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## TREATMENT OF SUGAR

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This invention relates to a method of manufacturing raw sugar, and more particularly to the addition of sodium hydrosulphite to solutions to improve the operations in the manufacture of raw sugar.

In a conventional process for the manufacture of raw sugar, the sugar is first expressed from the cane by a series of operations in which the cane is crushed and sprayed with water. The resulting raw cane juice contains dissolved oxygen, living organisms, colloidal materials and other materials which will interfere with the crystallization of the sugar. These impurities are partially removed in a defecation step, in the most conventional form of which lime is added to the raw cane juice under carefully controlled conditions and the solution is boiled to form a flocculent material which aids in the separation of impurities from the cane juice. The cane juice containing calcium salts, in addition to the aforementioned contaminants, is then separated from the coagulant by filtration or decantation to form a clarified solution containing approximately 15% sucrose.

The clarified juice is then passed through multiple effect evaporators which remove water from the solution to produce a thick syrup containing approximately 60% sucrose. Serious difficulty is encountered in the evaporators because of the formation of scale in the tubes of the evaporators which greatly reduces their heat transfer coefficient. The relatively high viscosity of the syrups, the "gummy" nature of many of the organic materials present in the cane juice and the lime aggravate the scaling condition.

The thick syrup is then passed into a vacuum pan in combination with varying amounts of added molasses where further evaporation of water from the sugar solution takes place. The evaporation is continued to form a massecuite (that is, a mass of sugar crystals suspended in a molasses). Ordinarily the massecuite is a highly viscous and sticky suspension which is relatively difficult to handle in the crystallizers and centrifuges.

The massecuite is centrifuged to separate the sugar crystals from the enveloping molasses. The molasses from the purer massecuite is returned to the vacuum pans for further exhaustion. The thoroughly exhausted molasses is recovered as "black strap" molasses.

The difficulties encountered in processing raw sugar solutions in this manner include:

1. Scaling in the calandria of preheaters and the evaporators;

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2. Formation of excessively viscous liquors and suspensions;
3. Presence of excessive gums and stickiness;
4. Growth of bacteria and mold;
5. Corrosion of metal and consequent discoloration of solution due to the presence of iron compounds;
6. Resistance of dispersed colloids to coagulation.

The important feature of the present invention resides in the marked improvement in the raw sugar manufacturing processes and in the refining properties of the raw sugar which result from the addition of sodium hydrosulfite ($Na_2S_2O_4$) to the solution. More specifically, the present invention embodies the addition of sodium hydrosulfite to the raw sugar liquor usually in the earlier stages of the process. It has been discovered that the judicious addition of sodium hydrosulfite during the early stages of processing raw sugar solutions results in:

1. Improved clarification;
2. Improved heat transfer in the pre-evaporators, evaporators and vacuum pans;
3. More brilliant, lighter in color, less viscous and less sticky thick syrup;
4. Diminished viscosity and stickiness in the massecuites and molasses;
5. Diminished color formation throughout the process as distinct from color bleaching;
6. Improved storage and refining characteristics of the resulting raw sugar.

These improvements make possible a series of economies both in the raw sugar house and in the refinery as will be subsequently described.

It is thought that these improvements arise from four basic functional characteristics of hydrosulfite compositions, which will now be discussed.

It is believed that one function of the hydrosulfite is to alter the temperature-solubility relations of the calcium salts which are responsible for the formation of calcium scale in the equipment, particularly in the calandria of the evaporators. Hydrosulfites, including sodium hydrosulfite, exhibit a widespread tendency to form double salts which have distinct temperature solubility relations from those of the single salts. The first function of the hydrosulfite is thus the improvement of heat transfer by reducing the calcium scale formation. It has even at times been observed that heavily scaled evaporators after evaporating sodium hydrosulfite containing solutions exhibit an appearance of scale attrition, as small particles of scale may be found

in the throughput of the evaporators. In such cases, an additional mechanism may be operative, namely, the deposition of hydrosulfite complex or double salts as scale instead of the normal single calcium salts; these hydrosulfite-calcium salts would tend to chip off of the calandria due to the gradual decomposition of the hydrosulfite. Whatever be the explanation, it has been discovered that when sodium hydrosulfite is added in small amounts to the sugar solutions before or during passage through the evaporator formation of scale is retarded.

The second function of the hydrosulfite is exhibited by a reduction in the gumminess or stickiness and of the viscosity of the massecuites and molasses. The viscosity and the gumminess of the massecuites and molasses are both intimately related to the colloids present in these masses and to the physical condition, particularly particle size, of these colloids. By reducing the viscosity and stickiness of the massecuites and molasses when added early in the process, hydrosulfite thus exhibits a basic action on the colloids. This basic action of hydrosulfite on the colloids is believed to be a coagulating action. This coagulating action of hydrosulfite on the colloids may arise from the adsorption of the doubly charged hydrosulfite ion on the surface of the dispersed colloid, the reduction of certain groups or linkages on the surface of the colloidal particles, such as the sulfide link in proteins and/or a complex or double salt formation with groups, such as the amino group, of the colloids. Whatever be the mechanism, sodium hydrosulfite has exhibited in practice a basic effect on the detrimental influence of colloidal formations.

The third function of hydrosulfite is its effect on the growth of living organisms during industrial processing. Even the boiling temperature present during defecation does not destroy all the living organisms present in sugar solutions and significant sugar losses frequently occur due to the action of organisms such as the gum-forming leuconostoc mesenteriods. Living organisms not only cause product loss but, what may be more important, also produce colloids and off colors. One encounters, for example, such troublesome organisms in stagnant paper pulp slurries which tend to turn black. Sodium hydrosulfite is toxic to many such living organisms in even very small concentration and thus reduces their detrimental influence in producing colloids and off-standard end products. The application of the toxic property of hydrosulfite on detrimental living organisms is clearly broader than the sugar industry.

The fourth function of hydrosulfite is an oxygen scavenging effect. Oxygen is injurious in the process industries for several reasons. In the first place, corrosion can only occur when oxygen is present together with water. Thus the presence of dissolved oxygen not only speeds the destruction of the equipment but also introduces color forming iron salts into the solutions and end products. In the second place, oxygen itself, or because of its formation of peroxides, is a catalyst for many side reactions particularly polymerization reactions. Thus the hydrosulfite in scavenging oxygen acts as an anti-corrosive, an anti-polymerization aid, and an inhibitor of color formation. This last is distinct from the well known color bleaching property of hydrosulfites.

In practicing the invention, a small quantity of the hydrosulfite can be profitably added directly under the presses to avoid growth of living organisms. However, sodium hydrosulfite is relatively unstable, especially at elevated temperatures and in contact with air, and is consumed by reducible substances present in the raw cane juice. For this reason, the major portion of the hydrosulfite is normally added to the process at the stage where the maximum result is desired. Thus to effect an improved clarification, including a more complete separation of defecation mud and/or a more compact and hence more easily filterable and washable filter mud as also a clearer juice, one would normally add the sodium hydrosulfite into, or immediately before, the defecator during or immediately prior to the defecation cook, preferably toward the end of the cook. In plants using continuous clarification systems of the "Dorr" type, the sodium hydrosulfite would be added continuously to the upper segments of the sedimentation trays.

On the other hand, to effect an optimum inhibition of scaling in the evaporators with a minimum of hydrosulfite, the sodium hydrosulfite would normally be added continuously to the clarified cane juice which feeds the evaporator and/or to the feed to the effect which causes most trouble, which usually is the last effect. My experiments have shown that a reduction in stickiness and viscosity of the massecuites and molasses can be obtained when the sodium hydrosulfite is added early in the process, as for example to the clarified juice; in fact my experiments have indicated a greater effect on the viscosity and stickiness when the sodium hydrosulfite is added to the clarified juice than when it is added to the vacuum pan. The greatest bleaching effect, of course, ensues when the sodium hydrosulfite is added to the vacuum pan in accord with the conventional practice of adding the hydrosulfite for bleaching as late in the process as possible to avoid reversion of color.

An optimum combination of the advantages of sodium hydrosulfite results from the continuous judicious addition of sodium hydrosulfite in partial increments at various stages of the process. A small part may be added under the crushing rolls. A major part may be added to the clarified juice before entering and/or while in the multiple effect evaporator and another part may be added to the thick syrup before entering the vacuum pan. The final decision as to the quantitative distribution of the additions of sodium hydrosulfite during the various early stages of processing will depend, of course, on the relative economic value of each of the advantages under the specific mill operating conditions and specific characteristics of the raw material being processed.

In practice, the amount of sodium hydrosulfite will vary with the mill operating conditions and with the amount of cane or other raw material used. However, one may reasonably expect to add in one or more steps a total of from 0.05 to 5 pounds of sodium hydrosulfite per ton of sucrose being processed. The following examples are given to illustrate the invention:

*Example 1*

From one to 1.5 pounds of sodium hydrosulfite per ton of sucrose in process was continuously added to the clarified cane juice just prior to entrance into the pre-evaporators and evaporators. The addition of sodium hydrosulfite was maintained for a two month period and the operation was compared with the operation before and after the period involving hydrosulfite

additions as also with previous years in which cane conditions were analogous.

A striking improvement in the scale condition was observed. The sugar mill in question had normally to shut down every seven days to clean the evaporators. With the hydrosulfite addition to the clarified juice, this mill found that it could easily run fifteen days or more between shutdowns. The evaporators were operating entirely satisfactorily at the end of fifteen days when shutdowns were ordered due to excessive accumulation of ash in the ovens. The scale which formed with hydrosulfite additions was entirely different in appearance and properties; it being almost black instead of grey, and it was now friable and of considerably less thickness. The thinner, almost black, friable scale which formed during the hydrosulfite additions was very soluble in the caustic wash and very easy to remove.

The thick syrup delivered by the evaporators during the operation with sodium hydrosulfite was considerably brighter, clearer and more sparkling, which to those practiced in the art implies improved subsequent processing.

The massecuites and molasses were markedly less viscous and less gummy, even the final blackstrap molasses was fluid during the hydrosulfite addition period.

Surprising improvement in purging was noted during the entire two months of hydrosulfite addition. A clocked run on seven hundred bags of sugar showed a reduction in purging time of raw sugar of 50%. The same polarization (96° to 97°) was obtained with half of the wash water previously used. Previously each centrifuge containing some two hundred and fifty pounds of raw sugar was washed with two liters of water in the case of primary strikes and with four liters of water in the case of secondary strikes; during the period with hydrosulfite addition to the clarified juice, one liter was used for primary strikes and two for secondary strikes.

The product raw sugar showed improved physical characteristics during the period with hydrosulfite addition. The raw sugar was lighter in color, the grain was harder and showed evidence of less molasses retention and less stickiness.

The refining operation of the raw sugars produced during the two months of hydrosulfite addition was materially improved. A 33% reduction in the quantity of affination wash water was obtained. Previously some fifteen liters of wash water had been required to wash three hundred pounds of affinated sugar. During the two months of hydrosulfite addition ten liters were used instead of the previous fifteen. The quantity of filter aid was reduced from 0.40 to 0.30 pound per one hundred pounds of sugar during the two months of hydrosulfite addition to the clarified cane juice and at the same time a 30% increase in filtering rate was obtained in the refinery.

*Example 2*

At a different sugar mill 0.75 pound of sodium hydrosulfite was continuously added to the clarified cane juice prior to entrance into the evaporators for a period of one month.

The striking improvement in the scale condition was again observed. Normal operation at this sugar mill involved a shutdown for cleaning the evaporator every ten days; during the month of hydrosulfite addition an interval of sixteen days without cleaning was easily reached and the shutdowns were finally made for reasons other than need to clean the evaporators.

The surprising improvement in purging was also observed at this mill during the month of hydrosulfite addition and a 50% reduction in the quantity of water used to wash the raw sugar occurred. Previously the primary sugar was washed with four liters of wash water per centrifuge-full and the secondaries with six liters. During the month of hydrosulfite addition, the primaries were washed with two liters and the secondaries with three liters.

The raw sugar product also showed improved brilliance, lighter color and harder grain during the month of hydrosulfite addition. Improved refining characteristics were also observed at this mill during the month of hydrosulfite addition in that a 25% reduction in affination wash water was possible.

In view of the foregoing, it is obvious that the use of sodium hydrosulfite gives rise to at least five distinct improvements. When the hydrosulfite is added prior to or during defecation, a more complete defecation, a more compact defecation mud, and a clearer, more clarified juice is obtained. It is believed that this is due in part to the coagulating or denaturing effect of the hydrosulfite on the colloids present in the sugar solutions, and in part to a more complete removal of the iron salts which enter largely by attrition of the crushing rolls. A more complete clarification improves all subsequent stages in the processing.

It has also been found that the addition of the sodium hydrosulfite prior or during passage through the heat transfer surfaces, particularly those of the evaporators, provides an improved heat transfer and less scale. It is believed that this improvement is due in part to all four of the basic functions of hydrosulfite which have been previously described. The scale in the evaporators arises in part from the inorganic and organic calcium salts and in part from the colloids present in the clarified juice; the colloids may in fact bind or occlude the calcium salts and cause them to adhere to the calandria as scale. Thus, in addition to the calcium scale inhibition due to the effect of hydrosulfite on the temperature-solubility relations of the calcium salts, the scale will also be reduced by the coagulating effect of hydrosulfite on colloids and by its toxicity to colloid forming organisms which will inhibit colloid scale formation and calcium scale occluded by colloids.

Furthermore, the effect of hydrosulfite in reducing the viscosity and gumminess of the syrups will occasion more turbulent flow and hence less scale formation. In addition, the oxygen scavenging effect of hydrosulfite will reduce corrosion and/or its concomitant roughening of the surfaces and thus reduce the tendency to retain scale. The economy of the scale reduction lies primarily in increasing the interval of operation between shutdowns for cleaning the evaporators and in the economies related thereto.

It has also been found that when the hydrosulfite is added early in the raw sugar process, before the evaporators, there is a reduction in viscosity and gummines of the massecuites and molasses. It is believed that this is primarily due to the basic effect of hydrosulfite in affecting the condition of aggregation of the colloidal materials. However, the oxygen scavenging effect of hydrosulfite and the consequent elimination of oxygen and peroxides, which are poly-

merization catalysts, could also well play a role in avoiding excessive viscosity and gum formation. The reduced viscosity and gumminess of the massecuites and molasses, occasioned by the addition of hydrosulfite early in the sugar process, results in more complete exhaustion of the molasses and hence larger yields of sugar; in a better circulation in the vacuum pan and hence less local overheating and inversion; in the formation of harder grains and more brilliance due to less occlusion of colloids and in a more complete and faster purging in the centrifuge. Moreover, the raw sugar produced with hydrosulfite addition early in the process requires less wash water on the centrifuge to bring it up to the required polarization. The reduction in wash water could be connected with the more complete purging described above which leaves less molasses to be washed out in producing raw sugar. As is known to those practiced in the art, the less wash water used the better will be the storing characteristics of the raw sugar.

The addition of the hydrosulfite early in the process also causes a reduction in the amount of color formed during the process, as distinct from the well known bleaching action of hydrosulfite after the formation of coloring matter. A major portion of the coloring matters in raw sugar and in its solutions is due to the presence of iron polyphenol compounds. The iron enters from the attrition of the crushing rolls and as the result of the corrosion of the equipment. Hydrosulfites tend to eliminate dissolved iron as insoluble iron sulfide and, furthermore, reduce the amount of iron salts which enter by corrosion in virtue of its oxygen scavenging effect. Furthermore, many polymerization products are colored and in eliminating peroxide catalysts, the hydrosulfite may indirectly reduce the formation of coloring matter in this manner. In any event, whatever be the explanation, it has been found that less coloring matter is formed in sugar solutions in the absence of oxygen than is formed in the presence of oxygen. Hydrosulfites are among the most efficient oxygen scavengers and in consequence less color is formed in the presence of hydrosulfite than in its absence.

Finally, the coloring matter which does form will in part be temporarily bleached by the well known bleaching action of hydrosulfites. The use of hydrosulfites to bleach the coloring matter in sugar is well known to those practiced in the art; it is also well known that such bleached sugars revert in storage and darken as the oxygen from the air re-oxidizes the coloring matter which was bleached by reduction by the hydrosulfite. For this reason, it is standard practice in all sugar mills or refineries which use hydrosulfite to bleach sugars to add the hydrosulfite as late in the process as possible; namely, in the vacuum pan where the massecuite is formed. The reason for adding the hydrosulfite late in the process, as has been done up to now, is so as to prevent darkening by re-oxidation after the hydrosulfite addition. Therefore, the hydrosulfite has always been added to bleach the coloring matter already formed and the fear of subsequent re-darkening has caused the addition of the hydrosulfite to be made as late in the process as possible.

This conventional bleaching procedure is quite distinct from the present invention for to inhibit the formation of coloring matter, as distinct from bleaching it after it forms, the hydrosulfite should be added as early in the process as feasible. The bleaching action of hydrosulfite added late in the process is temporary and the bleached coloring matter will revert and darken in air; the diminished formation of coloring matter due to oxygen scavenging by hydrosulfite added early in the process is permanent. In addition to this fundamental difference between the function of hydrosulfite added early in the process and hydrosulfite added late in the process, and in addition to the basic advantages described above which accrue only when the hydrosulfite is added early in the process, it should be noted that when the hydrosulfite is added to the vacuum pan in accord with the current art there is an incomplete and inadequate mixing of the hydrosulfite. Local over-concentrations occur in some places and under-concentration in others due to the high viscosity and inadequate circulation in the vacuum pan. This excess hydrosulfite is harmful to sugar solutions which are highly sensitive to a change in the pH at the temperatures of the vacuum pan. Therefore, the thorough mixing of the hydrosulfite is essential as well as economical. The thorough mixing can best be achieved by adding the hydrosulfite early in the process before high viscosity develops as a result of water evaporation and above all by adding the sodium hydrosulfite continuously rather than in batches.

Finally, the additions of hydrosulfite during the early stages of sugar processing improves the refining properties of the raw sugar. The formation of less coloring matter and a harder grain which is more resistant to dissolution by the affination syrups has already been mentioned. In addition, it has been discovered that at least two new improvements in refining characteristics as a result of hydrosulfite additions early in the raw sugar process are obtained. These include a considerable reduction in the quantity of affination wash water required to reach the desired polarization of approximately 99°, and improved filterability and reduction in the quantity of filter aid needed.

The judicious addition of sodium hydrosulfite can effect a more complete defecation, more compact defecation mud, and more clarified juice; an inhibition of scaling and/or improved heat transfer in the calandria of the evaporators and other heat transfer equipment; a more brilliant, lighter color, less viscous and less sticky thick syrup; a reduction in viscosity and stickiness of the massecuites and molasses, more complete purging and the use of less wash water for raw sugar; inhibition of color formation and inhibition of corrosion and improved storage and refining properties particularly as regards hardness of grain brilliance of raw sugar, affination and filterability.

I claim:

1. In a process for the manufacture of raw sugar from sugar cane in which sugar containing juices are expressed from cane, defecated, then evaporated to a thick syrup and sugar crystallized from the thick syrup, the improvement comprising the addition of sodium hydrosulfite to the sugar juice at any stage subsequent to grinding of the cane and prior to the discharge from the evaporators.

2. In a process for the manufacture of raw sugar from sugar cane in which sugar containing juices are expressed from cane, defecated, then evaporated to a thick syrup and sugar crystallized from the thick syrup, the improvement comprising the addition of sodium hydrosulfite to the

sugar solution immediately prior to the introduction of the solution into the evaporator.

3. A process for the manufacture of raw sugar from sugar cane characterized by the addition of sodium hydrosulfite to the cane juice during its initial concentration in evaporators.

4. In a process for the manufacture of raw sugar from sugar cane in which sugar containing juices are expressed from cane, defecated, then evaporated to a thick syrup and sugar crystallized from the thick syrup, the improvement comprising the addition of 0.5 to 4 pounds of sodium hydrosulfite per ton of sucrose in the sugar solution to the sugar juice at any stage subsequent to grinding of the cane and prior to its discharge from the evaporators.

5. In a process for the manufacture of raw sugar from sugar cane in which sugar containing juices are expressed from cane, defecated, then evaporated to a thick syrup and sugar crystallized from the thick syrup, the improvement comprising the addition of from 0.5 to 4 pounds of sodium hydrosulfite to the cane juice in partial increments during successive stages of the operation prior to the discharge of the juices from the evaporator.

6. In a process for the manufacture of raw sugar from sugar cane in which sugar containing juices are expressed from cane, defecated, and then evaporated to a thick syrup from which sugar is crystallized, the improvement comprising adding sodium hydrosulfite to sugar juices subsequent to defecation and prior to entering the vacuum pans whereby scaling of the evaporators is materially reduced.



7. In a process for the manufacture of raw sugar from sugar cane in which raw sugar juices are defecated, evaporated, and crystallized to form a raw sugar, the improvement comprising adding sodium hydrosulfite to sugar juices in the evaporation step substantially prior to the formation of grain.

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