This invention relates to the manufacture of refined sugar solutions and refined sugar. It relates to the removal of color-bodies from sugar solutions—preferably from hot sugar solutions—by means of strongly basic quaternary ammonium anion-exchange resins in the salt form.

It is conventional, in the manufacture of refined sugar solutions such as syrups and of refined crystallized sugar, to treat sugar solutions after affination and clarification with a variety of sorbing materials such as bone-char or powdered coal or other forms of carbon in an effort to remove by absorption or adsorption the various extraneous materials which are present as impurities in the sucrose solutions. This is done because such impurities, including color-bodies, lower the quality of the syrups and reduce the quantity and/or quality of the sugar which can be crystallized from the solutions.

It has also been shown, for example in U. S. Patents 2,551,519, 2,578,937, 2,578,938 and 2,635,061, that various combinations of cation-exchange materials and quaternary ammonium anion-exchange resins in the hydroxyl form can be used in the treatment of sugar solutions.

An object of this invention is to provide a method of purifying sugar solutions which has commercial advantages over processes known heretofore. An object is to provide a method which produces a better quality of refined syrup and a greater yield of refined sugar and lower quantities of molasses. Still another object is to furnish a method whereby larger amounts of more concentrated sugar solutions can be decolorized in a given time than by older methods. A further object is to accomplish this without destroying the adsorbent or without using objectionably large amounts of adsorbents such as bone-char.

These objects and other objects which will become evident are accomplished by the process of this invention which comprises treating—preferably at elevated temperatures—a solution of sucrose which contains color-bodies with a quaternary ammonium anion-exchange resin and wash with water. The resin is then treated with aqueous solutions of sodium chloride and sodium hypochlorite which remove the color-bodies, replace the adsorbed anions with chloride ions, and restore the resin to its original condition. Rinsing with water—or preferably with a dilute solution of ammonium hydroxide—completes the cycle.

While the description above is that of the preferred embodiment it is evident from the following discussion that variations in the process can be made without departing from the spirit of the invention.

The process of this invention can be applied to any sugar solution however dark in color and it will effect a real reduction in color. It is more reasonable, however, to apply the process to sugar solutions which have been affinated and also clarified with lime and phosphates. At least seventy percent of the color can be removed from such a solution by a single rapid treatment with the resin. Since other adsorbents such as bone-char, activated charcoal and powdered carbon also remove substantial quantities of color-bodies—but not all—and since their use up to a point is economical it is also practical to use them first to remove the color-bodies which are not adsorbed by the quaternary ammonium anion-exchange resins and then to remove essentially all of the remaining color-bodies by adsorption on the quaternary ammonium ion-exchange resin. It appears that the ion-exchange resins have a specificity for the color-bodies which are least readily adsorbed by conventional adsorbents and therefore they can be used most advantageously to remove the final traces of color from sugar solutions which have been partially decolorized.

The ion-exchange resins which are employed are those which contain quaternary ammonium salt groups—preferably chloride groups—as their polar groups. They are cross-linked, and hence insoluble, resins in granular or preferably spheroidal form and they contain in their structure quaternary ammonium salt groups. The quaternary ammonium salt groups are the functional groups on which adsorption of the anions take place and the adsorption salt form of the color-bodies is also believed to take place. Such resins are well known and are available commercially. Suitable resins are those which are made, for example, according to the processes of U. S. Patents 2,591,573 and 2,614,099 by first forming an insoluble, cross-linked copolymer of a monovinyl hydrocarbon and a copolymerizable cross-linking agent such as divinylbenzene, then haloalkylating the copolymer whereby alkylene halide groups become joined to the insoluble copolymer and finally aminating the haloalkylated resin with a tertiary amine such as trimethylamine or dimethylamino ethanol. Other quaternary ammonium anion-exchange resins are made by the process of U. S. Patent 2,540,885. While quaternary ammonium resins are ordinarily sold in the basic or hydroxyl form they are readily converted to the salt form by treatment with a solution of an inorganic salt or mineral acid.

What is required here is an insoluble quaternary ammonium anion-exchange resin of the strongly basic type which is in the salt form. What is also desired is that the resin be as porous as possible. As is well known, the degree of porosity of such a resin is inversely proportional to the amount of cross-linking agent which is employed and accordingly it is recommended that the quaternary ammonium anion-exchange resin be as low cross-linked as is consistent with other required properties such as insolubility and degree of swellability. For example, in the case of the resin which is made by the processes of U. S. Patents 2,591,573 and 2,614,099, it is most desirable that the amount of copolymerized cross-linker be not over 4% and preferably from about 0.5% to at least 2% on a molar basis. Here again, resins of this kind are available commercially as “quaternary ammonium anion-exchange resins of the porose grade.”

When employed in this process of sugar refining the resin is in the salt form—preferably in the chloride form. It can also be used in the bromide form which is fully
equivalent to the chloride form as far as color removal is concerned; but in the use of the bromide form more expensive regenerants are required and bromide ions which under these conditions are introduced into the sugar solutions. The resin can also be in the sulfate form, but when such is the case sulfate ions are either introduced into the sugar solutions being treated, or those present are not removed and this is undesirable since sulfate salts are much more difficult to remove from cryo-syrups in the crystallizing and also cause turbidity in the syrups. The quaternary ammonium aminoxone-exchange resin in the chloride form not only absorbs color-bodies but also exchanges its chloride ions for sulfate ions. This is most advantageous because sugars of lower ash-content are obtained, presumably because chloride salts are not occluded so tenaciously by sugar crystals as are sulfate salts and can be far more readily removed. It is much preferred that the sugar solutions which are purified by this process be hot. When the process is operated at elevated temperatures, the volume of sucrose solution which can be treated with a given amount of resin in a given time is far greater than when low temperatures are employed. Also of real importance is the fact that more concentrated solutions can be purified. Syrups at a temperature within the range of 110° to 210° F. have been treated and decolorized very successfully, but it is preferred that the temperature of the solutions be from 140° to 190° F. to fulfill these conditions solutions having a concentration at least as high as about 70° Brix have been rapidly and efficiently purified. The process is especially efficient when applied to sugar solutions having a concentration of 40° to 70° Brix. Also under these conditions the resins described above are stable and retain their capacity on repeated use in hundreds of cycles in contrast with quaternary ammonium anion-exchange resins in the hydroxyl form which gradually decompose under the same conditions.

During the decolorization process the resin absorbs color-bodies and other anions and ultimately becomes exhausted. At this point it is freed of the sugar solution, is usually rinsed, and is then regenerated. Two kinds of regenerants are required to restore the resin to its original condition; namely a solution of a water-soluble salt or mineral acid and a solution of a mild oxidizing agent. While these two kinds of regenerants can be mixed in the same solution it is preferred that they be used separately. The first kind of regernent—which is ordinarily sodium chloride or sulfuric acid—replaces adsorbed anions but fails to remove all of the adsorbed color-bodies from the resin. The color-bodies are removed, however, by the mild oxidizing agent. After the treatment with the two kinds of regenerants the resin is in condition to treat and purify more sugar solution.

Sodium chloride solutions are much preferred as regenerants and these can be of any reasonable and convenient concentration. In practice it is preferred to employ solutions containing about 1% to 15% salt. Solutions of other water-soluble chlorides such as hydrochloric acid, potassium chloride, calcium chloride and magnesium chloride have been used but these have no advantage over solutions of sodium chloride. What is evident from this, however, is that a solution of sodium chloride brine which contains other water-soluble chlorides as impurities can be used if desired. Hot solutions of sodium chloride at 130° to about 200° F. are particularly efficient.

Because the water-soluble chloride regenerant alone does not remove all of the color-bodies and hence fails in itself to restore the resin to its full capacity, it is necessary to employ in addition a solution of a mild oxidizing agent such as a solution of a water-soluble hypohalite—particularly a hypochlorite—or a solution of hydrogen peroxide. Solutions of sodium hypochlorite are recommended although other hypohalites such as potassium hypochlorite, potassium hypobromite, sodium hypo-

bromite and calcium hypochlorite can likewise be used. Strong oxidizing agents including potassium permanganate, nitric acid and chromic acid have also been used; and while these are effective in removing the color-bodies they are less satisfactory than the hypochlorites or hydrogen peroxide because they tend to degrade the resins. Solutions containing up to 10% peroxide or 15% sodium hypochlorite have been used but the particular concentration employed is a matter of choice. Usually more dilute solutions are preferred.

Under those conditions where the quantities of color-bodies in the sugar solutions are high and the amounts which are adsorbed are also high in comparison with the amounts of other anions which are simultaneously adsorbed, it is suggested that regeneration with both salt and oxidizing agent be carried out each time the resin becomes exhausted. In such cases it appears best to treat the exhausted resin first with a hot solution containing about 1% to 10% of the mineral acid or salt thereof, then with a 0.25% to 5% solution of a hypochlorite or of hydrogen peroxide at room or ambient temperature and then again with a hot solution of the mineral acid or salt.

On the other hand, when the ratio of adsorbed color-bodies to other adsorbed anions is low, it may be preferred to regenerate the resin a number of times with only a mineral acid or salt of a mineral acid, allow the color-bodies to be adsorbed more tenaciously and which are not removed by the first regeneration to be removed by means of a solution of a mild oxidizing agent.

The following examples serve to further illustrate this invention. In the examples the colors which are recorded are based on the American Maltoses Company's Color Standards which are described in Analytical Chemistry, vol. 24, page 832 (May 1952).

**Example 1**

A washed raw sugar melt having a concentration of 59.2° Brix at a temperature of 185° F., a pH of 6.9, a color of 15.5 and containing 28.5 units of color was percolated through a column containing particles of a relatively porous quaternary ammonium anion-exchange resin in the chloride form. The resin (Amberlite IRA-401, manufactured by Rohm & Haas Company, Philadelphia, Pennsylvania) was known to have been made by copolymerizing in aqueous suspension a mixture of 99% styrene, 0.5% ethylstrene and 0.5% divinylbenzene, on a molar basis; then chloromethylating the resultant copolymer; and finally reacting the chloromethylated copolymer with trimethylene. The column of resin beads was 24 inches in depth. The sugar solution was flowed at a rate of 62.5 gals. per square foot of column area per hour. A total quantity of sugar solution equivalent to 1500 pounds of solid sugar per cubic foot of resin was passed through the column. The effluent had a concentration of 58.7° Brix, a pH of 5.9, a color of 3 and contained 3.3 color units. Thus, a total of 88.5% of the color had been removed.

The ion-exchange resin was regenerated as follows: A 10% aqueous solution of sodium chloride, at a temperature of 175° F., was slowly percolated through the bed of resin over a total contact time of 20 minutes. The bed of resin was then washed thoroughly with water.

The whole procedure which comprises the treatment of the sugar solution, the removal of the color therefrom, and the regeneration of the resin constitutes one cycle of operation.

**Example 2**

The process of Example 1 was repeated 73 times in
2,785,998

the manner described, with essentially the same kind of washed raw sugar melt. The 75th cycle was run as follows: A washed raw sugar melt having a concentration of 60° Brix, a pH of 7.0, a color of 16, and containing 31 color units was percolated through the same column of anion-exchange resins. Here, as in the previous cycles, a total quantity of sugar solution equivalent to 1500 pounds of solid sugar per cubic foot of resin was passed through the column of resin at a rate of 62.5 gals./sq. ft./hour. The effluent had a concentration of 59° Brix, a pH of 6.3, a color of 6+, and contained 6.2 units of color.

It will be noted that about 80% of the color was removed. While this represents a real and very worthwhile improvement in the quality of the sugar solutions it is not as great a removal as was obtained in earlier cycles. The gradual loss of the capacity of the resin to remove color-bodies is due to the fact that some of the color-bodies are not removed from the resin by the step of regeneration, as explained above.

In this case, however, the same column of resin was used for 75 more cycles in the same manner described above. In the 150th cycle the same equivalent amount of washed raw sugar melt was passed through the same column of resin at the same rate and at the same temperature. The influent had a concentration of 60° Brix, a pH of 7, a color of 16+, and contained 32 color units. The effluent had a concentration of 59° Brix, a pH of 6.2, a color of 10+, and contained 8.6 color units. In this cycle about 79% of the color was removed.

After drained from the column of resin and the latter had been rinsed with hot water (sweetening off) the resin was regenerated as follows: A 10% aqueous solution of sodium chloride, at a temperature of 175° F., was slowly percolated through the bed of resin over a period of 1 hour. The bed of resin was thoroughly rinsed first with hot water and then with cold water. Next the bed was treated with a 2% aqueous solution of sodium hypochlorite at 80° F. for a total contact time of 60 minutes. Finally the column of resin was thoroughly rinsed with hot water.

In the 151st cycle, after the bed of resin had been regenerated with sodium chloride and with sodium hypochlorite as above described, a washed raw sugar melt was decolorized. The influent had a temperature of 180° F., a concentration of 60° Brix, a pH of 7.1, a color of 15 and contained 26 color units. The quantity of sugar solution and rate of flow were the same as described in Example 1. The effluent had a concentration of 59° Brix, a pH of 6.2, a color of 5, and contained 5.2 color units. In this cycle approximately 80% of the color was removed. This represents an improvement over the results of cycle No. 150 and shows the value and importance of using an oxidizing agent, at least periodically, in the regeneration of the ion-exchange resins.

Treatment of sugar solutions was continued in the manner described above using the same column of resin, the same rate of flow, the same regenerating procedure with sodium chloride every cycle and also employing the regenerating procedure with sodium chloride and sodium hypochlorite every thirteenth cycle. In the 410th cycle over 74% of the color was removed.

Example 3

The purpose of this example is to compare the decolorizing ability of a quaternary ammonium anion-exchange resin in the chloride form with that of the powdered activated carbon. The same washed raw sugar melt was employed and initially it had a concentration of 60° Brix, a pH of 7.0, a color of 16 and contained 31 color units.

A portion of this solution was treated in the conventional manner with powdered activated carbon in an amount equal to its adsorptive capacity in the solution. The resultant solution had a color of 9 and contained 8 units of color indicating that 74% of the color had been removed by the carbon.

Another portion of the washed raw sugar melt was treated in exactly the manner described above in Example 1. The product had a color of 3+ and contained 3.5 color units indicating that the resin had removed more than 88% of the color.

Example 4

A partially decolorized and filtered whole raw sugar melt having a concentration of 62 Brix, a pH of 5.5, a color of 22 and containing 123 color units was passed at a temperature of 170° F. through a column of anion-exchange resin in the chloride form. The resin was the same quaternary ammonium chloride resin described and employed in Example 1 above and the rate of flow was 71.2 gals./sq. ft./hr. An amount equivalent to 320 pounds of solid sugar per cubic foot of resin was thus treated. The effluent had a concentration of 60° Brix, a pH of 5.7, a color of 13 and contained 14.0 color units. From this it is evident that 98.7% of the color had been removed by the resin.

Example 5

In some cases, particularly where the quantities of color-bodies to be removed by the resin are high and many of the color-bodies are adsorbed tenaciously and are not removed by salt or acid alone during regeneration, it is preferred to regenerate the resin every cycle with a mild oxidizing agent, such as hydrogen peroxide or sodium hypochlorite. In such cases a very dilute solution of oxidizing agent can be used and/or the time of contact of the oxidizing agent with the resin can be decreased.

Accordingly, many portions of a washed raw sugar melt were passed through a column of the anion-exchange resin described in Example 1 above. The solutions all had an average concentration of 60° Brix, a pH of about 7.0, a color of 16-17, and contained about 31-34 color units. They were passed through the column at the rate of 62.5 gals./sq. ft./hour until the equivalent of 1500 lbs. of solid sugar had passed through per cubic foot of resin. The resin was then regenerated by means of a 2.5% aqueous solution of sodium chloride at 175° F. for a contact time of 20 minutes and with a 0.25% aqueous solution of sodium hypochlorite at 80° F. during a contact time of 20 minutes, followed in each case by thorough rinsing with water.

The effluent from the 75th cycle had a color of 3+ and contained 3.5 color units indicating a 90% removal of color. The effluent from the 150th cycle had a color of 3-4 and contained 3.7 color units, thus showing that 88% of the initial color had been removed.

We claim:

1. The process of purifying a sucrose solution which contains dissolved impurities including color-bodies which comprises bringing said solution, at a temperature from 130° F. to 210° F., into contact with a porous quaternary ammonium anion-exchange resin which is in the salt form.

2. The process of purifying a sucrose solution which contains dissolved impurities including color-bodies which comprises bringing said solution, at a temperature from 130° F. to 210° F., into contact with a porous quaternary ammonium anion-exchange resin which is in the chloride form.

3. The process of purifying an afined and clarified sucrose solution which contains dissolved impurities including color-bodies which comprises bringing said solution, at a temperature from 130° F. to 210° F., into contact with a porous quaternary ammonium anion-exchange resin which is in the chloride form.

4. The process of purifying a sucrose solution which contains dissolved impurities including color-bodies which comprises passing said solution at a temperature from 130° F. to 210° F., through a layer of particles of a porous quaternary ammonium anion-exchange resin
which is in the chloride form, thereby removing said color-bodies from said solution and adsorbing them on said resin, separating the resultant solution from said resin, and finally regenerating said resin and removing said adsorbed color-bodies from it by treating it with a solution of a water-soluble chloride and with a solution of a mild oxidizing agent.

5. The process of purifying a sucrose solution which contains dissolved impurities including color-bodies which comprises passing said solution at a temperature from 140°F. to 190°F. through a layer of particles of a porous quaternary ammonium anion-exchange resin which is in the chloride form, thereby removing said color-bodies from said solution and adsorbing them on said resin, separating the resultant solution from said resin and finally regenerating said resin and removing said adsorbed color-bodies from it by treating it with a solution of a water-soluble chloride and with a solution of a mild oxidizing agent.

6. The process of purifying an affinated and clarified sucrose solution which is at a concentration of 40° to about 70° Brix and which contains dissolved impurities including color-bodies which comprises passing said solution at a temperature from 140°F. to 190°F. through a layer of particles of a porous quaternary ammonium anion-exchange resin in the chloride form, thereby removing said color-bodies from said solution and adsorbing them on said resin, separating the resultant solution from said resin and finally regenerating said resin and said adsorbed color-bodies from it by treating it with a solution of sodium chloride and with a solution of sodium hypochlorite.

7. The process of purifying an affinated and clarified sucrose solution which is at a concentration of 40° to about 70° Brix and which contains dissolved impurities including color-bodies which comprises passing said solution at a temperature from 140°F. to 190°F. through a layer of particles of a porous quaternary ammonium anion-exchange resin in the chloride form, thereby removing said color-bodies from said solution and adsorbing them on said resin, separating the resultant solution from said resin, and finally regenerating said resin and said adsorbed color-bodies from it by treating it with a solution of sodium chloride and with a solution of hydrogen peroxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,301,669 Richter ---------------- Nov. 10, 1942
2,561,695 Gustafson -------------- July 24, 1951
2,578,358 Kunin ---------------- Dec. 18, 1951
2,650,177 Meijer ---------------- Aug. 25, 1953

FOREIGN PATENTS

489,173 Great Britain ------------ Jan. 20, 1937

OTHER REFERENCES

Serial No. 359,575, Smit (A. P. C.), published May 11, 1943.