

1

2,992,998

**FRUCTOHEPTONATE INHIBITED ALKALINE
DETERGENT SOLUTIONS**

Joseph V. Karabinos and Edwin J. Quinn, Joliet, Ill., assignors to Olin Mathieson Chemical Corporation, a corporation of Virginia

No Drawing. Filed Mar. 19, 1956, Ser. No. 572,215

6 Claims. (Cl. 252—156)

This invention provides improvements in that type of washing operation in which articles are washed with strongly alkaline solutions and in which deposits resulting from the presence of polyvalent metals, in particular, calcium and magnesium, in the wash water, reflected by spotting of the articles washed or by deposits on the washing machinery, have presented problems. In effect, the invention provides sequestering agents which are effective in highly alkaline wash solutions and inhibit or prevent or repress the depositions which are commonly encountered in such washing operations in the absence of a satisfactory sequestering agent.

In the washing of bottles in the dairy, soft drink and brewing industries, the bottles are washed with the use of hot solutions of sodium hydroxide, caustic soda, approximating 3% in strength, and sometimes as high as 5%. The water used is ordinary tap or well water, containing calcium and magnesium in the amounts present in ordinary water supplies, and there is a tendency for precipitates to deposit on both the wash machinery and the bottles, or the like, being washed. This deposition (milkstone) apparently takes place to the greatest extent in the first rinse tank, where in customary operation the pH of the rinse water is about 11.5, sometimes a little below 11.5, usually between 11.5 and 12. Precipitation results in the formation of scale on the machinery, plugging of the spray nozzles and discoloration or spotting of the bottles, or other objects being washed.

It has become common practice to use a so-called sequestering agent to reduce the precipitation in such operations, it being thought that a sequestering agent will serve to keep the calcium and/or magnesium in the wash or rinse solution, so that it does not deposit, or at least, will so condition the solution that the calcium and magnesium do not deposit as scale, discoloration of the bottles, or the like, or result in water spotting. Agents used in many washing operations such as the glassy phosphates and tripolyphosphate, which are useful in inhibiting the formation of films or precipitates with less alkaline detergents, as, for example, those used in domestic or commercial dishwashers, are ineffective with these more highly alkaline solutions, presumably because of hydrolysis. Sodium gluconate, in amounts ranging around 2% of the amount of caustic used, has been used as a sequestering agent to inhibit formation or deposition of precipitates in these highly alkaline washing operations. It is reasonably effective.

The present invention is based upon our discovery that the heptonates obtained by the cyanide carboxylation of fructose, and in particular, those prepared by the cyanide carboxylation of fructose under acid conditions, e.g., in the presence of ammonium chloride, are especially effective in inhibiting precipitation in washing operations in which highly alkaline solutions are used, as in the dairy, soft drink, and brewing industries. In particular, we have discovered that in contrast with the glucoheptonates prepared by the cyanide carboxylation of glucose, the fructoheptonates so prepared are more effective in repressing or inhibiting deposits where the rinse tank pH is slightly above 11.5 than where the pH is slightly below 11.5, an observation which we regard as wholly unexpected. We think that this discovery is significant in that we think that in the commonly used washing operations in the

2

dairy, soft drink and brewing industries, the major deposition takes place in the first rinse tank and as the washing machines are commonly operated the pH in this tank is above 11.5, that is, between 11.5 and 12, and not below 11.5.

For evaluation of the sequestering capacity of the sequestering agents for use with highly alkaline wash solutions, we have used a test method which represents a modification of a previously described test method, the modification giving a method which in our opinion more closely approximates actual service conditions than does the test method previously described. In our method a 10 foot length of steel chain weighing approximately 100 grams is circulated through 2 liters of tap water containing 60 grams of sodium hydroxide and 10 grams of the sequestering agent under test maintained at 150° F. followed by passage through a 3 liter bath of rinse tap water at 120° F. and back to the caustic solution with one revolution of the chain being made in approximately 2 minutes. Fresh tap water (250 p.p.m. hardness) is added to the rinse water at a continuous rate so that the pH in the rinse bath remains essentially constant. In one test series we maintained the rinse bath at a pH between 11 and 11.5, which we regard as on the low side from the standpoint of commercial operations. In another test series we maintained the rinse bath at a pH between 11.5 and 12, which we regard as closely approximating the pH in the first rinse tank of commercial machines, where we believe the greatest deposition of "milkstone" takes place. We have noted that as a chain is used in successive tests, with intermediate rinses in dilute HCl to remove deposits, it loses its original smooth surface and tends to absorb more deposit. In our tests reported below, we used a chain or chains which had been subject to several such treatments so that the factor of variability of chain surface is eliminated.

In the tests reported below we used a 6 hour running period. The results are set forth in the following table:

	Wt. of Scale in Grams	
	Rinse pH 11-11.5	Rinse pH 11.5-12
Blank	0.2808	0.4759
Sodium Gluconate	0.1017	0.1752
Sodium α -glucoheptonate	0.2059	0.0933
Sodium α - and β -glucoheptonates (prepared by adding NaCN to glucose with no NH_4Cl)	0.1321	0.1885
Sodium α - and β -glucoheptonates (prepared by adding NaCN to glucose with NH_4Cl)	0.0801	0.1325
Sodium α - and β -fructoheptonates (prepared by adding NaCN to fructose without NH_4Cl)	0.1313	0.0759
Sodium α - and β -fructophetonates (prepared by adding NaCN to fructose with NH_4Cl)	0.0938	0.0534

From the foregoing tests it is apparent that with sodium gluconate, and with the mixtures of glucoheptonates prepared by the cyanide carboxylation of glucose, the deposition of scale increases when the pH in the rinse is between 11.5 and 12 as compared with the deposition when the pH of the rinse is between 11 and 11.5, while with the mixture of fructoheptonates prepared by the cyanide carboxylation of fructose, the deposition is less when the rinse water is at a pH of 11.5 to 12 than it is when the rinse water is at a pH of 11 to 11.5. In addition, it should be noted that at the higher pH levels, the deposition is considerably less when the products obtained by the cyanide carboxylation of fructose are used than when sodium gluconate or the products obtained by the cyanide carboxylation of glucose are used. While the tests indicate that the use of sodium alpha-glucoheptonate

results in a lower level of deposition when the rinse water is in the pH range of 11.5 to 12 than results when the rinse water is at a pH of between 11 and 11.5, it is noteworthy that in both pH ranges there is considerably less deposit with the products obtained by the cyanide carboxylation of fructose than with the use of sodium alpha-glucuheptonate.

It will also be noted from the foregoing that the products obtained by the cyanide carboxylation of fructose in the presence of ammonium chloride are more effective than the products prepared by the cyanide carboxylation of fructose without the use of ammonium chloride. It is thought that the addition of ammonium chloride or some other acidic reagent to the reaction mixture of a sugar such as fructose and cyanide, or the use of hydrogen cyanide instead of sodium cyanide, tends to influence the relative proportions of the alpha and beta epimers formed. Thus, with glucose it is thought that when the reaction takes place under acid conditions, the formation of the alpha epimer is favored. With fructose, we have no information as to which of the two epimers, the alpha or the beta, is formed in greater proportions with such modification of the reaction conditions, but the fact which we have observed is that when the carboxylation takes place under acid conditions, the agent which is obtained is more effective under highly alkaline conditions than the agent which is obtained when the reaction is carried out under neutral or alkaline conditions. We have no explanation for this observed phenomenon.

The preparation of the fructoheptonic acids used in accordance with the present invention is simple. Advantageously, sodium cyanide is used, and in that case, all that is involved is adding sodium cyanide, with particular advantage together with ammonium chloride, to a solution of fructose as, for example, a 50% solution of fructose in water, maintaining the solution at a temperature of 18 to 20° C. or lower for several hours and then completing the reaction by heating to 60° C. for one or two hours, followed by heating to 95 to 100° C., or aerating at about 60° C. for several hours to convert all of the cyanides or other nitrogen-containing products to the carboxylate and to expel the ammonia. The product so obtained is the sodium salt of fructoheptonic acid, presumably a mixture, in proportions not known to us, of alpha- and beta-fructoheptonic acids. The product is conveniently used as a 50% solution in water. Of course, whether the product be used as the sodium salt, or the salt with some other cation, or whether it be converted to the free acid or lactone, when used as a sequestering agent in alkaline solutions the acids are essentially present as the ionized salt of whatever alkali metal is present in the solution, customarily sodium.

Preparation of the compositions used in accordance with the invention will be illustrated by the following example:

Example

To a 50% (by weight) solution of fructose in water containing 72.6 parts by weight of fructose is added 20 parts by weight of solid ammonium chloride followed by 19.8 parts by weight of technical sodium cyanide (96%) while maintaining the temperature at about 18 to 20° C. (tap water temperature). The mixture is then allowed to stand at room temperature overnight at which time the reaction is almost completed. It is completed by heating to 60° C. for one to two hours. The reaction mixture is then heated to 95 to 100° C. for several hours to convert all of the organic nitrogen-containing products to the carboxylate and expel the ammonia. The volume of the product is adjusted with water to give a solution of the sodium fructoheptonates containing 50 grams of heptonate in each 100 grams of solution, a convenient form in which to distribute and use the product.

Substantially the same technique with omission of the use of ammonium chloride or other acidic reagent also gives sodium fructoheptonates, but the products so ob-

tained, while effective sequestering agents in alkaline media, are not as effective as the products obtained with the use of ammonium chloride or other acidic materials. Instead of using sodium cyanide, hydrogen cyanide or potassium cyanide may be used, although for obvious reasons the use of sodium cyanide is the procedure of choice. Hydrogen cyanide used alone gives a product similar to that obtained from sodium cyanide and ammonium chloride. Other acidic agents may be used with sodium or potassium cyanide in place of the ammonium chloride to give similar products, although their use is less advantageous because they leave residual materials in the product.

The proportion of the fructoheptonates used, for optimum suppression of scale or other adherent deposits, will vary with the hardness of the water, the temperature, the caustic concentration, etc., but in general the amount used will be between 0.5 and 10% based on the caustic alkali—2% is a good average amount.

In use, the fructoheptonic acid mixture, usually in the form of the sodium salt, is simply added to the alkali solution used in the washing machine, as, for example, a machine for washing milk or cream bottles, soft drink bottles, beer bottles, or the like. Thus, with a bottle washing machine in a dairy using 250 p.p.m. hardness water with an initial charge of 1800 gallons of water and 400 lbs. of caustic soda, 2 gallons of a 50% solution of the sodium fructoheptonates may be included in the initial charge, followed by the addition of make-up water and caustic as required and about 100 ml. of the sodium fructoheptonate solution per day to give effective washing with minimized formation of deposits. Similar results are obtained even with 35 grain hardness water. Good results are also obtained with even more strongly caustic solutions, as, for example, the approximately 5% caustic solutions used in certain breweries.

We claim:

1. In the washing of articles with water containing dissolved calcium and magnesium salts with caustic alkali solutions, the method of inhibiting the formation of films and precipitates on the articles being washed which comprises incorporating into the wash solution in at least an amount sufficient to inhibit the formation of said films and precipitates, the mixture of fructoheptonic acids resulting from the cyanide carboxylation of fructose.

2. In the washing of articles with water containing dissolved calcium and magnesium salts with caustic alkali solutions, the method of inhibiting the formation of films and precipitates on the articles being washed which comprises incorporating into the wash solution in at least an amount sufficient to inhibit the formation of said films and precipitates, the mixture of fructoheptonic acids resulting from the cyanide carboxylation of fructose under acidic conditions.

3. In the washing of articles with water containing dissolved calcium and magnesium salts with caustic alkali solutions, the method of inhibiting the formation of films and precipitates on the articles being washed which comprises incorporating into the wash solution in at least an amount sufficient to inhibit the formation of said films and precipitates, the mixture of fructoheptonic acids resulting from the cyanide carboxylation of fructose in contact with ammonium chloride.

4. A washing solution comprising water, caustic soda as a detergent, and from about 0.5 to about 10% based on the caustic soda, of the mixture of fructoheptonic acids resulting from the cyanide carboxylation of fructose.

5. A washing solution comprising water caustic soda as a detergent, and from about 0.5 to about 10% based on the caustic soda, of the mixture of fructoheptonic acids resulting from the cyanide carboxylation of fructose under acidic solutions.

6. A washing solution comprising water, caustic soda

as a detergent, and from about 0.5 to about 10% based on the caustic soda, of the mixture of fructoheptonic acids resulting from the cyanide carboxylation of fructose in contact with ammonium chloride.

References Cited in the file of this patent.

UNITED STATES PATENTS

694,658	Meurant -----	Mar. 4, 1902
2,615,846	Dvorkovitz et al. -----	Oct. 28, 1952
2,650,875	Dvorkovitz et al. -----	Sept. 1, 1953

5 472,260

10

2,653,861
2,735,866

Meyer ----- Sept. 29, 1953
Clevenot ----- Feb. 21, 1956

FOREIGN PATENTS

Canada ----- Mar. 20, 1951

OTHER REFERENCES

Organic Chemistry, by Fieser et al., 3rd ed., pp. 350, 351, pub. by Reinhold Pub. Corp., N.Y. (1956).
Organic Synthesis, by Migrdichian, vol. 1, pp. 146, 147, 187, pub. by Reinhold Pub. Corp., N.Y., 1957.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,992,998

July 18, 1961

Joseph V. Karabinos et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 74, for "solutions" read -- conditions --.

Signed and sealed this 2nd day of January 1962.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents