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SUGAR SEQUESTERING AGENT

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This invention relates to washing compositions and particularly to such compositions having improved sequestering characteristics.

The commercial cleansing of bottles by dairies, breweries, soft drink bottlers, and other industries requiring reconditioning of glassware is conventionally reliant upon the employment of a strong caustic solution followed by a rinse. Such washing methods are generally satisfactory provided that some provision is made to prevent the precipitation of salts of calcium, magnesium, aluminum, iron and other insoluble metallic components. In the absence of such provisions, the insoluble metallic salts are precipitated as a scale, both on the glassware and on the washing machinery. Thus, sequestering agents, such as sugar acids, are normally employed in combination with the caustic solutions. Various sugar acids are now being used as sequestering agents in caustic solutions, particularly in the bottle washing field to prevent scale formation on machinery. These sequestering agents can be conveniently divided into two groups: gluconic acid prepared by fermentation, and various heptonic acids made by the cyanohydrin reaction on hexose sugars. While these sequestering agents have met with commercial acceptance, they are deficient in several respects. For example, they are relatively expensive and definitely limited in their sequestering capability. In addition, care must be taken in their storage and handling to prevent precipitation from solution.

It is, therefore, an object of this invention to provide a novel washing compound overcoming the disadvantages of the prior art. A more specific object of the present invention is to provide a new and novel stable sequestering composition of increased activity that can be economically prepared from readily available materials.

In accordance with this invention, generally stated, these and other objects are accomplished by reacting a concentrated caustic solution with a concentrated solution of a hexose sugar at an elevated temperature. More specifically, this invention contemplates a sequestering agent prepared by adding an aqueous solution containing at least 50% by weight caustic to an aqueous solution containing between about 70% and 85% by weight of a hexose sugar within a temperature range of approximately 90° C. to 100° C. and maintaining this temperature until the reaction is substantially complete. It has been found in most instances that the reaction can be completed in from about two to four hours. The caustic can be any water soluble alkali metal hydroxide. However, because of the economies involved, the hydroxides of sodium and potassium are preferred. Any hexose sugar, whether an aldose or a ketose, can be employed. Thus, materially improved sequestering agents can be prepared by the action of a caustic on glucose, fructose, sorbose or glucuronic acid, as well as mixtures and commercially available preparations of these sugars.

The original mixture prior to reaction consists essentially of one or more hexose sugars, an alkali metal hydroxide and water. Preferably the mixture contains in the neighborhood of 20% sodium hydroxide or other alkali metal hydroxide, 50% sugar or sugar mixture, and 30% water. However, the proportions of these materials can vary within limits without decreasing the activity of the resultant product. Thus, the original mixture can contain between 10 and 25 parts of an alkali metal hydroxide, between 30 and 60 parts of hexose sugars, and between 20 and 40 parts water. When other proportions of hexose sugars and alkali metal hydroxides are present in the original mixture, the superior sequestering agent of the present invention is not obtained. Likewise, the reaction mixture must be maintained at a temperature of at least about 90° C. for from about 2 to 4 hours to insure completion of the reaction and the formation of the active principle of the composition. Longer reaction times result in a decrease in activity of the sequestering agent.

The specific nature of the "active" ingredient in this reaction mixture is not known. The known individual components of conventional caustic-sugar reactions such as glucosaccharinic acid, isosaccharinic acid, metasaccharinic acid and lactic acid do not possess significant activity when compared with the present composition. In endeavors to identify and synthesize the "active principle" in the present hexose sugar-caustic reaction mixture, it has been determined that pyruvic acid, which gives a very high calcium acetate titration, is one of the active components. However, pyruvic acid is not the sole highly active sequestrant in the present composition. It is postulated that the compositions of the present invention contain other keto acids in addition to pyruvic acid. It is believed that these may be keto-glyceric acids or even alpha keto-hexonic acid. Since the "active principle" of the present invention cannot be positively identified, the present specification is directed to the product obtained by the treatment of concentrated hexose sugar solutions with concentrated caustic solutions rather than to a specific compound.

The invention will be more readily understood in view of the following detailed description of a preferred embodiment thereof. In this example and throughout the specification, all parts are expressed by weight unless otherwise indicated.

About 3,000 parts commercial glucose was dissolved in approximately 620 parts of water in a suitable reaction vessel provided with cooling coils. The resultant sugar solution was heated to about 90° C. and approximately 1,875 parts of a 50% aqueous sodium hydroxide solution was added over a period of about 2½ hours. During the sodium hydroxide addition, the temperature of the reaction mixture was maintained between about 90° C. and 95° C. by circulating cool water through the cooling coils. The reaction mixture was then maintained at a temperature between about 90° C. and 95° C. for approximately 4 hours and cooled to room temperature. The product thus obtained was a clear red-brown substance with a slight aromatic odor and a density of about 1.34 of 11.2 pounds per gallon (36.7° Baumé at room temperature). Its viscosity at room temperature is in the range of 90 to 100 centipoises. The product is alkaline (pH 11 in 1% aqueous solution) and is soluble in the full range of caustic solutions without development of an ammoniacal odor. The solution is exceptionally stable and does not

crystallize even at temperatures below −10° F. (−23° C.).

The calcium sequestering ability of this product was determined by the titration of 0.2 gram of the active material with 1% calcium acetate solution in 3% caustic solution in accordance with the process described by Mehltretter et al., Ind. Eng. Chem., 45, 2782 (1953). A 2% stock solution of the material was prepared and 10 ml. of this stock solution were diluted to 20 ml. with distilled water in a 50 ml. beaker. The diluted solution was mechanically stirred and a standard 1% calcium acetate solution introduced dropwise from a burette until the first appearance of permanent turbidity. In like manner, a number of sequestrants aside from hexose sugars were also treated with concentrated caustic at 90° C. and their sequestering ability determined by titration with calcium acetate solution. The results obtained are set forth below in the following table.

TABLE I

Sequestering Capacity of Various Sugars Treated With Concentrated Caustic at 90° C.

Sequestrant	Grams of calcium sequestered per 100 g. of sequestering agent as determined from the Calcium Acetate titration
Lactic Acid	2.54
Metasaccharinic Acid	2.8
Isosaccharinic Acid	3.18
Starch	1.91
D-glucosamine HCl	2.67
Sorbitol	2.54
Sucrose	2.16
D Xylose	9.1
L Rhamnose	7.9
D-Gala-L Mannoheptose	6.85
Lactose	6.4
Glucose	15.2
Fructose	15.9
Sorbose	14.7
Glucuronic Acid	13.8
Invert Sugar (equal mixture of glucose and fructose)	16.2

The sequestering agent of the present invention is identified in the aforegoing table as a glucose product. It will be noted that this material, as well as sequestering agents, produced by the action of concentrated sodium hydroxide on other hexose sugars, namely fructose, sorbose, glucuronic acid, and invert sugar exhibit a sequestering activity which is roughly twice as great as that of the other "sugar acids."

The activity of the present sequestrant toward calcium was also well illustrated by a direct scaling test. In carrying out this test, a concentrated solution of caustic containing a sequestering agent was metered into hard (250 p.p.m.) water at about 130° F. so that the diluted solution had a sodium hydroxide content of about 1% and a sequestrant content of about 0.025%. This solution was then passed over a series of 100 stainless steel screens about one inch in diameter impaled on a stainless steel wire for about 4 hours. The amount of scale deposited on the screens was then weighed directly. The results obtained using the sequestrant of the present invention, as well as other standard sequestrants, are tabulated below.

TABLE II

Scale Formation

Sequestrant:	Weight of scale in grams
None	4.306
Glucose treated with 50% caustic	0.025
Invert sugar treated with 50% caustic	0.020–0.030
Sodium gluconate	0.154
Sodium ethylene diamine tetraacetate	0.828
Sodium glucoheptonate	0.156

This test, which is fully described in an article entitled "Evaluation of Sequestrants in Bottle Washing," in Soap and Chemical Specialties, September 1957, pages 47–49, clearly illustrates the advantageous characteristics of the sequestrants under consideration.

While the sequestering agent of the present invention is generally satisfactory when used alone, additives can in some instances be used to advantage. For example, the addition of a small amount of an anionic or nonionic wetting agent (e.g. about 0.5 pound per 100 pounds of dry caustic) has been found desirable for washing soft drink bottles to effect a reduction in caustic carry-over.

Although the invention has been described in considerable detail in the foregoing, it is to be understood that the purpose of such detail is only for clarification of the invention and that many modifications can be made by those skilled in the art without departing from the spirit and scope of the invention, except as it is limited by the appended claims.

What is claimed is:

1. A process for the preparation of a sequestering agent which comprises mixing between about 30 percent and about 60 percent hexose sugar, between about 10 percent and about 25 percent alkali metal hydroxide and between about 20 percent and about 40 percent water and maintaining the temperature of the mixture between about 90° C. and 100° C. until the reaction is completed.

2. The process of claim 1 in which the hexose sugar is glucose.

3. The process of claim 1 in which the alkali metal hydroxide is sodium hydroxide.

4. A process for the preparation of a sequestering agent which comprises preparing an aqueous solution containing between about 70% and 85% hexose sugar, adding thereto a 50% aqueous solution of sodium hydroxide at a temperature between about 90° C. and 100° C. and maintaining the resultant mixture between about 90° C. and 100° C. until the reaction is completed.

5. A sequestering agent consisting essentially of the reaction product formed by the intermixture of between about 30% to about 60% hexose sugar, between about 10% and about 25% alkali metal hydroxide and between about 20% and about 40% water at a temperature between about 90° C. and 100° C.

References Cited in the file of this patent

Pigman: "The Carbohydrates" (1951), pages 60–69. (Copy in Sci. Lib.)

Chaberek et al.: "Organic Sequestering Agents" (1959), pages 335–338. (Copy in Sci. Lib.)