Patented Jan. 24, 1950 2,495,334

UNITED STATES PATENT OFFICE

2,495,334

METHOD OF REFINING SUGAR SOLUTIONS

William A. La Lande, Jr., Upper Darby, Pa., assignor to Porocel Corporation, Philadelphia, Pa., a corporation of Delaware

No Drawing. Application March 29, 1941, Serial No. 385,858

12 Claims. (Cl. 127—55)

1

The present invention relates to the refining of sugar solutions, particularly washed sugar liquors, by a combination treatment with a chemical bleaching agent and an adsorbent comprising activated bauxite.

An object of this invention is the substantial decolorization of sugar solutions by means of chemical bleaching agents and the treatment of the decolorized solutions with activated bauxite to remove from the solutions any excess of bleaching agent and products of the bleaching reaction, as well as a substantial proportion of the invert sugar, ash-forming constituents, and other impurities normally present in the sugar solutions.

A further object of this invention is the stabilization of the color of chemically-bleached sugar solutions by treatment of the color-unstable solutions with activated bauxite.

A further object of this invention is the prolongation of the life of decolorizing and refining adsorbents such as activated bauxite by pretreatment of the sugar solutions with chemical bleaching agents.

In the sugar refining industry, it is incumbent upon practically all refiners to process lower purity sugar solutions, such as wash syrups, as well as to process sugar solutions of relatively high purity, i. e., washed sugar liquors. In so doing, a refining adsorbent such as bauxite is first employed in the treatment of the high purity solutions, and then in the treatment of the low purity solutions. By operating in this sequence, the bauxite used in the treatment of the low purity solutions is already relatively heavily loaded with impurities removed from the high purity solutions first treated, and consequently has lost considerable of its original refining efficiency. However, by employing a chemical bleaching treatment prior to the treatment with bauxite, the color load upon the bauxite is markedly reduced, and the refining capacity or life of the bauxite is considerably increased. Thus, by utilizing a combination treatment with a chemical bleaching agent and activated bauxite, the overall efficiency of the refining process is substantially improved.

It has been proposed heretofore to decolorize sugar solutions by means of chemical bleaching agents such as hydrogen peroxide, sulfur dioxide, ozone, chlorine, hypochlorites, and the like, but treatment with such agents does not reduce the content of ash-forming constituents or lower the invert sugar content of the sugar solutions. In some cases the content of ash-forming constituents is actually increased, since in the bleaching reaction certain of the reaction products are non-volatile substances which are soluble in the sugar solution. The content of invert sugar and ash-forming constituents of sugar solutions decolorized solely by chemical bleaching agents must be reduced or eliminated entirely by vacuum concentration of the solutions, otherwise the subsequent crystallization of the sugar is rendered more difficult and the yield of finished sugar is lower. Sulfur dioxide, hydrogen peroxide and ozone readily decolorize sugar solutions without leaving in the decolorized solution additional ash-forming constituents, but some of the bleached coloring materials remain in the solutions, which on standing tend to become colored, due probably to a reversal of the decolorizing reaction. Any excess of bleaching agent in the decolorized solutions must be destroyed by the addition of other chemicals. Furthermore, the chemical bleaching agents may also exert a deleterious action upon the pH of the sugar solutions, which is reflected, for example, in the increase in invert sugar in subsequent refining operations.

2

I have found that the disadvantages of the prior art processes may be substantially obviated by a method involving simultaneous treatment with a chemical bleaching agent and an adsorbent, i. e., activated bauxite, or a treatment first with a bleaching agent and subsequently with activated bauxite.

In accordance with my invention, an impure sugar solution such as washed sugar liquor may be agitated with a suitable quantity of finely divided activated bauxite, for example, 5%–25% of through 100 mesh bauxite, with the simultaneous addition of a bleaching agent which may be either a solid, liquid or gas. The treatment may be carried out at temperatures up to about 200° F., and upon completion of the bleaching and refining reaction, the finely divided bauxite containing adsorbed reaction products, color bodies, ash-forming constituents, and unused bleaching agent may be separated from the refined sugar solution by filtration, centrifuging, or other suitable means. Alternatively, the impure sugar solution may be treated first with a chemical bleaching agent and thereafter contacted with finely divided bauxite. Bleaching agents such as hydrogen peroxide, sulfur dioxide, ozone, and chlorine are well adapted for simultaneous treatment, while alkali metal or alkaline earth metal peroxides, sulfites, hydrogen sulfites, hydrosulfites, hyposulfites, permanganates, hypo-

chlorites, and hypochlorous acid are preferably employed prior to bringing the sugar solution into contact with the adsorbent. When it is desired to employ a granular adsorbent, such as 10–30 mesh activated bauxite, the chemical bleaching agent may be added to the impure sugar solution and the solution then percolated or filtered through a bed of the adsorbent, or the bleaching agent may be incorporated in the impure solution substantially simultaneously with the percolation thereof through the bed of adsorbent. The percolation is perferably carried out at temperatures within the range of from about 150° F. to about 180° F. Activated bauxites which I have found suitable for use in accordance with my invention may be prepared by heating naturally occurring bauxite at temperatures of from about 500° F. to about 1600° F., and screening the activated material to the desired mesh size. Bauxites which have been heated between about 600° F. and 900° F. and which contain from about 2% to about 10% combined water are preferred, although bauxites activated by heating at higher temperatures may be employed.

By employing my combination treatment of chemical bleaching agent and adsorbent, the ash content and the invert sugar content of the sugar solution are reduced by the adsorbent, and the reaction products formed by the action of the bleaching agent upon components of the sugar solution are also largely removed, thus preventing reappearance of color in the finished sugar. The action of the bleaching agent decreases the color load on the adsorbent and consequently renders it more efficient in removing ash-forming constituents and invert sugar from the solution and lengthens its life as a decolorizing medium. Furthermore, the method of the present invention reduces the amount of ash and invert sugar to be eliminated in the boiling pans. In some cases it may be found desirable to adjust the pH of the sugar solution prior to or during treatment with a chemical bleaching agent or an adsorbent, by adding to the sugar solution a small amount of an acid or base.

My invention may be further illustrated by the following examples, which, however, are not to be construed as limiting the scope thereof:

(1) 0.316 lb. of $Ca(H_2PO_4)_2.H_2O$ was admixed with 0.45 gal. of water, and the resulting solution was added to 25 gallons of 60° Brix washed sugar liquor. The mixture was agitated for about 5 minutes at a temperature of 74° F. Then 0.32 lb. of calcium hypochlorite (chlorinated lime) was dispersed in 0.45 gal. of water, and 0.317 gal. of the resulting suspension was added to the phosphate-sugar solution above mentioned.

This mixture was stirred for 15 minutes at 74° F. and then heated to 175° F. and allowed to stand for one hour. The initial bleaching effect of the hypochlorite treatment at low temperature, i. e., 74° F., was partially offset by the heating to the elevated temperature of 175° F. to coagulate insoluble materials, and as a result, the color of the sugar solution darkened. A heavy scum comprising insoluble calcium phosphate and flocculated impurities was removed from the surface of the treated sugar solution, and the remainder of the calcium hypochlorite suspension was added, and the mixture stirred for about 10 minutes at 175° F. The first addition of hypochlorite is preferably made at a temperature between about 60° F. and 100° F., whereas the second addition is made at 125° F. to 200° F., and preferably at 150° F. to 175° F. While I have shown the use of monocalcium phosphate for the purpose of reacting with the metallic ion of the hypochlorite to produce an insoluble precipitate, I may employ other acid salts or acids supplying anions which form insoluble calcium salts to bring about a similar result. As a result of the second addition of hypochlorite, the color imparted to the solution by the heating was substantially removed. Then 0.5 lb. of a filter aid ("Hyflo Supercel") was admixed with the treated solution and the mixture filtered in a vacuum filter, whereby the filter aid and insoluble reaction products were removed from the treated sugar solution. A sample of the treated solution, when tested with $KI\text{-}H_2SO_4$, gave a positive test for ClO ions. The treated solution, as well as a sample of untreated washed sugar liquor, was filtered at a temperature of 165° F., through 10–30 mesh bauxite activated by heating at 700° F., each filter containing 12 lbs. of the granular bauxite. Analyses of the solutions and filtrates are given in the following table (dry basis).

Analysis	Wash liquor	Wash liquor, bauxite filtered	Wash liquor, hypochlorite treated	Wash liquor, hypochlorite treated, bauxite filtered	
Per cent sucrose	98.52	99.13	98.42	99.21	98.79
Per cent invert sugar	0.70	0.41	0.69	0.39	0.59
Per cent ash	0.26	0.06	0.28	0.07	0.16
Per cent undetermined	0.52	0.40	0.61	0.33	0.46
Color	65.3	6.2	6.5	1.1	3.2
pH	6.8	6.5	7.1	6.6	6.3
Filtrate yield, gallons		3.58		3.58	6.25
ClO ion in filtrate			positive	negative	negative
Per cent increase in sucrose		0.61	[1] 0.1	0.69	0.27
Per cent decrease in—					
Invert sugar		41.4	1.4	44.3	15.7
Ash		76.9	7.7	73.1	38.5
Undetermined		23.1	[2] 17.2	36.5	11.5
Color		90.4	90.5	98.3	95.1

[1] The sucrose content decreased
[2] The undetermined content increased.

From the above data it will be seen that while hypochlorite bleaching reduces the color of the washed sugar liquor to a substantial extent, the percent sucrose is not increased, the invert sugar is not decreased, and the ash content is changed only slightly. Furthermore, the treated liquor contains ClO ions, which must be removed by an additional treatment, and the original invert and ash content are carried to the crystallizing pans. On the other hand, filtration of the hypochlorite-bleached liquor through granular bauxite further reduces the color of the liquor, and at the same time decreases the ash and invert sugar content while increasing the percent sucrose. Moreover, since the ClO ion test is negative, no additional chemical treatment is necessary to remove the excess treating chemical, and less invert and

ash are carried to the vacuum evaporators. By eliminating the additional chemical treatment, a substantial reduction in refining costs is effected. Finally, a considerably higher yield of very light colored liquor is obtained by the combination treatment, the preliminary hypochlorite bleach reducing substantially the color load on the bauxite, thereby extending the decolorizing life of the adsorbent.

(2) A washed sugar liquor was admixed with 0.3% of 30% hydrogen peroxide (H_2O_2) and permitted to stand for 12 hours at a temperature of 75° F. The treated liquor was tested with KI-H_2SO_4 and found to contain an oxidizing agent. The treated, as well as untreated, liquor was filtered at a temperature of 165° F. through 20–60 mesh bauxite activated by heating at 1000° F., using 1 lb. of bauxite per 0.31 gal. of wash liquor. Analyses of the liquors charged to the filters, and of the filtrates, are given in the following table (dry basis).

Analysis	Wash liquor	Wash liquor, bauxite filtered	Wash liquor, ozone treated	Wash liquor, ozone treated, bauxite filtered
Per cent sucrose	98.36	99.15	98.28	99.20
Per cent invert sugar	0.59	0.40	0.61	0.38
Per cent ash	0.31	0.09	0.32	0.07
Per cent undetermined	0.74	0.36	0.79	0.35
Color	60.5	6.2	1.0	0.7
pH	7.1	6.4	6.0	5.9
Per cent increase in sucrose		0.79	[1] 0.08	0.84
Per cent decrease in—				
Invert sugar		32.2	[2] 3.4	35.6
Ash		71.3	[2] 3.2	77.4
Undetermined		51.3	[2] 6.7	52.7
Color		89.8	98.3	98.8

[1] The sucrose content decreased.
[2] The invert, ash, and undetermined content increased.

In the above examples, equal volumes of filtrates were taken from the filters, in which case the color of the ozone treated, bauxite filtered liquor was very much lighter than that of liquor which had been simply bauxite filtered. Had the ozone treated liquor been filtered to the same

Analysis	Wash liquor	Wash liquor, bauxite filtered	Wash liquor, H_2O_2 treated	Wash liquor, H_2O_2 treated bauxite filtered
Per cent sucrose	97.80	99.01	97.85	99.21
Per cent invert sugar	0.75	0.49	0.79	0.51
Per cent ash	0.34	0.09	0.35	0.085
Per cent undetermined	1.11	0.41	1.01	0.19
Color	50.4	4.8	4.8	1.2
pH	6.5	6.3	6.3	6.3
H_2O_2 in filtrate			positive	negative
Per cent increase in sucrose		1.21	0.05	1.41
Per cent decrease in—				
Invert sugar		34.7	[1] 5.3	32.0
Ash		73.5	[1] 2.9	75.0
Undetermined		63.1	9.0	82.9
Color		90.6	90.6	97.7

[1] The invert sugar and ash increased.

Again it will be noted that while the preliminary treatment with the chemical bleaching agent, i. e., H_2O_2, effected a substantial reduction in the color of the sugar liquor, the purity of the liquor expressed as percent sucrose, was substantially unchanged, as were the ash and invert sugar contents of the liquor. On the other hand, the combination treatment employed in accordance with the present invention not only increased the percent sucrose, and decreased the ash and invert sugar content, but gave a much lighter colored sugar liquor which required no chemical treatment to remove excess bleaching agent.

(3) Ozonized oxygen, containing 0.0043 lb. of ozone per cubic foot, was bubbled through 0.61 gal. of 60° Brix washed sugar liquor maintained at 165° F., at a rate of 0.71 cubic foot per hour, for a period of about 2 hours, at which time the bleaching or decolorizing action appeared to be complete. Excess ozone was then displaced from the sugar liquor by passing a stream of air through the solution for about 10 minutes. The treated, as well as the untreated liquors were then percolated through filters each containing 1.76 lb. of 10–30 mesh bauxite activated by heating at 800° F. for 20 minutes and cooled prior to use. Equal volumes of filtrates were obtained, equivalent to 2 lbs. of sugar solids per lb. of bauxite. Analyses of the liquors and filtrates are given in the following table (dry basis).

color as the untreated, bauxite filtered liquor, the yield would have been greatly increased.

(4) To a washed sugar liquor 0.1% $KMnO_4$, based on the solids content of the liquor, was added in the form of a saturated aqueous solution, and the mixture was permitted to stand for 10 hours at room temperature, at which time the bleaching action appeared to be complete, i. e., there was no further change in the color of the treated liquor. A precipitate comprising hydrated oxides of manganese was removed by decantation. The treated, as well as the untreated liquor was filtered at a temperature of 165° F. through 20–60 mesh bauxite activated by heating at 1000° F., using filters each containing 10.25 lbs. of the adsorbent. Analyses

of the liquors charged to the filters, and of the filtrates, are given in the following table (dry basis).

Analysis	Wash liquor	Wash liquor, bauxite filtered	Wash liquor, $KMnO_4$ treated	Wash liquor, $KMnO_4$ treated, bauxite filtered
Per cent sucrose	96.75	97.66	96.67	97.70
Per cent invert sugar	0.45	0.34	0.47	0.38
Per cent ash	0.17	0.12	0.24	0.02
Per cent undetermined	2.63	1.88	2.8	1.90
Color	31.5	5.5	8.4	5.9
pH	7.3	6.4	8.4	6.6
Filtrate yield, gallons		3.2		5.1
Per cent increase in sucrose		0.91	[1] 0.08	0.95
Per cent decrease in—				
Invert sugar		24.7	[2] 4.4	15.5
Ash		29.4	[2] 41.2	88.2
Undetermined		27.9	[2] 7.2	27.7
Color		93.3	89.7	92.6

[1] The sucrose decreased.
[2] The invert, ash and undetermined content increased.

(5) A washed sugar liquor was admixed with the volume of a saturated aqueous solution of potassium permanganate containing 0.1% $KMnO_4$, based upon the solids in the wash liquor, and the mixture was heated and maintained at a temperature of 165° F. for 2 hours, at which time the bleaching action of the permanganate appeared to be complete. To the permanganate-treated solution was then added 0.66% of sodium acid sulfite based on the solids content of the treated solution in the form of a 10% aqueous solution, and the mixture was permitted to stand until the action of the acid sulfite was complete. Samples of the untreated liquor, the permanganate-treated liquor, and the permanganate-acid sulfite treated liquor, were filtered, at a temperature of 165° F., through 20–60 mesh bauxite activated by heating at 1000° F., using filters each containing 11.85 lbs. of bauxite. Analyses of the liquors charged to the filters, and of the filtrates, are given in the following table (dry basis).

Analysis	Wash liquor	Wash liquor, bauxite filtered	Wash liquor, $KMnO_4$ treated	Wash liquor, $KMnO_4$ treated, bauxite filtered	Wash liquor, $KMnO_4$-$NaHSO_3$ treated	Wash liquor, $KMnO_4$-$NaHSO_3$ treated, bauxite filtered
Per cent sucrose	98.68	99.05	98.30	99.11	98.89	99.31
Per cent invert sugar	0.48	0.34	0.44	0.39	0.43	0.36
Per cent ash	0.19	0.12	0.34	0.10	0.38	0.06
Per cent undetermined	0.65	0.49	0.91	0.40	0.30	0.27
Color	46.0	4.0	27.4	2.5	17.7	2.6
pH	6.8	6.4	8.4	6.6	6.4	6.4
Yield filtrate, gallons		3.7		3.7		3.7
Per cent increase in sucrose		0.37	[1] 0.38	0.43	0.21	0.63
Per cent decrease in—						
Invert sugar		29.2	8.3	18.7	10.4	25.0
Ash		36.8	[2] 79.0	47.4	[2] 100.0	68.4
Undetermined		24.6	[2] 40.0	38.4	53.8	58.5
Color		91.3	40.4	94.5	61.5	94.2

[1] The sucrose content decreased.
[2] The ash and invert content increased.

From the foregoing it will be seen that the present invention provides a method of refining sugar solutions more efficiently than heretofore by the employment of a chemical bleaching agent and an adsorbent. By such method not only is the chemical bleaching treatment simplified but the useful life of the adsorbent is substantially prolonged.

What I claim is:

1. The method of treating a sugar solution that has been decolorized with active chlorine, which comprises contacting the solution at an elevated temperature and so containing returned color with a thermally activated bauxite.

2. The method of treating a solution of sugar decolorized with active chlorine which comprises heating the solution whereby color return is effected and treating said solution with a thermally activated bauxite.

3. The method of treating a solution of sugar decolorized with active chlorine which comprises heating the solution whereby color return is effected and percolating the decolorized sugar solution through a bed of thermally activated bauxite.

4. The method of treating a solution of washed sugar which comprises treating said solution with a quantity of a hypochlorite sufficient to substantially decolorize said solution and thereafter treating the decolorized solution at an elevated temperature, and so containing returned color, with activated bauxite.

5. The method of treating a solution of washed sugar which comprises treating said solution with a quantity of a hypochlorite sufficient to substantially decolorize said solution and with a reagent from the group consisting of acids and acid salts capable of forming an insoluble salt with the metal ion of the hypochlorite, separating insoluble material from said solution and thereafter treating said solution at an elevated temperature, and so containing returned color, with activated bauxite.

6. The method of treating a solution of washed sugar which comprises treating said solution with calcium hypochlorite and monocalcium phosphate in amounts sufficient to substantially decolorize said solution, separating insoluble material from said solution, and thereafter treating the so decolorized solution at an elevated temperature, and so containing returned color, with activated bauxite.

7. The method of refining a sugar solution which comprises treating said solution with a quantity of an alkaline earth metal hypochlorite sufficient to substantially decolorize said solu-

tion and with a reagent from the group consisting of acids and acid salts capable of forming an insoluble salt with the metal ion of said hypochlorite, separating insoluble material from said solution, and thereafter treating said solution at an elevated temperature, and so containing returned color, with activated bauxite.

8. The method of refining a sugar solution which comprises treating said solution with a quantity of an alkaline earth metal hypochlorite sufficient to substantially decolorize said solution and with a reagent from the group consisting of acids and acid salts capable of forming an insoluble salt with the metal ion of said hypochlorite, separating insoluble material from said solution, and thereafter treating said solution at a temperature between 150° F. and 175° F., and so containing returned color, with activated bauxite.

9. The method of refining a sugar solution which comprises treating said solution with a quantity of an alkaline earth metal hypochlorite sufficient to substantially decolorize said solution and with a reagent from the group consisting of acids and acid salts capable of forming an insoluble salt with the metal ion of said hypochlorite, separating insoluble material from said solution, and thereafter treating said solution at an elevated temperature with an additional quantity of said hypochlorite to effect further decolorization and with activated bauxite to prevent color return.

10. The method of refining a sugar solution which comprises treating said solution with active chlorine sufficient to substantially decolorize said

solution and thereafter treating said solution at an elevated temperature, with an additional quantity of said active chlorine to effect further decolorization, and with activated bauxite to prevent color return.

11. The method of refining a sugar solution which comprises treating said solution with active chlorine at a temperature below about 100 °F. to substantially decolorize said solution, and thereafter treating said solution at a temperature between 150° F. and 175° F. with an additional quantity of said active chlorine to effect further decolorization and with activated bauxite to prevent color return.

12. The method of refining a sugar solution which comprises treating said solution with active chlorine to substantially decolorize said solution, and thereafter treating said solution at a temperature between 150° F. and 175° F with an additional quantity of said active chlorine to effect further decolorization and with activated bauxite to prevent the color return.

WILLIAM A. LA LANDE, JR.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,989,156	Sanchez	Jan. 29, 1935
2,059,110	Ioannu	Oct. 27, 1936
2,211,727	La Lande	Aug. 13, 1940
2,216,753	Sanchez	Oct. 8, 1940