

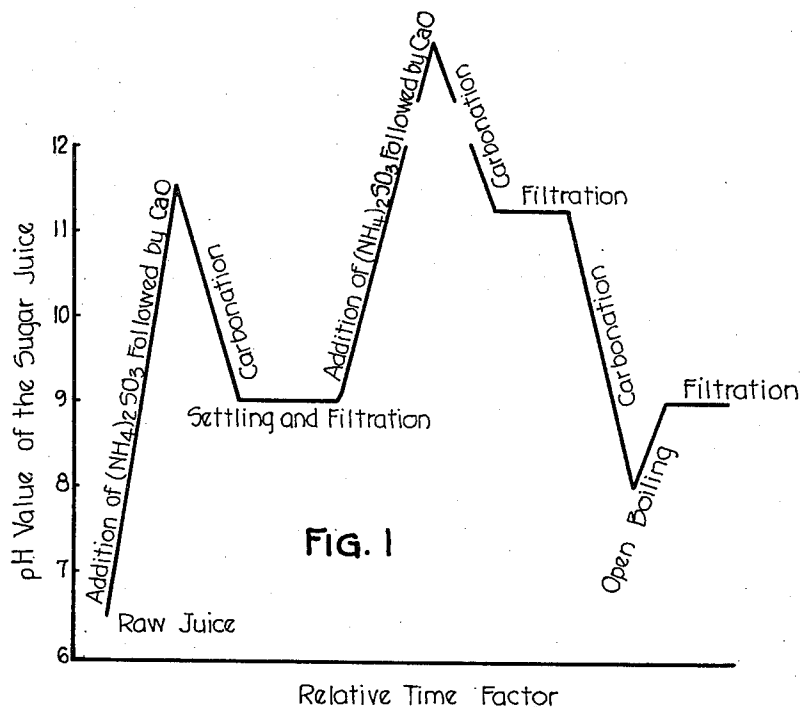
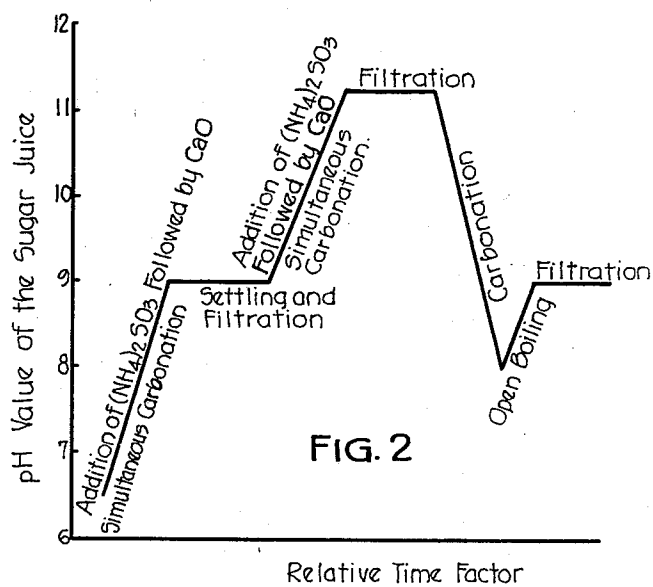
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PURIFICATION OF SUGAR JUICES

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PURIFICATION OF SUGAR JUICES

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This invention relates to the manufacture of sugar, and particularly to improvements in the carbonation process for purifying juices and syrups.

The disadvantages of the universally used carbonation processes have long been recognized. These include the use of excessive quantities of lime; the necessity for high juice temperatures to avoid filtration difficulties; the addition of sodium compounds which increase the losses of sugar as molasses; and inefficiency of purification, particularly as regards removal of colloidal material and residual calcium.

Many variations on the usual procedure such as the step-wise addition of the lime and the fractional removal of impurities under different conditions of alkalinity, as well as the use of supplementary reagents, including ammonia and its salts, have been suggested as improvements. In spite of these disclosures, a commercially feasible process which permits full realization of the benefits to be derived from such procedures has not heretofore been developed. This was inevitable because the optimum conditions of operation, particularly control of hydrogen ion concentration and temperature, had not previously been discovered.

In the following description of my invention and of a preferred method of carrying it out, particular reference is made to the manufacture of beet sugar although the principles involved are equally applicable to kindred arts, such as cane sugar manufacture, by proper adjustment of the conditions to meet the well known differences in character of the juices involved.

Sugar refiners have recognized the fact that the degree of clarification is related, inversely, to the amount of residual calcium salts left in the juice, provided the final calcium oxide elimination takes place at the optimum point pH 8.4 or hydrogen ion concentration of 2.5×10^{-9} .

In present processes alkali metal compounds, e. g. soda ash, are used to reduce the final calcium content of the juice, but the undesirability of the practice is universally admitted. As it is impossible to remove these compounds in later operations they increase the molasses losses. The use of ammonia has been suggested in this connection because it is capable of subsequent removal. But it has not been applied successfully commercially because of failure to properly control the hydrogen ion concentration and temperature of the juices.

I have found that the mere presence of ammonia, or its salts, in the final stages of clarification

is insufficient to bring about a pronounced reduction in dissolved calcium. It is not only necessary to assure a certain definite ammonia alkalinity, but it is also necessary to have in the solution sufficient suitable acid ions such as $\text{SO}_3^{=}$ or preferably carbonate ions obtained by carbonation to force the precipitation of the residual calcium.

The ammonia used may advantageously be made the carrier of useful acid radicals which form precipitates with lime possessing high sorptive capacity. Under these conditions the ammonium salt is introduced as the first step in the clarification, although further amounts may be added at later stages. In general the best results are obtained by introducing the ammonium salt before the addition of lime. By the mixing of the two reagents in solution a more rapid precipitation results than is possible in the standard methods now in use. The precipitate formed is more finely divided and a more effective sorptive agent. The sulfite has been found exceptionally effective but the carbonate, oxalate, phosphates, tartrate, or other such salts may also be used.

For economic commercial application of this invention a relatively low temperature procedure of carbonation is to be preferred because of the ammonia losses which accompany any evaporation of the juice. By operating at relatively lower temperatures substantial heat economies are also possible. A further advantage to be derived from "cold" operation, is a marked improvement in the sorption of colloidal material by the precipitates formed. Carbonation at temperatures below 85°C . has never previously been practicable because of the poor filtrability of the precipitates obtained. My procedure of control of hydrogen ion concentration, however, permits these operations to be carried out at much lower temperatures than 85°C . I can successfully operate at temperatures as low as 55 to 65°C .

This is made possible by the discovery of the possibility of arriving at a zone of clarification and rapid settling in the hydrogen ion concentration range of 3×10^{-9} to 10^{-10} or pH range of 8.5 to 10.0 by carbonating the limed sugar juice beyond the first zone of good settling which usually occurs at about the hydrogen ion concentration 5×10^{-11} to 2×10^{-12} (pH 10.7 to 11.2). In this zone of hydrogen ion concentration 3×10^{-9} to 10^{-10} the juices are of a red-brown color instead of the usual light yellow. They have been termed "burnt juices" when inadvertently encountered in the industry and have been studiously avoided from fear of their darker color.

have found this color to be of no importance, however, because it is readily eliminated in the subsequent steps of my process.

By first eliminating a part of the impurities in the zone of rapid settling where the pH=8.5 to 10 (hydrogen ion concentration 3×10^{-9} to 10^{-10}) a relatively small compact mud of comparatively high organic content is obtained. Because of its small amount, this precipitate can be of poor filtrability without reducing factory capacity below that of existing processes, even when the operations are carried out at low temperatures. This is in no way possible with any other process which has been suggested, for all involve as an essential feature the removal of the first impurities in a bulky precipitate representing an appreciable proportion of all the muds which have to be filtered.

Due to the fact that most of the disturbing organic substances will have been eliminated by this "pre-carbonation" treatment, filtration without settling is practicable after the main carbonation which follows. In this step the impurities are removed at a lower hydrogen ion concentration than in the first treatment. Again due to the previous removal of colloidal material, a more efficient sorption of that remaining is possible as the operations can be carried out nearer the true iso-electric point of such material as remains.

In the following description of a preferred method of carrying out my invention as applied to beet sugar manufacture, it will be understood that the well known variations in the character of the beets sliced will require corresponding variations in the quantities of reagents used and in the conditions of operation. This applies particularly to the hydrogen ion concentrations specified, it being recognized in present practice that the optimum may vary widely as from a hydrogen ion concentration of 6×10^{-11} to 6×10^{-12} (or pH 10.8 to 11.8) during the same campaign and even more for different campaign years.

According to my invention, raw diffusion juice at about 55 to 65° C. is treated with about 0.1% ammonium sulfite (all quantities of reagents will be expressed as percentages of the juice weight) followed by the addition of about 0.4% calcium oxide as milk of lime (or as calcium saccharate when operating in conjunction with the Steffen process). The resulting mixture, having a hydrogen ion concentration of about 10^{-11} to 10^{-12} or a pH value of about 11.0 to 12.0 is brought by carbonation in the usual way to a hydrogen ion concentration of about 3×10^{-9} to 3×10^{-10} or a pH of about 8.5 to 9.5, preferably more than a hydrogen ion concentration of 10^{-9} (pH 9). The resulting precipitate is settled, preferably in the Dorr thickener commonly employed for the first stage of separation in continuous methods of operation, and then filtered. The temperature during filtration need not be higher than 65° C. If desired, small quantities of lime, about 0.01-0.02%, may be added to the mud to facilitate filtration.

To the clear juice from the settling tank (Dorr overflow) about 0.05% $(\text{NH}_4)_2\text{SO}_3$ is added followed by about 0.4% CaO and the mixture carbonated in the usual way to a hydrogen ion concentration of about 3×10^{-11} to 10^{-12} or a pH of about 10.5 to 12.0, preferably a hydrogen ion concentration between 3×10^{-12} to 10^{-12} after filtration without settling, the carbonation of the filtrate is continued to a hydrogen ion concentration of about 10^{-8} to 2×10^{-9} or a pH value of about 8.0 to 8.2. The alkalinity of the juice may

then be raised by the addition of ammonia to a hydrogen ion concentration of 3×10^{-9} to 3×10^{-10} or a pH value of 8.5 to 9.5, or as is preferred, the unfiltered juice may be heated in the usual open boilers until this hydrogen ion concentration is attained as the result of the more rapid evolution of CO_2 as compared with NH_3 . In either case, a time interval at the lower hydrogen ion concentration of at least 10 minutes should be provided to allow an opportunity for the completion of precipitation before filtration.

The purified juice is then treated by the usual processes for recovery of the sugar.

When the ammonia content of the clarified thin juice is below 0.070% where the juice has a hydrogen ion concentration less than 3×10^{-9} there is no danger of appreciable corrosion of copper and brass apparatus or fittings. Where higher hydrogen ion concentrations are present even greater amounts of ammonia may be present without causing corrosion difficulties. It is not desirable, however, to allow the clarified thin juice to reach a hydrogen ion concentration higher than 10^{-8} as the subsequent elimination of ammonia then becomes difficult. It is to be noted that the total amount of ammonium sulfite used in the above described illustration of an application of my process, represents only about 0.045% ammonia or far below the amounts which produce corrosion.

By the use of automatic control apparatus of the hydrogen ion concentration of the juices, my invention may be carried out without permitting the alkalinity of the juices to materially exceed, during any one step of the operations, that at which the precipitated impurities are to be removed.

Both methods of operation are indicated diagrammatically in the drawing, wherein Figure 1 represents a flow-sheet of my process as carried out in batch operation, and Figure 2 a flow-sheet of the operations as carried out by continuous methods with automatic control of the pH value of the juices.

The relative time factor denoted in these figures is intended merely to show the order of the operations. The widths of the plateaus indicating filtration, for example, are not, in any sense, measures of the time required for these operations as compared with the other steps in the process.

The order of the various operations is designated by the labels and their effect on the pH value of the juice is indicated by the scale shown. The particular points used in the drawing are only representations of the pH ranges previously defined for the steps to which they refer. In Figure 1 no definite pH value has been assigned to the juice after the second addition of ammonium sulfite and lime because this may be varied widely by the use of different amounts of those reagents.

The present invention accordingly provides a practical commercially available process for purifying sugar juices which obviates the difficulties of the past. It provides a substantial economy in the use of lime not only as a result of the direct replacement of lime by another alkaline reagent, i. e. ammonium sulfite, but also as a result of the formation thereby of precipitates of much greater sorptive capacity. It makes the use of undesirable alkali-metal compounds entirely unnecessary. By eliminating the final SO_2 saturation, it gives improved sugars containing less residual SO_2 . Operation at lower temperatures, with the pre-carbonation treatment, results in less discoloration of the juice during clarification in the zone

of high alkalinity as well as much better sorption of colloids. Sorption of colloid impurities at their true iso-electric points, made possible by the precarbonation process, also greatly improves the removal of organic impurities. The result is a much better advance in degree of purity of the treated juice than is possible with previous processes. Not only are more colloids removed by my process, but also there is a more thorough removal of those colloids of a gummy nature (reversible type), consequently boiling and evaporation are improved and the difficulties of foaming reduced.

The introduction of $(\text{NH}_4)_2\text{SO}_3$ at the beginning of the clarification produces juices and sugars of greatly improved color. Another important feature of my invention is the presence of ammonium sulfite at each separation stage up to the evaporation stage. This results in greatly improved precipitation and in the formation of precipitates of increased sorptive capacity, settling rate and filtrability.

The thorough removal of calcium in the final stage of treatment results in juices which not only form no scale in the evaporators and heaters, but actually have been observed to dissolve the scale left in the apparatus by juices purified in the usual way. Moreover, this elimination of calcium results in lower sugar losses because less molasses is produced.

Some of the advantages of my process over the standard procedure of double carbonation and sulfur dioxide saturation are shown by the following results determined during various factory and small scale tests of my method.

	Standard procedure	Improved process
Consumption of CaO as milk of lime as percent of juice weight.....	2.12	1.64
Consumption of soda ash as percent of juice weight.....	0.10	None
Consumption of sulfur as percent of juice weight.....	0.07	None
Consumption of ammonium sulfite as percent of juice weight.....	None	0.12
Purity of clarified juice.....	90.9	92.4
CaO content of clarified juice as grams per 100 Brix.....	0.084	0.010
Color of clarified juice (pure water as zero) (product of standard procedure as 100).....	100	78
Sulfur content of final sugar as sulfite parts per 1,000,000.....	6.30	2.33
Color of final sugar (scale pure water=0).....	11	9

My invention is capable of many modifications. Where it may seem desirable not to make changes in equipment already installed or for other reasons the first step described above of removal of impurities in the range of hydrogen ion concentration of 3×10^{-9} to 3×10^{-10} may be entirely omitted and the impurities first removed at the lower hydrogen ion concentrations of about 5×10^{-11} to 2×10^{-12} employed in present practice. The full benefit of the use of ammonium sulfite, in savings of lime through the formation of precipitates of high sorptive capacity, more complete elimination of calcium, and improved purity of juices and color of sugar will still be obtained by following the remaining steps of my invention.

While I have in the foregoing described in some detail the preferred embodiment of my invention and some variants thereof, it will be understood that this is only for the purpose of making the invention more clear and that the invention is not to be regarded as limited to the details of operation described, nor is it dependent upon the soundness or accuracy of the theories which I

have advanced as to the advantageous results attained. On the other hand, the invention is to be regarded as limited only by the terms of the accompanying claims, in which it is my intention to claim all novelty inherent therein as broadly as is possible in view of the prior art.

I claim as my invention:

1. A method of purifying sugar solutions from which the bulk of the precipitable material has been removed, comprising carbonating the solution to a hydrogen ion concentration within the range 2×10^{-9} to 10^{-8} and adding ammonia thereto to reduce the hydrogen ion concentration thereof to a value within the range of 3×10^{-9} to 10^{-10} and subsequently removing the resulting precipitate.

2. A method of purifying sugar solutions prior to evaporation thereof comprising introducing at least one basic agent comprising free ammonia to bring the hydrogen ion concentration of said solution to a value not greater than about 10^{-8} while containing an ammonia concentration not greater than 0.07% and then evaporating said solution whereby scale formation in the evaporator and corrosion of copper-containing equipment is substantially avoided.

3. A method of purifying sugar solutions comprising as the first step the separation of precipitated impurities by carbonating the limes solution to a hydrogen ion concentration between 3×10^{-9} and 3×10^{-10} , then liming and carbonating the partly purified solution to effect a second separation of impurities within the hydrogen ion concentration range of about 3×10^{-11} to 10^{-12} .

4. A method of purifying sugar solutions comprising alkalinizing the solution then acidifying to a hydrogen ion concentration of about 3×10^{-9} to 3×10^{-10} removing the resulting precipitate and subsequently separating further impurities by treatment with alkaline and acid electrolytes to bring the hydrogen ion concentration first within the range 5×10^{-11} to 10^{-12} and subsequently within the range 3×10^{-9} to 3×10^{-10} .

5. A method of purifying sugar solutions from which the bulk of the precipitable material has been removed by acidifying the alkaline solution to a hydrogen ion concentration of about 5×10^{-11} to 10^{-12} comprising the adjustment of the hydrogen ion concentration thereof by treatment with acid and alkaline electrolytes to a point within the range 10^{-8} to 2×10^{-9} , then reduction of the hydrogen ion concentration before removal of impurities is effected to a point within the range 3×10^{-9} to 3×10^{-10} .

6. A method of purifying sugar solutions from which the bulk of the precipitable material has been removed by acidifying the alkaline solution to a hydrogen ion concentration of about 5×10^{-11} to 10^{-12} , comprising carbonating the solution in the presence of an ammonium salt to a hydrogen ion concentration of about 10^{-8} to 2×10^{-9} , then heating the solution to remove carbon dioxide therefrom and reduce the hydrogen ion concentration to a value of about 3×10^{-9} to 3×10^{-10} .

7. A method of purifying sugar solutions comprising as the first step carbonating the limes solution in the presence of an ammonium salt at a temperature below 85°C . to a hydrogen ion concentration of about 3×10^{-9} to 3×10^{-10} whereat precipitable material is caused to settle out, liming and carbonating the partially purified solution to a hydrogen ion concentration of about 5×10^{-11} to 10^{-12} , removing the resulting precipitate and subsequently further acidifying the solution and

effecting a final removal of impurities at a hydrogen ion concentration of about 3×10^{-9} to 3×10^{-10} .

8. A method of purifying sugar juices wherein the juice has been treated so as to be strongly alkaline, which comprises carbonating the juice to a hydrogen ion concentration of about 3×10^{-9} to 3×10^{-10} , whereat rapid settling of precipitable material takes place, filtering, strongly alkalinizing the filtrate and carbonating to a hydrogen ion concentration of about 5×10^{-11} to 10^{-12} , again removing precipitated material and acidifying and effecting a third separation of impurities at a hydrogen ion concentration of about 3×10^{-9} to 3×10^{-10} .
9. A method of purifying sugar solutions comprising treating the alkaline solution with an acid electrolyte in the presence of an ammonium salt to cause separation of impurities at a hydrogen ion concentration of first about 3×10^{-9} to 3×10^{-10} and then at about 5×10^{-11} to 10^{-12} and subsequently carbonating to a hydrogen ion concentration of about 10^{-8} to 2×10^{-9} and then heating to reduce the hydrogen ion concentration to about 3×10^{-9} to 3×10^{-10} .

10. A method of purifying sugar juices com-

prising carbonating alkalinized juice to a hydrogen ion concentration of about 3×10^{-9} to 3×10^{-10} , removing the material precipitated thereby, alkalinizing and carbonating the partially purified juice to a hydrogen ion concentration of about 5×10^{-11} to 10^{-12} , removing further precipitated material, carbonating to a hydrogen ion concentration of about 10^{-8} to 2×10^{-9} and subsequently lowering the hydrogen ion concentration to about 3×10^{-9} to 3×10^{-10} before final removal of impurities.

11. A method of purifying sugar solutions comprising treating the solution with ammonium sulfite and alkaline and acid electrolytes to bring the hydrogen ion concentration of the alkaline solution first to about 3×10^{-9} to 3×10^{-10} and then to about 5×10^{-11} to 10^{-12} , removing precipitated impurities in each of said hydrogen ion concentration ranges, acidifying the resulting solution to a hydrogen ion concentration of about 10^{-8} to 2×10^{-9} and subsequently lowering the hydrogen ion concentration to about 3×10^{-9} to 3×10^{-10} before final removal of impurities.

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