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(19)

(54) AN ALIPHATIC POLYAMINO POLYCARBOXYLIC ACID AND ITS SALTS AND THEIR USE AS CHELATING AGENTS

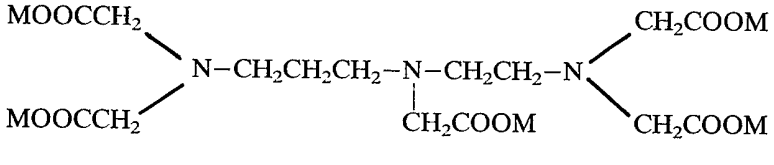
(71) We, REXOLIN CHEMICALS AKTIEBOLAG, a Swedish Body Corporate, of Industrigatan 125, Box 622, 25106 Helsingborg, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to novel compounds useful as chelating agents and to methods for preparing such compounds.

Methods are known for preparing certain aliphatic polycarboxylic amino acids or alkali metal salts thereof, see, e.g., Bersworth, U.S. Patents Nos. 2,407,645 and 2,387,735; Munz, U.S. Patent No. 2,130,505; and Singer et al, U.S. Patent No. 3,061,628. Singer et al also teach, in U.S. Patent No. 2,855,428, a method for preparing certain aliphatic polyaminonitriles (which are intermediates on the route of Singer et al to aliphatic polycarboxylic amino acids), and, in U.S. Patent No. 3,115,511, they teach a method for preparing iron chelates of such acids. Scanlon et al, U.S. Patent No. 3,780,099, teach a method for preparing an iron chelate of a salt of an aminoacetic acid.

The preseent invention provides:

(a) a chelating agent having the formula:



in which M is hydrogen or an alkali metal (e.g., K, Na, or Li) ion;

(b) methods for preparing said chelating agent; and

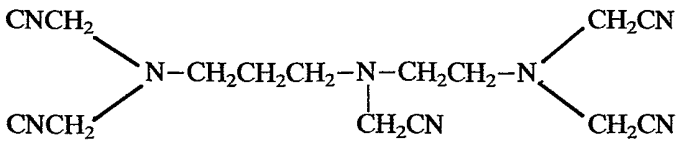
(c) chelates thereof with heavy metal ions which are defined as iron, zinc, cobalt, copper, manganese, calcium, chromium, or molybdenum ions.

This chelating agent has many uses including the production of chelates of trace elements (iron, zinc, manganese, cobalt, molybdenum and the like) which are useful for providing trace elements to growing plants.

The chelating agent is also useful to chelate ions of heavy metals such as iron and manganese when bleaching wood pulp for use in paper making, thereby to facilitate the

removal of such ions from the aqueous system comprising the pulp. For this purpose it has the advantage of being biodegradable.

This invention also provides a nitrile which is an intermediate for the said chelating agent, the said nitrile having the formula:



This nitrile can be designated "aminopropylethylenediaminepentaacetonitrile" which can be abbreviated to APEPAN.

When M is hydrogen the chelating agent of the present inventionn can be called.

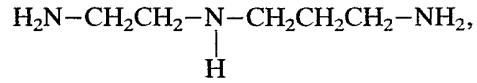
(a) pentacarboxymethylated aminopropyl ethylenediamine;
(b) N-(2-aminoethyl)-1,3-propanediamine, N,N,N′,N″,N″-pentaacetic acid;
(c) propanediamine, N-(2-aminoethyl)pentacarboxymethylate;
(d) propanediamine, N-(2-aminoethyl)pentaacetic acid; or
(e) aminopropylethylenediaminepentaacetic acid. When M is hydrogen, it can be designated "APEPA" and when M is an alkali metal ion the following designations (depending on the alkali metal ion) can be used:

Alkali Metal Ion	*Designation*
Potassium	APEPAK
Sodium	APEPANa
Lithium	APEPALi
"Alkali Metal" (generic)	APEPAM

Three general methods are known to be operable for preparing the chelating agent of this invention. These are:

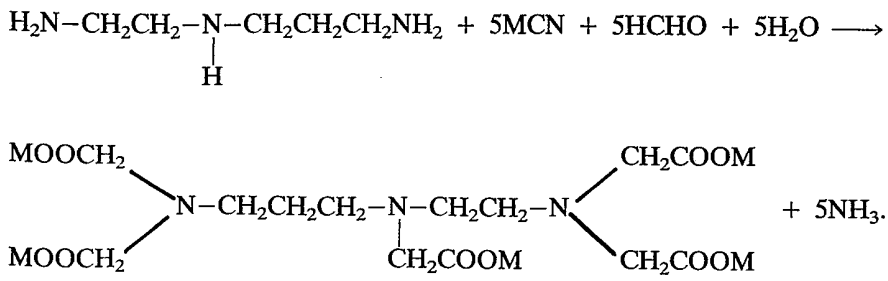
Method No. 1

2-aminoethyl-1,3-propanediamine,



which can be designated "APDA" is reacted in an alkaline aqueous medium with an alkali metal cyanide and formaldehyde to form an alkali metal salt of APEPA (e.g. APEPAK, APEPANa, or APEPALi). By-product ammonia is evaporated from the aqueous system as it (the ammonia) forms. The alkali metal salt of APEPA is recovered as a solid, e.g., by spray drying, or by evaporating (vaporizing) a substantial amount of water from the system and then cooling the aqueous residue to cause the alkali metal salt of APEPA to precipitate. The precipitated salt is recovered by filtration, decantation or centrifugation.

The following equation represents the reaction by which the salt APEPA is prepared when using Method No. 1:



M in the above equation represents an alkali metal ion.

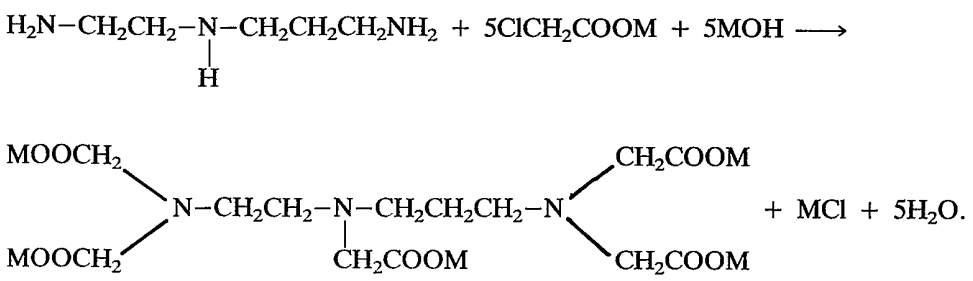
APDA is commercially available. It can be prepared by reacting ethylene diamine with acrylonitrile and hydrogenating the resulting product.

Example 1, infra, illustrates the preparation of APEPANa via method No. 1.

Method No. 2

APDA is reacted in an alkaline aqueous medium with an alkali metal salt of monochloroacetic acid and an alkali metal hydroxide to form an alkali metal salt of APEPA, water, and an alkali metal chloride. This salt of APEPA can be recovered by the techniques described in Method No. 1.

The following equation represents the reaction by which the alkali metal salt of APEPA is formed when using Method No. 2:

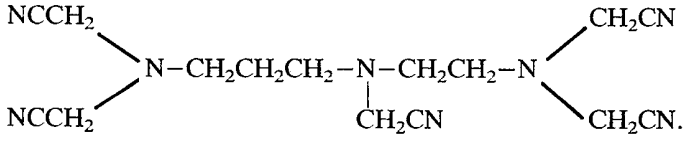


M, in the above equation, represents an alkali metal ion. For simplification, the above equation shows an alkali metal hydroxide (MOH); however, an alkali metal carbonate (e.g., potassium or sodium carbonate) ca be used to provide the alkalinity. Because of its low solubility, lithium carbonate is not recommended.

Procedure 1, infra, illustrates the preparation of APEPANa by Method No. 2.

Method No. 3

APDA is reacted in an acidic aqueous solution with HCN and formaldehyde to form a nitrile having the formula



This nitrile, which can be called aminopropylethylenediaminepentaacetonitrile, can be designated "APEPAN".

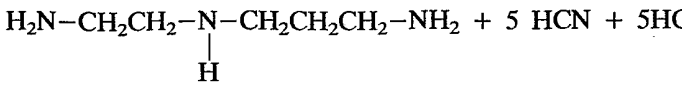
The APEPAN can be separated from the acidic mother liquor in which it is formed by evaporating (vaporizing) a substantial portion of water from the acid aqueous system comprising the APEPAN and cooling the resulting aqueous system (e.g., to 1 to 25°C, or 5 to 15°C.) to precipitate the APEPAN and recovering the precipitated APEPAN (e.g., by filtration, decantation, or centrifugation). If desired, the separated APEPAN can be washed with cold water to free it (the APEPAN) of acid.

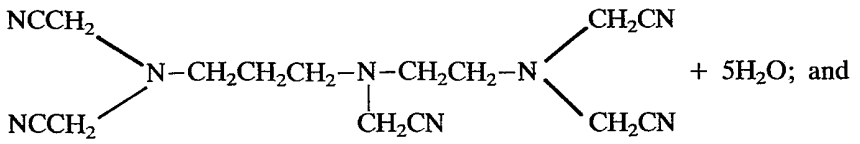
The separated APEPAN is reacted with an aqueous alkali metal hydroxide solution to

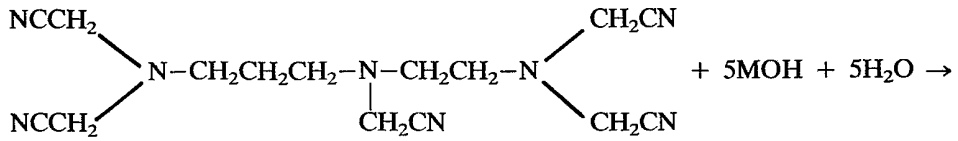
form an alkali metal salt of APEPA and byproduct ammonia which is evaporated from the reacting system.

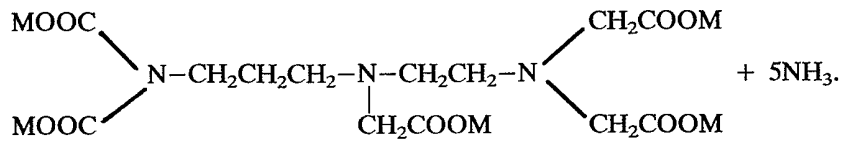
The alkali metal salt of APEPA can be recovered by the techniques described in Method No. 1.

The following equations represent the reactions by which the alkali metal salt of APEPA is prepared when using Method No. 3:









M, in the above equation, represents an alkali metal ion (e.g., potassium, sodium, or lithium).

Procedure 2, infra, illustrates the preparation of APEPAN and APEPANa by method No. 3.

The following examples and procedures further illustrate this invention. The examples were run. Although the procedures were not run, they will illustrate certain aspects of the invention.

EXAMPLE 1

(Preparation of APEPANa by Method No. 1)

An alkaline aqueous system was prepared by admixing in a vented reaction zone provided with a heating means, a cooling means, an agitating (stirring) means, and two inlet ports:

(a) 500 kg of water;

(b) 1172 kg (10,0 kilomoles) of APDA; and

(c) 80 kg (2,0 kilomoles) of sodium hydroxide added as a 50% aqueous solution. 4464 kg of an aqueous 37% formaldehyde solution (55.0 kilomoles of HCHO) and 8904kg of an aqueous 30% NaCN solution (54.5 kilomoles of NaCN) were added to the reaction zone while stirring the resulting reaction mixture therein and while maintaining said mixture at its boiling point to vaporize byproduct ammonia therefrom substantially as the ammonia was formed. The sodium cyanide solution and the formaldehyde solution were added at such rates that - until the reaction was substantially complete - the cyanide was present in slight excess over the formaldehyde.

The vaporized ammonia was recovered.

When the reaction was completed, and all of the sodium cyanide and formaldehyde solutions had been added, water was evaporated from the aqueous product until the total volume thereof was reduced by about 60% and the resulting concentrated aqueous product was cooled to atmospheric temperature (ca. 20°C) to facilitate the precipitation of APEPANa.

The precipitated APEPANa was separated by centrifugation and recovered.

If desired, APEPAK can be prepared by replacing the NaCN and NaOH with KCN and KOH, respectively, and APEPALi can be prepared by using LiCN and LiOH.

Alternatively, the APEPANa can be recovered by spray drying the aqueous product comprising the APEPANa before or after evaporating water therefrom in the above-mentioned concentrating step.

The sodium hydroxide is not a reactant but is added to control pH to assure that the system is alkaline at all times and to prevent the formation of HCN. When using formaldehyde that contains little or no acid, the sodium hydroxide can be omitted or the amount used can be reduced. However, it is preferred to operate at a pH above 9.

Paraformaldehyde or trioxane can be used as a source of formaldehyde.

EXAMPLE 2

(Using APEPANa in the Bleaching of Wood Pulp)

The use of chelating agents when bleaching wood pulp (e.g., when bleaching wood pulp to be used in paper making) is well-known in the art and is taught on page 191 of "The Bleaching of Pulp", TAPPI Monograph Series No. 27, Technical Association of the Pulp and Paper Industry (360 Lexington Avenue, New York, N.Y. 10017, USA), 1963.

Ground wood pulp from Utansjo was subjected to standard bleaching in a thermostated bath as follows:

H_2O_2	3% as 100% o.d. pulp
NaOH	1% as 100% o.d. pulp
Sodium Silicate	4%, ratio 1,6 53° Bé o.d. pulp
Time	3h.
Temperature	60°C.
Concentration	12%

1. in Runs Nos. 2 and 3 the chelating agents were charged in a pre-treatment (1 h., 40°C., Conc. 3%). This was followed by washing.
2. In Runs Nos. 4, 5, and 6 the chelating agents were added direct into the bleach-bath.

Dosage of Chelating Agent

0,2 and 0,4% of commercial grade product calculated on the weight of the dry pulp were charged. In the pre-treatment tap water was used and in the following washing stage demineralized water was used,

After the bleaching step the pulp was washed with demineralized water and sheets were made according to SCAN. The results are presented in the following table:

Run No.	*Chelating Agent Used*	*Chelating Agent kg/ton*	*Residual Peroxide*	*Brightness** % ISO*	*Point of Addition*
1	Control (none)	- 0 -	26	74,3	-
2	DTPA*	4	40	75.7	pre-treat
3	APEPANa	4	43	75.9	pre-treat
4	DTPA*	4	31	75.3	bleach-bath
5	APEPANa	2	28	75.0	bleach-bath
6	APEPANa	4	28	75,2	bleach-bath

*DTPA is diethylenetriaminepentaacetic acid pentasodium salt commercial grade.

**Brightnesses were measured on non acid-treated pulp.

The results of the above runs show that:

1. The test results for APEPANa, where charged into the bleach-bath, were as good as those for DTPA.

2. When charging the APEPANa in the pre-treatment a slightly improved result was achieved (brightness and residual peroxide) depending either on better efficiency in the more diluted solutions or the washing in the following stage.

While the above tests were made using APEPANa in a peroxide bleaching system, APEPANa, (or APEPA per se) is operable in other bleaching systems including but not limited to a hydrosulphite bleaching system (at pH 5 to 6), a chlorine bleaching system, and a chlorine dioxide bleaching system.

PROCEDURE 1

(Preparation of APEPANa by Method No. 2)

An aqueous alkaline reaction mixture can be prepared by admixing in a reaction zone provided with a stirring means and a heating means:

(a) 750 g of water;

(b) 117,2 g (1,0 mole) of APDA; 582,5 g (5,,0 moles) of sodium monochloroacetate ($ClCH_2COONa$); and 265 g (2,5 moles) of sodium carbonate. The reaction mixture can be maintained at 90-98°C. for 4-6 hours to form an aqueous product comprising APEPANa and a mother liquor.

The APEPANa can be recovered by boiling the aqueous product until about 60% or more of the water has been evaporated and cooling (e.g., to 1-25°C. or 5-15°C.) to precipitate the APEPANa which can be separated (e.g., by filtration, centrifugation, or decantation) and recovered. The recovered crude APEPANa can be washed with cold (e.g., 1-25°C. or 5-15°C.) water to remove water soluble impurities.

Spray drying can also be used to recover crude APEPANa.

If a purer grade of APEPANa is desired, the aqueous product comprising the mother liquor and APEPANa can be treated with acid (e.g., hydrochloric acid or sulphuric acid) to adjust the pH to about 1,3 to convert the APEPANa to APEPA which precipitates. The precipitated APEPA can be separated, washed with water if desired, and recovered. Alternatively, the separated APEPA can be converted to APEPANa by treating with about a stoichiometric amount of sodium hydroxide in an aqueous medium, separated, and recovered.

PROCEDURE 2

(Preparation of APEPAN and APEPANa by Method No. 3)

A 405,8 g portion of an aqueous 37% formaldehyde solution (5,0 moles of HCHO) and 135,2 g (5,0 moles) of HCN can be admixed in a vented reaction zone (the vent constituting a reflux means maintained below 15°C.), the reaction zone being provided with a cooling means, a heating means, two inlet ports, and a stirring means. The formaldehyde solution and HCN can be admixed and the pH of the resulting mixture can be adjusted to a pH below 1,0 with sulphuric acid while maintaining the temperature of the mixture below about 20°C.

An aqueous system comprising 750 g of water and 117,2 g (1,0 mole) of APDA can be added to the mixture in the reaction zone at such rate that:

(a) the temperature of the mixture in the reaction zone does not exceed about 60°C.; and

(b) the pH of said mixture remains below 1,0.

After all of the aqueous system comprising APDA has been added the material in the reaction zone can be heated to about 70-80°C. for about an hour and then cooled to about 15°C. Substantially all of the product (APEPAN) will precipitate at 15°C. The precipitated APEPAN can be separated by decantation, filtration, or centrifugation at about 15°C. If desired, the precipitated APEPAN can be washed with cold (e.g., 10-20°C.) water to free it (the APEPAN) from sulphuric acid.

The separated APEPAN can be recovered.

Alternatively, the formaldehyde solution and the APDA can be admixed to form a condensate which, after adjusting its pH to a value below 1,0 can be added to the HCN which is in the above-described reaction zone. The condensate should be added at such rate that the temperature of the resulting reacting mixture remains below about 60°C. After all of the condensate has been added to the HCN in the reaction zone the temperature of the material in the reaction zone can be adjusted to about 70-80°C. and maintained at such temperature for about an hour. The APEPAN product can be separated and recovered after cooling the material in the reaction zone to about 15°C.

APEPANa can be prepared by admixing 156,2 g (0,5 mole) of APEPAN and 650 g of water to form a slurry and adding said slurry to a vented reaction zone containing 108 g (2,7 moles) of sodium hydroxide present as an aqueous 25% sodium hydroxide solution. The

slurry is added at such rate that the resulting reaction mixture in the vented reaction zone boils gently. The vent serves as an outlet for byproduct ammonia which is recovered. The reaction zone is provided with a heating means, a cooling means, a stirring means, and an inlet port.

When hydrolysis is complete the material in the reaction zone can be boiled vigorously to remove about 40-60% of the water therefrom. The hot mixture can be cooled to about 20°C. and the resulting precipitated APEPANa can be separated and recovered. Alternatively, the APEPANa can be recovered by spray drying.

PROCEDURE 3

(Preparation of an Iron Chelate of APEPANa)

A solution of an iron (III) chelate of APEPANa can be prepared by admixing 548,8 g of an aqueous 25% iron(III) chloride solution (1,0 mole of $FeCl_3$) and 5173,0 g of an aqueous 10% APEPANa soluution (1,0 mole of APEPANa). While preparing the iron(III) chelate aqueous sodium hydroxide solution (ca 25% NaOH by weight) can be added as required to maintain the pH of the resulting iron(III) chelate solution at about 8.

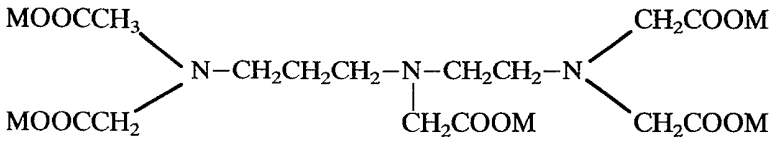
Other metallic chelate solutions (e.g., calcium, zinc, manganese, cobalt, or molybdenum) can be prepared by the above-described procedure by replacing the iron(III) chloride with calcium chloride, zinc chloride, manganese (II) chloride, cobalt chloride, or molybdenum(II) chloride, respectively, on a mole for mole basis.

If desired APEPANa can be replaced by APEPAK and the iron(III) chloride can be replaced with iron(II) chloride, iron(III) sulphate, or iron(II) sulphate on a mole for mole basis. Also, if desired, the sodium hydroxide can be replaced on a mole for mole basis by potassium hydroxide.

Alternatively, a chelate of iron (or other heavy metal) can be prepared by treating powdered iron with an aqueous APEPA slurry using the general procedure of U.S. Patent No. 3,115,511. If desired, the resulting chelate can be treated with sodium (or potassium) hydrogen carbonate to convert the APEPA ligand to an APEPAK ligand.

WHAT WE CLAIM IS:

1. A compound having the formula:



in which M is hydrogen, or an alkali metal ion.

2. A compound as claimed in claim 1, in which M is hydrogen.

3. A compound as claimed in Claim 1, in which M is an alkali metal ion.

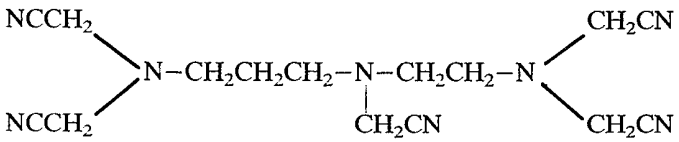
4. A compound as claimed in claim 3, in which the alkali metal ion is a sodium ion.

5. A compound as claimed in claim 3, in which the alkali metal ion is a potassium ion.

6. A heavy metal as hereinbefore defined chelate of a compound as claimed in claim 1.

7. A chelate as claimed in claim 6, in which M is sodium or potassium and the heavy metal is iron, manganese, calcium, cobalt, molybdenum or zinc.

8. The nitrile having the formula:



9. A process for preparing the nitrile of claim 8 comprising:

(a) reacting 2-aminoethyl-1,3-propanediamine, HCN, and formaldehyde in an acidic aqueous medium, and

(b) separating and recovering the resulting nitrile.

10. A process for preparing a compound as claimed in claim 1, in which M is an alkali metal ion, which comprises

(a) hydrolysing the nitrile of claim 8 with an alkali metal hydroxide in an aqueous medium, and

(b) separating and recovering the resulting compound as claimed in claim 1.

11. A process for preparing a compound as claimed in claim 1, in which M is an alkali metal ion which comprises

(a) reacting in an alkaline aqueous medium 2-aminoethyl-1,3-propanediamine, an alkali metal cyanide, and formaldehyde, and

(b) separating and recovering the resulting compound as claimed in claim 1.

12. A process for preparing a compound as claimed in claim 1, in which M is an alkali metal ion, which comprises reacting in an alkaline aqueous medium 2-aminoethyl-1,3-propanediamine and $ClCH_2COOM$, and separating and recovering the resulting compound as claimed in claim 1.

13. A process as claimed in claim 11 substantially as described in Example 1.

14. A compound as claimed in claim 1 when prepared by a process claimed in any one of claims 10 to 13.

15. A nitrile as claimed in claim 8 when prepared by a process as claimed in claim 9.

16. A process for bleaching wood pulp which comprises reacting the wood pulp with a bleaching agent in an aqueous system in the presence of, as chelating agent, a compound as claimed in any one of claims 1 to 5 or 14.

17. A process according to claim 16, in which the bleaching agent is a peroxide and M is sodium.

18. A process according to claim 17, in which the peroxide is hydrogen peroxide.

19. A process according to claim 16 substantially as described in Example 2.

20. Wood pulp bleached by the process of any one of claims 16 to 19.

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