facilitate the removal of gas bubbles and volatile substances.

The same company, also in 1938, published⁽⁷⁰⁾ the results of experiments with mannitol and sorbitol as raw materials for resins. It was reported that satisfactory ester gums and alkyds can be made from mannitol and sorbitol by carefully controlling the amounts and purity of the ingredients, heating schedules, agitation, and atmosphere. Ester gums thus prepared have properties intermediate between glycerol ester gums and modified phenolic types. When air-drying alkyds from sorbitol are tested in synthetic enamels

and baking enamels, they compare favorably with the corresponding glycerol resins and surpass the latter in resistance to cold check, salt spray, humidity, and hydrocarbons. The authors showed that these alcohols undergo internal etherification during polymerization, whereas glycerol does not, and they attribute to this fact the qualitative and quantitative differences between hexahydric and lower polyhydric alcohols in the formation of resinous esters.

A British patent⁽⁷¹⁾, in 1943, describes the formation of resinous ester products for enameling wire for insulating purposes by the reaction together of a cyclopentadiene adduct of maleic acid or anhydride with a polyhydric alcohol, such as sorbitol, and a monobasic fatty acid derived from a drying oil.

Sorbitol can be used to esterify *α*-chloroacrylic acid, and the esters can be polymerized to form useful plastics according to the patent⁽⁵³⁾ issued to the Pittsburgh Plate Glass Company in 1944, previously described.

Bruson⁽⁷²⁾ has patented a number of complex organic compounds in recent years, for use as plasticizers, in which sorbitol or mannitol is one of the components. As an example, a 1945 patent described the formation of 1, 2, 3, 4, 5, 6-hexakis (2-cyanoethoxy)hexane from sorbitol or mannitol and acrylonitrile, which, when refluxed with butyl alcohol, gave the compound $\text{ROCH}_2(\text{CH}(\text{OR}))_4\text{CH}_2\text{OR}$, where $\text{R} = -(\text{CH}_2)_2\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$. It is stated that such products are useful as plasticizers for synthetic resins, including cellulose nitrate or acetate, ethyl cellulose, polyvinyl chloride, polyvinyl acetals, phenolic formaldehyde resins, polyacrylates, and polymethacrylates.

By treating mannitol or sorbitol with allyl cyanide or crotononitrile in the presence of an aqueous alkaline condensing agent, 2-cyanoisopropyl ethers are prepared. During the condensation, the alkali transforms allyl cyanide to crotononitrile, which in turn adds the alcohol to its *α*, *β*-double bond, giving the same ether in either case. One or more *ω*-cyanoisopropyl groups may be introduced, depending upon the proportion of nitrile used. Bruson⁽⁷³⁾ states that these compounds, as sirups, are valuable as intermediates for the preparation of synthetic resins and plasticizers.

In another patent⁽⁷⁴⁾ taken out by the same inventor, a tri-dehydronordicyclopentadienyl ether of mannitol is described as an amber-colored resinous solid. It is formed by the reaction of dicyclopentadiene with mannitol in the presence of an acidic catalyst such as

boron trifluoride. This ether is polymerized when it is heated with 5 per cent of benzoyl peroxide at 100°C., or blown with air at 80-100°C. Both the polymers and the unpolymerized ethers are said to form varnish-like coatings.

The formation of allyl^(75,76) and β -methallyl⁽²⁸⁾ ethers of sorbitol and mannitol have been reported recently by Yanovsky and co-workers. These compounds are comparable to allyl sucrose, and can be polymerized to infusible insoluble resins by similar methods.

A patent was granted to J. B. Rust⁽⁷⁷⁾ in 1946, covering the preparation of resinous products by heating rosin esters, such as mannityl abietate, with unsaturated alcoholic esters of α -unsaturated α , β -dicarboxylic acids, such as diallylmalate, at 200-300°C.

Mannitol and sorbitol are included as polyhydric alcohols by M. O. Debacher⁽⁵⁷⁾ in the patent described previously covering partial esters of polyhydric alcohols and saturated fatty acids containing at least ten carbon atoms. These compounds are stated to be useful as plasticizers for polyvinyl acetal resins.

Anhydro derivatives of sorbitol and mannitol have been reported by a number of experimentors as suitable starting materials for plastic compositions. A patent⁽⁷⁸⁾ was issued in 1940, describing the condensation of dianhydro hexitols with monobasic acids, and non-hydroxylic dibasic acids to yield tasteless and colorless resins.

A number of articles⁽⁷⁹⁻⁸¹⁾ have been published recently concerning the formation and structure of 1, 4, 3, 6-dianhydro mannitol and sorbitol by Wiggins and collaborators. The acrylates and methacrylates of these compounds have also been made⁽⁸²⁾, and were found to polymerize rapidly, without the addition of a peroxide catalyst, to yield glass-like resins. The 2, 5-diacrylyl derivative of dianhydro sorbitol and the 2, 5-diacrylyl and 2, 5-dimethacrylyl derivatives of dianhydro mannitol are crystalline compounds which polymerize to hard, clear resins with heat alone, and which copolymerize with methyl methacrylate to yield clear resins which are harder than the polymer of methyl methacrylate mentioned above.

By treating anhydro-derivatives of sorbitol and mannitol with either the acid chlorides or the anhydrides of acrylic and methacrylic acids, Haworth and co-workers, in 1947, have patented⁽⁸³⁾ the preparation of esters which could be polymerized. In addition to the anhydro derivatives, the dimethylene, dibenzylidene, and monoacetone derivatives of these polyhydric alcohols were used.

An interesting plasticizer utilizing sorbitol has been patented recently covering an invention of the late R. M. Goepp, Jr.⁽⁸⁴⁾. It

describes sorbitol di- and tri-ketals of monochloroacetone as plasticizers for cellulose esters of a saturated straight chain fatty acid with from two to four carbon atoms. It is stated that this type of plasticizer is resistant to hydrolysis, has a low volatility, and acts as a flame-proofing agent.

MOLASSES

Polymerized molasses has found application as a road-surfacing material as well as for the formation of plastic articles. As early as 1908, experiments⁽⁸⁵⁾ were undertaken at Newton, Massachusetts, by the United States Department of Agriculture utilizing molasses as a road binder. The practical tests were tried after successful laboratory experiments had been completed. Some thirty years later, several papers⁽⁸⁶⁻⁸⁹⁾ were published by chemists in India describing the successful use of molasses, resinified by heat and acids, combined with coal tar and asphalt, to form an insoluble road material.

In the plastic field, a patent⁽⁹⁰⁾ was issued in 1934 for a process in which an acid liquor rich in organic acids and esters was extracted from molasses by the action of a mixture of sulfuric acid, alcohol, and an organic solvent such as ethyl acetate. The acid liquor is heated to about 100-120°C. in a concentrated solution to obtain a hard, non-inflammable, heat-resistant, insoluble, infusible resinoidal product which is suitable for use in making molded articles.

BAGASSE

Millions of tons of bagasse and other agricultural residues are available in the United States annually. To make the utilization of these agricultural residues attractive as raw material sources to industry, it is necessary to provide their continuous adequate supply to the manufacturing plant at a relatively low cost. The mechanical and economic problems of harvesting, collection, transportation, storage, and preservation will have to be better solved before substantial tonnages can be moved into industrial channels. In this respect, sugar cane bagasse is in a favorable position in that the cost of initial collection and defibering has already been absorbed in the manufacture of sugar. Costs of baling, storing, and transportation after receipt from the sugar mill, however, must be borne by the using industry.

Of the 423,000 tons of bagasse produced in continental United States and the 3,276,000 tons produced in insular United States per annum in the period 1931-1935⁽⁹¹⁾, probably 250,000 tons per

annum were used in the production of structural and insulating board. The major portion is burned for fuel at the sugar factories.

In 1933, the United States Forest Products Laboratory at Madison, Wisconsin, proposed methods for the production of plastic materials from sawdust, and allied substances. These methods^(92,93) consisted essentially of hydrolyzing or digesting the raw material at elevated temperatures and pressures with dilute acid or with aniline, and mixing the hydrolyzed residues with aniline. Subsequently, about 1938, the Agricultural By-Products Laboratory at Ames, Iowa, studied the effect of a number of variables on the above procedures applied to bagasse^(94,95).

The aniline bagasse plastic seemed to show the greatest promise. A comparison of certain physical characteristics of the bagasse plastic with those of the phenol-formaldehyde type is presented in the following table.

	Flexural Strength lbs./sq. in.	Moisture Absorption %	Specific Gravity	Hardness	Moisture in Air-Dry Molded Product %	Cost \$/lb.
Bagasse Plastic	6,900	2.99	1.38	90	0.86	0.054*
Phenol-Formaldehyde Plastic	7,063	0.34	1.34	98	0.25	0.14**

*Cost of labor, steam, etc., is not included.

**All costs are included.

The bagasse plastic compares favorably in all of the properties listed with the exception of its moisture content, and the latter has been improved in further experiments made in recent years.

A pilot plant for the production of molding powders from bagasse, based on the procedures developed at the Agricultural By-Products Laboratory, was erected in 1939 at a sugar mill in Louisiana, with a capacity of about 200 pounds of powder per day. The product offered for commercial use was an improvement over the laboratory product insofar as molding characteristics were concerned, but it did not meet with any commercial success⁽⁹⁶⁾. Chief among its shortcomings were the excessively long curing time required, poor flow qualities, and excessive gassing during molding. In view of these difficulties, attempts at marketing the product were discontinued for over a year, and all efforts were devoted to improving the material.

A product was finally developed which was comparable in most respects with the general purpose thermosetting compounds previously on the market, and which had certain advantages over many of

them in shortness of curing time, flow, and finish. A few tons of this material were manufactured, sold, and successfully used for commercial articles.

In the development work, the process was divided into two parts: the production of a resin from bagasse with complete destruction of the fibrous and non-reactive portions; and a parallel development of a satisfactory filler from bagasse. A resin was successfully developed, as well as a filler made from bagasse, which, when used in combination with the bagasse resin, was superior to wood flour and other common types of filler.

It was reported early in 1944⁽⁹⁷⁾ that a steadily growing demand for the thermosetting molding compounds based on bagasse had made it necessary to expand manufacturing facilities from the original pilot plant scale to a full-sized commercial unit. Research was directed toward the final development of two products—a general purpose and a semi-impact molding compound.

In the course of a search for a molding compound which could be manufactured without the use of any critical raw materials needed in the war economy, a new thermoplastic resin based upon bagasse was developed. The characteristics of this material suggested its use as a possible substitute for shellac in the manufacture of phonograph records, with the result that after a period of preliminary experimentation, commercial production was started in September, 1942.

The development of an alcohol-soluble bagasse resin showing some promise for use in laminating paper was continued during 1943. A water-soluble, thermosetting bonding resin, suitable for use with paper, cloth, and veneers, has been carried to the point of undergoing commercial tests. Its favorable characteristics include its extreme solubility in water, its rapid cure, and the relatively low temperatures and pressures required for complete curing. The resin is reported to have an unusual degree of flexibility after curing and to be very resistant to water.

Co-operative work between the Agricultural By-Products Laboratory and the automotive and rubber industries developed the fact that these molding powders can be compounded with both synthetic and natural rubbers. Steering wheels of molding powder-synthetic rubber have passed all laboratory and service tests. Gasket material of the same mixture has superior oil resistance, if not subjected to heat. It can also be substituted for part of the shellac used in the preparation of the hard, dense, lustrous materials used for fender

guards. The automobile industry, in addition, is interested in its use for buttons, knobs, dashboards, panels, and other automobile parts.

Other possible applications of the molded plastic include its use as electrical insulation material in the manufacture of radio and electrical equipment, and as tiles, table and desk tops, window frames, and numerous other articles of interest to the building and furniture industries.

In 1945, the heat-distortion temperature of a bagasse lignin type plastic called Valite #8003L was reported⁽⁹⁸⁾ as 151.0°C. This was one of the highest heat-distortion temperatures observed in a long list of various resins.

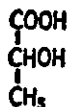
T. R. McElhinney, Technical Director of the Valite Corporation, has patented⁽⁹⁹⁾, in 1946, a process for making a synthetic resin of a type similar to the phenol-aldehyde resins. Aldehydes and ketones are liberated from bagasse by acid hydrolysis with live steam under pressure in the presence of phenol. In a short time, the contents of the autoclave are converted into a black resinous and viscous mass. The resulting basic resin (so-called "Novolak" resin) is then further treated to render it thermoplastic, or thermosetting. The process was described in another article, published in 1947⁽¹⁰⁰⁾, in which a number of the applications of this resin were listed. The thermosetting resin may be employed either for laminating cloth, paper, or glass, or it may be compounded with fine fillers to form a compound which can be filled into molds, giving articles of different sizes and shapes.

In the same year, an article appeared in an Indian journal⁽¹⁰¹⁾ describing a plastic obtained from bagasse. Its properties and mode of formation corresponded very closely with those of the bagasse plastic developed previously in the United States. Among its uses were listed the fabrication of laminated articles, molding powders, waterproofing of canvas, and as an ingredient of varnishes and paints.

A patent was granted to the Celotex Corporation in 1946⁽¹⁰²⁾ describing a cellulose-filled synthetic resin molded article, prepared in one step. A cellulosic fiber, such as bagasse, containing 7 to 11 per cent moisture is heated under a pressure of 500 to 1,500 pounds per square inch to 345-395°F. for ten to twelve minutes in a gas-tight mold. In this process, the lignins are converted to a synthetic resin which is firmly adhered to the cellulosic fiber. The product has a tensile strength of 1,600 to 4,000 pounds per square inch. Evidence for the formation of a resin is the decrease from 33 per cent of benzene-soluble material in the starting material to 1.9 per cent in the product and the impossibility of pulping the product.

Another patent using bagasse fiber as an ingredient of a plastic composition was granted in the same year to the Hercules Powder Company⁽¹⁰³⁾. It described the formation of a resinous composition by heating a ligneous material, such as bagasse fiber, water, and a higher fatty acid containing a conjugated system of double bonds, such as tung oil, at 240-330°C. under pressure until the cellular structure of the wood had disappeared, and recovering the resin by removing the water. The resins are characterized by freedom from cellular material and by a relatively dark color. They may be used in molding compositions and plastics, and as a binding material for different types of pressed boards.

LACTIC ACID



The importance of lactic acid plastics to the sugar industry lies in the fact that one of the raw materials used in large quantity in the manufacture of lactic acid is molasses, a by-product of the refining of sugar. It is also true of the other compounds to be discussed that sugar, or one of its by-products or derivatives, is directly or indirectly the raw material used in its manufacture. These include citric, aconitic, levulinic, citraconic, and itaconic acids.

The synthetic resins derived from these raw materials are, for the most part, alkyd resins. The generic name, alkyd, is here used to designate all possible resinous products of polyhydric alcohols and polybasic acids. Although alkyd resins are generally regarded as a comparatively new development of the last quarter-century, Berzelius⁽¹⁰⁴⁾ reported the formation of a resinous product from glycerol and tartaric acid as early as 1847. The popularly accepted beginning of the work on alkyd resins, however, is the discovery by Smith⁽¹⁰⁵⁾ of a resin from glycerol and phthalic anhydride in 1901. These resins are produced in large quantities for use as coatings and finishes, particularly for the manufacture of automobiles. A phenomenal growth has occurred in the volume of production of this type of synthetic resin which has increased from 13,000,000 pounds in 1931, to 128,000,000 pounds in 1941⁽¹⁰⁶⁾. It accounts for a high percentage of the total plastic industry's output, both in dollar volume and tonnage.

Lactic acid is also an important potential raw material for acry-

lic esters used in the manufacture of acrylic plastics. These plastics are not produced in as large quantities as alkyd resins, and are more expensive; but as they are of recent origin, their future growth should be substantial.

Lactic acid can be converted by suitable means into acrylonitrile, which is used as a copolymer with butadiene in the preparation of the Buna-N types of synthetic rubber⁽¹⁰⁷⁾. A patent⁽¹⁰⁸⁻¹¹⁰⁾ issued in February, 1944, to the E. I. du Pont de Nemours Company describes the acylation of lactonitrile by reacting a vinyl ester with lactonitrile in the presence of a tertiary amine. The resultant α -acetoxy propionitrile may become an important intermediate in the preparation of acrylonitrile.

Another application of these acids, in the form of their esters, is as solvents and plasticizers for various plastic materials. This usage antedates their polymerization into synthetic resins, and it is probable that, at the present time, the consumption of these compounds as plasticizers and solvents is greater than that as actual plastic raw materials.

In a number of instances, the principal deterrent to the large-scale application of the materials under consideration has been their relatively high cost; in other cases, the plastics derived from them have not had the desired properties. Research conducted during the past decade has already solved several of the problems concerned with both cost and quality. It seems safe to assume that the investigations now in process and those to be undertaken in the near future will assure a rapid and substantial growth in the consumption of many of these compounds.

Lactic acid is one of the oldest known organic acids and one of the most widely distributed in nature. It is the primary acid constituent of sour milk, from which it derives its name, one of the prevalent organic acids of the soil, and a normal constituent in the blood and muscle tissue of animals. Avery, of Littleton, Massachusetts, was the first person (1881) to produce lactic acid successfully on a commercial basis⁽¹¹¹⁾. Since 1881, its production by fermentation has become an important industry. It is manufactured by a comparatively high temperature fermentation from several inexpensive sugars, the cost of the raw material usually determining which sugar is to be used. Cane or beet molasses, invert sugar, lactose in whey, and starch from corn are used in the United States; potato starch is the common raw material in Germany. Yields of 90 per cent on the basis of the sugar fermented are not uncommon in controlled processes,

and higher yields have been obtained occasionally. About five million pounds of lactic acid, with a market value of nearly a million dollars, was produced from all sources in the United States in 1941⁽¹¹²⁾. In 1945, production had increased to about eight million pounds per annum⁽¹¹³⁾. An additional 250 thousand pounds of plastic grade, essentially free from chlorides, sulfates and heavy metals and most of the U. S. P. and C. P. grades are manufactured or imported. The leather industry is the principal consumer of lactic acid, utilizing probably 80 to 90 per cent of the entire consumption of the country.

An interesting application occurred in Germany during World War I⁽¹¹⁴⁾. Due to the need for a substitute for glycerol, which was required for the manufacture of many war materials, attempts were made to find a suitable replacement. Sodium and potassium lactates, called Perglycerine and Perkaglycerine respectively, were found to serve quite well as lubricants and in aqueous solutions as anti-freezing liquids. Their advantages were that, for friction purposes, a 45 per cent solution of Perglycerine was equivalent to a 65 per cent glycerine solution, and for cooling a lower concentration also sufficed. The substitutes proved to be about five times cheaper than glycerine.

Lactic acid esters have found a limited usage as a solvent for certain types of plastic materials. A German manufacturer⁽¹¹⁵⁾ reported in 1941 that methyl and ethyl lactates are among the best solvents for cellulose acetate, because they have a high boiling point, and consequently evaporate slowly to leave an even film. In contrast to tetrachloro-ethane, previously used, the fumes are non-poisonous. Esterification yields have been poor due to the use of aqueous solutions and the water solubility of the hydroxy acid. To avoid low yields, the esters were prepared by a special method under anhydrous conditions, using lactide, the cyclic dimer of lactic acid as the basic intermediate.

In a patent⁽¹¹⁶⁾, granted in the United States in June, 1944, esters, which are good plasticizers, especially for cellulose acetate, and good solvents for synthetic resins, are prepared by acetylating esters of lactyl lactic acid.

A method is described in a patent⁽¹¹⁷⁾ vested in the Alien Property Custodian in 1943, outlining the utilization of alkali lactates as softening agents for textiles, leather, paper, and plastics. Aqueous solutions of sodium lactate are used, for example, which contain a smaller proportion of an aliphatic hydroxy ether, such as a reaction product of ethylene oxide with a polyhydroxy alcohol.

An important application of lactic acid in the plastics industry is its use as one of the raw materials for plasticizers. It is usually esterified with another alcohol or acid, or both, when applied in this manner. Glyceryl lactate, for example, has been listed⁽¹¹⁸⁾ among the substances most commonly used as plasticizers, and a special method for its production was patented in 1943⁽¹¹⁹⁾. It comprised the preparation of glycerol dilactate by the reaction of a glycerol dihalohydrin, such as 1, 3-dichloro-2-propanol, with an alkaline salt of lactic acid.

In a patent issued in 1932⁽¹²⁰⁾ defining the use of an alkyd resin compatible with nitrocellulose, lactic acid is mentioned as a possible substitute for castor oil—that is, as a plasticizer.

E. I. du Pont de Nemours and Company were assigned a patent in 1938⁽¹²¹⁾ in which details are given for the preparation of esters of high molecular weight, such as dodecyl lactate, which are sirupy liquids of value as plasticizers with cellulose derivatives and in the preparation of lacquers, enamel and plastic compositions.

A patent⁽¹²²⁾ was granted to the Carbide and Carbon Chemicals Corporation in 1939, concerning the preparation of slightly viscous esters of high boiling point, suitable for use as solvents and plasticizers in lacquers and plastic compositions containing nitrocellulose and other cellulose derivatives or natural or synthetic gums and resins by treating a glycol or polyglycol with a hydroxymonocarboxylic acid, such as lactic acid, and then acylating. Details are given for the production of triethylene glycol di (butyryl lactate).

In 1945, H. V. Claborn⁽¹²³⁾ made a patent disclosure of various lactylactic esters made by heating under reflux dry lactide and various anhydrous alcohols in the presence of an acidic catalyst. These esters were considered to be suitable for use as plasticizers.

By a similar process, the American Cyanamid Company⁽¹²⁴⁾, in 1946, described the formation of 1-naphthyl methyl lactate in a patent. It was a light brown viscous sirup; had a very low vapor pressure; and was insoluble in water. It was stated to be a plasticizer for cellulose derivatives and to be compatible with other softening agents and with cellulose esters.

In two papers^(125, 126) presented at the September, 1947, meeting of the American Chemical Society, the synthesis of a number of lactic acid derivatives for use as plasticizers was described. In one, the preparation of twenty-three diglycol bis-carbonates of lactic esters by the action of diglycol bis-chloroformate on lactic esters was out-

lined. All the esters were compatible with either polyvinyl chloride-acetate (95-5) or cellulose acetate, and about one-third of them were miscible with both. All were compatible with ethyl cellulose. It was stated that these esters were prepared in good yield from commercially available and relatively inexpensive materials, and that several of them compared favorably with dioctylphthalate as plasticizers for vinyl resins.

In the other, a description of the preparation of a number of acyl derivatives of alkyl poly lactates was presented and the latter were evaluated as plasticizers for vinyl chloride polymers. Three methods of making alkyl poly lactates were discussed. The alkyl poly lactates were acylated with one of the following compounds: acetic anhydride, propionic anhydride, benzoyl chloride, lauroyl chloride, 2-ethylhexoyl chloride, or diglycol chloroformate. The products were mixtures of esters of monomeric, dimeric, trimeric, and polymeric lactic acid. The final products were almost colorless, high-boiling, viscous liquids. These esters were generally miscible with a 95 per cent vinyl chloride, 5 per cent vinyl acetate copolymer, and ethyl cellulose. However, they were not generally compatible with cellulose acetate.

The simplest form of plastic which can be manufactured from lactic acid is the product of its self-polymerization, since no additional chemicals would enter into the final product. Although the commercial usefulness of the acidic resin prepared by the self-esterification of lactic acid appears to be decidedly limited, due to its susceptibility to reversible polymerization, a number of articles and patents have been published describing the reaction. Condensation products, or polymers, of lactic acid are of interest because they occur in all aqueous solutions of lactic acid containing approximately 18 per cent lactic acid or more⁽¹²⁷⁾; the condensation polymers of intermediate molecular weight can be used as such or, after slight alteration, as plasticizers; and the condensation polymers of higher molecular weight can be converted into useful plastics by condensation with certain vegetable oils, glycols, and other chemicals. The alcohol and carboxyl groups present in poly lactic acid have frequently been used to prepare resinous materials. It is claimed that useful plastics can be made by treating poly lactic acid with alcohols⁽¹²⁸⁾, acids⁽¹²⁹⁾, acid chlorides⁽¹³⁰⁾, aldehydes⁽¹³¹⁾, and carbohydrates⁽¹³¹⁾.

A patent⁽¹³¹⁾ issued in 1932 to the Celanese Corporation of America describes a water-resistant resin formed by heating lactic acid as the sole reactant, until polymerization occurs. After distilling

any volatile part, a clear, hard, tough, and firmly adherent film is formed, which, in the undyed or unpigmented form, is almost colorless and fast to light.

In a later patent⁽¹³²⁾, granted in 1934 to G. L. Dorough, the dimer of lactic acid, lactide, is polymerized by heating it to a temperature approaching that at which decomposition of the polymerized product begins to occur, and the latter is then heated within such temperature range and at a pressure below 100 mm. of mercury to distill any residual monomeric lactide. The product is colorless when U. S. P. or C. P. lactic acid is used. It melts between 80 and 100°C., and has a molecular weight between 3,000 and 4,000. In 1938, the same inventor assigned a patent⁽¹²⁸⁾ to E. I. du Pont de Nemours and Company describing a method of increasing the molecular weight of polymerized lactic acid by condensing it with hydrogenated castor oil to form a tough, rubbery resin, which is soluble in aromatic hydrocarbons.

Filachione and Fisher⁽¹²⁷⁾ reported in 1944 the results of their experiments to determine optimum conditions for the production of lactic acid condensation polymers by both batch and continuous methods. Removal of water during the dehydration or self-esterification of lactic acid is facilitated by a relatively high temperature, reduced pressure, sulfuric acid, or similar esterification catalyst, and an entraining agent, such as benzene or toluene. Their experiments demonstrated that 80 per cent lactic acid of good quality can be dehydrated conveniently and continuously. Crude lactic acid was observed to be less suitable for conversion into the condensation polymers. The latter, which react readily with methanol, were found to be useful for making methyl lactate.

The resins just described are formed by the self-polymerization of lactic acid. Another, more important class of lactic acid plastics, however, includes substances formed by the reaction of lactic acid with another chemical compound prior to polymerization. At the present time, it is doubtful whether these lactic acid resins can compete in price with the glyptal, phenol-formaldehyde, or urea-formaldehyde types. Although these resins have as yet achieved no great prominence in the plastics field, it is felt that research laboratories have been laying the foundation on which such an industry could be established when conditions are more favorable. A brief survey of the patent and technical literature, therefore, should serve a useful purpose.

In an early patent⁽¹³³⁾ granted to the British Thomson-Houston Company in 1913, lactic acid is suggested for use with succinic acid, phthalic anhydride, and glycerol to impart improved plasticity to the finished product. In another English patent⁽¹³⁴⁾, issued in 1914, lactic acid is mentioned as replacing part of the phthalic acid in an alkyd resin. Also in 1914, the General Electric Company obtained a patent⁽¹³⁵⁾ covering a resin in which equal parts of lactic acid, phthalic anhydride, and glycerine were combined. It melted at 64°C. and was somewhat sticky.

The next patent⁽¹³⁶⁾ found in the literature was issued to the German General Electric Company (Allgemeine Elektrizitäts Gesellschaft) twenty-four years later, in 1938. In it, resins are prepared by completely esterifying a polyhydric alcohol such as glycerol with a hydroxy acid such as lactic acid and then condensing the product with a polycarboxylic acid such as phthalic acid. The products are soluble in acetone or alcohol-benzene mixtures, and may be used in lacquers and varnishes.

Chemists of the United States Department of Agriculture were granted a patent⁽¹³⁷⁾ in 1939, covering the formation of several plastic compositions utilizing lactic acid. Technical lactide can be esterified with glycerol to form glyceryl dilactate and the latter in turn forms the starting point for valuable resins by condensation with a polybasic acid. When phthalic anhydride is used di-(glyceryl dilactate)-triphthalate is formed which is compatible with nitrocellulose. In carrying out the above condensation with phthalic anhydride, the volatility of the latter makes it essential to operate at a very gradually increased temperature. With a long-chain aliphatic dibasic acid, on the other hand, this precaution is unnecessary, and resinification may then be completed in one day as compared with four days for the aromatic compound. Sebacic acid is a good example of the acid component, and the resulting di-(glyceryl dilactate)-trisebacate is a pale amber resin, which readily undergoes further polymerization to a harder product of reduced solubility.

The I. G. Farbenindustrie A.-G. reported in a patent disclosure⁽¹³⁸⁾ in 1939 that resinous condensation products are obtained by esterifying lactic acid with a polyhydric alcohol, such as glycerol, and then condensing the product with a polybasic acid, such as phthalic or succinic acid, and a monocarboxylic acid free from alcoholic hydroxyl groups, such as stearic acid. A solvent is advantageously added and water removed by azeotropic distillation, the removal being acceler-

ated by a current of indifferent gas. The resins obtained have good compatibility with pigments, such as zinc oxide, and with nitrocellulose.

In an article⁽¹³⁹⁾ published in 1940, the chemists of the United States Department of Agriculture, whose patent has been previously described, elaborated their earlier disclosure. They stated that a new type of alkyd resin had been prepared, starting from glycerol dilactate as the polyhydric alcohol and phthalic, maleic, azelaic, or sebacic acid as the dicarboxylic acid. Glycerol dilactate alkyds gel at lower average molecular weights than the corresponding glycerol alkyds, and some have, without further addition, a degree of flexibility which is imparted to the commercial alkyd resins only by modifying agents. The physical properties of the new resins are similar to those of the commercial alkyds. Modification of these resins with drying oils brings about solubility in low-cost paint thinners.

Very prolonged heating of the viscous mixture of lactyl lactic acid and lactide (resulting from low temperature treatment of lactic acid) with reactive compounds such as aldehydes and polyhydric alcohols has been found to yield alcohol insoluble varnish resins in the process of P. D. Watson, patented⁽¹⁴⁰⁾ in 1940. For example, the intermediate viscous mass, in admixture with 5 per cent of furfural, 10 to 15 per cent of glycerol, and 1 per cent of benzoyl peroxide as an accelerator, is baked in shallow aluminum pans at 159-170°C. for two weeks or longer. Baked coatings of these resins on tin plate in the absence of a primer are said to have resisted the action of 95 per cent alcohol for five months, and are claimed to be eminently suitable for the interior coating of beer cans.

A patent⁽¹⁴¹⁾ was issued in 1940, covering the formation of a resinous reaction product by fusing together lactic acid and isobutylamine, pyridine, dioctylamine, or aniline as principal reactants, at about 200°C.

Polyhydric alcohols are completely esterified with lactic acid and the ester is then condensed with one or a mixture of polycarboxylic acids in a German patent⁽¹⁴²⁾ issued in 1940. These condensation products are homogeneous, quick hardening resins, having good insulating properties.

A process for fractionating a resin derived chiefly from lactic acid by the use of petroleum ether and other solvents was patented⁽¹⁴³⁾ by P. D. Watson in 1940.

In a German patent⁽¹⁴⁴⁾, issued in 1943, lactic acid, or its

anhydride, is heated with a dicarboxylic acid which is used in a quantity sufficient at least to esterify the alcoholic hydroxyl radicals of the lactic acid, or its anhydride. In the product, the remaining carboxyls are esterified with a polyhydric alcohol.

In addition to its consumption in alkyd resins, an outlet for large quantities of lactic acid might be developed, if an inexpensive method of its esterification and pyrolysis to acrylic esters could be achieved, as the latter compounds are used in large quantities for the manufacture of acrylic resins. Methyl acrylate, as a copolymer with methyl methacrylate, is used extensively for the formation of thermoplastic polymers to replace glass. Although fairly good yields for the conversion of lactic acid into methyl acrylate are obtained, it is doubtful whether this procedure can compete, at the present time, with the synthesis of the latter from ethylene or ethylene oxide. Improvements in the conversion of lactic acid derivatives into esters and other derivatives of acrylic acid should make possible the economical production (through intermediates such as methyl acrylate and acrylonitrile) of acrylate resins, surface coatings, and rubberlike materials from abundant, domestic raw materials of agricultural origin. The resins made from acrylic acid derivatives have many desirable properties, and will probably be used in much larger quantities when production costs are lowered. The polymers of acrylic acid derivatives are characterized by colorless transparency, adhesive qualities, elasticity, and stability to light, moderate heat, and weathering. Resins made from acrylic acid derivatives, especially methyl acrylate, are particularly suitable as protective coatings, finishes for leathers, impregnating agents for textiles, and adhesives.

In 1935, several English workers reported⁽¹⁴⁵⁾ the conversion of methyl α -acetoxy propionate to methyl acrylate by pyrolysis in 90 per cent of the theoretical yield. Acetylation of lactic acid or its esters⁽¹⁴⁶⁾ with ketene gives α -acetoxy propionic acid or its esters⁽¹⁴⁷⁾; in 95 per cent yield. Because of the economic factors previously outlined, the Eastern Regional Research Laboratory of the United States Department of Agriculture undertook a study of some of the optimum conditions required for the conversion of methyl α -acetoxy propionate to methyl acrylate by pyrolysis, and published some of their results in 1942⁽¹⁴⁸⁾. Conditions were found under which the pyrolysis products, methyl acrylate and acetic acid, can be produced with low contact times—that is, with high throughput. At temperatures above approximately 550°C., it is possible to

convert virtually all of the methyl acetopropionate into methyl acrylate and acetic acid in one pass, and thus obviate the necessity of separating the unchanged starting material and recycling. In an extension of these experiments, a report⁽¹⁴⁹⁾ was made in 1944 of the synthesis of acrylic and methacrylic acids by thermal decomposition of their ethyl or higher alkyl esters. It seemed that this synthesis might be more practical than the alternative approach by hydrolysis. Alkyl acrylates were increasingly stable in the following order for alkyl groups: *s*-butyl < 2-cyanoethyl < ethyl and *n*-butyl < isobutyl. Yields as high as 97 per cent were recorded, and the process was stated to constitute a convenient method for preparing these unsaturated acrylic acids.

During 1943 and 1944, a number of articles⁽¹⁵⁰⁻¹⁵⁸⁾ covering various aspects of the utilization of lactic acid derivatives in the manufacture of acrylic plastics have been forthcoming from the same laboratory. A series of acrylic esters was prepared, including the methyl, allyl, methallyl, phenyl, tolyl, tetrahydrofurfuryl, and three homologous β -alkoxyethyl esters. In addition, higher *n*-alkyl acrylates, having two to sixteen carbon atoms in the alkyl group, were made as well as fourteen secondary and branched-chain alkyl acrylates. These compounds were polymerized, and the properties of the different polymers were discussed. In another paper⁽¹⁵⁹⁾ various aspects of the preparation of methyl acrylate were presented, the key compound from which most of the other esters were prepared by alcoholysis.

In the following years, much of the work of the Eastern Regional Research Laboratory mentioned in the previous paragraphs, was patented, and additional research was carried on. The latter was reported both in articles prepared for various scientific journals⁽¹⁶⁰⁻¹⁶⁸⁾ and in patents⁽¹⁶⁹⁻¹⁷⁴⁾.

In 1945, the lactates of several primary, secondary, and branched-chain alcohols were acetylated, and the resulting α -acetoxy propionates were pyrolyzed to obtain information of the relation between acetoxy propionate structure and the yield of acrylic ester⁽¹⁶¹⁾. In the same year, another paper⁽¹⁶²⁾ reported the preparation of unsaturated esters of lactic acid by acylating various lactic esters with acrylyl chloride, methacrylyl chloride, or methacrylic anhydride. The resulting acrylates and methacrylates were colorless liquids that exhibited the expected tendency to polymerize.

Later papers, in 1946, 1947, and 1948, referred to above, dealt

with various extensions of the previous work, increasing the number of acrylate type derivatives of lactic acid available for polymerization, and improving the methods of preparation.

Chemists of the Pittsburgh Plate Glass Company have patented⁽¹⁷⁵⁻¹⁹¹⁾, in recent years, the preparation of a number of complex allyl type derivatives of lactic acid which they claim can be polymerized to form useful laminates, coatings, plasticizers, and optical plastics. One series of such monomers was made by the reaction of an unsaturated ester of lactic acid with phosgene in the presence of an alkaline agent such as pyridine. All of these compounds can be polymerized by heating with benzoyl peroxide.

Bruson and co-workers⁽¹⁹²⁻¹⁹⁵⁾ have made a variety of monomers using derivatives of dicyclopentadiene in which lactic acid is one of the components. Patents covering these compounds were granted during 1945 and 1946. These derivatives are formed in the presence of acidic catalysts. The monomers polymerize readily to yield a hard, flexible, tough, insoluble, and infusible product.

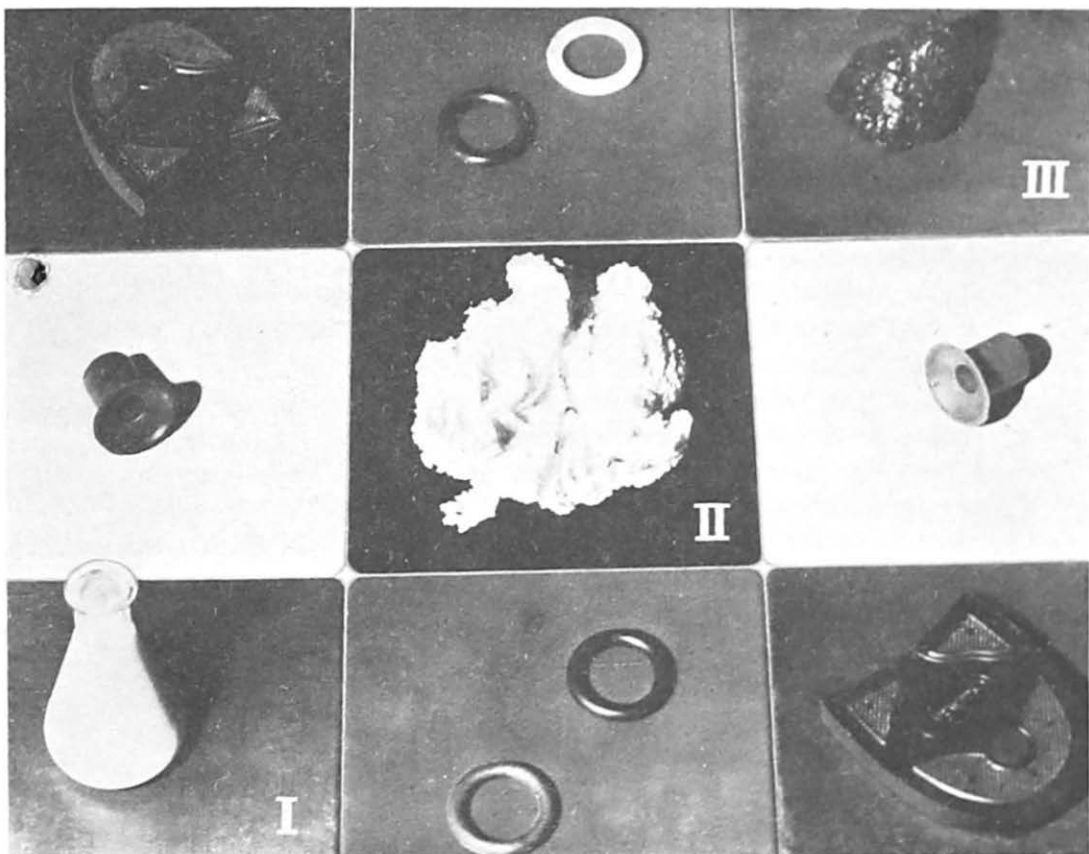
Several other patents have been granted in recent years in which lactic acid has been mentioned as one of the components of a plastic material. The E. I. du Pont de Nemours and Company patented⁽¹⁹⁶⁾ a glycolide resin in 1944 prepared from a mixture of lactic and glycolic acids.

The Eastman Kodak Company patented⁽¹⁹⁷⁾, in 1947, the formation of methyl acrylate in high yields by the pyrolysis of methyl lactate and ketene at 550°C. The process could be extended, according to the inventor, to the preparation of α , β -unsaturated nitriles, like acrylonitrile, from the corresponding α -hydroxy amides, nitriles, or ammonium salts.

A rather novel application of lactic acid was its use as a catalyst for the formation of a urea-formaldehyde type resin, as disclosed by a British patent⁽¹⁹⁸⁾ granted in 1947. For example urea was dissolved in water and combined with a mixture of thiocarbanilide and m-cresol. Thereafter, formaldehyde and lactic acid, in catalytic proportions, were added and the mixture was heated for several hours.

One of the most interesting and recent developments in the acrylics field has been the preparation of a new synthetic rubber⁽¹⁹⁹⁾, called "lactoprene" (figure 1), because of its relation to lactic acid, by the chemists of the Eastern Regional Research Laboratory. Unlike many polymerized methacrylic acid derivatives, polymers

prepared from the normal alkyl acrylates are soft and elastic at room temperatures⁽²⁰⁰⁾. It seemed that proper cross linkage, or vulcanization, might transform these essentially linear polymers into products more nearly resembling rubber. Acrylic ester copolymers containing vulcanizable unsaturation were prepared by polymerizing methyl acrylate or ethyl acrylate with small quantities



LACTOPRENE

An assortment of samples, including Lactoprene emulsion (I), the solid copolymer (II), compounded Lactoprene (III), and various molded specimens. (Photograph reproduced through the courtesy of the United States Department of Agriculture, M. C. Audsley, photographer.)

of polyfunctional monomers, such as butadiene, isoprene, and allyl maleate⁽²⁰¹⁾. Vulcanization with sulfur, accelerators, and other

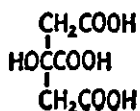
agents used in rubber compounding, transformed the acrylic resins into rubberlike products that appear to have attractive possibilities. Molasses, and several normally abundant carbohydrates, can be transformeed, through lactic acid as an intermediate, into approximately an equal weight of these new rubberlike materials.

These results were carried a step further by a study of saturated acrylic resins⁽²⁰²⁾. Although the vulcanizates prepared from copolymers of alkyl acrylates and unsaturated compounds were rubbery and seemed suitable as rubber replacements in some fields, polyfunctional monomers were generally objectionable because of their tendency to create cross linkages prematurely—that is, during polymerization. Vulcanization of saturated acrylic resins was therefore attempted. Polyethyl acrylate and various saturated copolymers of ethyl acrylate were vulcanized satisfactorily with red lead and quinone dioxime and also with benzoyl peroxide. The copolymers made from acrylonitrile, cyanoethyl acrylate, chloroethyl acrylate, chloropropyl acrylate, and phenyl acrylate were vulcanizable with certain sulfur-accelerator mixtures. The preparation of rubberlike materials by vulcanizing saturated acrylic resins instead of copolymers of the ethyl acrylate-butadiene type has the following advantages: agents and techniques to prevent cross linkage are not required; the polymers and copolymers are soluble, and hence the viscosity of the solutions can be used as an index of the molecular weight; and synthetic rubber cements can be made.

As previously mentioned, the formation of acrylic esters from lactic acid, at present production levels, cannot compete with the less expensive ethylene oxide process. It is an interesting speculation, however, to examine the future possibilities of this lactic acid application should the demand for acrylates and lactic acid approach 50 to 100 million pounds per annum. If lactic acid, or methyl lactate, could be manufactured profitably at a price of from 3 to 8 cents per pound, which does not seem unreasonable if the present rate of production is increased tenfold, it is probable that acrylic esters could be made more cheaply by the lactate method. It is understood that the present ethylene oxide process does not lend itself to any marked reductions in cost with increased volume. In connection with such a potential demand for lactic acid, an important consideration for the sugar industry is the competitive position of molasses with respect to whey, corn starch, etc., as raw materials for the production of lactic acid. Corn starch and other starchy

materials are probably too expensive for serious consideration in comparison with molasses, as they must first be saccharified at a considerable cost. Whey seems to be the most serious competitor, as it is usually a worthless by-product of cheese or casein manufacture. However, the 274,000,000 pounds of fermentable sugars in whey potentially available per annum⁽²⁰³⁾ are scattered among some five thousand establishments having outputs varying from a few thousand to over 50,000 pounds of whey per day. The cost of assembling the whey would therefore probably be prohibitive in comparison to that of molasses. Also, molasses appears to offer fewer manufacturing difficulties. As a result, assuming its return to the prewar price of 1 to 2 cents per pound, molasses would be the preferred raw material for lactic acid manufacture. The conversion of molasses to acrylic ester polymers would involve the following steps: fermentative production of lactic acid from molasses, esterification of lactic acid with methanol, acetylation of methyl lactate, pyrolysis of the acetylated methyl lactate, and polymerization of the acrylic ester monomer. Yields are high; in the case of lactoprene, one pound of carbohydrate can be transformed into approximately one pound of the synthetic rubber. Manufacturers are apparently already interested in this potential application of lactic acid in the acrylic plastic field, as five, or more, pilot plant investigations are reported to have been started.

CITRIC ACID



The commercial development of the fermentation process in the early nineteen-twenties revolutionized the citric acid industry. It has made the United States self-sufficient in respect to the citric acid supply and greatly changed world commerce in citric acid and calcium citrate. Cull lemons, limes, and pineapples are the principal sources⁽¹¹¹⁾ of natural citric acid, which is produced chiefly in Italy, and also in California, Hawaii, and the West Indies. In 1922, Italy produced approximately 90 per cent of the world's supply of calcium citrate, which is used in citric acid manufacture. Since 1927, however, very little calcium citrate or citric acid has been imported into this country. The following table⁽²⁰⁴⁾ illustrates the

changes which have occurred. These include a five-fold increase in annual production between 1914 and 1937, accompanied by more than a 50 per cent decrease in the average price per pound, resulting in slightly less than a threefold increase in dollar value.

UNITED STATES PRODUCTION OF CITRIC ACID FOR SALE

1914-1937

(From the U. S. Bureau of the Census)

Year	Pounds	Value	Average Price Per Pound
1914	2,657,840	\$1,516,326	\$0.53
1923	5,689,473	2,829,306	0.50
1929	10,755,789	4,832,984	0.46
1935	10,493,068	2,768,377	0.28
1937	18,138,263*	4,118,513	0.23

* See(205)

In 1929, the fermentation process accounted for 7,000,000 pounds of the total production, whereas 3,500,000 were produced from natural sources. Several factors have been responsible for this change: the production of citric acid by mold fermentation; an increase in the number of trees bearing lemons in the United States, importations of concentrated lemon juice, and high import duties. Maximum yields in the fermentation process have been secured, usually from sucrose and fructose, amounting to about 60 per cent of the weight of the sugar used in the medium. Occasionally glucose has given high yields, comparable with those from sucrose. For industrial fermentations, sucrose and technical glucose are best; maltose and molasses are less desirable.

According to the United States Department of Commerce(204), about 65 per cent of the domestic consumption was reported to be used for medicinal purposes, 15 per cent in foods, 9 per cent in candy, and the balance in miscellaneous applications.

Considerable interest has recently been manifested in synthetic resins derived from citric acid. The sharp decline in its price as a result of its large scale synthesis from sugar has placed it within the realm of possibility as a raw material for synthetic resins. Research on resins of the alkyd type has revealed the importance

of citraconic and itaconic acids and their anhydrides as raw materials. Since substantially better yields of these products from citric acid have recently been obtained, another potential use of this acid is indicated.

The citric acid resins, classed as alkyd resins, are obtained by condensing citric acid and glycerine. Commercial production is said to have started in Europe⁽²⁰⁶⁾, but there is no known domestic production as yet.

Van Bemmelen⁽²⁰⁷⁾, as far back as 1856, studied the reaction between glycerol and such acids as succinic and citric. He experimented with different proportions of acid and glycerol. In each case he obtained similar results: a thick sirup on heating at about 160°C. which, when further heated at about 210°C., was finally converted into a hard solid unaffected by water. Similar experiments were carried out by Lourenco⁽²⁰⁸⁾ in 1863, using citric acid.

A patent⁽²⁰⁹⁾ was issued to the Barrett Company in 1924, in which polyglycerols are heated with a polybasic aliphatic acid, such as citric acid, to obtain synthetic resins which are much stronger than the synthetic resins similarly prepared from glycerol.

In 1932, a patent⁽¹²⁰⁾ was granted covering a resin, compatible with nitrocellulose, formed from glycerol, phthalic anhydride, and castor oil, in which it was stated that citric acid may be used to replace phthalic anhydride.

In the patent disclosure⁽¹³⁶⁾ made by the German General Electric Company in 1938, previously described under lactic acid, citric acid is mentioned as a suitable alternate to lactic acid.

A Russian article⁽²¹⁰⁾ was published in 1939, describing the formation of resins from 94 per cent glycerol and crystalline citric acid which were either water-soluble or insoluble, depending upon the ratio of the ingredients used. A detailed description of the substances obtained under various reaction conditions is presented. The same author reported in another paper⁽²¹¹⁾ that films formed by a resin made from citric acid and glycerol were superior to linseed oil films in their hardness, permeability to water, and reversibility, and are equal to them in stretch and stability.

In a French patent⁽²¹²⁾ issued in 1939, alkyd resins susceptible to hardening are described which are produced by causing citric acid to react with glycols and condensing the triglycol esters obtained with a polybasic carboxylic acid.

Compounds like citric acid in which hydroxyl and carboxyl groups exist in the same molecule, polymerize to homocondensation products by the formation of polyesters, as pointed out by Carothers^(213, 214). The first product of the polymerization of citric acid at 190-200°C. has been described⁽²¹⁵⁾ as an almost water-white balsam. As heating is continued, and the fusion point attained, there is a violent evolution of water vapor. As the reaction proceeds, the product turns to a lemon-colored balsam and then to a dark orange-colored hard resin which is water soluble. Since the resinous product has a relatively high acid number, it appears that it is not due to an alkyd resin formation, but may rather be largely a polymer of itaconic anhydride. No practical application of this resin has been reported, but it is likely that reaction with other acids and alcohols might lead to useful products, as in the case of polymerized lactic acid.

A pale resin can be obtained from citric acid, according to certain British patents^(216,217) granted in 1939 and 1940, when it is heated with a mineral acid, turpentine oil, blown linseed oil, and linoleic acid, and is subsequently esterified with glycerine. Under these reaction conditions, citric acid changes readily to aconitic acid.

The General Motors Corporation, in 1941, patented⁽²¹⁸⁾ a fabric to be used as a coating for fuel pump diaphragms in which the resinous material was made from citric acid. A flexible fabric is imperviously coated with a resinous product made from glycerol, sebacic acid, and citric acid, and 5-20 per cent of lamp black is added to prevent solubility and scuffing off of the coating.

Two German patents^(219, 220) were granted in 1941 in which the use of citric acid for resin formation was cited. In the first, triglycol citrate is formed from citric acid and an aliphatic dihydric alcohol, and is condensed with a dicarboxylic acid to form an alkyd resin. In the second, citric acid di- or triglycol esters are condensed with citric acid, and the product is treated with a small quantity of an aldehyde to form a hard resin.

A citric acid varnish coating for copper wire has been patented⁽²²¹⁾ by the Thomson-Houston Company, Ltd. The resin is formed by the reaction of glycol and citric acid in a two-stage process, the alcohol being esterified in the first stage with a half equivalent of citric acid, and the remaining hydroxyl groups are condensed when the rest of the acid is added.

Despite the number and variety of patents which have been issued

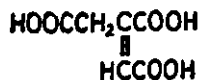
covering citric acid plastics, it was stated on competent authority⁽²²²⁾ in 1942, that citric acid resins have thus far attained only a theoretical interest. Citric acid esters, on the other hand, are being used extensively as plasticizers. In 1943, triethyl citrate was cited⁽¹¹⁸⁾ as one of the substances most commonly used as plasticizers. Four esters of citric acid were advertised⁽¹⁰⁷⁾ for sale in the same year. Triethyl citrate was described as "a solvent plasticizer for phenolic resins, cellulose esters and ethers, and most other plastic materials. As it is capable of holding considerable amounts of water in solution, it is recommended for investigation in connection with problems arising from blushing or the development of the orange-peel effect. Imparts resistance to oils." Tributyl citrate, on the contrary, was said to be "a plasticizer of low volatility and high water resistance. Has been found of value in inhibiting discoloration by light of products in which it has been incorporated." The acetyl derivatives of these two citrates were also described; that of the triethyl ester as of particular interest as a plasticizer for cellulose acetate, and that of the tributyl ester as a plasticizer for ethyl cellulose.

As evidence of a continuing interest in citric acid is the granting of a patent⁽²²³⁾, issued in 1944, to the American Cyanamid Company for the formation of an alkyd resin from citric acid, dipentaerythritol and an unsaturated fatty acid. The mixture is heated in an atmosphere free of oxygen to prevent discoloration and premature drying.

Also, in 1945, several patents were granted for the formation of polymeric materials in which citric acid was one of the components. A patent disclosure⁽²²⁴⁾ by D'Alelio assigned to the General Electric Company described synthetic resins which are stable in storage, and heat convertible without the addition of an accelerator. It consisted of a melamine-formaldehyde mixture to which a small amount of citric monoacid diamide had been added. The product was said to be useful in the preparation of coatings, laminating adhesives, casting resins, and molding powders.

The Pittsburgh Plate Glass Company patented a number of resins in the same year in which citric acid, or a derivative thereof, was the principal constituent. In one⁽¹⁸¹⁾, the monomer was bis (triallyl citrate) carbonate, formed by the reaction under special conditions of citric acid, allyl alcohol, and phosgene. In another⁽²²⁵⁾, an ester of triallyl citrate and allyl acid carbonate was prepared. Polymerization to useful plastics was accomplished in each instance by treatment with benzoyl peroxide.

ACONITIC ACID



Although aconitic acid has not been isolated from the fermentation of sugars by molds, Bernhauer and Bockl⁽²²⁶⁾, in 1932, found that one strain of *A. niger* produced citric acid in 20 per cent yield from aconitic acid and that citric acid could be converted into aconitic acid.

A method was described⁽²²⁷⁾, in 1945, for the preparation of aconitic acid with a 70 per cent yield by the catalytic dehydration of citric acid in a non-corrosive process. It had been prepared in limited quantities in the past by the mineral acid dehydration of citric acid. In one technique a non-solvent for citric and aconitic acids was used as the suspension medium for the acids and the catalyst; in a second method citric acid was mixed with the catalyst in the dry state, and the mixture was heated under vacuum at temperatures sufficient to fuse the reaction mass. A preliminary investigation indicated that aconitic and unconverted citric acid could be separated by the solvent extraction of a water solution of the two acids.

A more promising source of supply was described in 1941⁽²²⁸⁾. In it, aconitic acid is produced from sugar cane products. An investigation of the sediment which has been encountered in recent years in first and second molasses (and sometimes in sirup) produced in the western portion of the Louisiana sugar belt, and of the scale which forms on the heating surfaces when the sugar liquors originating in this territory are concentrated, revealed the fact that the sediment and some of the unusual scales were composed largely of calcium aconitate. This led to an examination of Louisiana sirups for their content of aconitic acid, and to the finding that this acid is present in larger proportions than formerly supposed. Hence it is possible that 'sugar cane juice may prove a convenient natural source of aconitic acid, the industrial development and utilization of which has been limited because its source heretofore has been the dehydration of citric acid.

In 1943, a Japanese investigator, Kimiyo Miti⁽²²⁹⁾, reported the isolation from Java Molasses of both transaconitic acid, and monoethyl aconitate, the latter in the amount of 0.7 gram from 4 kilograms of molasses. The aconitic acid and ester were first adsorbed on activated carbon from acidified molasses, followed by elution with 90 per cent ethanol.

Although it has long been known that aconitic acid is the principal organic acid in sugar cane juice⁽²³⁰⁾ and is also present in sorgo⁽²³¹⁾, no practical method of obtaining it from either of these natural sources had been found until Ventre discovered⁽²³²⁻²³⁴⁾ that, during the evaporation of sorgo juice for the production of sugar, an insoluble calcium aconitate separates from the evaporation sirups in quantities sufficient to make its recovery feasible. In a subsequent publication⁽²³⁵⁾, and in two additional patents^(236, 237), various improvements in the process were described. By introducing the use of both lime and calcium chloride, instead of the usual lime defecation, the recovery of aconitic acid from sorgo juices was increased from 42.9 per cent to 81.7 per cent of the available aconitic acid.

Balch and co-workers reported in 1945^(238, 239) the determination of aconitic acid in crusher juice and other factory products, as well as in the different portions of the sugar cane plant. Cane tops, and the sheaths and blades of the leaves were found to contain from three to five times as much aconitic acid as the millable cane. The authors state that there is as yet no practical method for removing the acid from the raw cane juice. It could be recovered economically, however, from cane tops or from immature cane especially grown for this purpose. Another good source of this compound would be blackstrap molasses, and it might be recovered as a by-product in the alcohol distillery.

Another insight into the problem of the isolation of aconitic acid from sugar cane sirups was furnished by an investigation⁽²⁴⁰⁾ of the insoluble aconitate obtained by Ventre. The properties of this salt were studied and compared with those of tri-calcium aconitate prepared from solutions of pure aconitic acid. The insoluble aconitates which separate from sugar cane and sorgo sirups were thus identified as calcium magnesium aconitates instead of tri-calcium aconitate, as previously surmised.

Although available in only limited quantities, triethyl aconitate and tri-n-butyl aconitate are listed as plasticizers in the 1943 annual catalog⁽¹⁰⁷⁾ of the plastic industry. Succinic and maleic acids and their derivatives, which can be obtained from aconitic acid, are valuable intermediates in the manufacture of plastics and plasticizers.

The preparation of an elastic alkyd resin from aconitic acid and glycerol was patented⁽²⁴¹⁾ in Japan in 1931 by Taturo Habu. The resin is prepared by heating the mixture at 170-180°C. for several hours. In 1935, the same inventor was granted two further

patents^(242, 243) in which the formation of plasticizers from aconitic acid was described. In one, a plasticizer is prepared by heating a mixture of aconitic acid and cyclohexanol at 155-160°C. It is a viscous semi-solid and is used as an additive ingredient to cellulose derivatives, or resins, and is resistant to water, acids, and alkalis. In the other, a plasticizer for cellulose derivatives or resins is made by heating aconitic acid with an aliphatic, aromatic, or terpene alcohol, or a mixture of these.

More recently, other derivatives of aconitic acid have been prepared and suggested for use as plasticizers. The American Cyanamid Company has obtained a patent⁽²⁴⁴⁾ for a method of forming esters of aconitic acid. In it, esters of citric acid are acetylated with acetic anhydride, followed by their dehydration to form the corresponding aconitates and acetic acid. The latter may be recovered. Yields of 91 per cent of both tri-butyl and tri-amyl aconitates are reported, and it is stated that these esters may be used as plasticizers for synthetic rubber.

By using a column of the desiccant "Florite" over a flask in which a mixture of octyl alcohol (technical 2-ethylhexanol) and aconitic acid was heated, a yield of 97 per cent of octyl aconitate was reported in 1945⁽²⁴⁵⁾. This method gives a simple means of making plasticizers from technical raw materials like aconitic acid.

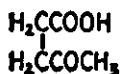
A patent⁽²¹⁷⁾ was granted in 1940 in Great Britain entitled "Condensation resins from aconitic acid and terpenes." If the condensation between aconitic acid and terpenes takes place in the presence of an unsaturated fatty acid, a resin of light color is produced. Persulfuric acid, sulfonic acids, and ethionic acid are suitable catalysts.

In a German patent⁽²⁴⁶⁾ issued in 1942, a synthetic resin is made by heating aconitic acid with an unsaturated fatty acid in the presence of a terpene alcohol, and the product is esterified with a polyhydric alcohol.

Aconitic acid was mentioned as a component of a plastic in two patents which were published in 1947. In one⁽²⁴⁷⁾, alkyl aconitate vinyl chloride copolymers were discussed. Organic solvent-soluble copolymers were prepared from vinyl chloride and trialkyl aconitates, such as trimethyl, triethyl, tripropyl, tributyl, and triamyl aconitate, by the standard polymerization techniques, preferably emulsion polymerization. The copolymers, thus formed, may be cast, milled, extruded, or molded at relatively low temperatures.

In the other⁽²⁴⁸⁾, a linear polymer was formed by the reaction of ethylene glycol, trimethylene glycol, sebacic acid, and aconitic acid. It was cured by heating in the presence of benzoyl peroxide to an infusible state.

LEVULINIC ACID



Levulinic acid has been synthesized by a variety of chemical methods. The most direct and practical method of preparation is to heat a hexose sugar, or a carbohydrate hydrolyzable to a hexose sugar, in an aqueous solution with a mineral acid. Numerous raw materials and conditions of reaction have been studied. In 1940, one manufacturer began its production on a commercial scale.

In 1931, Thomas and Schuette⁽²⁴⁹⁾ reported that levulinic acid could be made from glucose, fructose, sucrose, or starch, and in about the same yield from each of these starting materials. These experimentors also determined various optimum conditions for their reaction including the concentration of hydrochloric acid required and the effect of pressure.

The manufacture of levulinic acid from cane sugar was investigated^(250, 251) for several years prior to 1933 under a Multiple Fellowship of the Sugar Institute, Inc., at the Mellon Institute of Industrial Research. The published results indicated that the yield of levulinic esters from cane sugar had been improved by esterification of the crude acid and purification of the resulting esters. A yield of 40 per cent of the butyl ester was obtained. Four new alkyl esters of levulinic acid were also prepared.

The formation of levulinic acid from the residue from the distillation of an acid carbohydrate solution is described in a German patent disclosure⁽²⁵²⁾ made in 1940. The residue is dissolved in an alkaline or acid solution and heated. The insoluble residue is filtered off and from the filtrate is separated levulinic acid or its salt.

The E. I. du Pont de Nemours Company was granted two patents in 1940 concerning the formation of levulinic acid or one of its derivatives. In one⁽²⁵³⁾, the production of levulinic and homologous acids and intermediate compounds from dihalogen butenes was described. One of the halogen atoms was first selectively converted

to a cyano group, and subsequently in a two-stage hydrolysis, the cyano group was hydrolyzed to an acid and the residual halogen atom converted into a ketone. In the other⁽²⁵⁴⁾, levulinonitrile was prepared by reacting hydrogen cyanide with methyl vinyl ketone under anhydrous conditions in the liquid state.

Also in 1940, a patent⁽²⁵⁵⁾ was issued to the Corn Products Refining Company for a method of manufacture of levulinic acid which comprises heating a mixture containing a hexose sugar, a dilute, substantially non-oxidizing and non-reducing mineral acid and sodium chloride.

A study of the formation of levulinic acid from carbohydrates, published⁽²⁵⁶⁾ in 1941 and patented⁽²⁵⁷⁾ in 1943, showed promising results. Under ordinary circumstances, carbohydrates give, under the influence of mineral acids, humin-like decomposition products and levulinic acid in relatively poor yields. Hydrobromic acid, however, has a special effect. Using 10 per cent hydrobromic acid and heating for 24 hours at 130°C., dry glucose yielded 75.3 per cent of the theoretical amount of levulinic acid, starch 64.4 per cent, and crude sugar 69.3 per cent. Hexose containing natural materials also gave good yields.

A patent⁽²⁵⁸⁾ was issued to the A. E. Staley Manufacturing Company in 1942 in which was described a method of forming levulinic acid from a dextrose-producing carbohydrate. In the patented process a reaction mixture of a dextrose-producing carbohydrate, such as starch and hydrochloric acid, is subjected to heat and pressure to form levulinic acids and humin-type compounds, with sufficient mechanical agitation of the mixture to produce a granular type of humin compound.

More recently, a patent has been obtained by Haworth and Wiggins⁽²⁵⁹⁾ in 1944 in which several improvements in the preparation of levulinic acid from sucrose were recorded. In the first place, it was shown that hydrobromic acid was superior to sulfuric or hydrochloric acids as the catalyst in the reaction. Secondly, it was demonstrated that a low concentration, about 3 per cent, of sucrose greatly improved the yield of levulinic acid. Thirdly, it was found that a low concentration of sodium bromide could be used with hydrochloric acid to replace the more expensive hydrobromic acid as a catalyst, and, finally, by increasing the temperature, the reaction time was reduced from 12 hours to 2 to 3 hours.

In a later patent⁽²⁶⁰⁾, the same inventors described a two-stage

process for the preparation of 5-hydroxymethyl furfural⁽²⁶¹⁾ and levulinic acid from sucrose. Sucrose heated with oxalic acid at 150-170°C. yielded 5-hydroxymethyl furfural which was extracted with ethyl acetate. The residue was then treated with hydrobromic acid at 130-140°C. to yield formic and levulinic acids.

Improvements in the process for the production of hydroxymethyl furfural have been described in an article by Montgomery and Wiggins⁽²⁶²⁾ published in 1947. By heating sucrose in an aqueous solution under pressure at 160-170°C. for 2 hours, the same yield of hydroxymethyl furfural was obtained as by the older process using acid catalysts. Tetrahydrofuran 2, 5-dicarbino1, a hydrogenation product of hydroxymethyl furfural may be useful as a plasticizer for certain resins⁽²⁶³⁾.

A study of levulinic acid obtained as a reduction product of sugar by the use of high pressure hydrogenation was made in 1941 by the Hawaiian Sugar Planters Association⁽²⁶⁴⁾. Various derivatives were prepared and plastics made from them. The plastics were judged to be inferior to those produced from well-known available components.

Although levulinic acid derivatives were found to be inferior for plastic formation by the Hawaiian workers, esters of levulinic acid have been reported to be good solvents for synthetic resins. The properties of the alkyl esters, synthesized at the Mellon Institute^(250, 251) included their mutual solubility with water, stability of the esters in water, the solubility of gums and resins in the esters, and their miscibility with organic solvents. It was stated that the butyl and amyl esters are the most promising for commercial use. In another article⁽²⁶⁵⁾, published in 1939, describing the utilization of sugar derivatives, it is reported that the methyl, isopropyl, iso-amyl, and methylpropylcarbinol esters of levulinic acid are used for synthetic glass and artificial resin solvents.

The unique properties of levulinic acid indicate that it may find a valuable place as a plasticizer or as a constituent of synthetic plastic materials, despite the failure of the preliminary experiments already noted. The ease with which aldehydes react with it suggests interesting possibilities in the field of synthetic resins. In this connection, two patent disclosures were made in 1940. In the one⁽²⁶⁶⁾, issued to the du Pont Company, a water-soluble levulinic acid addition product of ethanolamine is described as a softener for a flexible, durable water-sensitive cellulosic structure. In the other⁽²⁶⁷⁾, an

artificial heat-setting resin is patented, obtained by fusing an organic amine and levulinic acid.

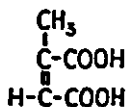
Within the last few years, a number of additional applications of levulinic acid as an ingredient of a plasticizer or plastic composition have been patented. The Dow Chemical Company disclosed in a patent in 1944⁽²⁶⁸⁾, the use of levulinic acid for the esterification of a bisphenol to form 2, 2-bis (4-β-levulinylloxyethoxyphenyl) propane which it is claimed is a very effective plasticizer for thermoplastic resins.

In 1946, Bruson⁽²⁶⁹⁾ patented the reaction of dicyclopentadiene with levulinic acid under acid conditions to yield the levulinate of hydroxydihydronordicyclopentadiene. It was stated that this ester is useful as a plasticizer for synthetic resins and natural and synthetic rubber.

The Wingfoot Corporation recently⁽²⁷⁰⁾ patented the copolymerization of a compound such as dichloroallyl levulinate with a conjugated butadiene to form a plastic mass.

Two other patents utilizing levulinic acid as an ingredient of a plasticizer were published in 1946. In one, the Commercial Solvents Corporation⁽²⁷¹⁾ disclosed its use in a special reaction. An alkyl levulinate is treated with 2-nitro-1,3-propanediol in the presence of an acid catalyst to form a cyclic ketal. The process is applicable only to the 2-nitro-1,3-propanediols. Other hydroxyl containing compounds do not react, or produce complex mixtures. The products are useful as plasticizers, particularly for the vinyl chloride polymers. In the other, the Pittsburgh Plate Glass Company⁽²⁷²⁾ has patented the use of methyl levulinate as a plasticizer for a styrene-maleic anhydride resin. It is stated that methyl levulinate is of outstanding merit for this purpose. By the addition of approximately 30 per cent methyl levulinate by weight, the resin, under appropriate conditions, sets to a transparent, hard, bubble-free, and well-plasticized solid, which is not subject to warping and cracking and which retains its properties well upon aging.

CITRACONIC ACID



The application of citraconic acid to the plastics industry has

been reported in relatively few instances. Its preparation from citric acid⁽²⁷³⁾ is accompanied by the formation of itaconic acid, which can be used in most cases to replace citraconic acid. Itaconic acid should become more readily available and less expensive than citraconic acid as the result of a new method of formation reported in 1944⁽²⁷⁴⁾.

A patent disclosure⁽²⁷⁵⁾ regarding the formation of citraconic and itaconic acids from citric acid was made in 1939. In it, concentrated aqueous solutions of citric acid are distilled under vacuum at 230°C., or over, to give a mixture of citraconic and itaconic acids or anhydrides.

In 1934, E. I. du Pont de Nemours and Company patented⁽²⁷⁶⁾ a process for the polymerization of esters of citraconic acid, which polymers could be combined with conjointly polymerized vinyl esters or styrene. The resultant plastics could be used as coating compounds to give clear films.

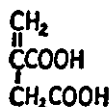
Carleton Ellis patented⁽²⁷⁷⁾ a process for the formation of a citraconic acid plastic in 1940. He formed an insoluble, infusible, resinous composition, suitable for castings or coatings, by treating citraconic acid with a glycol, heating the reaction mixture to an advanced stage of esterification at which substantially no further water can be eliminated, adding a polymerizing catalyst, such as benzoyl peroxide, and subjecting the resulting mixture to polymerizing conditions (suitably by heating at 100°C.) in the presence of air.

A patent was granted to the Standard Oil Development Company⁽²⁷⁸⁾ in 1945 covering the formation of a thermoplastic material from the reaction of citraconic anhydride with an olefin of the isobutenyl type such as dimethallylether, methallyl chloride, and acetate, diisobutenyl, or 2-methyl-1-heptene. The resins were claimed to be useful in impregnating fabrics and in molding compositions. Their resistance to heat and solvents should make them of use for electrical insulation, containers, ducts, and packing materials.

The Monsanto Chemical Company revealed the application of citraconic anhydride for the formation of a resin by condensation of it with rosin or terpinene, in a patent⁽²⁷⁹⁾ issued in 1945. The resins were formed by heating with water containing an alkali carbonate in an autoclave at 150-160°C. to yield an approximately half neutralized water-dispersible polymer useful for the sizing of paper pulp.

An alkyd resin formed by the esterification of citraconic acid with 2-(hydroxymethyl)-1-propen-3-ol was claimed to have novel properties by the Shell Development Company, in a patent obtained in February, 1948. The reaction proceeded in the usual three stages through the formation of a fusible, soluble resin, a fusible, insoluble resin, and finally an infusible, insoluble resin. It was stated that these polymers are suitable for the preparation of varnishes, baking enamels, adhesives, films, and floor coverings.

ITACONIC ACID



Kinoshita⁽²⁸⁰⁾, in 1931, reported a new species of *Aspergillus* mold, *A. itaconicus*, which produces very large amounts of itaconic acid on media containing potassium nitrate, as the nitrogen source, and 25 per cent of sucrose. Raistrick and co-workers⁽²⁸¹⁾ were also able to obtain itaconic acid using a strain of *A. terreus* Thom on an ordinary 5 per cent glucose medium in yields of as high as 11.8 per cent.

In September of 1944, Moyer, Lockwood, and Ward of the Northern Regional Research Laboratory of the United States Department of Agriculture described⁽²⁸²⁾ a relatively low cost method of producing itaconic acid. The process is an improvement of the mold fermentation, using *A. terreus*, previously reported by Raistrick and co-workers. The mold is seeded onto the surface of a 20 per cent sugar solution containing other necessary nutrients. It grows as a thick brown mat on the surface of the solution, which is kept in large shallow pans, and in the course of ten or twelve days produces one pound of recoverable itaconic acid for each four pounds of sugar used.

It can be produced by the new method at a raw material cost of approximately 22 cents a pound⁽²⁸³⁾. Further work concerning the factors affecting the production of itaconic acid by *A. terreus* in agitated cultures was reported⁽²⁸⁴⁾ from the same laboratory in 1946. Optimum conditions were developed for the pH of the solution and for the concentrations of its various constituents.

In 1945, Charles Pfizer and Company patented⁽²⁸⁵⁾ a fermentation process for the production of itaconic acid by *A. terreus*. Submerged

aerobic growth in a carbohydrate nutrient-containing medium was accomplished by suitable mechanical agitation with air or a mixture of air and oxygen-containing gases.

A large number of patents obtained in recent years by the General Electric Company indicate that itaconic acid may be useful in strengthening methacrylate-type resins. Prior to 1942, however, but little attention had been given it by the plastics industry.

In a British patent⁽²⁸⁶⁾, granted in 1925, dialkyl esters, or other suitable esters of itaconic acid, are heated to effect polymerization and obtain vitreous masses. Acids facilitate, and lime, piperidine, or other bases retard the reaction. The material may be molded previous to the completion of the final polymerization and hardening.

An article⁽²⁸⁷⁾ published in Germany in 1939 gives a description of an early attempt to use an artificial resin made of polymerized itaconic acid ester for the manufacture of an ornament.

Itaconic acid is mentioned as an alternate compound by Carleton Ellis in the patent⁽²⁷⁷⁾ described in the previous section under citraconic acid.

Several workers in the laboratories of the B. F. Goodrich Company published an article⁽²⁸⁸⁾ in 1941 in which polyethylene itaconate, an unsaturated polyester, is described as a typical polyester with recurring polymerizable groups. Polyethylene itaconate was prepared by esterification of equal molar proportions of ethylene glycol and itaconic acid. It was a viscous sirup which did not polymerize readily in bulk, even in the presence of benzoyl peroxide. A thin film, however, hardened in four days at room temperature to a tough, insoluble abrasion-resistant varnish. A number of the materials prepared in the course of these experiments seem to offer attractive possibilities for commercial development, especially in the paint and plastics industries. The liquid ester made from ethylene glycol and itaconic acid is the type of polyester which seems adaptable as a drying oil, and suggests interesting possibilities in this field.

A granulating agent for use in preparing synthetic resins from polymerizable esters of acrylic, methacrylic or itaconic acids was patented⁽²⁸⁹⁾ in 1942. It consists of a water-soluble salt, prepared by subjecting to alkaline hydrolysis polymerized alkyl esters of, among others, itaconic, citraconic, or aconitic acids.

In a series of eight patents⁽²⁹⁰⁻²⁹⁷⁾ issued to the General Electric Company during 1942 and 1943, G. F. D'Alelio has described the application of various esters of itaconic acid as copolymers with methacrylic esters and other polymerizable substances. In the initial

patent, the interpolymerization of di-sec-butyl itaconate and ethyl methacrylate is outlined. These compounds are polymerized by heating the mixture to about 70°C. for one to three days with 1 per cent of benzoyl peroxide in the proportion of 5 and 95 parts of the respective starting components. The resultant product is said to be suitable for molding and of higher flexural strength and impact than that of ethyl methacrylate when similarly polymerized alone. In six of the other patents, different esters of itaconic acid are likewise polymerized with ethyl methacrylate. These include bis (methoxyethyl), dihexyl, dibenzyl, bis-(isobutylcarbinol), and diallyl itaconates. In another patent⁽²⁹⁷⁾, entitled "Synthetic Rubberlike Compositions," a polyvinyl halide or polyvinylidene halide is used, together with an itaconic diester, such as dibenzyl or di-(phenoxyethyl) itaconate, in preparing a product suitable for use as an electrical insulation of cables.

Since 1943, D'Alelio has been granted four further patents. One⁽²⁹⁸⁾, in 1945, was for the copolymerization of acrylonitrile with various esters of itaconic acid. It was claimed that these copolymers could be formed into filaments, films, or tubes by extrusion or precipitation methods, and that they could be cold-drawn to yield crystalline bodies of high strength and flexibility. Another⁽²⁹⁹⁾, in the same year was granted for the copolymerization of vinyl chloride with a diester of itaconic acid in the proportion of more than 90 per cent of the chloride and less than 10 per cent of the ester. These copolymers had greater flexural and impact strengths than those of polyvinyl chloride. A third patent⁽³⁰⁰⁾ was issued in 1947 for the copolymerization of divinyl benzene and a monohydric alcohol ester of itaconic acid to form a soluble, fusible, heat-convertible polymer. Practically any monohydric alcohol can be used to form the ester, but the use of two unsaturated ester groups gave an uncontrollable reaction. The fourth patent⁽³⁰¹⁾ related to similar copolymers made from di-allyl maleate and saturated monohydric alcohol esters of maleic or fumaric acid.

The Wingfoot Corporation has utilized itaconic acid as a possible component of a polymeric substance in two patents, one⁽³⁰²⁾ issued in 1945, and the other⁽³⁰³⁾ in 1946. In the first, alicyclic keto esters of itaconic acid were prepared by the reaction of a metal salt of the acid and a halo-substituted ketone, thus splitting off a metal halide. The halo-substituted ketone may be 2-chlorocyclohexanone, cyclopentanone, chlorocamphor, and other substituted and unsubsti-

tuted alicyclic compounds. In the other, rubberlike masses were produced by copolymerizing butadiene and methyl itaconate.

A patent⁽³⁰⁴⁾ was granted to the Pittsburgh Plate Glass Company in 1946, covering the formation of an ester by the condensation of diethylene glycol and di-ethyl itaconate, followed by polymerization. It was claimed that a composition was formed which could be used to prepare transparent articles, as an impregnating agent or adhesive in the preparation of laminated cloth articles, or as a coating.

The British Thomson-Houston Company have patented⁽³⁰⁵⁾ the copolymerization of vinyl chloride with an ester of itaconic acid in the presence of a catalyst, such as benzoyl peroxide. It is claimed that such resins have a superior flexural and impact strength.

An interesting study⁽³⁰⁶⁾ of the mechanism of the emulsion copolymerization of styrene and itaconic acid was recently published. The results of this investigation strengthened the hypothesis that in emulsion copolymerizations the initial polymerization proceeds within the oil droplet or at its interface.

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