Styrene and Metastyrene

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The position of styrene polymers in the resin field is pointed out.

An improved method for the manufacture of ethylbenzene from ethylene and benzene is submitted. The conversion of ethylbenzene into styrene by the chlorination and elimination of hydrochloric acid is suggested. A new catalyst for accelerating the rate of polymerization of styrene in solution to give a soft polymer, α-m-styrene, is used.

THE relatively new and important styrene resin may be classified with the vinyl resins since it is a polymer of vinylbenzene. This product ranks high in molding property, for the polymer of styrene may be obtained ranging from a soft tacky material to a harder, nontacky, putty-like mass, and finally to a firm, transparent, colorless resin which is not brittle and can be machined easily. It ranks high in insulating property because of its hydrocarbon structure. A simple and low-cost method for making styrene would immediately increase the scope of use of this valuable plastic.

METHODS OF PREPARATION

For laboratory purposes styrene is most easily obtained by the dry distillation of cinnamic acid and its salts under atmospheric pressure. The use of this method of preparation on a commercial scale is prohibitive, because of the high cost involved in the preparation of cinnamic acid and the relatively poor yield obtained (*8–11, 20, 26, 30*).

The direct condensation of acetylene with benzene by means of aluminum chloride would be useful except for the fact that too high a percentage of by-products and tars are formed (*27, 34*).

The dehydration of methylphenylcarbinol gives styrene in good yield. The starting alcohol is not cheaply obtained, however (*1, 14, 17*).

Commercially styrene may be prepared from ethylbenzene by the removal of two hydrogens on the side chain. This may be accomplished either by passing the vapors of ethylbenzene through a hot tube or by first chlorinating and then splitting out hydrochloric acid. The first method has been investigated by Ostromislensky and others (*15, 23, 24*). The ethylbenzene is allowed to pass slowly through an iron tube, with or without catalysts, at about 600° C., washing through with carbon dioxide to keep the liquid moving and to prevent unnecessary polymerization and side reactions. Xylenes may be substituted for ethyl benzene:

$$C_6H_4(CH_3)_2 \xrightarrow{\text{Rearrangement}} C_6H_5CH_2CH_3 \longrightarrow C_6H_5CH{:}CH_2 + H_2$$

The above method has several disadvantages which hinder its use: (1) The conversion is in the neighborhood of 20 per cent. If one takes into consideration the recovered ethylbenzene, the yield is in the neighborhood of 30 per cent. (2) The styrene obtained is partially polymerized and mixed with dark colored decomposition products which reduce the amount of pure unpolymerized styrene obtained, as checked by the author, to less than the reported yield. Dehydrogenators such as sulfur have been suggested and applied, and a small increase in the percentage yield is claimed (*31*).

A method giving better yields, using ethylbenzene as the starting material and avoiding polymerization prematurely, goes through the following series of reactions. The ethylbenzene is first chlorinated (*5, 6, 16, 29, 32*):

$$C_6H_5CH_2CH_3 + Cl \longrightarrow C_6H_5CHClCH_3 + HCl$$

and hydrochloric acid is then split out by means of some suitable agent or by heat alone (*5, 16, 17, 23, 32*):

$$C_6H_5CHClCH_3 \longrightarrow C_6H_5CH{:}CH_2 + HCl$$

The styrene obtained is then polymerized by heat and pressure with or without the aid of a catalyst.

One of the major difficulties encountered in the above process is that pure ethylbenzene is not easily obtained by the usual methods, without at the same time forming large amounts of di-, tri-, and higher polyethylbenzenes. The condensation of ethylene or ethyl chloride with benzene by means of aluminum chloride yields large amounts of diethylbenzene and other polyethylbenzenes even when two to three times the calculated amount of benzene is employed. This has given rise to methods for transforming the polyethylbenzenes formed to monoethylbenzene. The polyethylbenzene is heated with aluminum chloride, or the catalyst formed in the ethylating reaction below, with an excess of fresh benzene (*28*):

$$C_6H_{6-x}(C_2H_5)_x + (x-1)C_6H_6 \longrightarrow xC_6H_5C_2H_5$$

Substituted styrenes, in connection with simple styrene, are used in manufacturing the resin. The diethylbenzene is chlorinated and hydrochloric acid is split out forming either a divinyl- or vinylethyl benzene. Ethyltolylbenzene, *p*-chloroethylbenzene, and other substituted ethylbenzenes are employed, giving rise to vinyl-substituted benzenes.

The problems which presented themselves were therefore as follows:

1. A method for making ethylbenzene from ethylene and benzene in good yield, in a rapid process, without the formation of large amounts of the polyethylbenzenes, and without the use of too high an excess of benzene.
2. A method for chlorinating ethylbenzene, with the formation of α-chloroethylbenzene in high yield, avoiding the formation of *p*-chloroethylbenzene or α,α-dichloroethylbenzene.
3. A method for the elimination of hydrochloric acid from the α-chloroethylbenzene without the use of expensive material or complicated methods, to give a colorless styrene.
4. A method for the rapid polymerization of styrene into a plastic polymer, avoiding the brittle polymer.

DISCUSSION OF METHOD EMPLOYED

In the manufacture of ethylbenzene, the condensation of ethylchloride with benzene by means of aluminum chloride was first tried (*7, 33*). Although twice the calculated amount of benzene was employed, the ratio of ethylbenzene to polyethylbenzenes formed was 280 to 175 grams. In addition to the above objection this method uses ethyl chloride, which can be made from ethyl alcohol, but incurs difficulty when prepared by the addition of hydrochloric acid to ethylene, special high-pressure apparatus being necessary (*4, 34*). The method next tried was one which had been studied by Balsohn (*3*). Ethylene was condensed directly with benzene, using aluminum chloride as the catalyst:

$$CH_2{:}CH_2 + C_6H_6 \longrightarrow C_2H_5C_6H_5$$

Balsohn reports that, on bubbling ethylene through benzene over aluminum chloride for several days, he obtained a mixture of ethylbenzene, diethylbenzene, and triethylbenzene in the ratio of 170–135 grams to 75 grams, respectively.

The author observed that, on passing ethylene through 1000 grams of benzene over 150 grams of aluminum chloride at 75° C., 20 hours were necessary for the absorption of 260 grams of ethylene, obtaining ethyl-, diethyl-, and triethylbenzene in the ratio of 400–225 grams to 85 grams, respectively. This method has the advantage of starting with ethylene directly but has the disadvantage of absorbing the ethylene too slowly, giving at the same time too high a yield of the polyethylbenzenes.

It is apparent from a careful study of this reaction that the condensation between ethyl chloride or ethylene with benzene is slower than the condensation of ethylene or ethyl chloride with ethylbenzene.

A method had to be found which would be more rapid and at the same time give none or very little of the polysubstituted compounds. It was observed that the first 5 hours were spent in transforming the powdery aluminum chloride into a heavy black liquid which formed a heavy oily layer at the bottom of benzene. As soon as this layer was formed, absorption was observable by the fact that the ethylene bubbles did not leave the liquid but were absorbed, the reaction being exothermic. This same oil was formed in a few minutes in the reaction between ethyl chloride and benzene. It was therefore deemed necessary to form this catalyst before the reaction would proceed with any speed. This was done by bubbling hydrochloric acid in with the first portions of ethylene. By this procedure the catalyst was formed completely in 40 minutes. Ethylene was then bubbled in alone. The reaction time was reduced to 12 hours, by this innovation, for the absorption of 200 grams of ethylene. However, the percentage of ethylbenzene over polyethylbenzenes was not increased.

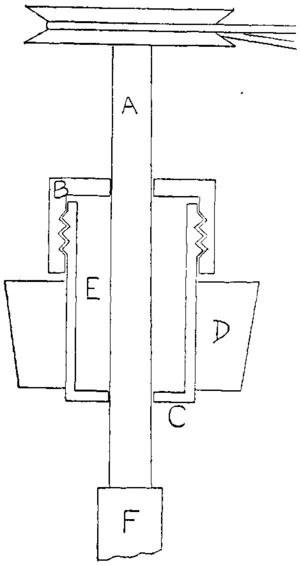

Figure 1. Arrangement for Preventing Leakage

A. Brass rod
B. Screw cap
C. Brass cup
D. Rubber stopper
E. Asbestos-graphite mixture
F. Rubber tubing to glass rod

It was observed that the catalyst remained at the bottom of the liquid except for the inefficient stirring brought about by the inflow of ethylene. Milligan and Reid (*21*) and Huber and Reid (*12*) have carefully studied the rapid increase of the speed of this reaction with efficiency in stirring. This is probably due to the dispersion of the catalyst through the reaction mixture. From the results these investigators report, it appears that stirring reduces at the same time the rate of formation of the polyethylbenzenes. This should follow from the constant removal of the ethylbenzene formed from the immediate sphere of action and should lower the chances of a second ethylation. Moreover, since the reaction was merely a direct addition of ethylene to benzene, with decrease in volume, it was obvious that pressure should favor the formation of the substituted benzene. The reaction being exothermic, too high a temperature was avoided, a temperature ranging between 70° and 75° C. being maintained. By these improvements the reaction time was reduced to 6 hours for the absorption of 200 grams; at the same time the yield of polyethylbenzenes was decreased, the yield of ethylbenzene being increased correspondingly. The pressure employed was equivalent to approximately 6 cm. of mercury. It is probable that greater pressures would have increased the speed of the reaction further.

The chlorination of ethylbenzene was attempted under various conditions of concentration of chlorine and of temperature, with or without the application of sunlight or bright artificial light. For the best results chlorination was carried out until about 60 per cent of the calculated amount of chlorine necessary was absorbed. Further chlorination of the ethylbenzene was much slower, the yield decreasing and the chlorine finding its way into the nucleus and attacking the carbon already chlorinated.

The elimination of hydrochloric acid from α-chloroethylbenzene has been the subject of numerous studies (*5*, *16*, *17*, *23*, *32*). The addition of equivalent quantities of tertiary bases and then decomposition of the quaternary salt formed is the most efficient but not the cheapest method for elimination of hydrochloric acid as pointed out by Klages and Keil (*18*) and Dorough (*5*). Catalysts, such as salts of aliphatic and aromatic bases, pyridine hydrochloride, aniline hydrochloride, dimethylaniline hydrochloride, trimethylamine hydrochloride, etc., have been suggested and give fairly good yields on either refluxing or distilling off the styrene as it forms. The α-chloroethylbenzene, floated on phosphoric acid, distills off styrene when heated. Sulfuric acid decomposes α-chloroethylbenzene to give a soft polymer of styrene. Inorganic salts, such as mercurous chloride, mercuric chloride, zinc chloride, mercuric oxide, mercuric sulfate, mercuric acetate, etc., will remove the hydrochloric acid from the chlorinated ethylbenzene to give styrene.

On heating the chlorinated ethylbenzene with 0.1 per cent of mercurous chloride in order to catalyze the elimination of hydrochloric acid, it was observed that invariably a relatively large amount of dark colored material was left in the distilling flask which would not come over at the boiling point of styrene and which would not steam-distill. It was also observed that the yield of styrene was never over 60 per cent on the basis of the chlorine absorbed. This is probably due to side reactions initiated by the mercurous chloride, coupled with the partial polymerization of styrene as it is rapidly formed. Dropping the chlorinated benzene into a decomposition chamber on the catalyst as rapidly as the styrene distills off, increased the yield to exactly 60 per cent.

Other catalysts were used in an attempt to increase the yield of styrene. Although none was found to do this to any extent, mercury-silver and mercury-copper couples were found to be more efficient but slower in action than the mercurous chloride. The yield of styrene rose to 65 per cent with the mercury-silver couple, the amount of residue decreasing.

The polymerization of pure styrene to a tough, nonbrittle polymer is easily accomplished. It is necessary only to heat the styrene in a sealed tube for approximately 8 to 10 hours when the styrene forms the desirable, so-called α-*m*-styrene. Heating in an open container gives the amber colored brittle modification. However, in cases where the styrene is dissolved in a solvent such as ethylbenzene, the time of polymerization increases up to 100 hours in a 40 per cent dilution.

Since the styrene, as obtained by the processes usually employed, contains varying amounts of ethylbenzene, a method or catalyst had to be found which would polymerize the styrene in solution. Among those suggested are: refluxing for long periods of time (*25*); using peroxides such as ozone (*19*); using benzoyl peroxide in hydrocarbon solution or hydrogen peroxide in aqueous emulsions (*13*); refluxing over alkalies or alkaline salts such as sodium hydroxide and potassium orthophosphate.

It was observed that heating with an excess of air invariably darkens the solution to an amber and eventually to a dark brown color. In the absence of air the resin remains transparent and colorless. From a survey of the literature, a catalyst most suited for the polymerization of this product should be a peroxide which would be soluble in ethylbenzene. Benzoyl peroxide fits this role and has been widely used.

A more efficient and cheaper polymerizing agent employed by the author is what might be called nascent benzoyl hydrogen peroxide. In order to avoid an expensive and involved method for the preparation of this compound, the fact that benzaldehyde forms this catalyst in its autoxidation was utilized. Benzaldehyde and an equivalent weight of oxygen were therefore used as the catalyst:

$$C_6H_5CHO + O_2 \longrightarrow C_6H_5COOOH \quad (2)$$

In a solution containing 45 per cent of styrene in ethylbenzene, polymerization was complete in 12 hours at 175° C. using 2 per cent of the catalyst.

Although considerable progress has been made in the last seven years in styrene chemistry, there is still a need felt for a method which would produce this resin as cheaply as the starting materials (benzene and ethylene or acetylene) warrant.

Preparation of Ethylbenzene

From Ethyl Chloride. One thousand grams of benzene were placed in a three-necked, 3-liter flask fitted with an efficient reflux condenser, thermometer, and inlet tube extending to the bottom of the flask. One hundred grams of aluminum chloride were added. To this mixture, by means of a closed dropping funnel, were added 50 grams of ethyl chloride. The temperature of the mixture was raised to 40° C. by means of a water bath, when a violent elimination of hydrochloric acid ensued. Slowly, over a period of one hour, by means of the closed dropping funnel were added 325 grams of ethyl chloride for a total of 375 grams. The ethyl chloride was previously cooled in an ice bath and added in small portions from a 50-cc. dropping funnel. After complete addition the temperature of the water bath was raised to 80° C. Heating was continued until all the hydrochloric acid had been given off. The total reaction time was about 2 hours. A heavy oil forms at the bottom of the reaction mixture as soon as the first portions of ethyl chloride have reacted.

The whole mixture was then poured into crushed ice, the lower layer reacting vigorously with water. If the reaction is to be repeated, the upper layer may be removed and fresh benzene and ethyl chloride added to the lower layer. The light yellow mixture obtained was then fractionated with a 2.5-foot (76.2-cm.) bulbed fractionating column, when a clear-cut separation of the products was obtained on one fractionation. The fraction boiling from 130° to 140° C. was collected as ethylbenzene. On refractionation 285 grams of a product boiling from 133° to 137° C. were obtained. The following table shows the yield of the various ethylated benzenes:

	Yield *Grams*	Boiling Point *° C.*
Ethylbenzene	285	133–37
Diethylbenzene	125	175–85
Triethylbenzene	35	210–20
Residue	15	....

The dark colored residue crystallized partially on standing, and consists, probably, of the higher alkylated benzenes; 610 grams of benzene were recovered.

From Ethylene without Stirring or Pressure. One thousand grams of benzene were placed in a 3-liter, three-necked flask, fitted with a reflux condenser and thermometer. A tube was led from the upper end of the condenser to a window because of the combustible ethylene. One hundred and fifty grams of aluminum chloride were added and hydrochloric acid was passed in until an increase in weight of 10 grams was noted. The hydrochloric acid generator was disconnected and a tank of ethylene was attached, using a mineral-oil bubble counter to help in adjusting the flow of ethylene. Sulfuric acid on sodium chloride (drying with calcium chloride) was used as the hydrochloric acid generator. The temperature of the mixture was raised until it reached 75° C. The powdered aluminum chloride became first yellowish and then dark red, forming a heavy oil which remained at the bottom of the liquid after 40 minutes. Absorption was then observable, for the large bubbles of ethylene entering the liquid at the bottom of the flask were seen to rise and grow smaller, disappearing eventually before they came to the top of the liquid. An increase in temperature did not increase the rate of absorption, the ethylene bubbling right through the liquid without being absorbed. The optimum temperature for the reaction appeared to be between 70° and 75° C. Little heat was applied, for the heat of reaction was almost sufficient to keep the temperature within the desired range. The ethylene was added at a rate such that any increase would cause large amounts of ethylene to leave the liquid unabsorbed. The addition was continued for 12 to 14 hours, when a 200-gram increase in weight was observed. The reaction mixture was poured into water and then fractionated as above:

	Yield *Grams*	Boiling Point *° C.*
Ethylbenzene	321	133–37
Diethylbenzene	173	175–85
Triethylbenzene	44	210–20
Residue	21	....

590 grams of benzene were recovered.

Under Pressure with Stirring. One thousand grams of benzene were placed in a 3-liter, three-necked flask fitted with a reflux condenser and an efficient stirring device, and 150 grams of aluminum chloride were added. The mechanical stirrer was started, and ethylene and hydrochloric acid were led in simultaneously below the level of the liquid for 10 to 15 minutes, when the powdered aluminum chloride was transformed completely into a light pinkish, heavy oil. The reflux condenser was replaced by a thermometer, and the inlet tube was lifted out of the liquid and attached to the source of ethylene which delivered the ethylene under a head of 3 feet (91.4 cm.) of water. Two 5-gallon (18.9-liter) jars were placed so that there was a difference of 3 feet in their elevation. A three-hole rubber stopper was placed in the lower jar and a two-hole rubber stopper in the upper. A glass tube was led from the bottom of the lower jar through the two stoppers to the bottom of the upper jar. The second opening of the upper jar was left open to the atmosphere. Through a second opening in the lower jar was passed the ethylene directly from the tank by means of a glass tube. The third opening in the lower jar led to the three-necked ethylating flask after having passed through a safety flask, calcium chloride, a mineral-oil bubble counter, and a second safety flask. The opening leading to the ethylating flask was closed by means of a clamp, and ethylene was led into the lower jar, forcing the water up into the upper jar which was fitted with a two-hole rubber stopper to allow an opening to the atmosphere. The clamp leading to the ethylating flask was then opened, supplying from the tank, at the same time, the lower jar at such a rate as to keep it three-fourths full of ethylene at all times. During the addition it was necessary to lift the rubber stopper of the thermometer twice to allow nonreactive gases which accumulate to be swept out (air, etc.). The reaction mixture was kept between 60° and 70° C. by means of a water bath. The heat of reaction was almost sufficient to keep the mixture at that temperature. In order to prevent leakage through the stirring apparatus, a 3-inch (7.6-cm.) mercury seal may be used; however, a simpler method is shown in Figure 1.

The brass cup is overfilled, packing down tight, with an asbestos fiber–graphite mixture, and the cover is screwed down tight to force the graphite against the brass rotating rod in order both to seal and lubricate. This arrangement can withstand relatively high pressures if carefully made.

For an increase in weight of 190 grams, from 6 to 8 hours were necessary. The same catalyst may be used for two runs. In order to reactivate it for the third run, 2 grams of aluminum foil may be added before the addition of the hydrochloric acid–ethylene mixture, when the aluminum dissolves, bringing back the volume of the catalyst to what it was before the first run (*22*). The reaction mixture obtained was poured into water and fractionated:

	Yield *Grams*	Boiling Point ° *C.*
Ethylbenzene	430	133–37
Diethylbenzene	97	175–85
Triethylbenzene	29	210–20
Residue	14	....

420 grams of benzene were recovered.

Chlorination of Ethylbenzene

Method A. One thousand grams of ethylbenzene were placed in a 3-liter, three-necked flask which was fitted with a thermometer and a reflux condenser leading by means of a tube to an open window. Chlorine, passed directly from a tank and dried with calcium chloride, was passed in below the level of the ethylbenzene, keeping the temperature of the mixture at 100° to 110° C. by means of a small flame which was assisted by the heat of the reaction. Two and a half hours were necessary for an increase in weight of 200 grams. The mixture was then fractionated in vacuum, collecting the fraction between 87° and 93° C. at 20 mm.; 672 grams of α-chloroethylbenzene were obtained. This is an 85 per cent yield on the basis of the chlorine employed.

Method B. Chlorine was bubbled into 1000 grams of ethylbenzene using the apparatus as above. The rays of a General Electric Sunlamp S-1 were directed at the solution, no effort being made either to cool or heat the solution. Absorption was slow, taking from 6 to 7 hours for an increase in weight of 200 grams. The increase in weight was noted after the lamp had caused to react any dissolved residual chlorine, the solution becoming colorless. The product was distilled in vacuum, collecting the fraction as above; 679 grams of α-chloroethylbenzene were obtained for an 86 per cent yield.

Method C. One thousand grams of ethylbenzene were chlorinated as above, except that the flask was placed in bright sunlight, keeping the temperature between 10° and 15° C. by means of an ice bath, until an increase in weight of 200 grams had taken place, the solution being colorless. On fractionation as above, 670 grams of α-chloroethylbenzene were obtained for an 84 per cent yield on the basis of the chlorine absorbed.

Elimination of Hydrochloric Acid to Form Styrene

One thousand grams of ethylbenzene were chlorinated as in method A and were transferred directly to a distilling flask. To this mixture was added 4 grams of silver foil which had been rubbed in mercury until it had absorbed one gram of mercury. The mixture was then slowly heated so that the vapors came off below 155° C. Large amounts of hydrochloric acid were evolved, and these were drawn off with mild suction from the receiving flask. When half the liquid had gone over, the flame was raised so that the liquid distilled over up to 165° C. After no more liquid would distill over, the distillate (765 grams) was washed with water and then 5 per cent sodium hydroxide solution until it was neutral to litmus. It was then washed with water and dried over anhydrous potassium carbonate. The ethylbenzene was then distilled off in a one-foot (30.5-cm.) fractionating column, distilling off everything which came over up to 140° C. The remainder was distilled in vacuum, collecting the fraction which distilled from 40° to 45° C. at 35 mm. This was redistilled in vacuum, collecting the fraction which distilled from 41° to 44° C. at 35 mm.; 204 grams of styrene were obtained and 79 grams of styrene polymer were left in the distilling flask. This does not represent the total amount of styrene obtained, for an appreciable amount comes over with the ethylbenzene; 140 grams of residue were left in the flask with the catalyst which would not steam-distill. If one gram of mercurous chloride was used in place of the silver-mercury amalgam, 155 grams of residue were obtained and 750 grams of distillate after washing free from hydrochloric acid.

Polymerization of the Styrene in Solution

The liquid obtained directly after the decomposition with the silver-mercury amalgam or mercurous chloride was placed in an autoclave. Oxygen was bubbled in until an increase in weight of 0.6 gram was observed for every 100 grams of liquid. Two grams of benzaldehyde for every 100 grams were added. The autoclave was then heated to 150° C. and kept there for 12 to 18 hours. The pressure developed as noted on the gage was between 10 and 15 pounds. The autoclave was then allowed to cool to room temperature, and the liquid was steam-distilled. The residue in the steam-distilling flask was taken up in carbon tetrachloride and dried over anhydrous potassium carbonate. The carbon tetrachloride was evaporated at 50 mm. on a water bath. The *m*-styrene obtained was a relatively soft, clear, transparent, and almost colorless resin which could be hardened to the desired degree by heat and pressure. Heating at 200° C. in air for one hour converted it quantitatively into the amber, brittle polymer (yield, 340 to 379 grams) for the total amount of *m*-styrene obtained from the chlorination of 1000 grams of ethylbenzene to an increase in weight of 200 grams.

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Purification and Acidification of Polysaccharide Solutions by Electricity

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An apparatus suitable for the acidification and purification of polysaccharide solutions on a semi-commercial scale by means of electrodialysis and the experimental procedure involved in its use are described. The interrelationships between the current density, concentration of the solutions, rate of flow of the solutions through the process, percentage of ash removed from the solutions, and the final pH produced in them have been studied and reported. The cost of the current consumed, the dilution produced, and the amount of colloidal material coagulated are also given. The effect of the permeability of the diaphragms used upon the efficiency of the process is studied.

IN THE preparation of a palatable sirup from polysaccharide-containing products such as Jerusalem artichokes, dahlias, chicory, corn, etc., two problems are of considerable importance: (1) the conversion of the polysaccharides to simple sugars and (2) the removal of undesirable nonsugar material naturally occurring in the plant. The first has usually been accomplished by one of two methods: (1) the addition of an inorganic acid or of the salt of such an acid and a weak base which would give the required pH, the undesirable ions being later precipitated from the solution, or (2) by the addition of an acid which was later neutralized to give a soluble salt which would not impair the taste of the finished sirup. The first method offers the difficulty that few, if any, salts are completely insoluble in a sugar solution which is suitable for filtration, more precipitate being formed in the final concentration of the sirup. A difficulty encountered in the second method is that the number of soluble salts that will not impair the taste of the finished sirup is definitely limited; even a small amount of sodium chloride, the commonest example, is undesirable for certain uses of the sirup. The removal of undesirable nonsugar material naturally occurring in the plant is usually accomplished by preliminary defecation of the juice by one of several methods, or by a preliminary precipitation and removal of the polysaccharide or sugar desired.

Since certain disadvantages and difficulties are inherent in all of these processes, it was considered desirable to study the purification and acidification of polysaccharide solutions by means of electricity without the addition of any chemicals. This laboratory has been interested for some time in the production of a palatable levulose sirup from the Jerusalem artichoke (*Helianthus tuberosus*) without preliminary precipitation and removal of the levulose from the extract obtained with a diffusion battery (*4*). The work reported in this paper was therefore carried out upon diffusion battery extracts from artichokes. Preliminary work, in which a three-compartment apparatus (two electrode compartments with a central juice compartment separated from them by suitable diaphragms) was used, was done by Heubaum[2] of this laboratory (*5*), and the results obtained were such that a study of the process on a semi-commercial scale seemed justified. It is the purpose of this paper to describe apparatus suitable for semi-commercial scale production, and to give the results of a study of the interrelationships between the current density, concentrations of the solutions, rate of flow of the solutions through the process, percentage of ash removed from the solutions, final pH produced, and cost of current consumed.

Apparatus

The apparatus used was an electroösmose outfit with six double electroösmose cells obtained from the Central Scientific Company for use with a 110-volt, direct current circuit. A photograph of the apparatus set up for use with only eight juice compartments is given in Figure 1; a sketch of the cells and wiring used is given in Figure 2:

Compartments *B* are those containing the juice under treatment. Compartments *C* are the cathode compartments, and *A* the anode compartments. The electrode compartments are filled with water and a slow stream of water is allowed to flow through them, coming in through the small funnels shown in Figure 1 and flowing out through the ducts, *D*, of Figure 2, into the trough as shown in Figure 1. The rate of flow of this wash water can be altered at will by means of screw plugs. The juice flows in series through all of the *B* compartments, which are connected with siphons, entering at one end and flowing out of the other end through an automatic siphon as shown. The capacity of the apparatus is about 8 liters of juice and about the same amount of water. The frames serving as walls for the compartments are of rubber, and the plates (*E* of Figure 2) separating the cells from each other are of hard rubber. The frames and plates can be compressed by means of the three screws shown in Figure 1 so that the whole apparatus is water-tight.

The cathodes are constructed of zinc plates 11 × 19 cm. and 3 mm. in thickness, and the anodes of especially prepared magnetite plates 10 × 20 cm. and 5 mm. in thickness. The distance between the electrodes is 3.5 cm. since each frame is 17 mm. thick.

The diaphragms used in separating the juice from the water in the adjoining electrode compartments are of 12-ounce (340.2-gram) Wamsutta canvas painted with a solution of para-gum in benzene. The solution was applied in successive coats just until no more sugar diffused through it when it served as a wall between a sugar solution and water for 4 hours. Diaphragms thus prepared have served for about 200 hours over a period of 2.5 months without any noticeable alteration in their properties. The area of diaphragm in contact with the juice during the run was about 2.75

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[2] U. S. and foreign patents applied for by Heubaum.