United States Patent Office 3,412,180
Patented Nov. 19, 1968

3,412,180

PRODUCT OF GLUCOHEPTONIC ACID OR ITS ALKALI METAL SALTS AND ALKALI METAL HEXAMETAPHOSPHATE

Hoyt M. Corley, Midlothian, Ill., assignor to W. H. Miner, Inc., Chicago, Ill., a corporation of Delaware

No Drawing. Filed Nov. 6, 1964, Ser. No. 409,555
4 Claims. (Cl. 260—920)

ABSTRACT OF THE DISCLOSURE

Combining glucoheptonic acid or a salt thereof, such as sodium glucoheptonate or potassium glucoheptonate, with an alkali metal phosphate, such as sodium hexametaphosphate, provides a new and highly useful sequestrant.

This invention relates to new and useful compositions of matter and the production thereof. More particularly it relates to unique compositions having unusually high sequestering ability.

Compounds having sequestering ability, particularly for multivalent alkaline earth ions, have long been known. Those which are of significant industrial importance are represented by the amino-carboxylic acids, such as the alkylene polymaine polyacetic acids and the nitriloacetic acids; the sugar acids, such as the gluconic and glucoheptonic acids; and the alkali salts of various phosphates, such as sodium tetrametaphosphate, sodium hexametaphosphate, sodium tripolyphosphate, tetrasodium pyrophosphate, and the like.

Neither the organic nor the inorganic materials above referred to are entirely satisfactory, either because they have low specific sequestering ability, or are too expensive for many uses, or decompose under conditions necessary for use.

It is therefore an object of this invention to provide novel compositions which are generally applicable for the sequestration of objectionable multivalent metal ions.

A further object is to provide a composition which has exceptionally high specific sequestering ability, which is chemically stable under conditions of normal use, and which is low enough in cost to be economically attarctive.

Other objects and advantages of the invention will become apparent from the description thereof which follows.

Sugar acids are believed to form water-soluble complexes with multivalent metal ions because of the ability of the carboxyl and hydroxyl groups in those acids to bind the cations in ring form by means of coordinate and covalent bonds.

They find their greatest field of utility in highly alkaline solutions where sequestration of iron is important. Exactly how the iron is sequestered by the sugar acids in alkaline solution is not fully understood. Apparently carboxyl groups are not required, although a carbonyl group adjacent to the carboxyl appears to enhance sequestering ability. It may be that the hydroxyl groups on sugar acids form complexes with both ferric and ferrous ions. A most important industrial use of the sugar acids is as a component of highly alkaline derusting and metal cleaning compounds and in bottle washing operations in highly alkaline solutions, generally containing 3% caustic soda along with other chemicals. On the other hand, the sugar acids are poor sequestering agents for calcium, magnesium, iron, chrmoium, etc, in the pH range of 4–10. The alkylene polyamine-polyacetic acids are the favored agents for sequestering these metals under mild conditions of acidity or alkalinity. The latter mentioned sequestrants have less ability to hold iron within the pH range of 4–10 and almost no iron sequestering ability under conditions of high alkalinity such as is encountered in alkaline cleaning operations.

I have discovered, however, that when the sugar acids and particularly glucoheptonic acid and its sodium or potassium salts are combined with an alkali metal phosphate such as sodium hexametaphosphate, that for some unexplainable reason the combination has a tremendously increased sequestering ability over that which would be expected from the calculated values determined for the individual compounds. The synergistic increase in the sequestering ability of these two compounds when combined is illustrated in the following table, which compares the sequestering ability of the individual compounds against combinations thereof in various proportions. In said table the sequestering ability of the individual compounds and combinations were tested for the amount of calcium carbonate sequestered using calcium phosphate as the indicator for determining the end point of sequestering activity.

TABLE I.—SEQUESTERING ABILITY OF SODIUM HEXAMETAPHOSPHATE ADDITIONS TO SODIUM GLUCOHEPTONATE

Formulation	Mg $CaCO_3$/gm. of Sequestrant at pH 10		
	Found	Calc.	Synergistic Affect Dif.
1. Sodium glocoheptonate (35% sol)	200.4		
2. Sodium hexametaphosphate 98%	421.6		
3. 99% #1, 1% #2	217.8	202.6	15.2
4. 98% #1, 2% #2	251.4	204.8	46.6
5. 96% #1, 4% #2	366.8	209.2	157.6
6. 95% #1, 5% #2	467.3	211.4	255.9
7. 94% #1, 6% #2	508.9	213.6	295.3
8. 93% #1, 7% #2	593.2	215.8	388.4
9. 90% #1, 10% #2	788.5	222.5	56.10

In the above examples it will be noted that the synergistic improvement is pronounced and where the sodium glucoheptonate solution is combined with at least 5% of the sodium hexametaphosphate, has a synergistic improvement over 100%. My tests indicate that these formulations also have a very high sequestering power for copper, magnesium and iron as well as calcium in the pH range of 6–11. There are 32 possible isomers of glucoheptonic acid and in this patent wherever glucoheptonate is referred to it is intended to cover the mixture of such isomers that are normally present in the commercial production of glucoheptonic acid and its salts. Also by sodium hexametaphosphate I mean a sodium phosphate which has a ratio of Na_2O to P_2O_5 in the range of 1.121/1 to 1.321/1. Preferably I use a material having a P_2O_5 content of 66–67% and a pH of a 1% solution of 7.8 to 8.0.

I have found that even greater synergistic sequestering abilities are demonstrated when I combine the sodium glucoheptonate solution with an alkali metal salt such as sodium hexametaphosphate in the presence of heat.

Example 1

For example, 100 grams of sodium glucoheptonate solution having a concentration of 50% solids was rapidly heated to 185° F. As soon as the temperature reached 185° F., 50 grams of granular sodium hexametaphosphate was added. At the end of 5 minutes the mass was cooled down to 120° F. as rapidly as possible and then to room temperature. Under these conditions there seems to be a definite chemical reaction between the sodium glucoheptonate and the sodium hexametaphosphate. There is a noticeable temperature increase to the boiling point of the liquid with steam vapor being given off and the final reaction product is quite fluid. The total liquid volume changes very little during the reaction, not more than 2–4%. In the above example, the sodium glucoheptonate solution which comprised the starting material was found in two separate tests to have a sequestering ability of 74.7 and 78 when measured according to the buffered phosphate method of testing which will be described below. The sodium hexametaphosphate by the same test

method showed a sequestering ability of 400. The calculated sequestering ability of these proportions of sodium glucoheptonate and hexametaphosphate is 285 mg. of calcium carbonate per gram of sequestrant. However the actual sequestering ability of this reaction product as determined by the phosphate testing method was 3703 in one test and 3564 in the duplicate test.

Glucoheptonic acid and its salts are conventionally synthesized from aldehyde sugars by the well-known Kiliani Synthesis, which consists in reacting a cyanide with an aldehyde group in an organic compound. In accordance with the present invention the aldehyde sugar may be obtained from any one of the commonly available sugars, such as cane sugar, or syrup made from any of the starches of wheat, potatoes, soybeans, hard woods and the like. The cyanide reaction with the aldehyde sugar is exothermic, causing a considerable temperature rise in the reaction mass. The end of the reaction can therefore be determined by the point at which there is no further temperature rise. The aldehyde enolizes to form an unstable hydroxy group at the aldehydic oxygen. This unstable hydroxy group reacts with the cyanide to form a nitrile of the organic compound and a hydroxide with the anion on the starting cyanide compound. When this reaction is conducted with an organic compound having multi-functional groups, the nitrile is easily hydrolyzed to a carboxyl group. One molecule of water reacts with the nitrile to give the corresponding amide. Then a second molecule of water reacts with the amide to give a carboxyl group and releases ammonia. The carboxyl group is stable and can be subjected to numerous additional reactions.

Example 2

In another example, sodium glucoheptono-hexametaphosphate reaction product of Example 1 was produced by charging 281 lbs. of water into a jacketed autoclave equipped with an agitator and a sparger in the bottom to accomplish aeration. The water was heated in the autoclave to 60° F. and with the agitator in operation it was charged with 304 lbs. of an aldehyde sugar obtained from cornstarch. The particular cornstarch used in the example is sold under the trade name Sweetose C and is described by its manufacturer as follows:

Degree of conversion	High.
Type of conversion	Acid-enzyme.
Dextrose equivalent	64%.
Fermentable extract	76%.
Dextrose (monosaccharides)	39%.
Maltose (dissacharides)	33%
Maltotriose (trisaccharides)	12%.
Higher saccharides	16%.
Commercial Baumé	43°.
Total solids	82%.
Moisture	18%.
pH	5.
Acidity as HCl	0.015%.
Viscosity	50 poises at 100° F.
Boiling point	233° F.
Weight, lbs. per gal. at 100° F.	11.8
Percentage ash (sulphated) of resin-refined corn syrup less than 0.02%.	
Percentage ash of bone—0.3% char or vegetable—carbon refined corn syrup	0.3%.

After charging the autoclave with the sweetose C a few minutes are allowed to obtain a homogeneous solution, the temperature of the syrup in the autoclave being brought to 60° F. As soon as the solution is uniform and the syrup temperature reaches 60° F., 40½ lbs. of sodium cyanide was added. An immediate rise in temperature was noted and during the early stages of the reaction the increase was at the rate of 2° per minute. It ceased to rise at approximately 182–186° F. which indicated the reaction to produce sodium glucoheptonate was complete.

As soon as the temperature rise stopped 260 lbs. of granular sodium hexametaphosphate was added to the autoclave. The temperature rose approximately 212° F. with the evolution of steam. Aeration was started just before the hexametaphosphate was added and was continued until after the reaction was completed. After a delay of 5 minutes the mass was cooled as rapidly as possible until the temperature reached 120° F., at which time the agitation and aeration were stopped.

Ideally, the concentrated sodium glucoheptono-hexametaphosphate reaction product is diluted with cold water at the end of the first 5 minutes of reaction time in an amount sufficient to give a final sequestering ability of 250–500 mg. of calcium carbonate per gram of diluted solution depending upon the sequestering ability it is desired to have in the finished product. By using large volumes of water to dilute the concentrate, it is possible to greatly expedite the cooling of the reaction mass and also prevent decomposition of the unreacted polysaccharides as well as the glucoheptono-hexametaphosphate reaction product.

One of the problems of this reaction is the heat instability of sugar, syrups and sodium glucoheptonate, which easily decompose at elevated temperatures. I have found, however, that limiting the time the reaction mass is held at 185° F., coupled with rapid cooling of the reaction product minimizes degradation. For example, we have found that maintaining the 185° F. temperature in the reaction mass for 15 minutes, after the sodium hexametaphosphate has been added, reduces the sequestering ability of the reaction product by approximately 50%. It also greatly increases the viscosity of the solution and darkens it substantially. Solutions held for 15 minutes at 185° F. are black as compared with the brown coloration obtained during the five-minute time required for reaction.

Example 3

For comparison purposes, a commercial form of sodium glucoheptonate, a light colored, 97%.
pure, sodium glucoheptonate in powder form, was tested for its sequestering ability and was then used for reacting with sodium hexametaphosphate according to the present invention. In this instance 4.1 grams of the above-mentioned 97% sodium glucoheptonate was mixed with distilled water to produce 10 ml. of solution. This 41% solids mixture gave a sequestering ability of 84.6 in the first test and 74.7 mg. of calcium carbonate per gram of solution in the second test. 8 grams of this sodium glucoheptonate solution was heated to 185° F. Aeration was started and 4 grams of granular hexametaphosphate added to the solution. Heating and aeration was continued for 5 minutes, after which the reaction mass was rapidly cooled. The sequestering ability of the mixture of these two materials should have been 256 by calculation. In the first test its sequestering ability was actually determined to be 2,119.8 and in the second test to be 2,189.5 mg. of calcium carbonate per gram of test solution.

The method employed for determining the sequestering ability of the glucoheptonate and its esters of hexametaphosphate in the above examples was conducted as follows:

A sample of the sequestering agent to be tested was made up as a 0.3% solution in distilled water, and 10 ml. of saturated potasium dihydrogen phosphate (KH_2PO_4) was added per 100 ml. of solution. The concentration of KH_2PO_4 in the test solution was 2.2 grams per 100 ml. The pH of the solution to be tested was adjusted as necessary by the addition of sodium hydroxide solution. Test solutions of calcium, magnesium and iron were made such that their concentrations were 1 milligram of metallic ion per ml. In the case of magnesium the solution was magnesium sulfate, in the case of calcium the solution was calcium chloride, and in the case of iron the solution was

ferric chloride. In making each titration, the solution of the test ion was added slowly to the solution of the sequestering agent, and the end point considered to be that at which the first permanent turbidity appeared. The pH was monitered during the course of each titration and was adjusted as necessary in order to maintain a constant pH.

It is assumed that sequestering agents work on a mole to mole basis, that is, one mole generally of a sequestrant can adsorb and hold one mole of heavy metal ion only. However, in the sodium glucoheptono-sodium hexametaphosphate product which we obtain, some 4–10 moles of multivalent metal ion per mole of glucoheptono-hexametaphosphate product are being sequestered and this ability to sequester multiple ions per mole of sequestrant is not yet explainable to my satisfaction; however, my testings substantiate its existence. In the above example I have found that one gram mole of sodium glucoheptonosodium hexametaphosphate product will hold 4 gram moles of calcium ion in aqueous solution whereas on a 1 to 1 mole proportion basis it should require 848 grams of this complex to hold 40 grams of calcium ion (equivalent to 100 grams of calcium carbonate) in solution.

Thus having described my invention, I claim:

1. The sequestrant obtained by combining from about 50 to 99 parts of a material from the group consisting of glucoheptonic acid and the sodium and potassium salts thereof with from about 50 to about 1 parts of an alkali metal phosphate having an Na_2O to P_2O_5 ratio in the range of 1.121/1 to 1.321/1.

2. The product obtained by combining from about 50 to 99 parts of sodium glucoheptonate with from about 50 to 1 parts of a sodium phosphate having an Na_2O to P_2O_5 ratio in the range of 1.121/1 to 1.321/1.

3. The sequestrant obtained by adding to an aqueous solution containing sodium glucoheptonate, which solution is at a temperature of about 185° F., an amount of sodium hexametaphosphate equal to the amount of sodium glucoheptonate and after about 5 minutes, cooling the reaction mixture.

4. The sequestrant obtained by heating an aqueous solution of alkali metal glucoheptonate to about 185° F., combining granular alkali metal hexametaphosphate therewith at said temperature, and after about 5 minutes, cooling the reaction mixture, the amount of said glucoheptonate being equal to the amount of said hexametaphosphate.

No references cited.

CHARLES B. PARKER, *Primary Examiner.*

A. H. SUTTO, *Assistant Examiner.*