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(54)

Tablet for processing silver halide color photographic light-sensitive materials.

(57)

A solid photographic processing tablet is disclosed. The tablet comprises a thiosulfate salt, a ferric complex salt of an amino polycarboxylic acid and a polymer selected from the group consisting of polyethylene glycols, polyvinylpyrrolidones and polyvinyl alcohols.

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Field of the Invention

The present invention relates to a tablet for processing a silver halide color photographic light-sensitive material, and more particularly relates to a tablet for preparing a processing solution of a silver halide color photographic light-sensitive material having sufficient strength and excellent storage stability.

Background of the Invention

A silver halide photographic light-sensitive material after being exposed is photographically processed through a development step, a desalting step, a washing step and a stabilization step. The photographic processing is ordinarily conducted using an automatic processing machine. On such an occasion, a replenisher replenishing system is commonly used wherein the processing solution in a processing tank is controlled so that the degree of activity thereof is kept constant. In the case of the replenisher replenishing system, the purposes thereof include dilution of materials dissolved from the light-sensitive material, and replenishment of consumed components, usually resulting in an occurrence of a large amount of an overflowing waste solution and an empty vessel.

There has been a world wide movement for making regulations prohibiting disposal of photo-effluent directly into ocean and regulations plastic materials. In addition, safety regulations on packaging materials have been strengthened for maintaining safety in transportation of liquid hazardous substances, resulting in creased cost. Accordingly, a new development of a processing system wherein a photographic disposal is reduced remarkably and bottles for processing agents are not used is demanded.

In mini lab shops using compact processing machines which have recently been spreading rapidly, development of technologies for controlling exposure for a print has been advanced and a system wherein anybody can conduct printing operation is being introduced. However, dissolving operation of the replenishing solution and control of the processing solution are still difficult so that a critical error to dissolve a wrong processing agent and to erroneously replenish the processing solution may easily occur. Thus, this conventional replenishment system has resulted complaints frequently.

Accordingly, in the photographic industry, it has strongly been demanded to develop a replenishment system using solid chemicals wherein substantially no photographic waste solution occurs, no bottles for processing agents are used and no dissolution operation is necessary. As a method to meet this demand, Japanese Patent O.P.I. Publication No. 119454/1993 discloses a method to make up almost all processing components into a solid processing agent and to charge it to a processing tank directly.

However, among the tablets described in the above-mentioned patents, the surface of tablets for bleach-fixing employing an amino polycarboxyl acid ferric complex salt and a thiosulfate becomes pasty under high humidity, since the thiosulfate absorbs moisture. Even when humidity-proof package is used therefor, for long-term storage, the above-mentioned problem still occurs due to initial humidity inside the package or moisture inside the tablet itself. As a result, tablets coagulate each other or they stick to the inner surface of the package. During use, the tablet agent is difficult to remove from a package or a cartridge. Specifically, when the tablet is shipped from Japan to East South Asia, the Middle-East and Africa by a ship of 2 to 4 weeks duration, the temperature extremes between day and night during the transportation may reach 15 to 20 °C, and the humidity may vary by 20 to 30 %RH. Accordingly, in such cases, the above-mentioned problem becomes more apparent.

Summary of the Invention

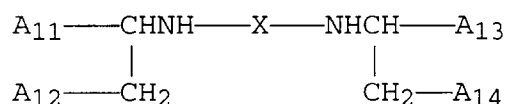
An object of the invention is to provide a photographic solid processing tablet for fix-bleach having excellent storage stability and handling property.

The above object can be attained by a solid processing tablet for processing a silver halide color photographic light-sensitive material wherein the tablet comprises at least one thiosulfate salt, at least one ferric complex salt of an amino polycarboxylic acid and at least one compound selected from the group consisting of polyethylene glycols, polyvinylpyrrolidones and polyvinyl alcohols or a method for preparing a solid photographic processing tablet comprising a thiosulfate salt, a ferric complex salt of an amino polycarboxylic acid and a polymer selected from the group consisting of polyethylene glycols, polyvinylpyrrolidones and polyvinyl alcohols, comprising the steps of:

- granulating a first composition comprising the ferric complex salt;
- granulating a second composition comprising the thiosulfate salt;
- mixing the resulting granulates with the polymer; and
- molding the resulting mixture by applying pressure to obtain the tablet.

wherein A_1 to A_4 may be the same with or the different from each other and represent each a hydrogen atom, a hydroxy group, $-\text{COOM}$, $-\text{PO}_3(\text{M}_1)_2$, $-\text{CH}_2\text{COOM}_2$, $-\text{CH}_2\text{OH}$ or a lower alkyl group, provided that at least one of A_1 to A_4 represents $-\text{COOM}$, $-\text{PO}_3(\text{M}_1)_2$ or $-\text{CH}_2\text{COOM}_2$; and M , M_1 and M_2 represent each a hydrogen atom, an ammonium group, an alkali metal or an organic ammonium group.

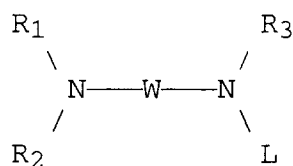
Formula (A-II)



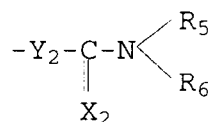
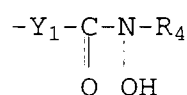
wherein A_{11} to A_{14} may be the same with or the different from each other and represent each $-\text{CH}_2\text{OH}$, $-\text{COOM}_3$ or $-\text{PO}_3(\text{M}_4)_2$; M_3 and M_4 represent each a hydrogen atom, an ammonium group, an alkali metal or an organic ammonium group; X represents an alkylene group having 2 to 6 carbon atoms or $-(\text{B}_1\text{O})_n-\text{B}_2-$ in which n is an integer of 1 to 8 and B_1 and B_2 may be the same with or the different from each other and represent each an alkylene group having 1 to 5 carbon atoms.

In the above-given Formula (A-II), the alkylene groups represented by X include, for example, the groups of ethylene, propylene or butylene. In $(\text{B}_1\text{O})_n-\text{B}_2-$ represented by X , the alkylene groups represented by B_1 and B_2 include, for example, methylene, ethylene and trimethylene. These alkylene groups may also have a substituent including, for example, a lower alkyl group such as a methyl group, an ethyl group, or a hydroxy group.

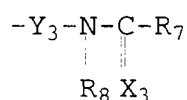
Formula (A-III)



wherein R_1 to R_3 represent each a hydrogen atom, a substituted or unsubstituted alkyl or aryl group; L represents either one of the following formulas,



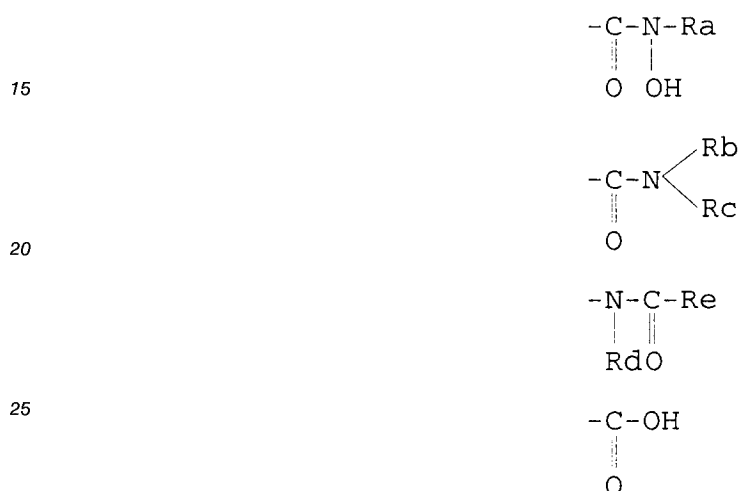
or



wherein Y_1 to Y_3 represent each an alkylene or arylene group; X_2 and X_3 represent each an oxygen atom or a sulfur atom; and R_4 to R_8 represent each a hydrogen atom, an alkyl group or an aryl group; and W represents a divalent linking group.

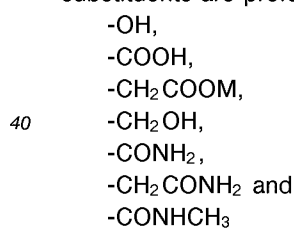
In the above-given Formula (A-III), the alkyl groups represented by R_1 through R_3 include, for example, those of the straight-chained, the branched and the cyclic, each having 1 to 10 carbon atoms and, among

them, a methyl group and an ethyl group are particularly desirable. The aryl groups represented by R₁ through R₃ include, preferably, a phenyl group. When R₁ through R₃ represent each an alkyl or aryl group, each of these groups may have a substituent. The substituents for R₁ through R₃ include, for example, an alkyl group, an aralkyl group, an alkenyl group, an alkynyl group, an alkoxy group, an aryl group, a substituted amino group, an acylamino group, a sulfonylamino group, a ureido group, a urethane group, an aryloxy group, a sulfamoyl group, a carbamoyl group, an alkylthio group, an arylthio group, a sulfonyl group, a sulfinyl group, a hydroxy group, a halogen atom, a cyano group, a sulfo group, a carboxy group, a phosphono group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyl group, an acyloxy group, a carbonamido group, a sulfonamido group and a nitro group. The preferable substituents include those having the following formulas:



wherein Ra, Rb, Rc, Rd and Re represent each a hydrogen atom, an alkyl group or an aryl group.

In the above-given Formula (A-III), the alkylene groups represented by Y₁ through Y₃ include, for example, a methylene group, an ethylene group or a propylene group. The arylene groups represented thereby include, for example, a phenylene group. Each of the alkylene groups and arylene groups represented by Y₁ through Y₃ may have each a substituent. The substituents applicable thereto include, for example, those given for the substituents of R₁ through R₃ and, among these substituents, the following substituents are preferable.



(in which M represents a hydrogen atom, an alkali metal or an ammonium group.)

In the foregoing Formula (A-III), the divalent linking groups represented by W include, desirably, an alkylene group having 2 to 8 carbon atoms (including a cyclohexylene group), an arylene group having 6 to 10 carbon atoms,



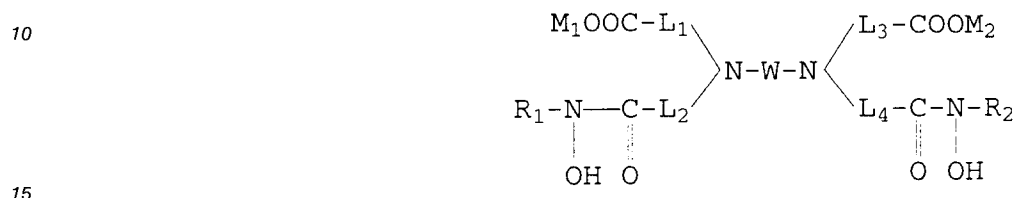
wherein B₁ and B₂ represent each an alkylene or arylene group and n is an integer of 1 to 3.



wherein Z represents a hydrogen atom, an unsubstituted alkyl or aryl group, or an alkyl or aryl group substituted with -COOM, -SO₃M or -OH; and M represents a hydrogen atom, an alkali metal or an ammonium group. These divalent linking groups may be combined with each other.

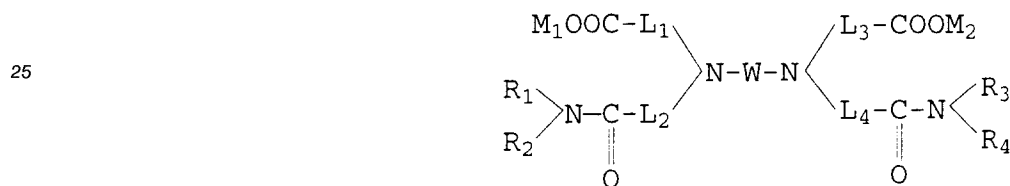
Among the compounds represented by Formula (A-III), the preferable ones include the compounds
5 represented by the following Formula (B-I) or (B-II).

Formula (B-I)



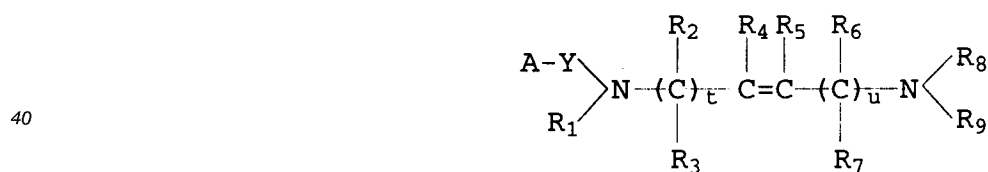
wherein R₁ and R₂ represent each a hydrogen atom, an alkyl group or an aryl group; L₁ through L₄ represent each an alkylene group or an arylene group; and M₁ and M₂ represent each a hydrogen atom, an alkali metal, an ammonium group or an organic ammonium group.

Formula (B-II)



wherein R₁ through R₄ are each synonymous with R₁ and R₂ each denoted in Formula (B-I), and L₁ through L₄ and M₁ and M₂ are each synonymous with those denoted in Formula (B-II).

Formula (A-IV)

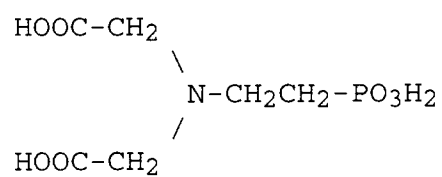


wherein R₁ to R₃ and R₆ to R₉ represent each a hydrogen atom or a substituted or unsubstituted alkyl or aryl group; R₄ and R₅ represent each a hydrogen atom, a halogen atom, a cyano group, a nitro group, an acyl group, a sulfamoyl group, a carbamoyl group, an alkoxy carbonyl group, an allyloxy carbonyl group, a sulfonyl group, a sulfinyl group or a substitutable alkyl or aryl group, provided, R₄ and R₅ may be associated so as to form a 5-membered or 6-membered ring; A represents a carboxy group, a phosphono group, a sulfo group, a hydroxy group or an alkyl metal salt or ammonium salt thereof; Y represents an alkylene group or an arylene group, provided, Y may have a substituent; and t and u are each an integer of 0 or 1.

The typical examples of the compounds represented by Formula (A-I), (A-II), (A-III) or (A-IV) will be given below. The compounds represented thereby shall not, however, be limited thereto.

A-I-6

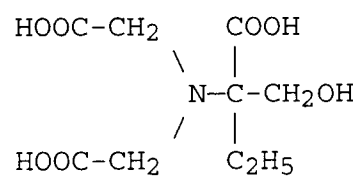
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A-I-7

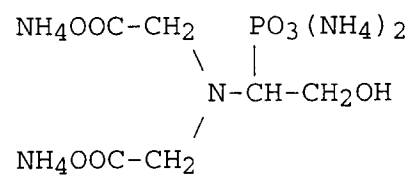
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A-I-8

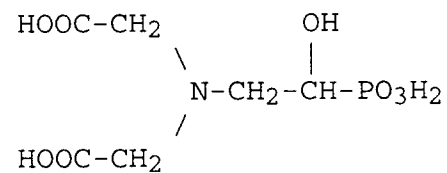
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A-I-9

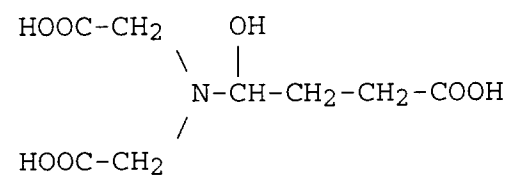
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A-I-10

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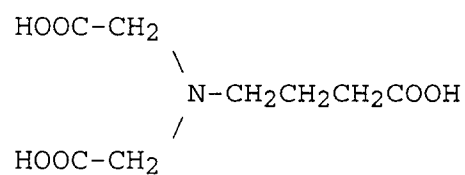


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A-I-11

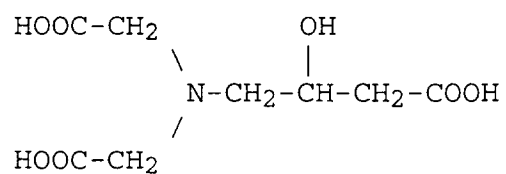
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A-I-12

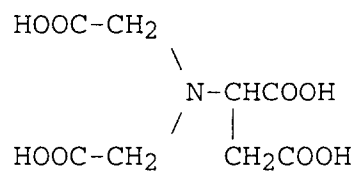
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A-I-13

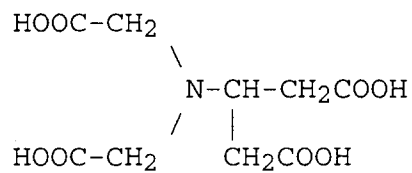
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A-I-14

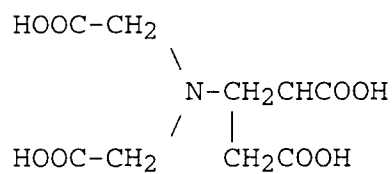
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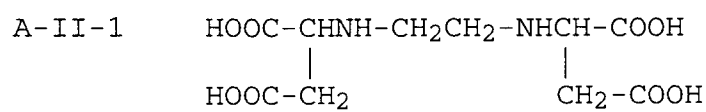
A-I-15

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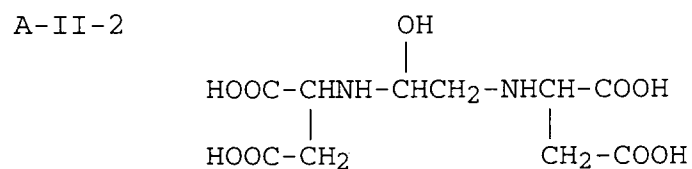


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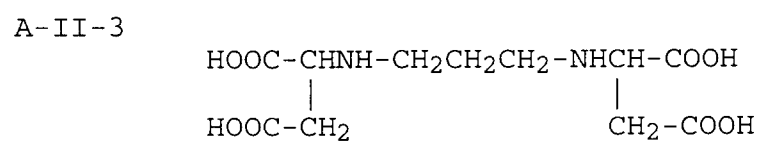


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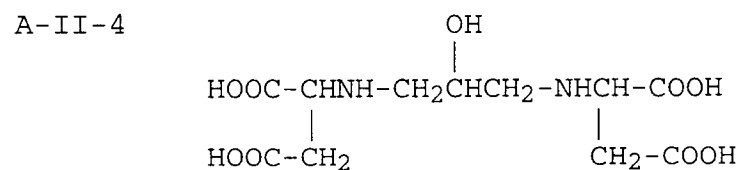


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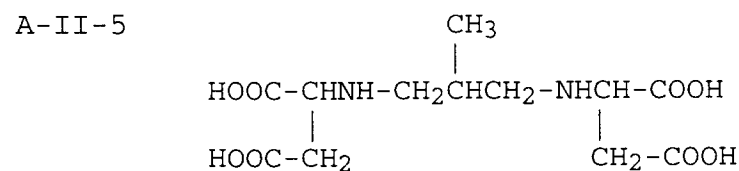


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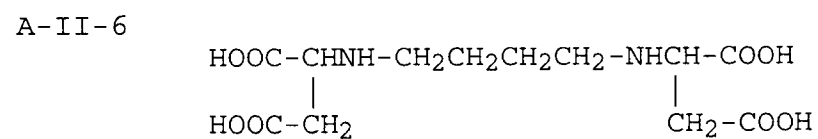


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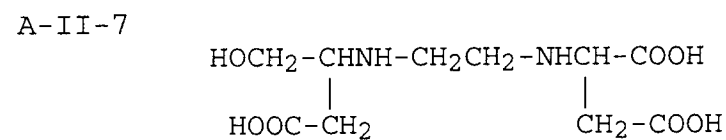


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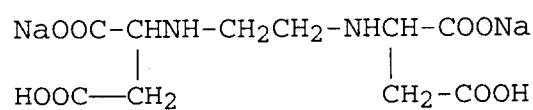


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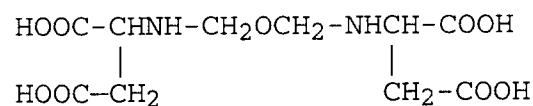
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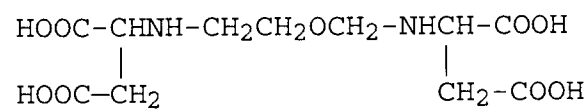
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A-II-10

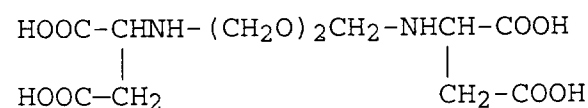
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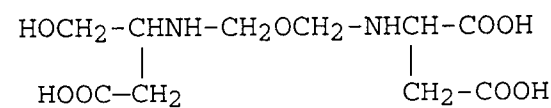
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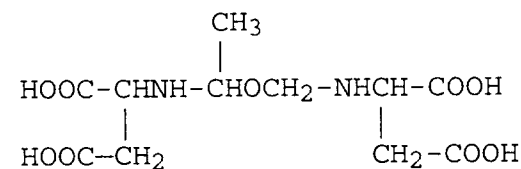
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A-II-13

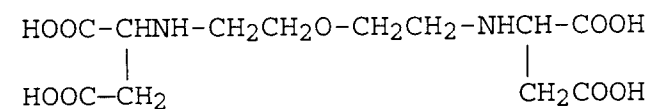
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A-II-14

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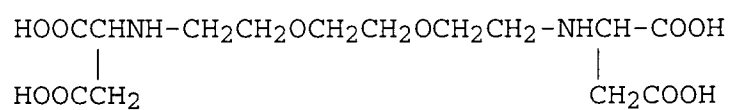


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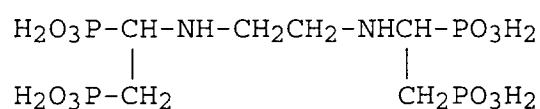
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A-II-16

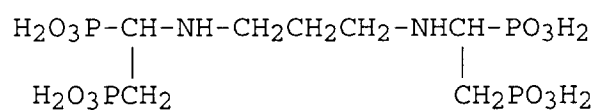
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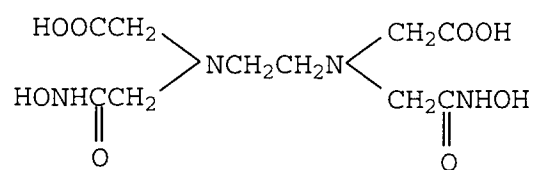
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A-III-1

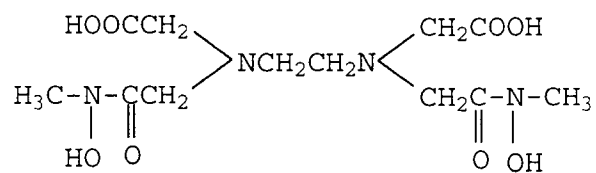
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A-III-2

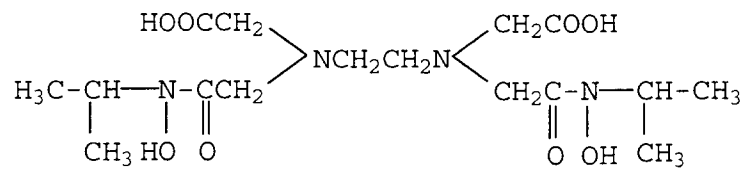
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A-III-3

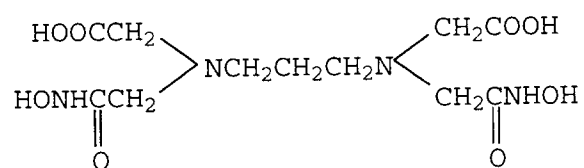
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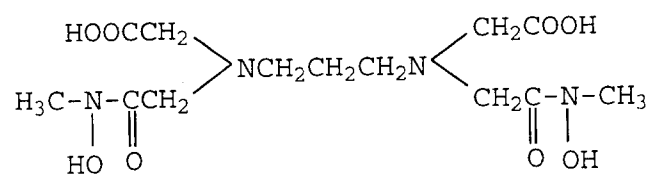
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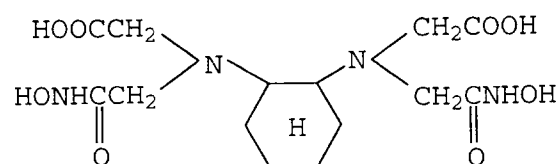
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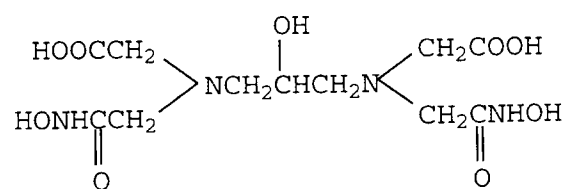
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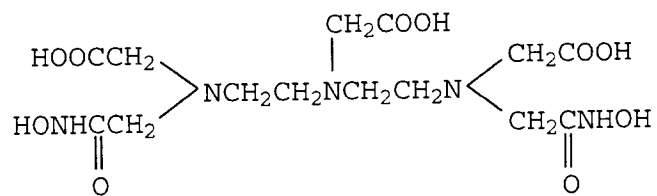
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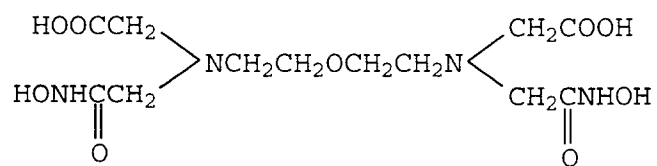
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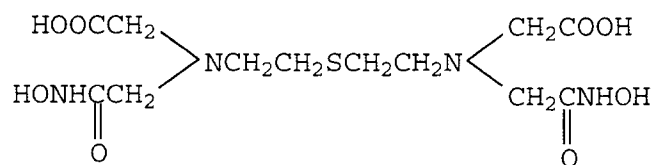
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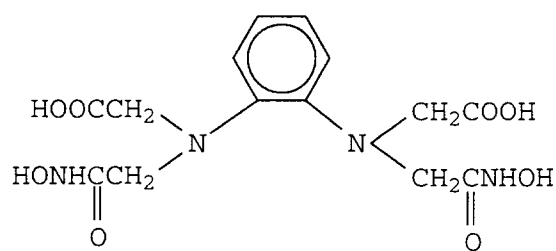
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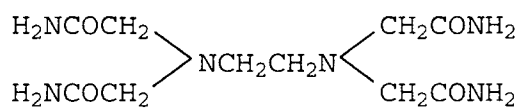
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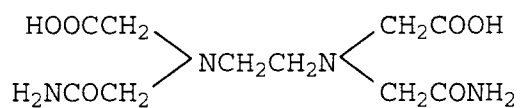
A-III-11



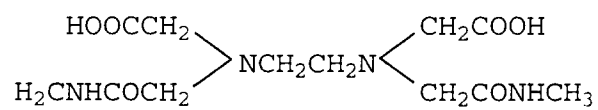
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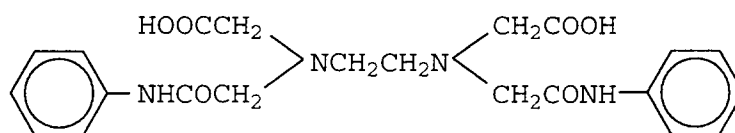
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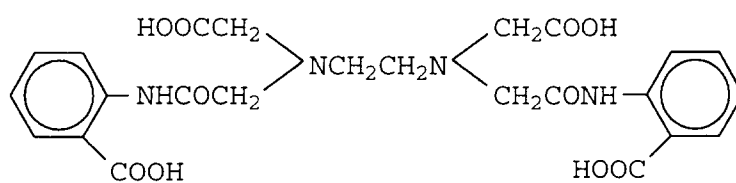
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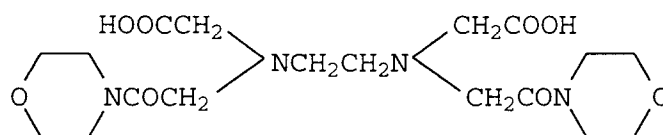
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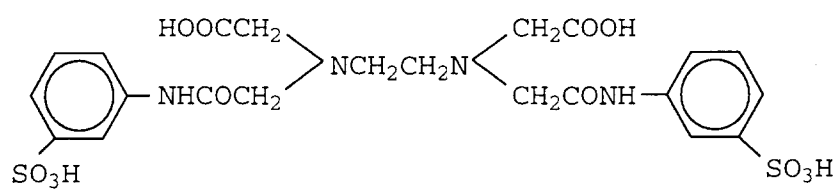
A-III-16



A-III-17

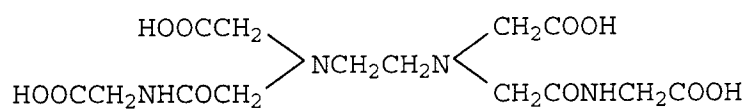


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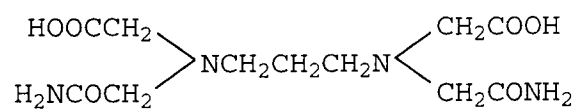
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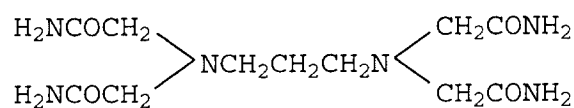
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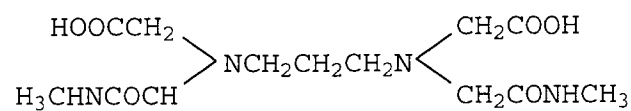
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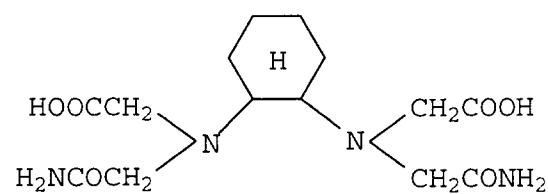
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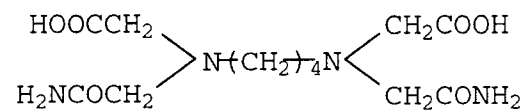
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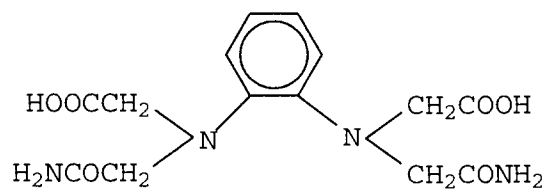


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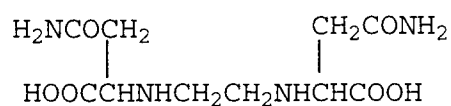
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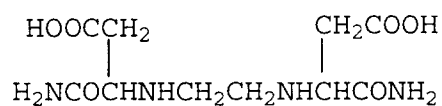
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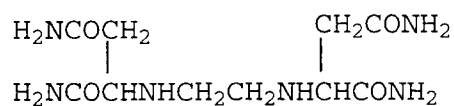
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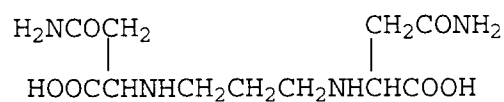
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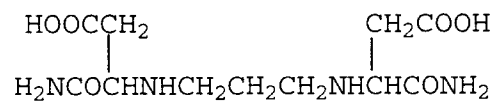
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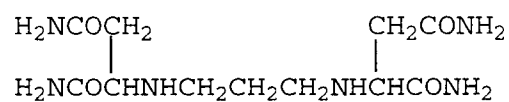
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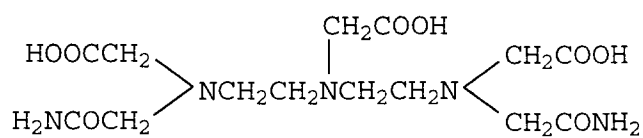
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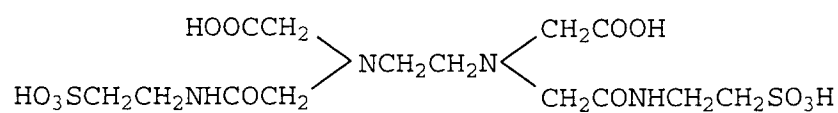
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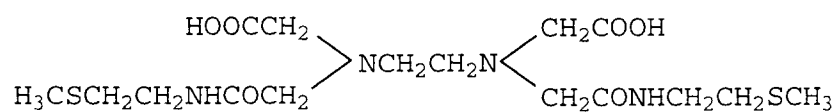
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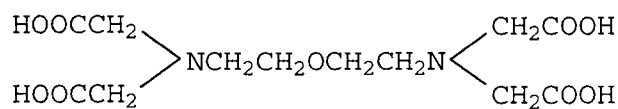
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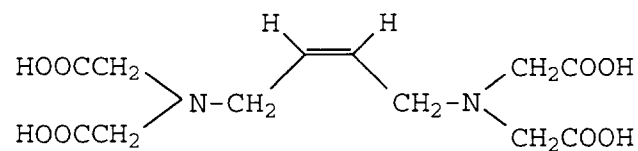
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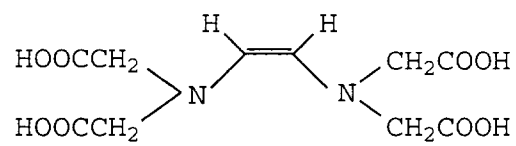
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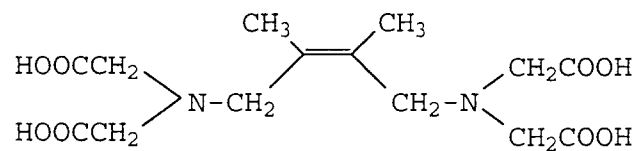
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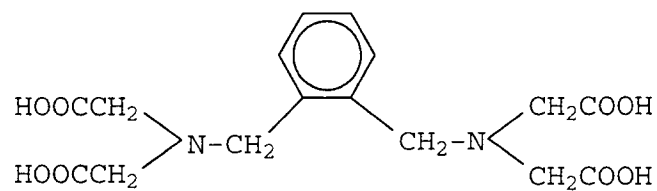
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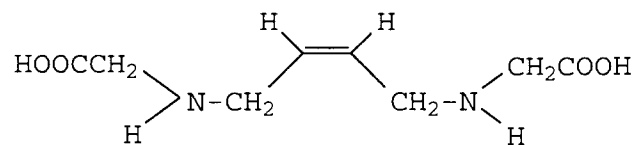
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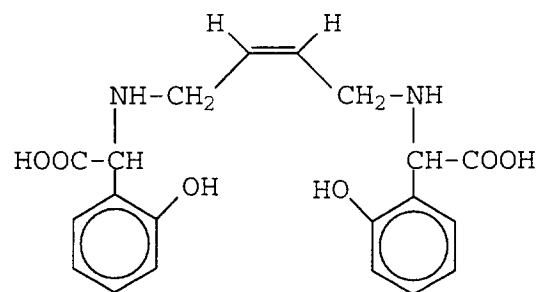
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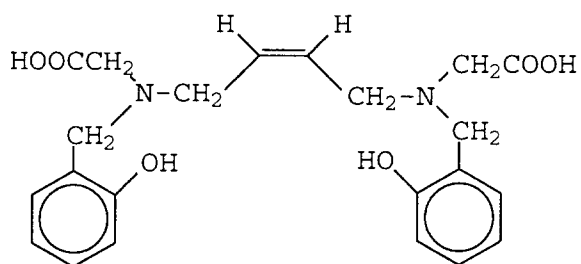
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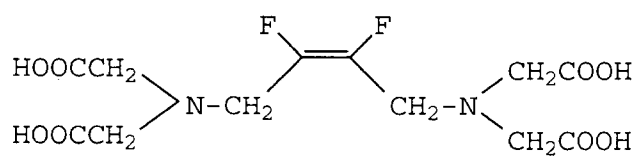
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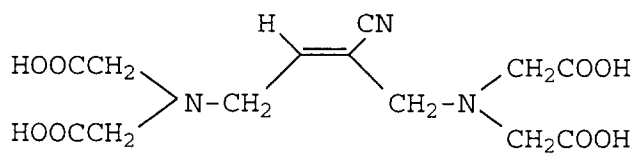
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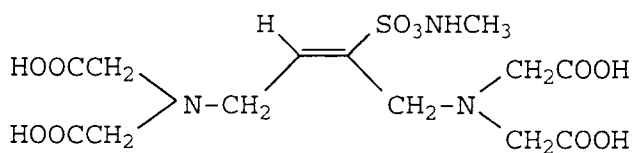
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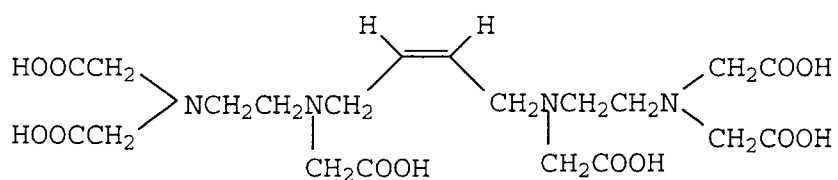
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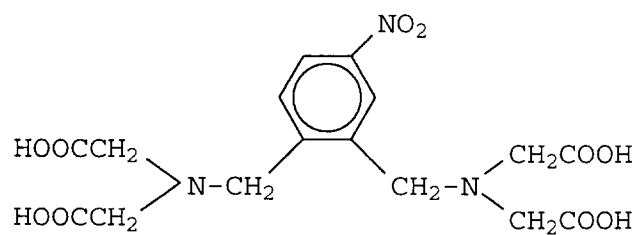


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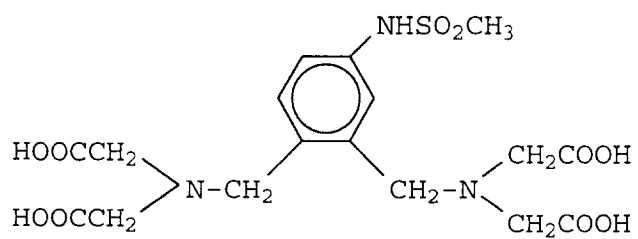
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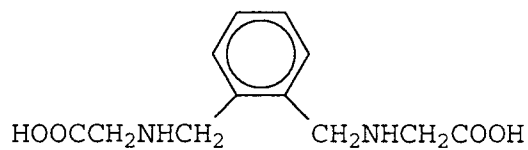
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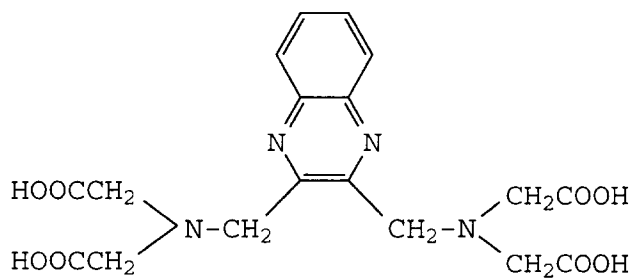


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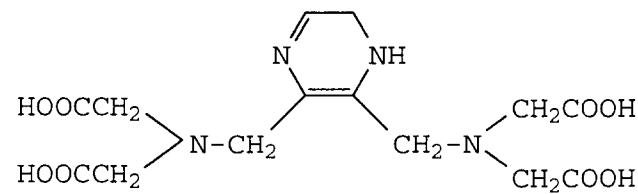
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A-IV-16

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In the present invention, ferric complex salts of the following compounds can be used as bleaching agents for the (hereinafter referred to as) bleacher or bleach-fixer in addition to the ferric complex salts of the above compounds.

A'-1: Ethylenediaminetetraacetic acid

5 A'-2: Trans-1,2-cyclohexanediaminetetraacetic acid

A'-3: Dihydroxyethylglycinic acid

A'-4: Ethylenediaminetetrakis(methylenephosphonic) acid

A'-5: Nitrilotris(methylenephosphonic) acid

A'-6: Diethylenetriaminepenta(methylenephosphonic) acid

10 A'-7: Diethylenetriaminepentaacetic acid

A'-8: Ethylenediaminediortho(hydroxyphenyl)acetic acid

A'-9: Hydroxyethylethylenediaminetriacetic acid

A'-10: Ethylenediaminedipropionic acid

A'-11: Ethylenediaminediacetic acid

15 A'-12: Hydroxyethyliminodiacetic acid

A'-13: Nitrilotriacetic acid

A'-14: Nitrilotripropionic acid

A'-15: Triethylenetetraminehexaacetic acid

A'-16: Ethylenediaminetetrapropionic acid

20 A'-17: 1,3-propylenediaminetetraacetic acid

A'-18: glycoltherdiaminetetraacetic acid

There can be also used exemplified compounds 1-71 described on pages 7 through 11 of Japanese Patent O.P.I. Publication No.174432/1992 and exemplified compounds 1-36 described on pages 25 through 30 of Japanese Patent O.P.I. Publication No.204533/1992.

25 The content of the compounds represented by the above-given Formulas (A-I) through (A-IV) is preferably 10 to 70 % by weight and more preferably 20 to 60 % by weight per tablet, in view of storage stability.

In terms of the effects of the present invention, the weight of the tablet agent of the invention is preferred to be 1 to 50 g.

30

Examples

The invention will be described in detail in the following Examples 1 through 5.

35 Example 1

A tablet sample was prepared according to the following procedures.

1. Preparation of a tablet sample for a bleach-fixing composition for color paper use

40

Procedure (1)

45 In a bandamu-mill 3600 g of ferric ammonium diethylenetriamine pentaacetic acid monohydrate and 36 g of diethylenetriamine pentaacetic acid was pulverized up to have an average particle size of 30 μ m or less. The resulting fine particles were mixed for 10 minutes in a stirring granulator available on the market and were granulated by adding 50 ml of water thereto. Thereafter, the granules were dried at 65 °C for 2 hours in a fluid-bed type drier to completely remove the moisture and to obtain granule sample A.

Procedure (2)

50

In the same manner as in Procedure (1) 2800 g of ammonium thiosulfate, 700 g of sodium sulfite and 175 g of Pineflow (produced by Matsutani Chemical Co.) were pulverized and mixed, and the mixture was granulated by adding 130 ml of water thereto. Thereafter, the granules were dried at 60 °C for 2 hours in a fluid-bed type drier to completely remove the moisture and to obtain granule sample B.

55

Procedure (3)

Compounds shown in Table 1 was added to granule sample A in an amount shown in Table 1 and mixed. Granule sample B in an amount of 3675 g and 35 g of sodium N-lauroylsarcosine were added to 3259 g of the mixture and mixed for 30 minutes. Thereafter, the resulting mixture was compression-tabulated by applying a pressure of 12 tons, making use of a tabulating machine, a remodeled Tough Press Correct Model 1527HU manufactured by Kikusui Mfg. Works to obtain a tablet having a weight of 12.0 g. Thus, 580 tablets were prepared for each of tablet sample Nos. 1-1 through 1-25, each tablet having a diameter of 30 mm.

2. Preparation of comparative tablet sample A

Procedure (4)

In the same manner as in Procedure (1) 3600 g of ferric ammonium diethylenetriamine pentaacetic acid salt monohydrate and 36 g of diethylenetriamine pentaacetic acid were pulverized and mixed. Thereafter, the resulting mixture was granulated and dried to obtain granulate sample A.

Procedure (5)

Procedure (2) was repeated to obtain granule sample B.

Procedure (6)

Granule sample A in an amount of 3259 g, 3675 g of Granule sample B and 35 g of sodium N-lauroylsarcosine were mixed and the resulting mixture was compression-tabulated in the same manner as in Procedure (3) to obtain 580 pieces of tablet sample A.

Using tablet samples obtained through the above-mentioned procedures, the following experiments were conducted. Experiment 1: Evaluation of adhesiveness

Five tablets of each of the samples were placed and seal-packaged tightly in a packing material made of a high density polyethylene, and stored for 4 weeks under 40 °C and 80 %RH. Thereafter, the package was unpacked, the appearance of the tablets and the adhesion of the tablets to the packing material were evaluated as follows:

A Tablets are smooth on the surface, and their adhesion to the packing material and the adhesion between tablets were not observed.

B Adhesion of the tablets to the packing material and the adhesion between tablets were only slightly observed, and not problematic.

C Partial adhesion of the tablets to the packing material was observed.

D Significant adhesion of the tablets to the packing material was observed and it was difficult to remove the tablets from the package.

Experiment 2: Evaluation of anti-abrasion property

Five tablet samples were inserted in a tester for the degree of abrasion of tablet (modified from one produced by Sugaki Irika Kogyo Co., Ltd.). The tester was rotated for 5 minutes at 20 rpm. The occurrence ratio of powder after rotation was calculated, with the occurrence ratio before rotation defined as 0 %. The larger this value was, the higher the occurrence ratio of powder. Accordingly, this value represents the easiness of the abrasion of tablet.

Table 1 shows the results thereof.

Table 1

Sample No.	Polymer:12wt%	Adhesivene ss	Degree of abrasion	
1-1	PEG 600	B	0.52	Invention
1-2	PEG 1000	B	0.50	Invention
1-3	PEG 4000	A	0.53	Invention
1-4	PEG 6000	A	0.55	Invention
1-5	PEG 10000	A	0.56	Invention
1-6	PEG 2000	A	0.51	Invention
1-7	PVA-1	B	0.95	Invention
1-8	PVA-2	B	0.96	Invention
1-9	PVA-3	B	0.91	Invention
1-10	PVP-1	B	0.83	Invention
1-11	PVP-2	B	0.81	Invention
1-12	PVP-3	B	0.85	Invention
1-13	—	D	1.14	Comparative

PEG 600: Polyethylene glycol #600 (produced by Nihon
Yushi)

PEG 1000: Polyethylene glycol #1000 (produced by Nihon
Yushi)

PEG 4000: Polyethylene glycol #4000 (produced by Nihon
Yushi)

PEG 6000: Polyethylene glycol #6000 (produced by Nihon
Yushi)

PEG 10000: Polyethylene glycol #10000 (produced by Nihon
Yushi)

PEG 20000: Polyethylene glycol #20000 (produced by Nihon
Yushi)

PVA-1: Polyvinyl alcohol MW: 10000 (produced by Aldrich)

PVA-2: Polyvinyl alcohol MW: 22000 to 31000 (produced by Aldrich)

PVA-3: Polyvinyl alcohol MW: 80000 to 100000 (produced by Aldrich)

PVP-1: Polyvinyl pyrrolidone K-15 (produced by Tokyo Kasei)

PVP-2: Polyvinyl pyrrolidone K-30 (produced by Tokyo Kasei)

PVP-3: Polyvinyl pyrrolidone K-60 (produced by Tokyo Kasei)

It is apparent from the above-mentioned Table 1 that the surface of the tablet of the present invention was not changed, and remained smooth after storage for a long period. In addition, the occurrence of fine powder was insignificant showing excellent tablet strength. Accordingly, it is understood that the tablet of the present invention is extremely superior in terms of handling property.

Example 2

1. Preparation of tablet sample A

Procedure (7)

In a Hammer-mill available on the market, 6000.0 g of ferric ethylenediamine tetraacetic acid sodium salt trihydrate, 300.0 g of ethylenediamine tetraacetic acid and 400.0 g of sodium carbonate monohydrate were pulverized to have an average particle size of 80 μ m or less. Pineflow in an amount of 600.0 g was added to the resulting fine particles, mixed for 10 minutes in a stirring granulator available on the market, and granulated by adding 200 ml of water thereto. Thereafter, the granules were dried at 60 °C for 3 hours to completely remove the moisture and to obtain granules.

Procedure (8)

Ammonium thiosulfate of 8000.0 g, 3000 g of sodium metabisulfite were pulverized and 400.0 g of Pineflow was added thereto and mixed in the same manner as in Procedure (7), and the mixture was granulated by adding 170 ml of water thereto. Thereafter, the granules were dried at 60 °C for 2 hours to completely remove the moisture and to obtain granules.

Procedure (9)

Polyethylene glycol #4000 (produced by Nihonyushi co. Ltd.) was added in an amount as shown in Table 2 to a mixture of granules obtained in Procedures (7) and (8) and mixed for 10 minutes using Cross-rotary mixer available on the market, and 90.0 g of sodium N-lauroylsarcosine was added thereto and mixed for 3 minutes to obtain mixed granules. Thereafter, the resulting granules was tableted using a rotary tableting machine to obtain a tablet having a diameter of 30 mm and a weight of 11.0 g. Thus, 1700 tablets were prepared for each of tablet sample Nos.A-1 through A-10.

2. Preparation of tablet sample B

Procedure (10)

5 In a Hammer-mill available on the market, 6000.0 g of ferric ethylenediamine tetraacetic acid sodium salt trihydrate, 300.0 g of ethylenediamine tetraacetic acid, 400.0 g of sodium carbonate monohydrate, 8000.0 g of ammonium thiosulfate, and 3000 g of sodium metabisulfite were pulverized to have an average particle size of 80 μm or less. Pineflow in an amount of 1000.0 g and Polyethylene glycol #4000 (in an amount as shown in Table 2) were added thereto and mixed for 10 minutes using a cross-rotary mixer
 10 available on the market, and 90.0 g of sodium N-lauroylsarcosine was added thereto and mixed for 3 minutes to obtain mixed granules. Thereafter, the resulting granules were tableted using a rotary tableting machine to obtain a tablet having a diameter of 30 mm, a thickness of 10 mm and a weight of 12.5 g. Thus, 1700 tablets were prepared for each of tablet sample Nos.B-1 through B-10.

15 3. Evaluation

The above obtained tablets were evaluated as follows:

Evaluation 1: Adhesiveness

20 Five tablets of each of the samples were placed and seal-packaged tightly in a packing material made of a high density polyethylene, and stored for 4 weeks under 40 °C and 80 %RH. Thereafter, the package was unpacked, the appearance of the tablets and the adhesion of the tablets to the packing material were evaluated as follows:

- 25 A Tablets are smooth on the surface, and their adhesion to the packing material and the adhesion between tablets were not observed.
 B Adhesion of the tablets to the packing material and the adhesion between tablets were only slightly observed, and not problematic.
 C Partial adhesion of the tablets to the packing material was observed.
 30 D significant adhesion of the tablets to the packing material was observed and it was difficult to remove the tablets from the package.

Evaluation 2: Anti-abrasion property

35 Ten tablets of each of the samples were placed and tightly seal-packaged in a packing material of high density polyethylene, and stored at 50 °C for one month. Thereafter, the package was unsealed and the ten tablets were weighed. Then, the tablets were repackaged in the packing material and the resulting package was subjected to a vibration test using Vibration Tester BF-UA produced by IDEX Co., Ltd. The five minutes' vibration test was repeated 24 times under 5-67 Hz cycle. The degree of abrasion property was
 40 evaluated from the following Equation:

Abrasion degree (wt%) = (the difference between the weight of ten tablets before and after the vibration test) $\times$ 100/(the weight of ten tablets before the vibration test)

- 45 A Abrasion degree below 0.01 %: The tablets were not abraded and no powder was observed on the packing material.
 B Abrasion degree 0.01 - 0.1 %: The tablets were slightly abraded and slight powder was observed on the packing material, and not problematic for practical use.
 C Abrasion degree from more than 0.1 to 0.4 %: The tablets were partially abraded and more powder
 50 residue was observed on the packing material.
 D Abrasion degree over 0.4 %: The tablets were abraded significantly, and, when unpacked, the powder flies in the air.

Evaluation 3: Tableting property

55 Adhesion of components to be tableted on the surface of a compression-molding device on tableting was evaluated.

- A Adhesion of the components on the surface of the compression-molding device was not observed.

B Adhesion of the components on the surface of the compression-molding device was slight, and not problematic for practical use.

C Adhesion of the components on the surface of the compression-molding device was observed and the obtained tablets had fine protrusions and concavities on the surface. D Adhesion of the components on the surface of the compression-molding device was significant, and made the tableting procedure difficult.

The results are shown in Table 2.

Table 2

	PEG (wt%)	Adhesiveness	Anti-abrasion property	Tableting property	Remarks
A-1	0	D	D	D	Comparative
A-2	1	B	B	C	Invention
A-3	8	B	B	C	Invention
A-4	10	B	A	B	Invention
A-5	15	A	A	A	Invention
A-6	20	A	A	A	Invention
A-7	30	B	A	A	Invention
A-8	50	B	A	B	Invention
A-9	55	B	B	C	Invention
A-10	60	B	B	C	Invention
B-1	0	D	D	D	Comparative
B-2	1	C	B	C	Invention
B-3	8	C	B	C	Invention
B-4	10	B	B	B	Invention
B-5	15	B	B	A	Invention
B-6	20	A	B	A	Invention
B-7	30	B	B	A	Invention
B-8	50	B	B	B	Invention
B-9	55	B	B	C	Invention
B-10	60	C	B	C	Invention

As is apparent from Table 2, tablets containing the polymer of the invention in an amount of 10 to 50 wt% improve tableting property, i.e., tablets productivity as well as the adhesiveness or strength of the tablets even in a long storage period. The above effects of the invention was more remarkable in tablets prepared by a method comprising the steps of preparing granules containing ferric complex salt of amino polycarboxylic acid and granules containing a thiosulfate separately, and mixing the resulting granules, followed by tableting.

Example 3

Tablet samples were prepared in the same manner as in Sample A-5 of Example 2, except that ferric complex salt of exemplified compound A-I-2, A-II-1, A-III-3, or A-IV-1 was used instead of sodium ferric ethylene diamine tetraacetic acid trihydrate. The thus obtained tablets were processed and evaluated in the same manner as in Example 1. The results were the same as those of Example 1.

Example 4

Tablet samples were prepared in the same manner as in sample A-5 of Example 2, except that sodium thiosulfate or potassium thiosulfate was used instead of ammonium thiosulfate. The thus obtained tablets were processed and evaluated in the same manner as in Example 1. The results were the same as those of Example 1.

Example 5

Tablet samples 4-1 through 4-11 were prepared in the same manner as in Sample A-5 of Example 2, except that the diameter and thickness of the tablet were varied as shown in Table 3. The thus obtained tablets were processed and evaluated in the same manner as in Example 2. The results are shown in Table 3.

Table 3

Sample	Diameter d (mm)	Thickness (mm)	d/h	Adhesiveness	Abrasion proper
4-1	30	4	7.5	B	B
4-2	30	5	6.0	A	B
4-3	30	10	3.0	A	A
4-4	30	20	1.5	A	A
4-5	30	30	1.0	A	B
4-6	30	35	0.9	B	B
4-7	10	4	2.5	A	A
4-8	15	5	3.0	A	A
4-9	20	5	4.0	A	A
4-10	40	10	4.0	A	A
4-11	50	10	5.0	A	B

As is apparent from Table 3, tablets having a x/h within the range of 1.0 to 6.0 exhibit improved results in adhesiveness and abrasion.

Example 6

A tablet sample was prepared according to the following procedures.

[0037]

1. Preparation of a tablet sample for a bleach-fixing composition for color paper use

Procedure (11)

In a bandamu-mill 3600 g of ferric amino polycarboxylic acid ammonium salt monohydrate (shown in Table 1) and 36 g of amino polycarboxylic acid (shown in Table 1) was pulverized up to have an average particle size of 30 μm or less. Polyethylene glycol 6000 in an amount of 625 g was added to the resulting fine particles, mixed for 10 minutes in a stirring granulator available on the market, and granulated by adding 200 ml of water thereto. Thereafter, the granules were dried at 45 °C for 4 hours in a fluid-bed type drier to completely remove the moisture and to obtain granule sample A'.

[0038]

Procedure (12)

In the same manner as in Procedure (1) 2800 g of ammonium thiosulfate, 700 g of sodium sulfite and 175 g of Pineflow (produced by Matsutani Chemical Co.) were pulverized and mixed, and the mixture was granulated by adding 130 ml of water thereto. Thereafter, the granules were dried at 60 °C for 2 hours to completely remove the moisture and to obtain granule sample B'.

[0039]

Procedure (13)

5 Sodium N-lauroylsarcosine in an amount of 35 g was added to a mixture of 3259 g of granule sample A' obtained in Procedure (11) and 3675 g of granule sample B' obtained in Procedure (12) and mixed for 10 minutes. Thereafter, the resulting mixture was compression-tabulated by applying a pressure of 12 tons, making use of a tabulating machine, a remodeled Tough Press Correct Model 1527HU manufactured by Kikusui Mfg. Works to obtain a tablet having a weight of 12.0 g. Thus, 580 tablets were prepared for each of
10 tablet sample Nos. 5-1 through 5-25, each tablet having a diameter of 30 mm.

[0040]

2. Preparation of comparative tablet sample B' Procedure (14)

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In the same manner as in Procedure (1) 3600 g of ferric amino polycarboxylic acid ammonium salt monohydrate and 36 g of amino polycarboxylic acid were pulverized and mixed. Thereafter, the resulting mixture was granulated and dried to obtain granulate sample A".

20 [0041]

Procedure (15)

Procedure (2) was repeated to obtain granule sample B".

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[0042]

Procedure (16)

30 Sodium N-lauroylsarcosine in an amount of 35 g was added to a mixture of 3259 g of granule sample A" obtained in Procedure (14) and 3675 g of granule sample B" obtained in Procedure (15) and mixed for 10 minutes. Thereafter, the resulting mixture was tabulated in the same manner as in Procedure (3) to obtain 580 pieces of tablet sample B'.

35 [0043]

[Experiment]

a) Measurement of hardness

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The hardness of 20 pieces of the tablet samples obtained in accordance with the above-mentioned procedure was measured by means of a tablet hardener (Speed checker produced by Okada Seiko Co., Ltd.) and the average value thereof was calculated.

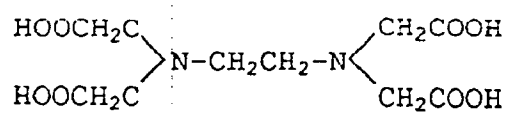
45 [0044]

b) Measurement of the degree of abrasion

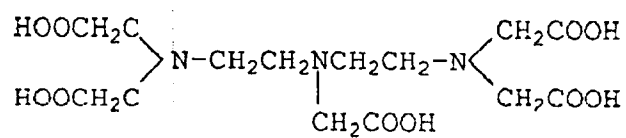
50 Five pieces of the tablet samples obtained in accordance with the above-mentioned procedure was placed in a tester for the degree of abrasion of tablet (produced by Sugaki Irika Kogyo Co., Ltd.). The tester was rotated for 5 minutes at 20 rpm. The occurrence ratio of powder after rotation was calculated when the occurrence ratio before rotation was defined to be 0 %. The larger this value is, the higher the occurrence ratio of powder is. Accordingly, this value represents the easiness of the abrasion of tablet. Table 4 shows the results thereof. In addition, the amino polycarboxylic acid in Table 4 are shown below.

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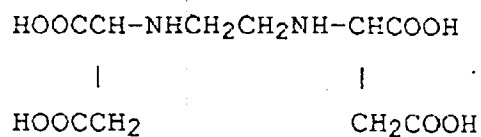
[A'-1]



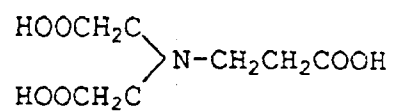
[A'-7]



[A-II-1]



[A-I-2]



[A-IV-1]

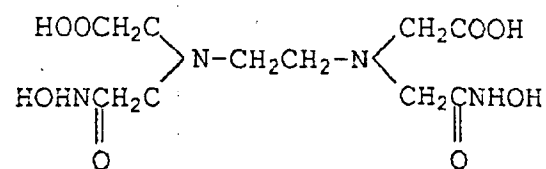


Table 4 (continued)

Sample No.	Amino polycarboxylic acid	Addition rate of PEG 6000 (wt%)	Hardness (kg)	Abrasion (wt%)	Category
B'-3	Illustrated compound A-II-1	0	40.3	6.06	Comp.
5-11	Illustrated compound A-II-1	8	62.1	1.01	Inv.
5-12	Illustrated compound A-II-1	10	74.4	0.60	Inv.
5-13	Illustrated compound A-II-1	30	89.2	0.40	Inv.
5-14	Illustrated compound A-II-1	50	90.1	0.36	Inv.
5-15	Illustrated compound A-II-1	65	91.0	0.28	Inv.
B-4'	Illustrated compound A-I-2	0	49.3	4.22	Comp.
5-16	Illustrated compound A-I-2	8	59.3	2.10	Inv.
5-17	Illustrated compound A-I-2	10	62.4	1.22	Inv.
5-18	Illustrated compound A-I-2	30	80.3	1.01	Inv.
5-19	Illustrated compound A-I-2	50	82.7	0.98	Inv.
5-20	Illustrated compound A-I-2	65	84.8	0.95	Inv.

Table 4 (continued)

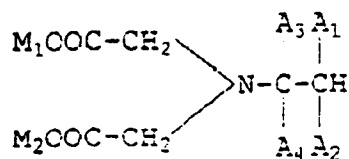
Sample No.	Amino polycarboxylic acid	Addition rate of PEG 6000 (wt%)	Hardness (kg)	Abrasion (wt%)	Category
B'-5	Illustrated compound A-IV-1	0	48.4	5.36	Comp.
5-21	Illustrated compound A-V-1	8	64.2	3.88	Inv.
5-22	Illustrated compound A-V-1	10	67.8	1.82	Inv.
5-23	Illustrated compound A-V-1	30	85.3	1.69	Inv.
5-24	Illustrated compound A-V-1	50	86.7	1.53	Inv.
5-25	Illustrated compound A-V-1	65	87.1	1.41	Inv.

From Table 4 above, it can be understood that the water-soluble polymer of the present invention provides more desirable results compared to the results of Example 1 when it is incorporated in the granules of an amino polycarboxylic acid ferric salt.

Claims

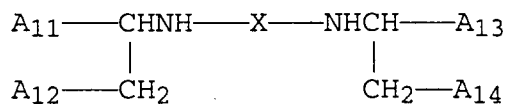
1. A solid photographic processing tablet comprising a thiosulfate salt, a ferric complex salt of an amino polycarboxylic acid and a polymer selected from the group consisting of polyethylene glycols, polyvinylpyrrolidones and polyvinyl alcohols.
2. The tablet of claim 1, wherein the polymer content of the tablet is 10 to 50 % by weight.
3. The tablet of claim 1, wherein the thiosulfate content of the tablet is 20 to 70 % by weight.
4. The tablet of claim 1, wherein the ferric salt content of the tablet is 10 to 70 % by weight.
5. The tablet of claim 1, wherein said polymer is polyethylene glycols.
6. The tablet of claim 1, wherein said amino polycarboxylic acid is selected from the group consisting of compounds represented by the following Formulas (A I), (A II), (A III), [and] (A IV) and the following compounds A'-1 through A'-18:

Formula (A-I)



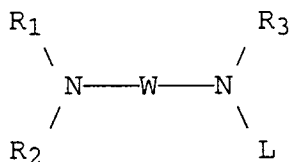
wherein A_1 , A_2 , A_3 and A_4 represent each a hydrogen atom, a hydroxy group, $-\text{COOM}$, $-\text{PO}_3(\text{M}_1)_2$, $-\text{CH}_2\text{COOM}_2$, $-\text{CH}_2\text{OH}$ or a lower alkyl group, provided that at least one of A_1 through A_4 represents $-\text{COOM}$, $-\text{PO}_3(\text{M}_1)_2$ or $-\text{CH}_2\text{COOM}_2$; and M , M_1 and M_2 represent each a hydrogen atom, an ammonium group, an alkali metal or an organic ammonium group,

Formula (A-II)

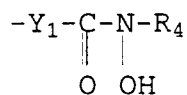


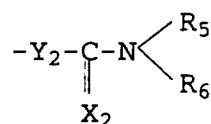
wherein A_{11} , A_{12} , A_{13} and A_{14} represent each $-\text{CH}_2\text{OH}$, $-\text{COOM}_3$ or $-\text{PO}_3(\text{M}_4)_2$ in which M_3 and M_4 represent each a hydrogen atom, an ammonium group, an alkali metal or an organic ammonium group; and X represents an alkylene group having 2 to 6 carbon atoms or $-(\text{B}_1\text{O})_n-\text{B}_2-$ in which B_1 and B_2 represent each an alkylene group having 1 to 5 carbon atoms and n is an integer of 1 to 8,

Formula (A-III)

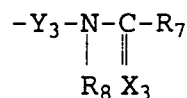


wherein R_1 , R_2 and R_3 represent each a hydrogen atom, a substituted or unsubstituted alkyl or aryl group; L represents the following formula:



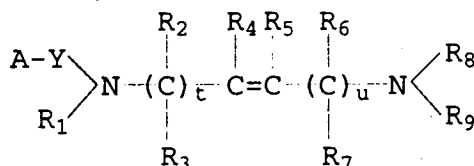


or



in which Y_1 , Y_2 and Y_3 represent each an alkylene or arylene group, X_2 and X_3 represent each an oxygen atom or a sulfur atom, and R_4 , R_5 , R_6 , R_7 and R_8 represent each a hydrogen atom, an alkyl group or an aryl group; and W represents a divalent linking group,

Formula (A-IV)



wherein R_1 , R_2 , R_3 , R_6 , R_7 , R_8 , and R_9 represent each a hydrogen atom or a substituted or unsubstituted alkyl or aryl group; R_4 and R_5 represent each a hydrogen atom, a halogen atom, a cyano group, a nitro group, an acyl group, a sulfamoyl group, a carbamoyl group, an alkoxy-carbonyl group, an allyloxy-carbonyl group, a sulfonyl group, a sulfinyl group or a substituted or unsubstituted alkyl or aryl group, provided that R_4 and R_5 may combine to form a 5-membered or 6-membered ring; A represents a carboxy group, a phosphono group, a sulfo group, a hydroxy group or an alkali metal salt or ammonium salt thereof; Y represents an alkylene group or an arylene group; and t and u are each an integer of 0 or 1,

A'-1: Ethylenediaminetetraacetic acid

A'-2: Trans-1,2-cyclohexanediaminetetraacetic acid

A'-3: Dihydroxyethylglycinic acid

A'-4: Ethylenediaminetetrakis(methylenephosphonic acid)

A'-5: Nitrilotrismethylenephosphonic acid

A'-6: Diethylenetriaminepentakis(methylenephosphonic acid)

A'-7: Diethylenetriaminepentaacetic acid

A'-8: Ethylenediaminediortho-hydroxyphenylacetic acid

A'-9: Hydroxyethylethylenediaminetriacetic acid

A'-10: Ethylenediaminedipropionic acid

A'-11: Ethylenediaminediacetic acid

A'-12: Hydroxyethyliminodiacetic acid

A'-13: Nitrilotriacetic acid

A'-14: Nitrilotripropionic acid

A'-15: Triethylenetetraminehexaacetic acid

A'-16: Ethylenediaminetetrapropionic acid

A'-17: 1,3-propylenediaminetetraacetic acid

A'-18: glycoletherdiaminetetraacetic acid

7. A method for preparing a solid photographic processing tablet comprising a thiosulfate salt, a ferric complex salt of an amino polycarboxylic acid and a polymer selected from the group consisting of polyethylene glycols, polyvinylpyrrolidones and polyvinyl alcohols, comprising the steps of:
 - granulating a first composition comprising the ferric complex salt;

granulating a second composition comprising the thiosulfate salt;
mixing the resulting granulates with the polymer; and
molding the resulting mixture by applying pressure to obtain the tablet.

5 **8.** The method of claim 7 wherein the polymer content of the tablet is 10 to 50 % by weight.

9. A method for preparing a solid photographic processing tablet comprising a thiosulfate salt, a ferric complex salt of an amino polycarboxylic acid and a polymer selected from the group consisting of polyethylene glycols, polyvinylpyrrolidones and polyvinyl alcohols,
10 comprising the steps of:
 granulating a first composition comprising the ferric complex salt and the polymer;
 granulating a second composition comprising the thiosulfate salt;
 mixing the resulting granulates; and
 molding the resulting mixture by applying pressure to obtain the tablet.

15 **10.** The method of claim 9, wherein the polymer content of the tablet is 10 to 50 % by weight.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 6615

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
P,X	EP-A-0 542 283 (KONICA CORPORATION) 19 May 1993 * page 3, line 6 - page 3, line 18 * * page 49, line 32 - page 56, line 19 * * examples 6,7 * ---	1-6	G03C7/42 G03C7/44
A	EP-A-0 405 238 (AGFA-GEVAERT AG) 2 January 1991 * page 2, line 1 - page 2, line 46 * D & JP-A-3 039 735 (...) 20 February 1991 ---	1-10	
A,P	EP-A-0 540 990 (KONICA CORPORATION) 12 May 1993 * page 1, line 3 - page 1, line 8 * * page 2, line 3 - page 3, line 52 * * page 4, line 41 - page 7, line 6 * -----	1-10	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			G03C
Place of search MUNICH		Date of completion of the search 18 July 1994	Examiner MARKOWSKI, V
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