

1

2

3,294,689

SYNERGISTIC SEQUESTERING AGENT

John S. Pierce, 813 Rosemeath Road,
Richmond, Va. 23221

No Drawing. Filed Oct. 24, 1963, Ser. No. 318,519
1 Claim. (Cl. 252-82)

This invention relates to a sequestering agent which is a composition of matter containing one or more polyhydroxyamines and one or more water soluble alpha-hydroxy acids. More particularly, it relates to a sequestering agent which is a composition of matter with the structural and other relationships described below.

The main object of this invention is to provide a sequestering agent of wide utility. The need for this wide utility is demonstrated by the following facts:

Industrial waters, through contact with pipes, alloys and metal coatings, frequently contain one or more of the cations Fe^{++} , Cu^{++} , Ni^{++} , Al^{+++} and Cd^{++} . In textile processing, as stated by Chaberek and Martell in "Organic Sequestering Agents," page 323, (publisher, John Wiley and Sons, Inc., New York, 1959 Edition), "it is frequently important to remove even trace element impurities, since some of the heavy metals in amounts of even less than 1 p.p.m. can seriously affect the quality of the finished textile, as well as the economics of various processing operation." In solutions for kier boiling, bleaching, rayon manufacture and dyeing, metal ion contaminants can prove highly injurious to the fabrics. Trace amounts of Fe^{++} , Cu^{++} and Mn^{++} are injurious in bleaching of cotton cloth. Traces of Fe^{++} , Mn^{++} , Cu^{++} and Cr^{+++} tend to cause rancidity in edible oils.

The following is quoted from Sutermeister's "Chemistry of Pulp and Paper Making," page 396. (Publisher, John Wiley and Sons, Inc., 1941 Edition.)

"The presence of iron in water is very objectionable in all pulp and paper-making processes because cellulose has the property of absorbing this and other metals from dilute solutions. This results in the yellowing of white papers and the diluting of colored ones, especially light tints. Iron is especially troublesome in the manufacture of photographic papers, particularly, if it is present in such form that it may collect in pipes, reservoirs, etc., as such sludge may break away at times and cause endless trouble. It is also claimed to hasten the deterioration of rosin sizing when paper is exposed to light.

"Iron may be present in either the ferrous or ferric condition; in ground waters it is usually in solution as ferrous carbonate, while in surface water it is nearly always present as hydrated ferric oxide. . . .

"Manganese in a water supply may be exceedingly troublesome—even more so than iron—because of the black oxide deposits which may cause clogging of pipe lines."

Ferrous ion is oxidized readily to the ferric state, particularly in a basic solution.

Further reference is had to "Organic Sequestering Agents," (supra); from pages 354 and 356 the following is quoted:

"Since for many metals the best electroplating characteristics are obtained with alkaline plating baths, complexing agents are necessary to maintain the metal ions in soluble form. Also, metal deposits obtained from solutions containing metal complexes usually have better physical properties than those obtained from solutions of the aquo metal ions."

"The shift in . . . redox potential which occurs on complex formation makes possible selective electroplating of two metals which are normally deposited together, if a chelating or complexing agent can be found which differentiates between them. Since the electrode poten-

tial is directly related to the stability constant, the chelating agent chosen for selective electrodeposition should have different affinities for the two (or more) metal ions involved. Many potentially important applications of sequestering agents in the electroplating field should thus be possible. . . ."

A general object of the present invention is to provide a composition of matter for use as a sequestering agent in the textile field and in the manufacture of paper.

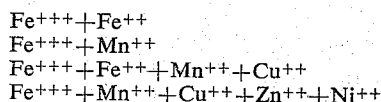
Another general object is to provide a sequestering agent for use in other industries in which the presence of appreciable concentrations of the heavy metal ions, generally found in industrial waters, proves harmful to the products manufactured.

Another general object is to provide a sequestering agent for use in an electroplating bath which evolves no toxic fumes and which holds in alkaline solution low ionic concentrations the ions from copper, cadmium, iron, and certain other metals.

Another general object is to provide a composition of matter, as described below, for use as a sequestering agent for any cation and for any group of cations which are held in solution in low ionic concentrations better by this composition of matter than by either the polyhydroxyamine (or polyhydroxyamines) or the alpha-hydroxy acid (or alpha-hydroxy acids) present in this composition of matter; that is, when used alone.

A specific object of this invention is to provide a composition of matter to sequester Fe^{+++} under widely different conditions of temperature and pH, particularly in basic solution.

Another specific object of this invention is to provide a composition of matter to sequester the following combinations of cations, under widely different conditions of temperature and pH, particularly in basic solution:



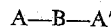
Another specific object of this invention is to provide a composition of matter to be used as a sequestering agent in the electroplating of copper.

Another specific object of this invention is to provide a composition of matter to be used as a sequestering agent in the electroplating of cadmium.

Another specific object of this invention is to provide a composition of matter to be used as a sequestering agent in the electroplating of iron.

Now, to explain more fully, this invention is for a composition of matter containing one or more polyhydroxyamines and one or more water-soluble alpha-hydroxy acids, in which the polyhydroxyamines and the alpha-hydroxy acids have the following limitations:

Each polyhydroxyamine has the structure



in which



is a member made up of the group



and



and A and A' each is a member made up of the group which is a monovalent alkanolamino radical, each radical containing one nitrogen and at least two alcoholic hydroxyls, each being two carbons removed from the nitrogen and in each radical there being an alcoholic hydroxyl/carbon ratio of at least 1/2; and in each alpha-

hydroxy, which is water-soluble, the ratio of the sum of alcoholic hydroxyls and carboxyl hydroxyls to carbon is at least 1/2 and the molar ratio of polyhydroxyamine to alpha-hydroxy acid has limits of 4/1 and 1/4.

Tables I and II are given to illustrate polyhydroxyamines and alpha-hydroxy acids, respectively, which fall within the scope of this invention. In Table I, for each polyhydroxyamine of structure A—B—A', the groups A and A' are equivalent.

TABLE I.—POLYHYDROXYAMINES

	Formulas	Names
1.....	$(\text{HOCH}_2)_3\text{CNHCH}_2\text{CH}_2\text{NHC}(\text{CH}_2\text{OH})_3$	N,N'-Bis[tris(hydroxymethyl)methyl]-ethylenediamine.
2.....	$(\text{HOCH}_2)_3\text{CNHCH}_2\text{CHOHCH}_2\text{NHC}(\text{CH}_2\text{OH})_3$	1,3-Bis[tris(hydroxymethyl)-methylamino]-2-propanol.
3.....	$(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$	N,N'-Bis[di(β -hydroxyethyl)]-ethylenediamine.
4.....	$(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CHOHCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$	1,3-Bis[di(β -hydroxyethyl)amino]-2-propanol.
5.....	$(\text{HOCH}_2)_2\text{C}(\text{CH}_3)\text{NHCH}_2\text{CH}_2\text{NHC}(\text{CH}_2\text{OH})_2$	1,2-Bis[methyl-di(hydroxymethyl)-methylamino]ethane.
6.....	$(\text{HOCH}_2)_2\text{C}(\text{CH}_3)\text{NHCH}_2\text{CHOHCH}_2\text{NHC}(\text{CH}_2\text{OH})_2$	1,3-Bis[methyl-di(hydroxymethyl)-methylamino]-2-propanol.

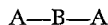
TABLE II.—ALPHA-HYDROXY ACIDS

	Formulas	Names
a.....	HOCH_2COOH	Glycolic acid.
b.....	$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	Lactic acid.
c.....	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COOH}$	Alpha-hydroxybutyric acid.
d.....	$\text{HOOCCH}(\text{OH})\text{CH}_2\text{COOH}$	Malic acid.
e.....	$\begin{array}{c} \text{COOH} \\ \\ \text{CHOH} \\ \\ \text{CHOH} \\ \\ \text{COOH} \end{array}$	Tartaric acid.
f.....	$\begin{array}{c} \text{CH}_2\text{COOH} \\ \\ \text{C}(\text{OH})\text{COOH} \\ \\ \text{CH}_2\text{COOH} \end{array}$	Citric acid.
g.....	$\begin{array}{c} \text{COOH} \\ \\ \text{HCOH} \\ \\ \text{HOCH} \\ \\ \text{HCOH} \\ \\ \text{HCOH} \\ \\ \text{COOH} \end{array}$	Gluconic acid.

PREPARATION OF SOLUTIONS OF SEQUESTERING AGENTS

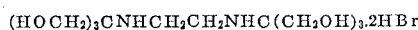
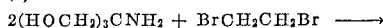
The salts of the alpha-hydroxy acids used in this study were purchased or were formed from the acid and sodium or potassium hydroxide, with the exception of sodium alpha-hydroxy butyrate, which was prepared by the hydrolysis of alpha-bromo-butyric acid with two molar quantities of sodium hydroxide solution.

In general, the methods outlined by Pierce and Wotiz in "J. Am. Chem. Soc., 66," page 879 (1944) were used for the preparation of alkanolamines of structure

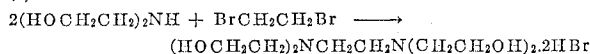


The reactions were as follows:

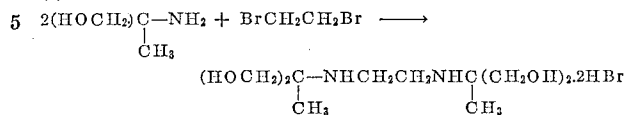
(1)



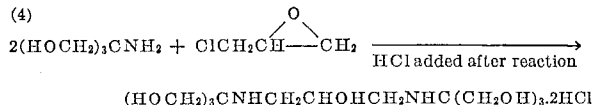
(2)



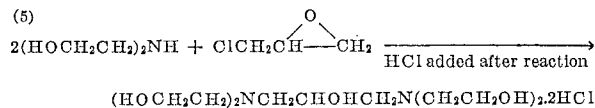
(3)



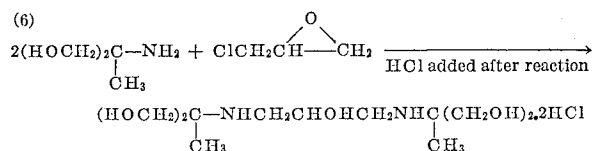
35 (4)



40 (5)



45 (6)



55

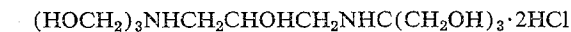
Sodium hydroxide, potassium hydroxide or sodium bicarbonate can be used to remove halogen acid and to increase the yield of desired polyhydroxyamine.

When the reaction is complete, excess halogen acid can be added to convert all polyhydroxyamines to the corresponding salts. Hydrobromic acid serves for the compounds formed in equations 1–3 and hydrochloric acid serves for the alkanolamines formed in equations 4–6.

60

Purification of the polyhydroxyamine salts can be effected, as with the same or similar compounds of Pierce and Wotiz, (supra), by use of organic solvents. Ethanol can be used to extract the polyhydroxyamines from inorganic salts. When the polyhydroxyamine dihydrohalide crystallizes readily from alcohol, as does

70



purification can be effected by recrystallization from ethanol. Also, aqueous ethanol can be used when the solubility in water is not too high. For the products of structure A—B—A which form dihydrohalides which are quite soluble in ethanol, a non-solvent, such as cyclo-

75

5

hexane, can be used to throw the polyhydroxyamine salt out of solution.

Usually, molar solutions were prepared of the alpha-hydroxy acids as sodium or potassium salts and of the alkanolamines as hydrochlorides or hydrobromides. The cations also were prepared as molar solutions, usually as the nitrates. In some cases the cation solutions were diluted to 0.1 molar solutions before being measured to form solutions for the sequestering tests. Graduated pipettes were used for the final measurements in most cases.

Early in this study, volumes of solution from 10 to 100 ml. were used in the solubilization tests. Later a volume of 4 ml. was used and still later a volume of 2 ml. was used for most of the tests. The use of the small volume enables one to carry out simultaneously nine tests, each with four test tubes. Thus, if an error should be made in making up the solutions of cations, the same error would appear in the tests with single sequestering agents and with the synergistic combinations.

In these tests, except a few at the end of this specification, the polyhydroxyamines were used as the hydrochlorides or hydrobromides; the alpha-hydroxy acids were used as the sodium or potassium salts. The relative amounts of polyhydroxyamine free base and cation of the polyhydroxyamine and relative amounts of the alpha-hydroxy acid and anion of the acid at any particular time depend to a great extent on the pH of the solution. Thus, in a solution which is acidic or neutral, the polyhydroxyamine exists largely in the form of the cation; but, in a solution which is strongly alkaline, the polyhydroxyamine likely exists largely as the free base or hydrated free base and to a slight extent as a cation. Similarly, in a strongly alkaline solution the alpha-hydroxy acid exists largely as the anion while in a strongly acidic solution it exists mainly as the free acid. Therefore, for convenience, both in the specification and in the claims, the solubilizing agents usually are referred to as "polyhydroxyamines" "polyalkanolamines" or "alkanolamines" and as "alphahydroxy acids." These terms are meant and are to be understood herein to include the cations of the polyhydroxyamines and the anions of the alpha-hydroxy acids.

All the temperature readings in this specification are on the Centigrade scale.

At the outset of the present study, the synergistic sequestering effect on Fe^{+++} of 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol and citric acid was the main interest.

Example 1

Solutions were made with ferric chloride in molar concentrations of 10^{-6} , 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} and 10^{-1} and with 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol dihydrochloride,



and potassium citrate, each in molar concentrations approximately four times that of the ferric chloride. The solutions were heated in test tubes in a boiling water bath. Sodium hydroxide solution was added slowly to each solution to change the pH gradually from less than 7 to over 13. No visible precipitate of iron occurred. Each solution was evaporated to less than half of the original volume. Still no precipitate of iron occurred; nor did it occur when the solutions were frozen.

In the above test, it is noted that the polyhydroxyamine and citrate are in equimolar amounts. In other tests, it was observed that neither 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol nor citrate alone holds Fe^{+++} in hot solution as the pH changes gradually from below 7 to high alkalinity but that together these two sequestering agents, through a wide range of ratios of

6

molar concentrations, do hold Fe^{+++} in solution as the pH is changed gradually from below 7 to beyond 11.

This synergistic sequestering action of the above polyhydroxyamine and alpha-hydroxy acid on Fe^{+++} was noted when the molar ratio of polyhydroxyamine to citrate was 4/1 and when it was 1/4. Also, it was noted in appreciably lower ratio of molar concentrations than 1/4 and in and appreciably higher ratio than 4/1. That is, the combined sequestering power of the above polyhydroxyamine and alphahydroxy acid is much greater for Fe^{+++} than the action of either alone, over a wide ratio of molecular concentrations. The synergistic sequestering action of 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol and citrate over a wide ratio of molar concentrations is illustrated by the following example:

Example 2

Seven solutions were prepared, each containing 1 ml. of M Fe^{+++} in a total volume of 10 ml. The number of milliliters of M 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol and of M citrate are indicated below:

No. sample	Alkanolamine, M, ml.	Citrate M, ml.
1.....	0	4
2.....	1	4
3.....	2	4
4.....	4	4
5.....	4	2
6.....	4	1
7.....	4	0

To each of the solutions, in a hot water bath, 1 drop of 6 N sodium hydroxide solution was added each 10 minutes for 2.5 hours. Sample No. 1 gave a precipitate before any sodium hydroxide was added. The precipitate increased quite a bit as base was added and it persisted throughout the test. Sample No. 7 also gave a distinct precipitate before any base was added and the precipitate increased as the first few drops of base were added and persisted throughout the experiment. Samples 2, 3, 4, 5 and 6 gave no precipitate throughout the experiment.

It is well known in the rayon field that certain cations, particularly Cu^{++} , Mn^{++} , and Ni^{++} , catalyze oxidative degradation of cellulose. Therefore, in the production of rayon, it is highly desirable that the purification process should remove as much as possible of the undesirable cations. Furthermore, many manufacturers employ alkaline desulfuring solutions, the alkalinity of which varies according to the particular type of rayon being prepared as well as the time available in the process for desulfuring and the equipment in use. Also, in the preparation of rayon, large quantities of zinc sulfate are used, and while a trace of Zn^{++} left in the rayon does not cause extensive oxidation degradation, as do the three cations mentioned above, the presence of Zn^{++} in the final product is undesirable. Furthermore, the extensive use of iron equipment makes the presence of some iron in solution quite probable.

In view of the objectionable properties of Fe^{+++} , Cu^{++} , Mn^{++} , Ni^{++} and Zn^{++} , if left in rayon or other industrial products, it seemed advisable to carry out tests on the ability of polyhydroxyamines in Table I and of alpha-hydroxy acids in Table II to act as sequestering agents on these cations.

Tests for the following two examples were carried out in 150 ml. beakers and with the sequestering agents 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol dihydrochloride and potassium citrate.

Example 3

The sequestering agents were molar. The cations were Fe^{+++} , Mn^{++} , Cu^{++} , Zn^{++} and Ni^{++} . In the stock test cation solution each cation was 0.2 M so the total cation concentration was molar. The volumes used are indicated below:

Test No.	Polyalkanolamine, ml.	Alpha-Hydroxy Acid, ml.	Cation, ml.
1-----	8.0	0	1.0
2-----	8.0	2.0	1.0
3-----	8.0	8.0	1.0
4-----	2.0	8.0	1.0
5-----	0	8.0	1.0

Each solution was diluted to 50 ml. To each beaker was added a boiling stone and the solutions were heated to gentle boiling on a hot plate. Water was added from time to time to keep the volume near 50 ml.

To each of the five solutions was added 1 drop of 6 M sodium hydroxide solution each minute for 1 hour.

In beaker No. 1 there was a fairly heavy precipitate when the solution reached the boiling temperature and the precipitate persisted throughout the experiment.

In beaker No. 5 a distinct precipitate was noted in 34 minutes and it became quite heavy by the end of the experiment.

In beakers Nos. 2, 3 and 4, no precipitate was formed during the experiment.

Example 4

The sequestering agents were molar. The cations were Fe^{+++} , Fe^{++} , Mn^{++} , Cu^{++} , Zn^{++} , Cd^{++} , Ni^{++} , Co^{++} , Cr^{+++} and Al^{+++} . In the stock test solution each cation was 0.1 M so the total cation concentration was molar. The volumes used are indicated below:

Test No.	Polyalkanolamine, ml.	Alpha-Hydroxy Acid, ml.	Cation, ml.
1-----	8.0	0	1.0
2-----	8.0	2.0	1.0
3-----	8.0	8.0	1.0
4-----	2.0	8.0	1.0
5-----	0	8.0	1.0

Each solution was diluted to 50 ml. To each beaker was added a boiling stone and the solution was heated to gentle boiling on a hot plate. Water was added from time to time to keep the volume near 50 ml. To each of the five solutions was added 1 drop of 6 M sodium hydroxide solution each minute for 1 hour.

In beaker No. 1 there was a fairly heavy precipitate by the time the solution reached the boiling point. The precipitate became quite heavy within 6 minutes and the heavy precipitate persisted throughout the experiment.

In beaker No. 5 a slight precipitate appeared in 35 minutes, it became quite heavy within 38 minutes and persisted throughout the experiment.

No precipitate was noted in any of the other three beakers during the experiment.

Not only does 1,3 - bis[tris(hydroxymethyl)methylamino]-2-propanol have synergistic sequestering action on certain cations deleterious to industry when used with citrate, but also when used with each of the other alpha-hydroxy acids listed in Table II.

Not only does citrate have synergistic sequestering action on certain cations deleterious to industry when used with 1,3 - bis[tris(hydroxymethyl)methylamino] - 2 - propanol but also when used with each of the other polyhydroxyamines in Table I.

Furthermore, each of the six polyhydroxyamines in Table I, when used with each of the alpha-hydroxy acids

in Table II, in molar concentration ratios of 1/4 and 4/1 has been demonstrated to have superior sequestering properties on some cation or group of cations to either the alkanolamine or acid, in the absence of the other sequestering agent.

Each of the six polyhydroxyamines in Table I, when used with all of the alpha-hydroxy acids in Table II, in molar ratios of polyhydroxyamine to alpha-hydroxy acid of 1/4 and 4/1, has been demonstrated to have superior sequestering properties on some cation or group of cations, to either the polyalkanolamine or alpha-hydroxy acids, in the absence of the other type of sequestering agent.

All of the polyhydroxyamines in Table I, when used with each of the alpha-hydroxy acids in Table II, in molar concentration ratios of polyhydroxyamines to acid of 1/4 and of 4/1, have been demonstrated to have superior sequestering action on some cation or group of cations than the alkanolamines or acid, in the absence of the other type of sequestering agent.

Also, using a table of random numbers to choose the particular polyhydroxyamines and alpha-hydroxy acids in each combination, the following combinations were made:

Alpha-Hydroxy acids	Polyhydroxyamines	No. of Tests
1 with-----	2, 3, 4 and 5-----	4
2 with-----	1, 2, 3, 4, 5 and 6 (all)-----	6
3 with-----	1, 2, 3, 4, 5 and 6-----	6
4 with-----	1, 2, 3, 4, 5 and 6-----	6
5 with-----	1, 2, 3, 4, 5 and 6-----	6
6 with-----	1, 2, 3, 4, 5 and 6-----	6
7 with-----	2, 3, 4 and 5-----	4

In each of the above combinations, greater sequestering action was noted on some cation or group of cations with the combination of polyhydroxyamines and alpha-hydroxy acids, in ratios of molar concentration of polyalkanolamines to alpha-hydroxy acids of 4/1 and of 1/4, than with the polyhydroxyamines or alpha-hydroxy acids, in the absence of the other type of sequestering agent.

In each of the tests mentioned above, one or more cations, which are deleterious in industry, were used.

Example 5 is given to show the method used for most of the early study. In this test, the polyhydroxyamine used was 1,3-bis[tris(hydroxymethyl)methylamino]-2-propanol and the acid was tartaric. The alkanolamine was used as the dihydrochloride and the acid was used as the sodium salt.

Example 5

Four ml. of solutions were prepared of the molar concentrations indicated below:

Test No.	Cations				Polyhydroxyamine	Acid
	Fe^{+++}	Mn^{++}	Ni^{++}	Cu^{++}		
1-----	0.01	0.01	0.01	0.01	0.20	00
2-----	0.01	0.01	0.01	0.01	0.20	0.05
3-----	0.01	0.01	0.01	0.01	0.05	0.20
4-----	0.01	0.01	0.01	0.01	00	0.20

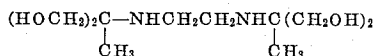
The solutions were placed in test tubes suspended in a boiling water bath. At ten minute intervals 1 drop of N sodium hydroxide was added to each of the solutions. A heavy precipitate was in test tube No. 1 before any sodium hydroxide was added and the precipitate did not clear up. A heavy precipitate was in test tube No. 4 after 40 minutes heating and it remained throughout the experiment. No precipitate was observed in either test tube No. 2 or test tube No. 3 after 2 hours heating.

In Examples 6, 7 and 8, below, the initial volume for each test was approximately 2 ml. in order that as many

tests as possible could be carried out simultaneously. To support the test tubes in the hot water bath, three rows of holes were drilled in a piece of plywood. Thus, nine sets of four test tubes each were used simultaneously.

Example 6 is given below to illustrate the synergistic effect when a particular polyhydroxyamine in Table I is used with all of the alpha-hydroxy acids in Table II.

For Example 6, the amino alcohol was



It was used as the dihydrobromide.

Example 6

Two ml. solutions were prepared of the molar concentrations indicated below:

Test No.	Cations	Polyhydroxyamines	Alpha-Hydroxy Acids (all in Table II)
1	Cu ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Z ⁺⁺ ; Each 0.005 M.	0.40	0.00
2	do	0.40	0.10
3	do	0.10	0.40
4	do	0.00	0.40

The solutions were placed in test tubes suspended in a water bath near boiling. At ten minute intervals 1 drop of N sodium hydroxide solution was added to each of the solutions. A slight precipitate was observed in test tube No. 1 at the end of 20 minutes. It became quite heavy at the end of 50 minutes. A slight precipitate was observed in test tube No. 4 at the end of 20 minutes. It became quite heavy at the end of 30 minutes. No precipitate was observed in either test tube No. 2 or test tube No. 3 after 1 hour of heating.

Example 7 is given to illustrate the synergistic effect noted when all of the polyhydroxyamines in Table I are used with a particular alpha-hydroxy acid in Table II.

Example 7

Two ml. solutions were prepared of the molar concentrations indicated below:

Test No.	Cations		Polyhydroxyamines (all in Table I)	Alpha-Hydroxy Acid Malic
	Fe ⁺⁺⁺	Mn ⁺⁺		
1	0.025	0.025	0.40	0.00
2	0.025	0.025	0.40	0.10
3	0.025	0.025	0.10	0.40
4	0.025	0.025	0.00	0.40

The solutions were placed in test tubes suspended in a boiling water bath. At ten minute intervals 1 drop of N sodium hydroxide solution was added to each of the solutions. A distinct precipitate was obtained in test tube No. 1 before any sodium hydroxide was added and the precipitate persisted throughout the experiment. A heavy precipitate was obtained in test tube No. 4 after 20 minutes heating. No precipitate was obtained in either test tube No. 2 or test tube No. 3 at the end of one hour.

Example 8 is given to illustrate the synergistic effect noted when all of the polyhydroxyamines in Table I are used with all of the alpha-hydroxy acids in Table II.

Example 8

Two ml. solutions were prepared of the molar concentrations indicated below:

Test No.	Cations				Polyhydroxyamines (all in Table I)	Alpha-Hydroxy Acids (all in Table II)
	Fe ⁺⁺⁺	Mn ⁺⁺	Zn ⁺⁺	Cd ⁺⁺		
1	0.005	0.005	0.005	0.005	0.40	0.00
2	0.005	0.005	0.005	0.005	0.40	0.10
3	0.005	0.005	0.005	0.005	0.10	0.40
4	0.005	0.005	0.005	0.005	0.00	0.40

The solutions were placed in test tubes suspended in a boiling water bath. Drops of N sodium hydroxide solution were added to each solution as indicated below:

Time, minutes:	Drops added
10	1
20	3
40	3
100	3
115	3
120	3

A heavy precipitate was obtained in test tube No. 1 before any sodium hydroxide was added and the precipitate persisted throughout the experiment. A distinct precipitate was obtained in test tube No. 4 after 40 minutes. No precipitate was noted in either test tube No. 2 or test tube No. 3 after 160 minutes.

The tests on synergistic sequestering action of the polyhydroxyamines in Table I and the alpha-hydroxy acids in Table II were carried out by the slow addition, usually dropwise, of sodium hydroxide solution to the hot solutions of the cations listed in Tables III and IV (below), and by the same general method as used in Examples 6, 7 and 8. Usually, but not always, the initial volume for each test was approximately 2 ml. In Tables III and IV and subsequent tables, the polyhydroxyamines or polyalkanolamines are designated by the numbers assigned to them in Table I. The alpha-hydroxy acids are designated by the letters assigned to them in Table II.

The ethylenediamine derivatives were used as the dihydrobromides; the derivatives of 1,3-diamino-2-propanol were used as the dihydrochlorides.

The alpha-hydroxy acids were used as the sodium or potassium salts. Either potassium or sodium salts can be used in these tests.

In each of these examples, four test tubes with the same cation and same initial volume of solution were used. If x is taken as the lowest molar concentration in any test tube containing sequestering agent, the tubes had the following concentrations of sequestering agents:

Tube No.	Polyhydroxyamine	Alpha-Hydroxy Acid
1	4x	0
2	4x	x
3	x	4x
4	0	4x

In Table III are included the data on the three Examples No. 6, No. 7 and No. 8, immediately preceding, and also numerous other examples.

TABLE III.—SYNERGISTIC ACTION OF SYMMETRICAL POLYHYDROXYAMINES AND ALPHA-HYDROXY ACIDS AS SEQUESTERING AGENTS

Test No.	Polyhydroxyamines	Alpha-Hydroxy Acids	Cations
1	1	a	Fe ⁺⁺⁺ .
2	1	b	Fe ⁺⁺⁺ .
3	1	c	Fe ⁺⁺⁺ .
4	1	d	Fe ⁺⁺⁺ .
5	1	e	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ , Co ⁺⁺ .
6	1	f	Fe ⁺⁺⁺ .
7	1	g	Fe ⁺⁺⁺ , Zn ⁺⁺ .
8	2	a	Fe ⁺⁺⁺ .
9	2	b	Fe ⁺⁺⁺ .
10	2	c	Fe ⁺⁺⁺ .
11	2	d	Fe ⁺⁺⁺ .
12	2	e	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ , Co ⁺⁺ .
13	2	f	Fe ⁺⁺⁺ .
14	2	g	Fe ⁺⁺⁺ , Zn ⁺⁺ .
15	3	a	Fe ⁺⁺⁺ .
16	3	b	Fe ⁺⁺⁺ .
17	3	c	Fe ⁺⁺⁺ .
18	3	d	Fe ⁺⁺⁺ .
19	3	e	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ , Co ⁺⁺ .
20	3	f	Fe ⁺⁺⁺ .
21	3	g	Fe ⁺⁺⁺ , Zn ⁺⁺ .
22	4	a	Cu ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ .
23	4	b	Fe ⁺⁺⁺ .
24	4	c	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ , Co ⁺⁺ .
25	4	d	Fe ⁺⁺⁺ .
26	4	e	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Zn ⁺⁺ .
27	4	f	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ .
28	4	g	Fe ⁺⁺⁺ , Mn ⁺⁺ .
29	5	a	Fe ⁺⁺⁺ .
30	5	b	Fe ⁺⁺⁺ .
31	5	c	Fe ⁺⁺⁺ .
32	5	d	Fe ⁺⁺⁺ .
33	5	e	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Zn ⁺⁺ .
34	5	f	Fe ⁺⁺⁺ .
35	5	g	Fe ⁺⁺⁺ , Zn ⁺⁺ .
36	6	a	Fe ⁺⁺⁺ .
37	6	b	Fe ⁺⁺⁺ .
38	6	c	Fe ⁺⁺⁺ .
39	6	d	Fe ⁺⁺⁺ .
40	6	e	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ , Co ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ .
41	6	f	Fe ⁺⁺⁺ .
42	6	g	Fe ⁺⁺⁺ , Zn ⁺⁺ .
43	1	a, b, c, d, e, f, g	Cu ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ .
44	2	a, b, c, d, e, f, g	Cu ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ .
45	3	a, b, c, d, e, f, g	Cu ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ .
46	4	a, b, c, d, e, f, g	Cu ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ .
47	5	a, b, c, d, e, f, g	Cu ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ .
48	6	a, b, c, d, e, f, g	Cu ⁺⁺ , Cd ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ , Mn ⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ .
49	1, 2, 3, 4, 5, 6	a	Fe ⁺⁺⁺ , Mn ⁺⁺ .
50	1, 2, 3, 4, 5, 6	b	Fe ⁺⁺⁺ , Mn ⁺⁺ .
51	1, 2, 3, 4, 5, 6	c	Fe ⁺⁺⁺ , Mn ⁺⁺ .
52	1, 2, 3, 4, 5, 6	d	Fe ⁺⁺⁺ , Mn ⁺⁺ .
53	1, 2, 3, 4, 5, 6	e	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ , Co ⁺⁺ , Ni ⁺⁺ , Cr ⁺⁺⁺ , Al ⁺⁺⁺ .
54	1, 2, 3, 4, 5, 6	f	Fe ⁺⁺⁺ , Mn ⁺⁺ .
55	1, 2, 3, 4, 5, 6	g	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
56	1, 2, 3, 4, 5, 6	a, b, c, d, e, f, g	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .

In each of the fifty-six tests above, the combined polyhydroxyamine (or polyhydroxyamines) and alpha-hydroxy acid (or alpha-hydroxy acids), in molar ratios of 4/1 and 1/4, kept the cation (or group of cations) in solution better than did either type of sequestering agent in approximately the same molar concentration as the more concentrated one, in the absence of the other type of sequestering agent.

Thus, it is evident that the polyhydroxyamines in Table I and the alpha-hydroxy acids in Table II have useful synergistic sequestering action on certain cations which prove harmful in the textile industry, the paper industry and other important industries. This synergistic action is observable in a ratio of molar concentration of polyhydroxyamine to alpha-hydroxy acid of 4/1 and of 1/4.

With a table of random numbers as a guide, combinations of polyhydroxyamines and alpha-hydroxy acids were chosen at random from Table I and Table II. The number of alpha-hydroxy acids and polyhydroxyamines in the various combinations are as follows:

One alpha-hydroxy acid with 2, 3, 4 and 5 polyhydroxyamines (four combinations).

Two alpha-hydroxy acids with 1, 2, 3, 4, 5 and 6 polyhydroxyamines (six combinations).

Three alpha-hydroxy acids with 1, 2, 3, 4, 5 and 6 polyhydroxyamines (six combinations).

Four alpha-hydroxy acids with 1, 2, 3, 4, 5 and 6 polyhydroxyamines (six combinations).

Five alpha-hydroxy acids with 1, 2, 3, 4, 5 and 6 polyhydroxyamines (six combinations).

Six alpha-hydroxy acids with 1, 2, 3, 4, 5 and 6 polyhydroxyamines (six combinations).

Seven alpha-hydroxy acids with 2, 3, 4 and 5 polyhydroxyamines (four combinations).

Each of the thirty-eight combinations above was tested as a sequestering agent for one or more cations which prove deleterious in the paper and textile industry. The results are summarized in following Table IV.

Note: The following combinations are not included in Table IV since they are in Table III:

(a) One alpha-hydroxy acid with one polyhydroxyamine.

(b) One alpha-hydroxy acid with six (all) polyhydroxyamines.

(c) Seven alpha-hydroxy acids (all) with one polyhydroxyamine.

(d) seven alpha-hydroxy acids (all) with six polyhydroxyamines (all).

the cations listed were carried out with symmetrical polyhydroxyamines. That is, in the generic formula



5 A' is equivalent to A. However, such an equivalence is not necessary to obtain a synergistic sequestering action with the alpha-hydroxy acids in Table II, and the prepara-

TABLE IV.—SYNERGISTIC ACTION OF SYMMETRICAL POLYHYDROXYAMINES AND ALPHA-HYDROXY ACIDS AS SEQUESTERING AGENTS

Test No.	alpha-Hydroxy Acids	Polyhydroxyamines	Cations
1	d	2,6	Fe ⁺⁺⁺ , Mn ⁺⁺ .
2	b	1,2,4	Fe ⁺⁺⁺ , Mn ⁺⁺ .
3	e	2,3,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
4	a	1,3,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ .
5	a, d	2	Fe ⁺⁺⁺ , Mn ⁺⁺ .
6	c, g	1,5	Fe ⁺⁺⁺ , Mn ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ , Co ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ .
7	b, d	2,3,6	Fe ⁺⁺⁺ , Mn ⁺⁺ .
8	c, e	2,3,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ .
9	d, f	1,2,3,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
10	d, e	1,2,3,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
11	e, f, g	3	Fe ⁺⁺⁺ , Zn ⁺⁺ .
12	b, f, g	3,4	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
13	a, e, f	1,2,4	Fe ⁺⁺⁺ , Mn ⁺⁺ .
14	b, c, e	1,3,4,6	Fe ⁺⁺⁺ , Mn ⁺⁺ .
15	c, d, e	1,3,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ .
16	b, c, g	1,2,3,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ .
17	a, b, d, g	6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ , Co ⁺⁺ , Al ⁺⁺⁺ , Cr ⁺⁺⁺ .
18	c, e, f, g	5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
19	a, b, d, g	1,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Zn ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Cd ⁺⁺ , Cr ⁺⁺⁺ , Al ⁺⁺⁺ .
20	a, b, d, g	1,2,4,5	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Zn ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Cd ⁺⁺ , Cr ⁺⁺⁺ , Al ⁺⁺⁺ .
21	a, d, f, g	1,2,3,4,5	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Zn ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Cd ⁺⁺ , Cr ⁺⁺⁺ , Al ⁺⁺⁺ .
22	b, c, e, f	1,2,3,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Zn ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Cd ⁺⁺ , Cr ⁺⁺⁺ , Al ⁺⁺⁺ .
23	a, b, e, f, g	5	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
24	a, c, d, f, g	1,3	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
25	a, b, e, f, g	2,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
26	a, c, e, f, g	1,3,4,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
27	a, b, c, e, f	1,2,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
28	a, b, c, d, g	1,2,3,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
29	a, b, c, e, f, g	5	Fe ⁺⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
30	a, b, c, d, f, g	1,4	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
31	a, b, d, e, f, g	1,3,5	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
32	a, b, d, e, f, g	1,2,4,5	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
33	b, c, d, e, f, g	2,3,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
34	a, b, c, d, f, g	1,2,3,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
35	a, b, c, d, e, f, g	3,5	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
36	a, b, c, d, e, f, g	2,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
37	a, b, c, d, e, f, g	2,3,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .
38	a, b, c, d, e, f, g	1,2,4,5,6	Fe ⁺⁺⁺ , Mn ⁺⁺ , Zn ⁺⁺ , Cd ⁺⁺ .

The data in Tables III and IV may be summarized as follows:

The synergistic sequestering action of polyhydroxyamines and alpha-hydroxy acids on certain cations, including several objectionable cations in various industries, is displayed by all of the polyhydroxyamines in Table I and all of the alpha-hydroxy acids in Table II. This synergistic sequestering action is noted as follows:

(a) when each polyhydroxyamine in Table I is used with each alpha-hydroxy acid in Table II

(b) when each polyhydroxyamine in Table I is used with all the alpha-hydroxy acids in Table II

(c) when all of the polyhydroxyamines in Table I are used with each alpha-hydroxy acid in Table II

(d) when all of the polyhydroxyamines in Table I are used with all of the alpha-hydroxy acids in Table II

(e) when the sequestering agents from Table I and Table II are chosen by use of a table of random numbers.

The above synergistic sequestering action is noted when the ratios of molar concentrations of polyhydroxyamines to alpha-hydroxy acids is 4/1 and when it is 1/4. When two or more polyhydroxyamines are used in any test, each alkanolamine is present in the same molar concentration and the concentration specified is the total molar concentration of alkanolamines. Similarly, when two or more alpha-hydroxy acids are used in any test, each alpha-hydroxy acid is present in the same molar concentration and the concentration specified is the total molar concentration of alpha-hydroxy acids.

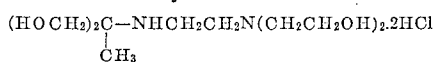
As stated, the above tests on synergistic sequestering action of polyhydroxyamines and alpha-hydroxy acids on

tions of typical unsymmetrical compounds of structure A—B—A' are given in following Examples 9 and 10.

Example 9

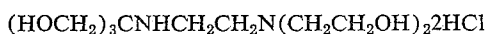
A solution of 71.8 g. (0.5 mole) of 1-bromo-2-chloroethane in 95% ethanol was refluxed while a solution of 52.5 g. (0.5 mole) of 2-amino-2-methyl-1,3-propanediol in 200 ml. of 95% ethanol was added over a two-hour period. The resulting solution was refluxed 18 hours, then evaporated to a low volume. The residue was dissolved in 95% ethanol along with 52.5 g. (0.5 mole) of diethanolamine and refluxed for twenty hours. After standing 8 days, the mixture was treated with 42.0 g. (0.5 mole) of sodium bicarbonate and refluxed 4 hours. After standing 4 days the mixture was filtered and the precipitate discarded. The filtrate was saturated with dry hydrogen chloride and filtered while hot. The resulting filtrate was cooled in an ice-water bath and filtered. The precipitate was saved and the filtrate was treated with two volumes of acetone. An oil came out and, on treatment with absolute alcohol, the oil became crystalline. This crystalline material was combined with the precipitate saved above and analyzed, showing the presence of some bromide. The combined precipitates were then dissolved in 250 ml. of 95% ethanol and refluxed with 22.4 g. (0.4 mole) of potassium hydroxide dissolved in 20 ml. of water. At the end of one hour, 40.0 g. (0.4 mole) of potassium bicarbonate was added and the refluxing was continued for 18 hours. Two layers formed; the lower, being mainly water, was taken up with solid potassium carbonate. The resulting mixture was filtered and the filtrate was saturated with dry hydrogen chloride. A precipitate,

which came out, was removed by filtration and dried in the oven at 120°. The yield of

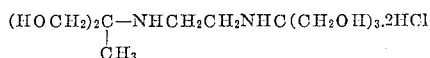


was 14.1 g.

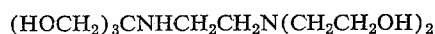
The same general procedure was followed for the preparation of



and

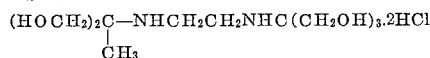


In the preparation of the first of these two compounds, 2-amino-2-hydroxymethyl-1,3-propanediol was condensed with a large excess of ethylene bromochloride and the intermediate of the structure $(\text{HOCH}_2)_3\text{CNHCH}_2\text{CH}_2\text{Cl}$ (likely with some $(\text{HOCH}_2)_3\text{CNHCH}_2\text{CH}_2\text{Br}$), after removal of excess ethylene bromochloride by evaporation and ether extraction, was condensed with diethanolamine. In the conversion of

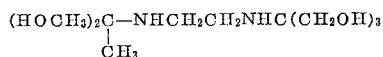


to the dihydrochloride, dry hydrogen chloride was used.

In the preparation of



2-amino-2-methyl-1,3-propanediol was condensed with a large excess of ethylene bromochloride and the beta-haloethyl derivative, thus formed, after removal of excess ethylene bromochloride by evaporation of ether extraction, was condensed with 2-amino-2-hydroxymethyl-1,3-propanediol. Dry hydrogen chloride was used to convert

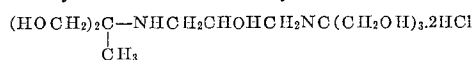


to the dihydrochloride.

Example 10

A mixture of 26.3 g. (0.25 mole) of 2-amino-2-methyl-1,3-propanediol, 27.8 g. (0.3 mole) of epichlorohydrin, 30 ml. of water and 90 ml. of methanol was refluxed gently for 5 hours and then left standing 18 hours. The reaction mixture was then treated with 200 ml. of ether and 100 ml. of n-butanol. A green oil settled out and the ether-butanol layer was decanted and discarded, the last traces of ether being removed from the oil on an evaporator. The oily residue was dissolved in 150 ml. of 95% ethanol along with 30.3 g. (0.25 mole) of tris

and refluxed for one hour. On standing for three days, a solid lower layer formed, was removed by filtration and discarded. The ethanolic filtrate was diluted to 350 ml. with 95% ethanol and saturated with dry hydrogen chloride. The resulting mixture was cooled in an ice-water bath and a gummy precipitate came out. The gum was discarded. The alcoholic layer gave a precipitate after standing two days. The precipitate was filtered off and the filtrate again treated with dry hydrogen chloride. A gum settled out on cooling and the alcohol was decanted. The gum became crystalline after standing with 75 ml. of absolute ethanol. The ethanolic layer was treated with an equal volume of ether. More gum settled out and crystallized on standing. The two precipitates were combined, washed with absolute ethanol and placed in an oven to dry at 120°. The total yield of



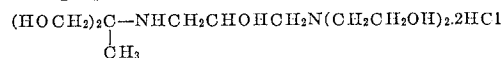
was 14.4 g.

In the preparation of



epichlorohydrin was first condensed with tris(hydroxymethyl)aminomethane and the resulting alkylation product was treated with diethanolamine and sodium hydroxide solution. The desired polyalkanolamine was converted to the dihydrochloride with concentrated aqueous hydrochloric acid.

In the preparation of



epichlorohydrin was first condensed with 2-amino-2-methyl-1,3-propanediol and the resulting alkylation product was converted to the desired polyalkanolamine by reaction with diethanolamine and sodium hydroxide solution. Concentrated hydrochloric acid was used to form the desired dihydrochloride.

In the procedures given in Examples 9 and 10, provision is not made for complete separation of the impurities of A—B—A₂HCl and A'—B—A'₂HCl from the desired product, A—B—A'₂HCl. It is possible that trace amounts of A—B—A₂HCl and of A'—B—A'₂HCl are left in each sample of A—B—A'₂HCl in following Table V. Thus, the melting points recorded may not represent pure compounds. However, the data are given for identification purposes.

The compounds in following Table V were prepared by the methods of Examples 9 and 10, with slight modifications in some cases. The numbers assigned to these unsymmetrical polyalkanolamines in Table V are used to designate them in Tables VI and VII.

TABLE V.—UNSYMMETRICAL POLYHYDROXYAMINES

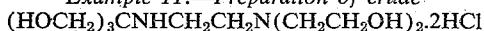
	M. P., ° C. (Uncor.)	Chloride, Percent	
		Calc'd.	Found
7..... $(\text{HOCH}_2)_3\text{CNHCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2\cdot 2\text{HCl}$	(1)	21.55	21.90
8..... $(\text{HOCH}_2)_3\text{CNHCH}_2\text{CHOHCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2\cdot 2\text{HCl}$	144-146	20.00	20.31
9..... $(\text{HOCH}_2)_2\underset{\text{CH}_3}{\text{C}}-\text{NHCH}_2\text{CH}_2\text{NHC}(\text{CH}_2\text{OH})_3\cdot 2\text{HCl}$	146.5-148	21.85	21.95
10..... $(\text{HOCH}_2)_2\underset{\text{CH}_3}{\text{C}}-\text{NHCH}_2\text{CHOHCH}_2\text{NHC}(\text{CH}_2\text{OH})_3\cdot 2\text{HCl}$	(2)	29.00	20.25
11..... $(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NHC}(\text{CH}_2\text{OH})_3\cdot 2\text{HCl}$	226-228	22.98	23.40
12..... $(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CHOHCH}_2\text{NHC}(\text{CH}_2\text{OH})_3\cdot 2\text{HCl}$	(3)	20.90	20.80

¹ Gummy semi-solid.
Gum.

Each of the unsymmetrical polyhydroxyamines in Table V, when used with each of the alpha-hydroxy acids in Table II, in molar ratios of polyhydroxyamine to alpha-hydroxy acid of 4/1 and of 1/4, kept in solution certain cations, including Fe^{+++} and Mn^{++} , better than did either sequestering agent alone in approximately the same molar concentration as the agent in higher molar concentration or the sum of the concentrations of both sequestering agents. The cations used with each sequestering agent and combination of sequestering agents are given in Table VI, below.

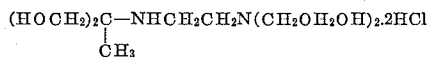
Purification of the unsymmetrical compounds of structure A—B—A' proved to be quite difficult. Therefore crude samples of each of the compounds of Table V were prepared for testing as synergistic sequestering agents with the alpha-hydroxy acids of Table II. These polyhydroxyamines were prepared by the general procedures outlined below, modified slightly in some cases:

Example 11.—Preparation of crude

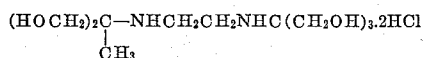


A solution of 30.3 g. (0.25 mole) of tris(hydroxymethyl)aminomethane and 35.9 g. (0.25 mole) of 1-bromo-2-chloroethane in 50 ml. of 95% ethanol was refluxed for 5 hours. At the end of this time, 26.3 g. (0.25 mole) of diethanolamine was added and the refluxing was continued for 18 hours. Partial neutralization of the hydrochloride was accomplished by refluxing the mixture with 21 g. (0.25 mole) of sodium bicarbonate and the mixture was evaporated to a low volume. The residue was dissolved in water, the pH of the solution was adjusted to about 3 with hydrochloric acid and water was added to make a total volume of 250 ml.

In the preparation of crude

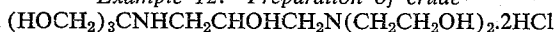


and



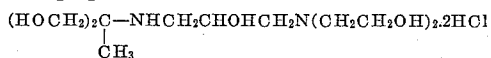
the first reaction was with 2-amino-2-methyl-1,3-propanediol and $\text{BrCH}_2\text{CH}_2\text{Cl}$. The syntheses were completed as above with slight modifications.

Example 12.—Preparation of crude

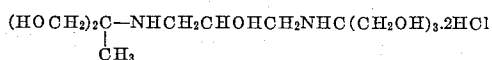


A mixture of 60.5 g. (0.50 mole) of tris(hydroxymethyl)aminomethane, 46.3 g. (0.50 mole) of epichlorohydrin and 200 ml. of methanol was left standing for 24 hours. The mixture was halved and one portion was treated with 26.2 g. (0.25 mole) of diethanolamine and 10.0 g. (0.25 mole) of sodium hydroxide dissolved in 10 ml. of water. The resulting mixture was left standing for 3 days and then was evaporated to low volume. The residue was dissolved in water and the solution was adjusted to a pH of about 3 with hydrochloric acid and diluted with water to 250 ml.

In the preparation of crude



and



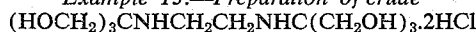
the first step was the reaction of 2-amino-2-methyl-1,3-propanediol with epichlorohydrin. The syntheses were completed as above, with slight modifications.

Tests with samples of each of the crude products of Table V showed that the impurities present do not prevent the synergistic sequestering action of each of these unsymmetrical polyhydroxyamines with each of the alpha-hydroxy acids of Table II.

While isolation of the pure polyhydroxyamines of Table I was less difficult than the purification of the

compounds of Table V, the purification of the symmetrical compounds of structure A—B—A was the most tedious step in their preparation. Therefore, crude samples of each of the polyhydroxyamines of Table I were prepared for testing as synergistic sequestering agents with each of the alpha-hydroxy acids of Table II. These compounds were prepared by the general procedures given below, modified slightly in some cases.

Example 13.—Preparation of crude



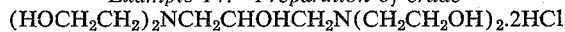
A mixture of 60.5 g. (0.50 mole) of tris(hydroxymethyl)aminomethane, 47.0 g. (0.25 mole) of ethylene bromide, 50 ml. of methanol and 25 ml. of water was refluxed for 24 hours. The mixture was treated with 34.6 g. (0.25 mole) of solid potassium carbonate and refluxed for 24 hours, then left standing for 7 days. The mixture was heated to boiling and filtered while hot. The precipitate was heated with 200 ml. of methanol and the solution was decanted and combined with the filtrate from above. The methanol was removed by evaporation and the residue was dissolved in water. The solution was adjusted to a pH of about 3 with hydrochloric acid and was diluted to 250 ml.

The other compounds of structure



were prepared by the same general procedure as just outlined, modified slightly.

Example 14.—Preparation of crude



A mixture of 52.5 g. (0.5 mole) of diethanolamine, 23.1 g. (0.25 mole) of epichlorohydrin and 50 ml. of methanol was left standing for 24 hours. The mixture was treated with 10.0 g. (0.25 mole) of sodium hydroxide dissolved in 15 ml. of water. A solid came out and was filtered off after the reaction mixture had stood for 6 days. The filtrate was evaporated to a low volume and the residue was dissolved in approximately 175 ml. of water. The pH of the solution was adjusted to about 7 with hydrochloric acid and water was added to make a total volume of 250 ml.

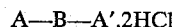
The other compounds of structure



were prepared by the same general procedure as just outlined, modified slightly.

Tests with samples of the crude polyhydroxyamines of Table I showed that the impurities present do not prevent the synergistic sequestering action of each of these compounds with each of the alpha-hydroxy acids of Table II.

In the preparation of molar solutions of the crude polyalkanolamines of Tables I and V, for use in Examples 15–21 and in getting data for Tables VI and VII, the calculated molarity was based on the assumption that complete reaction took place to yield the desired products



It is recognized that this assumption is not correct so the concentrations of the polyhydroxyamines listed in the examples and in the data in Tables VI and VII are incorrect only to the extent that the predicted reaction did not take place.

Thus, the claims for synergistic sequestering action of polyhydroxyamines and alpha-hydroxy acids over certain molarity ratios should be based, as they are, on the tests with purified polyhydroxyamines. Since the data with the crude polyhydroxyamines show that the claims do hold when these crude compounds are used with the alpha-hydroxy acids of Table II, it is probable that the limits for the ratio of alpha-hydroxy acid to polyhydroxyamine could be increased somewhat.

Each of the alpha-hydroxy acids in Table II was used in one of the following illustrative examples. In Examples 15, 17, 19 and 21, purified polyhydroxyamines from Table V were used. In Examples 16, 18 and 20, crude polyhydroxyamines were used. The stock test solutions of polyhydroxyamines and of alpha-hydroxy acids were molar.

In each of these examples, except No. 19, and in all of the tests tabulated in Tables VI and VII, except those involving tartrate, the total initial volume of solution was approximately 2 ml.

In practically all of the tests in the following illustrative examples and in the data tabulated in Tables VI and VII, the pH of each test solution was 3 or lower at the outset of the test. Tartrate, however, in some cases was used at a pH near 7, as a precipitate, likely potassium bitartrate, was obtained when an attempt was made to adjust the pH to near 3. This precipitate dissolved on dilution with 2 ml. of water and on heating so that it did not interfere with the tests involving tartrate indicated below.

Below are given the combinations of cations and the molarity of each cation in the stock test solutions used in the following illustrative examples Nos. 15-21 and in the tests tabulated in Tables VI and VII.

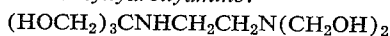
No. of Cations	Cations	Molarity of each Cation
2	Fe ⁺⁺⁺ , Mn ⁺⁺	0.25
5	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Zn ⁺⁺ , Ni ⁺⁺	0.20
8	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Zn ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Cd ⁺⁺ , Cr ⁺⁺⁺	0.10
9	Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Zn ⁺⁺ , Ni ⁺⁺ , Co ⁺⁺ , Cd ⁺⁺ , Cr ⁺⁺⁺ , Al ⁺⁺⁺	0.10

Since only these four combinations of cations are used in Tables VI and VII, the number of cations rather than their symbols are given.

In the tests for each example below, four test tubes were used. The sequestering agents as molar solutions, and cations used in each test tube and their volumes are given.

The tubes were heated in a water bath boiling or near boiling.

Example 15.—Polyhydroxyamine:



(used as purified dihydrochloride)

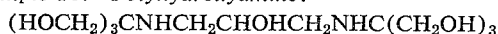
Alpha-Hydroxy Acid: Glycolic.

Cations: Fe⁺⁺⁺, Mn⁺⁺, Cu⁺⁺, Zn⁺⁺, Ni⁺⁺.

No. Tube	Polyhydroxyamine, ml.	Alpha-Hydroxy Acid, ml.	Cations, ml.
1	1.0	0	0.1
2	0.8	0.2	0.1
3	0.2	0.8	0.1
4	0	1.0	0.1

One drop of N sodium hydroxide solution was added to each test tube each five minutes for one hour. At the end of this time the pH of each tube was adjusted to about 7.8. Readings were taken after 1 hour 55 minutes. A heavy precipitate was in test tubes Nos. 1 and 4. No precipitate was visible in tubes Nos. 2 and 3.

Example 16.—Polyhydroxyamine:



(used as crude dihydrochloride)

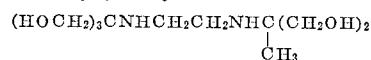
Alpha-Hydroxy Acid: Lactic.

Cations: Fe⁺⁺⁺, Mn⁺⁺, Cu⁺⁺, Zn⁺⁺, Ni⁺⁺, Co⁺⁺, Cd⁺⁺, Cr⁺⁺⁺, Al⁺⁺⁺.

No. Tube	Polyhydroxyamine, ml.	Alpha-Hydroxy Acid, ml.	Cations, ml.
1	1.0	0	0.1
2	0.8	0.2	0.1
3	0.2	0.8	0.1
4	0	1.0	0.1

One drop of N sodium hydroxide solution was added to each test tube every 5 minutes. At the end of 30 minutes the pH of the contents of tube No. 4 was approximately 8; so, no more base was added to this tube. This tube had a heavy precipitate which persisted throughout the experiment. Addition of base at the same rate of one drop each 5 minutes was continued with tubes Nos. 1, 2 and 3 for a period of 1 hour 55 minutes. A slight precipitate was noted in tube No. 1 at the end of 23 minutes. This precipitate persisted throughout the experiment. No precipitate was noted in tubes Nos. 2 and 3 at any time during the experiment.

Example 17.—Polyhydroxyamine:



(Used as the purified dihydrochloride)

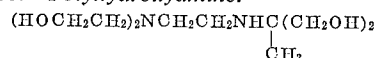
Alpha-Hydroxy Acid: Alpha-Hydroxybutyric.

Cations: Fe⁺⁺⁺, Mn⁺⁺, Cu⁺⁺, Zn⁺⁺, Ni⁺⁺, Co⁺⁺, Cd⁺⁺, Cr⁺⁺⁺, Al⁺⁺⁺.

No. Tube	Polyhydroxyamine, ml.	Alpha-Hydroxy Acid, ml.	Cations, ml.
1	1.0	0	0.1
2	0.8	0.2	0.1
3	0.2	0.8	0.1
4	0	1.0	0.1

One drop of N sodium hydroxide solution was added to each test tube every 5 minutes for a period of 45 minutes. Then the pH of each tube was adjusted to about 7.2. When readings were taken at 1 hour 15 minutes and 1 hour 45 minutes, a heavy precipitate was in tube No. 1, a medium precipitate was in tube No. 4 but no precipitate was in tubes Nos. 2 and 3.

Example 18.—Polyhydroxyamine:



(used as crude dihydrochloride)

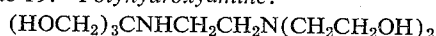
Alpha-Hydroxy Acid: Malic.

Cations: Fe⁺⁺⁺, Mn⁺⁺, Cu⁺⁺, Zn⁺⁺, Ni⁺⁺, Co⁺⁺, Cd⁺⁺, Cr⁺⁺⁺, Al⁺⁺⁺.

No. Tube	Polyhydroxyamine, ml.	Alpha-Hydroxy Acid, ml.	Cations, ml.
1	1.0	0	0.1
2	0.8	0.2	0.1
3	0.2	0.8	0.1
4	0	1.0	0.1

One drop of N sodium hydroxide solution was added to each tube every 5 minutes for a period of 1 hour 45 minutes. At this time there were medium precipitates in tubes Nos. 1 and 4 but no precipitate in either tube No. 2 or tube No. 3. After 2 hours 7 minutes 10 drops of N sodium hydroxide solution were added to each tube. When readings were taken at 2 hours 10 minutes a medium precipitate was in tube No. 1, a heavy precipitate was in tube No. 4 but no precipitate was in either of the other tubes.

Example 19.—Polyhydroxyamine:



(used as purified dihydrochloride)

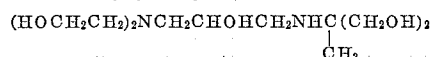
Alpha-Hydroxy Acid: Tartaric.

Cations: Fe⁺⁺⁺, Mn⁺⁺, Cu⁺⁺, Ni⁺⁺, Zn⁺⁺.

No. Tube	Polyhydroxy-amine, ml.	Alpha-Hydroxy Acid, ml.	Cations, ml.
1.....	1.0	0	0.2
2.....	0.8	0.2	0.2
3.....	0.2	0.8	0.2
4.....	0	1.0	0.2

When hydrochloric acid was added to these tubes, to adjust the pH to about 3, a white crystalline precipitate, likely potassium bitartrate, was formed in tube No. 3 and tube No. 4. On dilution of each of these four solutions with 2 ml. of water and on heating in a water bath, the precipitates dissolved. One drop of N sodium hydroxide solution was added to each tube every 5 minutes for a period of 1 hour. At the end of this time a fairly heavy precipitate was in tube No. 1, a heavy precipitate was in tube No. 4 but no precipitate was in tube No. 2 or tube No. 3. The pH of each sample was adjusted to about 9.3. At the end of 2 hours 10 minutes readings were taken. The precipitates in tubes No. 1 and No. 4 were distinctly less than at the end of 1 hour. No precipitate was in tube No. 2 or tube No. 3.

Example 20.—Polyhydroxyamine:



(used as crude dihydrochloride)

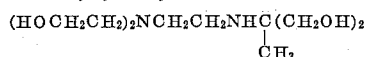
Alpha-Hydroxy Acid: Citric.

Cations: Fe⁺⁺⁺, Mn⁺⁺.

No. Tube	Polyhydroxy-amine, ml.	Alpha-Hydroxy Acid, ml.	Cations, ml.
1.....	1.0	0	0.2
2.....	0.8	0.2	0.2
3.....	0.2	0.8	0.2
4.....	0	1.0	0.2

One drop of N sodium hydroxide solution was added to each tube every 5 minutes for 1 hour. At the end of this time there was a heavy precipitate in tube No. 1, a fairly heavy precipitate in tube No. 4 but no precipitate in tube No. 2 or tube No. 3. The pH values of the solutions in tubes Nos. 1, 2, 3 and 4 were approximately 8.0, 8.5, 9.0 and 8.2, respectively.

Example 21.—Polyhydroxyamine:



(Used as pure dihydrochloride)

Alpha-Hydroxy Acid: Gluconic.

Cations: Fe⁺⁺⁺, Mn⁺⁺, Cu⁺⁺, Zn⁺⁺, Ni⁺⁺, Co⁺⁺, Cd⁺⁺, Cr⁺⁺⁺.

No. Tube	Polyhydroxy-amine, ml.	Alpha-Hydroxy Acid, ml.	Cations, ml.
1.....	1.0	0	0.1
2.....	0.8	0.2	0.1
3.....	0.2	0.8	0.1
4.....	0	1.0	0.1

One drop of N sodium hydroxide solution was added to each tube every 5 minutes for a period of 1 hour. Then the pH of the contents of each tube was adjusted to about 10.5. Readings were taken after 1 hour 30 minutes. A heavy precipitate was in tube No. 1, a fairly heavy precipitate was in tube No. 4 but no precipitate was in either tube No. 2 or tube No. 3.

The test with each alpha-hydroxy acid tabulated in following Tables VI and VII was carried out approximately as was the test with the same acid in the illustrative examples just above.

In illustrative Examples 15-21, if x is taken as the lowest molar concentration of sequestering agent in this particular example, the tubes had the following molar concentrations of sequestering agents:

Tube No.	Polyhydroxyamine	Alpha-Hydroxy Acid
1.....	5x	0
2.....	4x	x
3.....	x	4x
4.....	0	5x

The same ratios of concentrations were used in all the tests in Table VII and all in Table VI except Nos. 8-14, 22, 23, 27, 36-39, 41 and 42. In these tests, the tubes had the following relative concentrations of sequestering agents:

Tube No.	Polyhydroxyamine	Alpha-Hydroxy Acid
1.....	4x	0
2.....	4x	x
3.....	x	4x
4.....	0	4x

Each of the crude polyhydroxyamines in Table I and in Table V, when used with each of the alpha-hydroxy acids in Table II, in molar ratios of polyhydroxyamine to alpha-hydroxy acid of 4/1 and of 1/4, kept in solution certain cations, including Fe⁺⁺⁺ and Mn⁺⁺ better than did either type of sequestering agent along in approximately the same molar concentration as the sum of the concentrations of the individual sequestering agents. The cations and sequestering agents used are given in following Table VII.

TABLE VI.—SYNERGISTIC ACTION OF UNSYMMETRICAL POLYHYDROXYAMINES AND ALPHA-HYDROXY ACIDS AS SEQUESTERING AGENTS

No. test	Polyhydroxyamine	Alpha-Hydroxy Acid	Cations, Number
1.....	7	a.....	5
2.....	7	b.....	5
3.....	7	c.....	5
4.....	7	d.....	5
5.....	7	e.....	5
6.....	7	f.....	8
7.....	7	g.....	8
8.....	8	a.....	9
9.....	8	b.....	9
10.....	8	c.....	9
11.....	8	d.....	2
12.....	8	e.....	9
13.....	8	f.....	2
14.....	8	g.....	9
15.....	9	a.....	9
16.....	9	b.....	9
17.....	9	c.....	9
18.....	9	d.....	9
19.....	9	e.....	9
20.....	9	f.....	9
21.....	9	g.....	9
22.....	10	a.....	2
23.....	10	b.....	2
24.....	10	c.....	5
25.....	10	d.....	5
26.....	10	e.....	5
27.....	10	f.....	2
28.....	10	g.....	5
29.....	11	a.....	8
30.....	11	b.....	8
31.....	11	c.....	8
32.....	11	d.....	8
33.....	11	e.....	5
34.....	11	f.....	8
35.....	11	g.....	8
36.....	12	a.....	2
37.....	12	b.....	2
38.....	12	c.....	9
39.....	12	d.....	9
40.....	12	e.....	9
41.....	12	f.....	2
42.....	12	g.....	8

TABLE VII.—SYNERGISTIC ACTION OF CRUDE POLY-HYDROXYAMINES AND ALPHA-HYDROXY ACIDS AS SEQUESTERING AGENTS

No. test	Polyhydroxyamine	Alpha-Hydroxy Acid	Cations, Number
1.	1	a	9
2.	1	b	2
3.	1	c	2
4.	1	d	2
5.	1	e	9
6.	1	f	2
7.	1	g	9
8.	2	a	9
9.	2	b	9
10.	2	c	9
11.	2	d	9
12.	2	e	9
13.	2	f	9
14.	2	g	9
15.	3	a	9
16.	3	b	9
17.	3	c	9
18.	3	d	9
19.	3	e	9
20.	3	f	9
21.	3	g	9
22.	4	a	9
23.	4	b	9
24.	4	c	9
25.	4	d	9
26.	4	e	9
27.	4	f	9
28.	4	g	9
29.	5	a	9
30.	5	b	9
31.	5	c	9
32.	5	d	9
33.	5	e	9
34.	5	f	9
35.	5	g	9
36.	6	a	2
37.	6	b	2
38.	6	c	2
39.	6	d	9
40.	6	e	9
41.	6	f	9
42.	6	g	9
43.	7	a	9
44.	7	b	9
45.	7	c	9
46.	7	d	9
47.	7	e	9
48.	7	f	9
49.	7	g	9
50.	8	a	9
51.	8	b	9
52.	8	c	9
53.	8	d	9
54.	8	e	9
55.	8	f	9
56.	8	g	9
57.	9	a	9
58.	9	b	9
59.	9	c	9
60.	9	d	9
61.	9	e	9
62.	9	f	9
63.	9	g	9
64.	10	a	9
65.	10	b	9
66.	10	c	9
67.	10	d	9
68.	10	e	9
69.	10	f	9
70.	10	g	9
71.	11	a	9
72.	11	b	9
73.	11	c	9
74.	11	d	9
75.	11	e	9
76.	11	f	9
77.	11	g	9
78.	12	a	2
79.	12	b	2
80.	12	c	2
81.	12	d	2
82.	12	e	9
83.	12	f	2
84.	12	g	9

Most of the above tests were to show that the polyhydroxyamines and alpha-hydroxy acids of the present specification over a wide ratio of molar concentrations have synergistic sequestering action on certain cations which are deleterious when present in industrial waters.

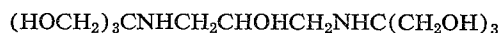
The following examples give the preparation of the crude free base,



and its synergistic sequestering action with citric acid.

Example 22

A mixture of 60.5 g. (0.50 mole) of 2-amino-2-hydroxy-methyl-1,3-propanediol, 23.1 g. (0.25 mole) of epichlorohydrin, 50 ml. of water and 50 ml. of methanol was left standing for 3 days. The mixture was treated with 12.0 g. (0.30 mole) of sodium hydroxide in 15 ml. of water and was refluxed for 3 hours. The methanol was vacuum-evaporated and the residue was dissolved in the minimum amount of water. The solution was diluted to 125 ml. giving a solution approximately 2 molar in



assuming complete reaction of 2-amino-2-hydroxymethyl-1,3-propanediol and epichlorohydrin.

Example 23

The following tests were carried out in 150 ml. beakers. To each beaker was added 2.0 ml. of crude 2 M



2.0 ml. of 2 M citric acid, 1.0 ml. of the cation or cations indicated below, 45 ml. of water and a boiling stone. The cations used and their concentrations are given below:

No. Test.	Cation(s)	Molarity, each
1.	Fe ⁺⁺	1.0
2.	Fe ⁺⁺⁺	1.0
3.	Fe ⁺⁺ , Fe ⁺⁺⁺	0.5
4.	Mn ⁺⁺	1.0
5.	Fe ⁺⁺ , Fe ⁺⁺⁺ , Mn ⁺⁺	0.33
6.	Fe ⁺⁺ , Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺	0.25
7.	Fe ⁺⁺ , Fe ⁺⁺⁺ , Mn ⁺⁺ , Cu ⁺⁺ , Ni ⁺⁺ , Zn ⁺⁺ , Co ⁺⁺ , Cd ⁺⁺ , Cr ⁺⁺⁺ , Al ⁺⁺⁺	0.10

The solutions were heated to gentle boiling and 1 drop of N sodium hydroxide solution was added to each solution every minute for 1 hour. Water was added as needed to keep the volume approximately 50 ml. No precipitate was noted in any case. From 1 hour to 1.5 hours, 1 drop of 6 N sodium hydroxide solution was added every minute. No precipitate was noted in any case. On continuation of the addition of 1 drop of 6 N sodium hydroxide solution every minute, distinct precipitates were noted in beakers No. 1 and No. 3 after 100 minutes and in beaker No. 2 after 105 minutes. At the end of 2 hours, there was a slight cloudiness in each of the other four beakers.

Example 24

To a hot solution containing 2.0 ml. of crude 2 M



2.0 ml. of 2 M citric acid, 1.0 ml. of Fe⁺⁺⁺, Mn⁺⁺, Cu⁺⁺, Zn⁺⁺ and Ni⁺⁺ (each 0.2 molar) and approximately 45 ml. of water, there was added every minute for 1 hour 1 drop of N sodium hydroxide solution. No precipitate was noted. For the second hour 1 drop of 6 N sodium hydroxide solution was added every minute. No precipitation was noted.

The present study demonstrates that polyhydroxyamines and alpha-hydroxy acids, of structures specified, have synergistic sequestering action on certain cations.

The polyhydroxyamines listed in Tables I and V, and others which come within the scope of the present invention, are synthesized readily from chemicals available in large amounts and at low cost from ethylene, propylene, formaldehyde, nitromethane and nitroethane.

The symmetrical polyhydroxyamines of Table I can be prepared in crude form in simple equipment with a minimum of chemical control (see Example 22). The crude polyhydroxyamines are effective sequestering agents when used with each of the alpha-hydroxy acids of Table II, particularly the acids with two or three carboxyl groups.

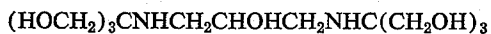
Practical applications of the properties of the inexpensive sequestering agents of the present specification will

25

occur to those industrial chemists skilled in sequestering technology.

The lack of toxic fumes and the high sequestering action of certain combinations on many cations over a pH range of from below 7 to over 13 should make these solutions particularly useful.

For example, preliminary tests indicate that an alkaline solution of equimolar amounts of



and citrate is an effective solvent for electroplating of copper, cadmium and iron.

From the following solution, iron was electroplated in a coating resembling blue steel:

111.3 g. $(\text{HOCH}_2)_3\text{CNHCH}_2\text{CHOHCH}_2\text{NHC}(\text{CH}_2\text{OH})_3$.
2HCl

97.2 g. $\text{K}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$

54 g. $\text{FeCl}_3 \cdot \text{H}_2\text{O}$

150 ml. 6 N sodium hydroxide solution

Water, to make a volume of 1 liter.

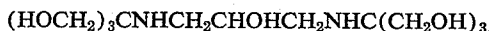
Copper and cadmium were deposited as adherent coats from alkaline solutions of the two sequestering agents above.

I claim:

A synergistic sequestering composition of matter of wide

26

utility which, when dissolved in water, consists essentially of an aqueous solution of



and citric acid, in which the molar ratio of polyhydroxy-amine to citric acid has limits of 4/1 and 1/4.

References Cited by the Examiner

UNITED STATES PATENTS

10	2,408,096	9/1946	Pierce et al. ----	252—158	XR
	2,544,649	3/1951	Bersworth.		
	2,674,523	4/1954	McDonald et al.		
	2,712,544	7/1955	Bersworth.		
	2,862,880	12/1958	Clemens -----	252—175	XR
15	3,000,829	9/1961	Arden -----	252—80	
	3,099,521	7/1963	Arensburg -----	252—175	XR

OTHER REFERENCES

Zussman: "Metal Complexing Agents in Soap and Detergent Products," Soap and San. Chem. (November 1952), pp. 79, 81, 83 and 139.

LEON D. ROSDOL, *Primary Examiner.*

25 JULIUS GREENWALD, *Examiner.*

W. E. SCHULZ, *Assistant Examiner.*