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REFINING OF SUGAR AND SUGAR SIRUPS

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This invention relates to a process for decolorizing sugars and sugar sirups by treatment with peracids or their salts. More particularly, our process relates to the treatment of sugar sirups, such as any of the common commercial sugar products, with a solution containing a peracid or a salt of a peracid for the purpose of decolorizing and refining those products. Our improved process is of general applicability in the refining of the various types of sugar products prepared for commercial sale.

The use of hydrogen peroxide and of other oxidizing agents in methods for decolorizing sugar products has already been suggested. Some of these decolorizing agents have been used in the past or are now being used to a greater or less extent in commercial sugar refining operations. While certain of these oxidizing agents such as hydrogen peroxide have been effective agents for the commercial clarification of sugar and sugar liquors, we have now found that the peracids, specifically, peracids such as peracetic acid, monopersuccinic acid, monoperphthalic acid, monopersulfuric acid (Caro's acid), and the salts of these peracids, are greatly superior in their action to oxidizing agents such as hydrogen peroxide. The peracids and their salts have been found to possess greater decolorizing activity than hydrogen peroxide or other per compounds, when employed in amounts giving equivalent active oxygen concentrations, which increased activity results in greater decolorization at less cost. Moreover, the peracids and their salts have been found to be more rapid in their action when utilized for decolorizing sugar and sugar sirups and, in fact, they operate to effect clarification with greater rapidity than any of the other per compounds previously utilized or suggested for this purpose in the sugar refining industry. It has also been found that the peracids and their salts function satisfactorily at lower temperatures than those previously considered necessary when utilizing per compounds such as hydrogen peroxide for sugar decolorization. In addition, the peracids and their salts have been found to be very efficient agents for effecting permanent removal of the red coloration which is normally present in most sugar sirups.

It is accordingly one of the objects of our invention to develop a process for the refining of sugar and sugar sirups which will utilize the very active and effective peracids and their salts. Another object of this invention is the development of a process for the decolorization of sugar and sugar sirups, utilizing peracids as the active agents, which process will effect more permanent color removal than can be now secured by the use of the various agents previously suggested for use in sugar decolorization. Still another object of this invention is the development of a process employing the peracids in the decolorization of sugar, which process will be generally applicable for treating the various types of sugar liquors which are ordinarily subjected to decolorization and refining in commercial operations as, for example, raw sugar liquors, soft sugar liquors, affination liquor, etc. These and other objects of this invention, which will become apparent hereinafter, may be summarized by stating that the primary aim of our process is the utilization of the peracids and their salts in the commercial refining of sugar and sugar sirups obtained from cane, corn, and beet sugar sources.

The peracids which we have found effective for use in the treatment of sugar sirups may be readily prepared by various methods now known to the art. One method involves reacting the anhydride of the acid and a peroxide such as hydrogen peroxide or an alkali metal peroxide, or a per compound such as an alkali metal perborate, under certain suitable controlled conditions. This results in an aqueous solution containing the peracid or the persalt, the particular form in which the peracid radical is present depending principally on the pH of the aqueous liquid and on the presence and amount of metallic ions in the solution. While we have found that peracids or their salts prepared by other processes are equally satisfactory when used in our sugar refining method, ordinarily we prefer to prepare an aqueous solution of the peracid or persalt in this manner by reacting the particular acid anhydride selected with a peroxide such as commercial 100 volume hydrogen peroxide or sodium peroxide. We have secured very satisfactory decolorizing action with various organic peracids such as peracetic acid, monoperphthalic acid, monopersuccinic acid, monopermaleic acid and other monoperacids prepared in this way, as well as with the inorganic peracid, monopersulfuric acid (Caro's acid).

The sugar solution which is to be decolorized in accordance with our improved refining process may be derived from either cane, corn, or beet sugar sources. Sugar sirups of various kinds have been satisfactorily decolorized by the use of the various peracids, both organic and inorganic, as the active agents. For example, we have utilized the peracids in refining various types of beet sugar sirups, as well as cane sugar liquors

such, for example, as those known in the trade as raw sugar liquor, washed sugar liquor, turbinado sirup, affination liquor, and soft sugar liquor.

The peracid or salt of the peracid, ordinarily in aqueous solution, may be prepared and then added directly to the particular sugar sirup which it is desired to decolorize. An alternative way of proceeding involves first adding a definite amount of a peroxide such as hydrogen peroxide, or a solution of an alkali metal peroxide such as sodium peroxide, to the sugar liquor, and then adding the desired acid anhydride in amount sufficient to react with the peroxide and form the peracid in the sugar liquor. This involves forming the peracid or the salt of the peracid in situ in the sugar sirup.

In actual practice, the amount of the peracid employed will be controlled by the extent of decolorization desired. We have found that even small amounts of peracids possess effective action in the decolorizing of sugar sirups. Efficient decolorization has been obtained at temperatures as low as room temperature or below, and as high as 180° F. or even higher. The pH value of the solution is not especially critical and, during the major portion of the decolorizing step, may vary from 5.0 to 11.0. We have found that the peracids and their salts possess most effective decolorizing and refining action within this pH range.

While the extent of color removal for equal amounts of active agents is greater at the lower temperatures, assuming that the peracid and the sugar liquor remain sufficiently long in contact, the speed of the decolorizing action is greater at higher temperatures. For this reason, it may be desirable to employ a temperature more elevated than room temperature in order to secure more rapid decolorization, thus shortening the period of time necessary. We have found that the time required for complete decolorization will vary largely with the temperature and with the amount of peracid present. For example, at 75° F. a period of up to one hour may be required to secure complete clarification, while at 180° F. substantially complete decolorization has been secured with some sirups at the end of only one minute.

In practice, the temperature selected for use during the refining operation will be determined largely by the temperature encountered in actual manufacturing processes, as well as by the rate of decolorization desired. While any pH value within the range 5.0 to 11.0 has been found effective and the pH is not especially critical, somewhat better results are secured at a pH of about 7 or 8. Ordinarily, since acid or highly alkaline conditions tend to cause inversion of sucrose to dextrose, the pH selected will be determined largely by the amount of inversion allowable in the sugar liquor.

Our improved process for the decolorization of sugar liquors may of course be employed in conjunction with any of the refining treatments now utilized in the sugar industry, such as, for example, those which involve treatment of the sugar liquors with bone-char, activated carbon, and other refining agents. It is particularly applicable for use in the decolorization of low-purity sirups such as the so-called soft liquors employed in the manufacture of yellow and brown sugars. We have, moreover, found that the peracids are especially efficient in the decolorization of high purity sugar liquors, and that it is generally unnecessary in the case of these sugar sirups to employ, as an additional step, the customary treatment with bone-char, activated carbon treatment, or other adsorbent. In the use of our process in the decolorization of high-purity sugar liquors, the expense incident to bone-char and activated carbon may thus ordinarily be saved. The peracids have been found especially useful for sugar refining operations in which no adsorbent agent is ordinarily employed, such as in the decolorization and refining of beet sugar liquors.

As examples of our improved process, the following may be given:

Example I

An aqueous solution of peracetic acid was prepared by adding an equimolar quantity of acetic anhydride to a solution of sodium peroxide of 1.0 volume concentration. The volume concentration of a solution of an active oxygen compound is the number of cubic centimeters of oxygen gas, measured at 0° C. at 760 mm. pressure, that will be released from one cubic centimeter of the solution measured at 20° C. A solution of sodium peroxide of 1.0 volume concentration has a Na_2O_2 concentration of substantially 0.72%. After reacting the acetic anhydride with the sodium peroxide in aqueous solution, the pH of the solution was reduced to 7.6 by the addition of sulfuric acid.

Three 50 cc. samples of a raw sugar liquor containing 60 grams of solids per 100 cc. and having a Lovibond number, as measured in a 0.5" cell, of 120.5 were treated with three different amounts of peracetic acid, prepared in the manner described. One of these 50 cc. samples was treated with three cc. of the peracetic acid solution (equivalent in active oxygen concentration to 0.072% Na_2O_2). The second sample was treated with 10 cc. of the peracetic acid solution (equivalent to 0.24% Na_2O_2). The third sample was treated with 20 cc. of the peracetic acid solution (equivalent to 0.48% Na_2O_2). The sirups were allowed to bleach overnight at 80° F. and were then filtered to remove suspended solids. At the conclusion of the bleaching, the color of all three samples was determined in a Lovibond tintometer, measured in a 0.5" cell. The first bleached sample had a Lovibond number of 60.3, the second bleached sample, a Lovibond number of 36.0, and the third bleached sample, a Lovibond number of 24.5. It is obvious that in all cases remarkable decolorization was secured with relatively small amounts of peracetic acid.

Example 2

Various samples of turbinado sirups, each 100 cc. in volume and containing 62 grams of sugar per 100 cc., were treated with various amounts of the peracetic acid solution referred to in Example I. The sirups were allowed to bleach overnight at room temperature (80° F.) and the color was then determined in a Lovibond tintometer and compared with the color of the untreated sirup. The results are summarized below:

Peracetic acid used in treatment equivalent to per cent Na_2O_2	Lovibond number of treated sirup in 1.0" cell
None (untreated)	4.5
0.0117	3.0
0.0234	2.2
0.0585	0.7
0.117	0.4
0.234	0.3

Example 3

Peracetic acid solution was prepared by adding an equimolar quantity of acetic anhydride to a solution of sodium peroxide of substantially 1.0 volume concentration (0.72% Na_2O_2).

A sample of a soft sugar liquor, containing 67 grams of solids per 100 grams of liquor, was treated with an amount of the aqueous peracetic acid solution equivalent to substantially 0.125% Na_2O_2, based on the weight of the solids in the sugar liquor. The sirup was allowed to stand for thirty minutes at 160° F. and the color of the treated sirup was then determined in a Lovibond tintometer and compared with that of the untreated sirup measured in the same way. The untreated sugar sirup had a Lovibond number of 35.5, as compared with the Lovibond number of 7.6 for the sirup which had been decolorized with peracetic acid. This corresponds to 79% decolorization.

The same soft sugar liquor, when treated with 0.156% of H_2O_2 in the form of the 100 volume commercial hydrogen peroxide solution, and then heated to 160° F. for thirty minutes yielded a product wherein the color was only 20% removed. This comparative test shows the greater effectiveness of the peracid.

Example 4

A washed sugar liquor was treated with various amounts of a solution of peracetic acid prepared as in Example I. The resulting solutions were allowed to stand overnight, and the color was then measured and compared with the color of the untreated sirup. The amount of peracid, in the table which follows, is based on the percentage of sodium peroxide used in preparing it. This table shows the Lovibond number, as measured in a 1" cell, of samples of the sirup treated with various amounts of the peracetic acid solution, as well as the Lovibond number of the untreated sugar sirup:

Amount of sodium peroxide used to prepare peracetic acid with which the sugar sample was treated	Lovibond number as measured in 1" cell
None (intreated)	16.2
0.0116%	11.6
0.0232%	7.5
0.058%	4.5
0.116%	3.0
0.232%	2.1

Example 5

A sample of beet sugar sirup having a Lovibond number of 8.5 as measured in a 0.5" cell was treated with an aqueous solution containing 0.25% of monopersulfuric acid. Previous to its addition to the beet sugar sirup, the solution of persulfuric acid was adjusted to a pH of substantially 5.5 by the addition of sodium bicarbonate.

The decolorization treatment was carried out at room temperature and after but a few minutes of contact between the monopersulfuric acid and sugar sirup, the Lovibond number of the sirup was found to be 3.5. When the sample was heated for a period of an hour at 160° F. under a vacuum, the Lovibond number was found to be 4.0.

As a comparison, a sample of the untreated sirup was heated at 160° F. under a vacuum for a period of an hour and the Lovibond number was found to be substantially unchanged, being 8.6 as compared with 8.5 before the heating.

Example 6

To 100 cc. of a turbinado sirup containing 62 grams of sugar, there were added 10 cc. of a solution of sodium monopersuccinate which had been prepared by adding an equimolar amount of succinic anhydride to an aqueous solution of sodium peroxide of substantially 1.0 volume concentration. The sirup was allowed to stand in contact with the sodium monopersuccinate for three hours at a temperature of 80° F. The pH of the treated sirup was then adjusted to substantially the same pH as that of the untreated sirup, and color values were measured using a Lovibond tintometer. The color values, as measured in a 1.0" cell, were found to be 4.5 for the untreated sirup and 0.9 for the treated sirup.

Example 7

The decolorization described in Example 6 was repeated using 10 cc. of a solution of sodium monoperphthalate instead of the sodium monopersuccinate. The sodium monoperphthalate solution was prepared by adding an equimolar quantity of phthalic anhydride to an aqueous solution of sodium peroxide of substantially 1.0 volume concentration. The color value of the sirup treated in this way was found to be 1.0, as compared with the Lovibond number of 4.5 for the untreated sirup.

In the foregoing examples, percentages, where given are by weight based on the dry weight of the solids in the sugar liquor.

Although any peracid, inorganic or organic, is suitable for use in our process, ordinarily we prefer to utilize peracetic acid or peracetate salts of this acid. This treatment agent is especially active, is economical to use, and is prepared relatively easily from inexpensive starting materials.

To those skilled in the art, many widely different embodiments and applications of our invention in the general field of decolorizing and refining sugar and sugar sirups will be apparent. It should be understood that the details of our preferred procedure as described, including the concentrations, conditions under which the bleaching is carried out, and other factors involved, may be subjected to some change without departing from either the spirit or the scope of our invention. It is intended that our invention is not to be restricted to specific preferred embodiments, minor details, or specific modes of operation described as illustrative, as we have found the peracids and their salts to be generally useful for decolorizing the various types and classes of sugars and sugar liquors normally encountered in the cane, corn and beet sugar industries.

In the appended claims, the terms "peracid" or "peracids" are intended to include not only the acids themselves, but the various salts of those peracids. Similarly, the term "sugar" or "sugars," as employed in the claims, is intended to refer to the various types of sugar sirups, sugar liquors, and sugar containing liquids which are ordinarily decolorized and/or refined.

We claim:

1. The process of decolorizing sugar which comprises subjecting said sugar to the decolorizing action of an organic monoperacid.

2. The process of decolorizing sugar which comprises treating said sugar with a peracid selected from the group which consists of peracetic acid, monopersuccinic acid, monoper-

phthalic acid, monopermaleic acid, and monopersulfuric acid.

3. The process of decolorizing sugar which comprises subjecting said sugar to the action of peracetic acid.

4. The process of decolorizing sugar which comprises subjecting said sugar to the action of monopersuccinic acid.

5. The process of decolorizing sugar which comprises subjecting said sugar to the action of monopersulfuric acid.

6. The process of refining sugar which comprises subjecting said sugar to the action of an organic peracid, the treatment being carried out in aqueous solution, at a temperature within the range room temperature to 180° F., said solution having a pH value during said treatment falling within the range 5 to 11.

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