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PURIFICATION OF SUGAR SOLUTIONS

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This invention relates to the purification of aqueous sugar solutions and similar aqueous liquids, and is concerned primarily with improvements in the production of sucrose, dextrose and the like.

A principal object of the invention is an improvement in methods for purifying solutions of sucrose, particularly those obtained from sugar beets and from sugar cane.

Another object of the invention is to provide an improvement in the manufacture of dextrose, particularly corn sugar.

Another object of the invention is an improvement in the production of sugars of increased purity and diminished ash constituents.

Other objects of the invention will become apparent on the further reading of this specification and the appended claims.

In the manufacture of commercial sugars from practically any source it is highly desirable that the non-sugar constituents be kept or reduced as low as possible in order to improve the quality and increase the yield of crystallizable sugar and to decrease the amount of residual low-value molasses. Even in the production of the modern so-called "liquid sugars," which are sold as concentrated syrups, without crystallization of solid sugar, a correspondingly high degree of purity is usually required.

It is in the production of the solid sugars, however, that the purity of the sugar juices is of most obvious importance since it bears a direct relation to the quality of sugar and the amounts of the various grades of sugar and of molasses which are the primary factors in the operation and economy of a sugar mill or plant. These factors and relationships are well understood by those skilled in the sugar art, and so need not be given more than brief mention here.

The non-sugar constituents of raw sugar juices may be either organic or inorganic. Usually they are both, the amount and proportion of each depending largely on the nature of the sugar source and on methods of processing. In beet juice, for example, the diffusion juice contains relatively large amounts of both organic and inorganic non-sugars. The principal effect of the several steps of liming and carbonization used in purifying diffusion juice is to remove a large part, but far from all, of the organic impurities without, however, accomplishing a corresponding reduction in the amount of inorganic ash constituents. For example, typical beet "thin juices" that have been subjected to the usual purification procedures may still contain inorganic ash constituents to the extent of 2000 to 5000 parts per million, consisting mostly of potassium and sodium compounds several of which have been shown to be highly melassigenic. The remaining organic non-sugars and metal salts of organic acids also contribute to the formation of molasses, in addition to which may may seriously affect the quality of the crystallized sugar.

In the manufacture of dextrose by acid hydrolysis of a starch, such as corn starch, a large amount of inorganic non-sugars is formed as a result of neutralizing with alkali the free acid (usually hydrochloric or sulfuric) in the liquor after hydrolysis. The salt formed as a result of this neutralization constitutes the principal source of inorganic non-sugars in this case, since the ash constituents of starch are usually quite low. In addition, however, the acid converter liquor resulting from the hydrolysis contains relatively large amounts of organic impurities such as amino-acids, other proteins, carbohydrates and the like, all of which it would be desirable to remove if practical because of their deleterious effect, as in the case of the inorganic non-sugars, on the quality and yield of sugar obtained.

In the case of production of sugar from sugar cane, the purification of the juice is normally directed particularly to the removal of organic colloids, defecation being accomplished principally by a relatively small dosage of lime, together with one or more of a variety of special clarifying agents which have been introduced in recent years in an effort to improve the vitally important removal of organic non-sugars. The production of refined white sugar from raw cane sugar follows much the same general principles.

It will be apparent from the foregoing discussion that in all cases the elimination of organic non-sugars, especially organic colloids, constitute an essential step in the purification of sugar juices and syrups. While there are many ways in which the various organic non-sugars are objectionable, one of the most obvious is the objection of color resulting from the presence of certain of these substances; great care and effort therefore are almost universally employed to secure as complete decolorization as possible.

The removal of inorganic salts or ash constituents, on the other hand, is a consideration the importance of which will naturally vary with the particular sugar and manufacturing process involved; and it is only in recent years that any serious effort has been made to reduce the ash constituents, even though their deleterious effect

has long been recognized, especially in the manufacture of beet sugar.

It has been found that the inorganic salts of beet sugar juice may be reduced practically completely by subjecting the juice to treatment first with a substance having hydrogen-exchange properties and then with a substance having acid-adsorbing properties. Specifically, the ash from a typical thin juice in one of the important beet sections of the United States may be of the order of 4000 to 5000 parts per million. Of this amount, about 700 to 1100 parts per million may be composed of alkaline compounds, principally the carbonates of potassium, sodium, and calcium, while the remainder consists mostly of the sulfates and chlorides of potassium and sodium together with inorganic residue resulting from the ignition of metal salts of organic acids. When such a juice is contacted with a hydrogen exchange body under suitable conditions the salts are converted to the corresponding hydrogen compounds; thus, the carbonates (and bicarbonates) are converted to carbonic acid (carbon dioxide and water), the sulfates and chlorides are converted to free sulfuric and hydrochloric acids respectively, and the metal-organic salts are largely converted to the free organic acids. When subsequently the thus-treated juice is contacted with a body having acid-adsorption properties, the free sulfuric and hydrochloric acids, and part of the free organic acids, are removed from solution, leaving nothing in their place. In other words, it is possible by this method to remove practically completely the metal salts present in the juice, with a resultant increase in purity the degree and importance of which will be at once evident to the sugar chemist.

Among the hydrogen exchange bodies suitable for the first step in this treatment may be mentioned the so-called carbonaceous zeolites, usually prepared by the treatment with strong sulfuric acid of wood, lignite, coal or the like, in methods well-known to the art; suitable also are the cation-exchange synthetic resins, such as the condensation products of polyhydric phenols and formaldehyde described by Adams and Holmes in the Journal of the Society of Chemical Industry, January 11, 1935. These hydrogen exchange bodies, preferably employed in beds of granular material through which the liquid to be treated is passed, are regenerated with a solution of a strong acid, such as sulfuric or hydrochloric acid.

Among the acid-adsorption or acid-removal bodies (frequently called also "anion-exchange" bodies) may be mentioned the m-phenylene-diamine-formaldehyde resins, aniline-aldehyde resins and other resins also described by Adams and Holmes (loc. cit.) and by several other recent authors and patentees. Inorganic acid-adsorbents have also been proposed, particularly such as the oxides of iron and aluminum in the form of gels or other highly porous structures.

Similarly, in the case of the manufacture of dextrose from starch, it has been proposed to lower the ash content of the neutralized converter liquor by treating the acid liquor before neutralization with an acid-adsorbing body for the removal of free mineral and organic acids, thus making neutralizing unnecessary and consequently avoiding the large amount of salt heretofore formed as a result of the neutralization. In this case, obviously, the free acid to be removed is already present, and does not have to be formed by a hydrogen exchange step. It has been proposed to utilize for this acid adsorption the synthetic resins or other acid-removal substances just described.

The present application is not concerned broadly with the methods of sugar purification just described and I make no broad claim to such methods. My invention is concerned with novel improvements in these and similar methods which have been found to increase their utility and economy to such a marked degree that in several cases for the first time the commercial practicality of such methods is definitely assured.

One of the principal obstacles, as previously noted, to the complete elimination of non-sugars from juices, syrups, etc., is the difficulty of removing from them certain of the organic colloids and other organic substances, among which may be mentioned particularly those imparting color to the liquids. The effect of some of these impurities is out of all proportion to the actual weight present. Any practical method for bringing about the more complete removal of these substances is therefore an accomplishment of great importance and utility.

I have found that this result may be accomplished by interposing between the hydrogen exchange treatment and the acid-adsorbing treatment, described in detail above for the treatment of beet juice, a step in which the liquid is contacted while in the acid condition with an active carbon, preferably a decolorizing carbon. An activated carbon of the decolorizing type is especially suitable. I prefer to use the carbon in granular form and in a bed through which the acidic sugar liquor is passed, color and other organic colloids and organic dissolved impurities being removed in the passage. The size of the carbon particles should generally be as small as hydraulic and other operating conditions will permit in order to provide maximum surface of the carbon particles per unit of volume. I have found a particle size of 20 to 40 mesh, for example, quite satisfactory for several types of this work, although there is obviously considerable latitude in this respect. The depth of bed is likewise subject to considerable variation depending on circumstances. In most cases, however, I prefer to employ a depth of bed from about 2 to 4 feet; while there is a cumulative and disproportionate increase of adsorbent capacity with increased depth of bed up to a certain point, structural and operating considerations are usually limiting factors so that it may sometimes be found desirable to employ two or more comparatively shallow beds in series rather than one bed of excessive depth.

The rate of flow to be employed in passing the liquid through the carbon bed will naturally vary with each particular set of conditions, and will depend chiefly on the amount of impurity to be removed, the depth of carbon bed, the size of the carbon particles, and similar factors. With 20 to 40 mesh carbon particles in beds of 2 to 4 feet in depth, rates of flow from 1 to 4 gallons per square foot per minute will generally be found satisfactory.

The carbon bed interposed between the hydrogen exchange treatment and acid-adsorbing treatment accomplishes another result in addition to the highly important removal of organic impurities just mentioned. Unless the carbon bed is thus interposed, there is a marked tendency for the acid-removal bodies to adsorb to a greater or lesser extent the organic colloids and other organic impurities, particularly those of an acidic nature, which tend to clog and foul

the acid-adsorbent bed and make it inactive and unsuitable for use even after the usual regeneration with alkali. The synthetic resins employed for acid-adsorption now commercially available are quite expensive, costing from ten to twenty times as much as activated carbon. It follows that replacement of a bed of such synthetic resins constitutes a very substantial item of operating expense, whereas the replacement of a bed of activated carbon would not be a serious handicap even if replacement was necessary comparatively frequently.

Frequent replacement of the activated carbon bed is not necessary, however, in carrying out the improved process of my invention; for I have discovered that if the carbon is used to adsorb organic colloids from sugar juices while these are definitely acid, that is, with a pH substantially less than 7, and preferably less than about 4.3, the spent carbon bed may be reactivated quite successfully and a great many times by simple treatment with a solution of an alkali, preferably sodium or potassium hydroxide or carbonate, as for example, a one-half to five per cent solution of sodium hydroxide. For example, I have found in certain cases that 30 gallons of 1% caustic soda solution per cubic foot of carbon bed accomplishes effective regeneration for a large number of cycles; and in favorable conditions much smaller amounts of alkali will suffice. In a case in point, the activated carbon bed had been used to decolorize approximately 300 gallons of juice per cubic foot of carbon in each cycle before regeneration with the alkali solution.

A particularly useful and economical method of reactivating the spent activated carbon bed with alkali is to employ all or part of the same alkaline solution that has previously been employed for regenerating the acid-adsorbing body such as the synthetic resins already mentioned. In this way the excess alkali (frequently 30 to 50 per cent of the total alkali) used in regenerating the acid-adsorbing body is utilized in reactivating the carbon, thus saving not only alkali but water as well—a factor frequently of considerable importance, particularly where the disposal of waste liquids is a problem.

As a specific example of what has actually been accomplished in this field, I may mention the purification of a highly colored beet thin juice (Brix about 11) having the essential inorganic chemical characteristics of the juice above mentioned—that is, an ash of 4000 to 5000 parts per million, total alkalinity of 700 to 1000 parts per million, hardness of 75 to 100 parts per million (the last two values being expressed in terms of calcium carbonate), sulfate about 300 parts per million, and chloride about 40 parts per million. After subjection to hydrogen exchange treatment with a carbonaceous zeolite (sulfonated coal) regenerated with sulfuric acid, the pH of the juice was about 2.3 at the beginning and during most of the run; it eventually began to rise and the run was cut off at a pH of about 3.0 when the conversion of the inorganic and organic salts to the corresponding free acids was evidently ceasing to be complete. The effluent from the hydrogen exchange treatment was passed continuously through a bed of granular "Darco" decolorizing carbon and then through a bed of synthetic acid-adsorbing resin. The carbon reduced the color of the juice passed through it from an intense straw color to practical water-whiteness.

The purity of the juice entering the three-stage treating system ranged from about 90 to 91, and of the effluent about 98 to 99. In other words, the rise in purity resulting from this three-stage treatment was consistently about 8 points; and the effluent purity of 98 to 99 obviously means to the sugar chemist not only a crystallized sugar of exceptionally high quality, but also practically the complete elimination of molasses.

The activated carbon bed used in these tests was repeatedly reactivated in series with the acid-adsorbing resin by the spent alkali solution (½ per cent sodium hydroxide) used first for regenerating the resin. So successful was this method of reactivating both acid-adsorbing resin and activated carbon in pilot plant operation that at the end of 100 cycles both units were operating with the same capacity and efficiency as when new.

Tests made in the laboratory showed conclusively that when the acidic sugar juices were decolorized by passing through the bed of granular activated carbon in the manner above described, and the bed subsequently activated with alkali (e. g. sodium hydroxide) the color removed from the carbon by the reactivation was equal to that removed from the juice, proper pH correction of the spent regenerant being made to provide a fair basis for comparison.

Prior to regeneration the carbon is preferably drained and washed with a minimum volume of water, the washing having the twofold purpose of loosening and cleansing the bed and also removing sugar that may be recovered. The alkali regenerating solution may be applied to the carbon cold or hot. A hot solution is sometimes more effective. The time of application may be varied, but I have usually found a period of 15 to 30 minutes to be effective. After the application of alkali the bed is again washed with water. Many decolorizing carbons have a decided tendency to retain alkali, especially the hydroxides, rather tenaciously, thus prolonging the washing operation; I have found it possible to shorten this washing period when desirable by treating the carbon with an acidic substance, such as sulfuric or hydrochloric or other strong acid, but preferably carbon dioxide in the form of carbonated water or by bubbling carbon dioxide or a mixture of flue or kiln gases through the bed or in other ways; the alkali carbonate or bicarbonate, particularly the bicarbonate (like the neutral salt formed when a strong acid has been employed instead of carbon dioxide), washes out much more quickly than the hydroxide.

The alkali solution that has been used to reactivate the carbon, with or without having previously regenerated the acid-adsorbing body also, may be treated in appropriate manner for recovery of substances contained in the liquid.

The activated carbon may be employed also in powdered form in the processes of my invention; but it will be obvious that the use of beds of granular carbon fits in much more conveniently in the three-stage purification system just described.

I am aware, of course, that active carbon in the form of bone-black, activated carbon and the like has been used for a number of years in the purification of the juices and syrups of beet sugar, cane sugar, corn sugar and the like, and I make no claim to such broad use. My method of utilizing active carbon in sugar purification, however, differs radically from those of the prior art in many respects. For example, all prior use of activated carbon in beet sugar manufacture has been in the highly alkaline pH range char-

acteristic of treated beet juices before evaporation, the range being typically from pH 9 to 10. This high pH range results naturally from the large dosages of lime used in processing the juice, and is lowered only to a limited extent by the carbonation (and sulfitation) steps. As a matter of fact, a high pH in the juice is deliberately and carefully maintained, even to the point of adding alkali at various points along the line, if necessary, in order to avoid inversion of the sucrose.

Similarly, in the case of cane juice and dextrose converter liquor the liquids are quickly brought to a pH of at least 7, and usually between 7 and 8.5 before powdered activated carbon is applied—although obviously in the case of the dextrose, the pH of at least 7 is maintained for purposes other than that of preventing the inversion of sucrose which is so carefully guarded against with cane sugar and beet sugar.

I have found that activated carbon functions much less efficiently for the removal of color and other colloidal substances from sugar juices in the high pH environment that characterizes present practice, and that the removal proceeds much more satisfactorily if the pH of the liquid is substantially less than 7, and preferably less than about 4.3. In other words, the present methods of employing activated carbon in sugar purification are diametrically opposed to efficient utilization of the carbon. As a matter of fact, the high pH of the sugar liquors, especially in the case of beet sugar liquors, actually tends to prevent rather than promote adsorption by the carbon. Striking confirmation of this statement is found in the fact that the bed of granular activated carbon employed in the processes of my invention for the removal of organic substances from acidic sugar liquors may be reactivated quite effectively by a very dilute alkali solution, for example a one-half per cent sodium hydroxide solution. It will thus be seen that, in addition to the particular use of carbon in the polystage treatment of sugar juices and syrups herein described, my method of utilizing the carbon for sugar purification is basically new both in its application to acidic liquors and to its subsequent and cyclic use and reactivation with alkali.

This method is perfectly practical even in the case of sucrose because the low pH at which adsorption by the carbon takes place is almost immediately increased to a safe value by the acid-adsorption step which follows, thus avoiding any loss whatsoever from inversion. If for any reason, it is desired still further to increase the pH of the liquid that has been treated by the acid-adsorption body, this result may be accomplished by the addition (preferably after removal of carbon dioxide from the liquor by boiling or aeration) of an extremely small amount of an alkali, such as sodium hydroxide, as the liquor by this time has been freed almost completely of buffering substances.

The basic principles of my invention may be modified in many details for most advantageous adaptation to a specific problem or set of conditions. Thus, in the case of sugar solutions of such initial low ash content that decrease of this ash is relatively unimportant, the benefit of treating with active carbon the sugar liquor in acidic condition may be secured simply by adding the requisite amount of acid as such, as for example, sulfuric, hydrochloric, or acetic acid, rather than through the mechanism of hydrogen exchange previously described. In such cases acidification is carried out to a pH substantially less than 7, and preferably less than about 4.3. The acidic liquor, after treatment with the active carbon, is then treated for removal of free acid, as by contact with one of the anion-removal bodies previously mentioned, or by direct neutralization with an alkali, or in some cases by simple boiling or aeration in the event that a readily volatile acid has been employed for the acidification.

Other modifications of the basic processes of my invention will be suggested to those skilled in the art on reading of this specification. Alternative or equivalent materials may be employed, as for example, types of acid-adsorbing bodies or of active carbon other than those specified. All such modifications are contemplated as coming within the scope of the invention as defined in the appended claims.

I claim:

1. A process for the purification of a sugar bearing solution which comprises contacting the solution successively with a hydrogen exchange body, with an active carbon, and with an acid-adsorbing body.

2. A process for the purification of a sucrose solution which comprises converting dissolved salts to corresponding free acids by hydrogen exchange treatment, removing colloids from the thus-acidified liquor by treatment with active carbon, and subsequently removing the free acids by treatment with an acid-adsorbing body.

3. A cyclic process for the purification of a sugar bearing solution which comprises passing the sugar bearing solution through a bed of a hydrogen exchange material, then through a bed of active carbon and finally through a bed of an acid adsorbing material, and regenerating the bed of the hydrogen exchange material by passing a dilute solution of a strong acid therethrough, and the beds of acid adsorbing material and active carbon by passing a stream of a dilute solution of alkali first through the acid adsorbing material and then through the active carbon.

4. The process according to claim 1 in which the hydrogen exchange body, the active carbon and the acid-adsorbing body are all in granular form.

5. In combination with a process for the purification of a sugar solution which comprises contacting the solution successively with a hydrogen exchange body, with an active carbon, and with an acid-adsorbing body, the method of regenerating said carbon which comprises treating said carbon with a solution of an alkali, then treating said alkali-regenerated carbon with an acidic substance, thereby expediting the washing of alkali from the carbon, and thereafter washing said carbon with water.

6. A process as described in claim 5 in which the acidic substance comprises carbon dioxide.

7. The process for the purification of a sugar solution containing organic and inorganic impurities, which comprises contacting the solution with a hydrogen exchange body to exchange H^+ for cations of salts in said solution, said exchange body being inherently capable of forming acid in said sugar solution as said cations in said solution are exchanged, and powdered active carbon to remove color from said solution, and finally contacting said sugar solution with an acid-adsorbing body.

8. In the process for the purification of a sugar bearing solution which includes contacting a solution successively with a hydrogen exchange body and an acid adsorbing body, the improvement which comprises treating the solution com-

ing from the hydrogen exchange body with an active carbon prior to the said treatment with the acid adsorbing body.

9. In the method of refining a sugar bearing solution which comprises clarifying the solution to remove impurities, and subjecting the thus clarified solution to the sequential exchange action of a bed of hydrogen exchange material and a bed of acid adsorption material, the improvement which comprises subjecting the solution coming from the hydrogen exchange bed to treatment with an active carbon prior to treatment with the acid adsorption material.

10. A process for the purification of a sucrose solution which comprises treating the solution with a hydrogen exchange body to convert the dissolved salts to the corresponding free acids and reduce the pH of the solution to between 4.3 and 7.0, removing colloids from the thus acidified liquor by treatment with active carbon, and subsequently removing the free acids by treatment with an acid adsorbing body.

11. A process for the purification of a sucrose solution which comprises treating the solution with a hydrogen exchange body to convert the dissolved salts to the corresponding free acids and reduce the pH of the solution to between 2.3 and 4.3, removing colloids from the thus acidified liquor by treatment with active carbon, and subsequently removing the free acids by treatment with an acid adsorbing body.

12. A process for the purification of a sucrose solution which comprises converting dissolved salts to corresponding free acids by hydrogen exchange treatment, removing colloids from the thus acidified liquor by treatment with active carbon, subsequently removing the free acids by treatment with an acid adsorbing body, and regenerating the spent active carbon with a solution of an alkali previously employed for regeneration of the acid adsorbing body.

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