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(54) **Solid processing composition for silver halide color photographic light-sensitive materials.**

(57) A solid processing composition for a silver halide color photographic light-sensitive material is disclosed, the composition comprising an amino polycarboxylic acid ferric complex hydrate, wherein the drying weight reduction at 50 °C of the composition is 0.1 to 10.0 % by weight.

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## FIELD OF THE INVENTION

The invention relates to a solid composition in the form of powder or tablets for a silver halide color photographic light-sensitive material.

## BACKGROUND OF THE INVENTION

A silver halide photographic light-sensitive material is usually processed using a color developer, a bleach, a bleach-fixer, a fixer and a stabilizer to obtain an imagewise image. The components of the processing solutions used herein are packaged in plastic bottles for easy use in the form of one or more concentrated solutions and are supplied as a processing solution kit to consumers. The consumers dilute the component solutions of the kit with water to prepare the processing solutions (as starter solutions or replenisher solutions) and use them.

Recently, in the photographic processing industry small-scaled developing store, so-called mini-labs, which process a photographic material using a small automatic processor, rapidly increased and the amount of the processing kits used also increased. The processing kit in concentrated solution form still requires much storage space. Further, the cost for transport is not low. The discarded plastic bottles increase year by year and should be recovered, however the recovering is difficult and therefore, development of a processing system in which waste plastics are reduced is demanded.

Powder photographic processing agents are considered in order to reduce storage space, transport cost and the amount of the plastic waste. However, the powder agents produce loose powder when it is dissolved in water, and operators breathe in loose powder particles, resulting in health hazard. Further, the present inventor has found that other photographic solutions may be contaminated with the components of the loose powder and there occurs the possibility of other trouble in developing process.

Japanese Patent O.P.I Publication No. 3-39739/1991 discloses a granular agent of an amino polycarboxylic acid ferric complex containing an re-halogenating agent having a specific average particle diameter. This method can prevent the occurrence of loose powder because the agent is not powder, but powder is likely to occur during transport because of its brittleness. Further, the inventors have found that the adherence of the granules to a package or aggregation of the granules is caused during storage such as transport under a high temperature.

Japanese Patent O.P.I Publication No. 5-119454/1993 discloses a tablet agent of an amino polycarboxylic acid ferric complex. It has been found, however, that in this method powder is likely to occur during transport because of its brittleness.

Japanese Patent O.P.I Publication No. 5-119450/1993 discloses a tablet agent having excellent storage stability and improved strength by controlling a moisture content of a tablet and further discloses a tablet composition having a moisture content of 0.5 to 10.0 wt%. However, there is no description in this reference of an amino polycarboxylic acid hydrate or a drying weight reduction of the solid composition. This method is considered to attain the excellent storage stability and improved strength, but is not satisfactory for the adherence of the tablets to a package or aggregation of the tablets during transport. Japanese Patent O.P.I Publication No. 5-232656/1993 discloses a tablet agent containing a hydrate salt of an amino polycarboxylic acid ferric complex, but there is no description of the control of a moisture content and the agent is not satisfactory for the prevention of moisture absorption and aggregation of the tablets which is the effects of the invention.

In processing a silver halide photographic light-sensitive material a single step comprising bleaching and fixing as a desilvering step is widely employed. However, there is a problem that the step is unstable since a bleaching agent, an oxidizing agent and a sulfite, a reducing agent are present in the bleach-fixing solution.

When a bleach-fixing agent is prepared as a solid processing composition, the problem of storage stability still remains, and various studies have been made to solve the problem. Japanese Patent O.P.I. Publication No. 4-19655 discloses a method of packaging under vacuum a composition in which a bleaching agent layer and a fixing agent layer are separated and a third layer is provided between them. Japanese Patent O.P.I. Publication No. 5-142708 discloses tablets obtained by compression-molding granules having an average particle diameter of 100 to 800 μm.

The present inventors have found that it is difficult obtain a solid processing composition having a stable property and less powder occurrence as above described using the above methods, since the influence of vibration during transport, heat during storage or atmospheric moisture during production or usage is great.

## SUMMAY OF THE INVENTION

A first object of the invention is provide a solid processing composition for a silver halide color photographic light-sensitive material in which fine powder occurrence is reduced during vibration. A second object is to provide a solid processing composition for a silver halide color photographic light-sensitive material preventing an adherence under a high temperature.

A third object of the invention is to provide a solid processing composition for bleach-fixing in the form of granules or tablets for a silver halide color photographic light-sensitive material giving high storage stability during storage under high temperature. A fourth object is to provide a solid processing composition for bleach-fixing in the form of granules or tablets for a silver halide color photographic light-sensitive material which does not cause fine powder occurrence due to vibration during transport or atmospheric moisture during production or usage.

In the invention the solid processing composition for bleaching is distinguished from the solid processing composition for bleach-fixing. The solid processing composition for bleaching of the invention refers to a solid processing composition containing an amino polycarboxylic acid ferric complex and not containing a fixing agent. The solid processing composition for bleach-fixing of the invention refers to a solid processing composition containing an amino polycarboxylic acid ferric complex and a fixing agent such as a thiosulfate or a thiocyanate.

The solid processing composition for bleaching is preferable in view of prevention of adherence under a high temperature. The solid processing composition for bleach-fixing is preferable in view of high storage stability under a high temperature.

## DETAILED DESCRIPTION OF THE INVENTION

The objects of the invention can be attained by the following:

(1). A solid processing composition for bleaching a silver halide color photographic light-sensitive material, the composition comprising at least one amino polycarboxylic acid ferric complex hydrate, wherein the drying weight reduction at 50 ° C of the composition is 0.1 to 10.0 % by weight.

(2). The solid processing composition of Item (1), wherein the mole ratio of crystal water to the ferric complex hydrate is $0.3 \leqq H_2O/\text{the ferric complex (mole)} \leqq 3.0$.

(3). The solid processing composition of Item (1) or (2), further comprising at least one selected from a water-soluble polymer and a saccharide.

(4). The solid processing composition of Item 1, 2 or 3, wherein the composition is compression-molded into tablets.

(5). A solid processing composition for bleach-fixing a silver halide color photographic light-sensitive material, the composition comprising at least one amino polycarboxylic acid ferric complex and at least one fixing agent, wherein the amino polycarboxylic acid ferric complex contains water and the drying weight reduction at 50 ° C of the composition is 0.1 to 10.0 % by weight.

(6). The solid processing composition of Item (5), wherein the composition is in the form of granules and the content of granules having a particle diameter of less than 149 $\mu$m is not more than 30 % by weight.

(7). The solid processing composition of Item (5) or (6), wherein the composition comprises granules containing an amino polycarboxylic acid ferric complex.

(8). The solid processing composition of Item (5), (6) or (7), wherein the fixing agent is at least one thiosulfate.

(9). The solid processing composition of Item (5), (6), (7) or (8), wherein all or a part of the thiosulfate is in the form of granules.

(10). The solid processing composition of Item (5), (6), (7), (8) or (9), wherein the composition contains at least one compound selected from a water-soluble polymer and a saccharide and the content of the compound is 1 to 30 % by weight based on the total weight of the composition.

(11). The solid processing composition of Item (5), wherein the composition comprising at least one of an amino polycarboxylic acid ferric complex hydrate and at least one fixing agent in admixture is compression-molded into tablets.

(12). The solid processing composition of Item (11), wherein the fixing agent is at least one thiosulfate.

(13). The solid processing composition of Item (11) or (12), wherein the composition comprises granules containing an amino polycarboxylic acid ferric complex.

(14). The solid processing composition of Item (11), (12) or (13), wherein the amino polycarboxylic acid ferric complex hydrate is in one granules and the fixing agent is in other granules.

(15). The solid processig composition of Item (11), (12), (13) or (14), wherein the composition further contains at least one selected from a saccharide and a water soluble polymer in an amount of 1 to 30 % by weight.

The invention will be detailed below.

The inventors have studied a solid composition for a silver halide color photographic light-sensitive material and found the following:

It has been found that in the solid processing composition comprising an amino polycarboxylic acid ferric complex hydrate, the weight reduction at 50 ° C, upper limit temperature which is happened to be, of the ferric complex hydrate has a great influence on the above problem.

In the solid composition comprising an amino polycarboxylic acid ferric complex, when the amino polycarboxylic acid ferric complex in the composition is anhydrous, the solidified amino polycarboxylic acid ferric complex is broken to fine powder due to vibration during transport and a problem of the resulting powder scatter occurs. Further, the appearance also varies under a high temperature or humidity.

Assuming the temperature till the usage of the composition, storage stability of a solid processing composition containing the complex hydrate and a fixing agent was evaluated and there occurred a new problem that a thiosulfate in the composition changed in quality and water-insoluble matter was produced. There is a serious problem that insoluble matters in the processing solution clog a filter of a processing machine, adhere to the surface of a light-sensitive material to be processed or give damage to the material.

When the drying weight reduction at 50 ° C of the composition exceeds 10.0 % by weight, the solid processing composition adheres to a package and the aggregation of the composition due to adherence of water drops to the surface thereof, so-called blocking phenomenon causes. The composition containing a fixing agent produces insoluble matter during storage under high temperature. When the drying weight reduction at 50 ° C of the composition is less than 0.5 % by weight, solid components other than an amino polycarboxylic acid ferric complex are broken to fine powder due to vibration. Further, the appearance also varies due to moisture absorption.

The solid composition is sometimes exposed to a high humidity, at a temporary time other than time packaged and isolated from atmospheric air, for example, at dissolution before its usage or its packaging on production. It has been found that in such cases the composition containing a fixing agent absorbs atmospheric moisture to damage and causes powder occurrence, resulting in a serious problem on handling it.

They have made detailed studies based on the above results and found that when the drying weight reduction at 50 ° C of a solid processing composition for a silver halide color photographic light-sensitive material is 0.5 to 10.0 % by weight, the composition is obtained which has no substantial influence on temperature or vibration during manufacture, transport or usage thereof, no powder occurrence and no aggregation phenomenon.

It has been found that the above solid processing composition for a silver halide color photographic light-sensitive material compression-molded into tablets exhibits the effects of the invention markedly as compared with the conventional one, and the sliding property thereof is also improved. This is because the initial moisture content remained in tablets on compression is considered to be controlled within the constant range.

It has been found that the above mentioned effects are obtained by a composition containing an amino polycarboxylic acid ferric complex hydrate and having a drying weight reduction within the range of the invention, but not obtained only by controlling the moisture content of a solid processing composition.

The reason that the temperature condition of the drying weight reduction in the invention is 50 ° C is that the temperature corresponds to upper limit occurred during distribution. The different temperature may give a different weight reduction but the reduction is within the scope of the invention in view of the object of the invention.

According to the invention, the drying weight reduction at 50 ° C of the composition may be 0.1 to 10.0 % by weight, however, in view of the effects of the invention, in the case of the composition not containing thiosulfate or thiocyanate the reduction is preferably 0.5 to 8.0 % by weight, and more preferably 1.0 to 6.0 % by weight.

According to the invention, the drying weight reduction at 50 ° C of the composition containing a fixing agent is preferably 0.3 to 5 % by weight, and more preferably 0.5 to 3 % by weight.

The drying weight reduction at 50 ° C of the composition herein referred to is a percentage of a value obtained by dividing the weight reduced after the composition is heated at 50 ° C to the constant weight by the weight before drying and is calculated from the following equation:

$$\text{Weight Reduction} = (\text{weight before drying} - \text{weight after drying}) / (\text{weight before drying}) \times 100\ (\text{weight }\%)$$

In the solid processing composition of the invention it is essential to contain at least an amino polycarboxylic acid ferric complex hydrate, and different two or more kinds of complexes may be used in combination. In such a case one half or more of the complex hydrate is preferably used in view of the effects of the invention. The amino polycarboxylic acid ferric complex•hydrate used in the invention is in a crystal form or in other solid forms (e.g., amorphous or gel), and contains water as crystal water, coordinate water or others. The water may be contained in any ratio in the complex hydrate. The amino polycarboxylic acid ferric complex hydrate of the invention includes one having no uniform composition in which an optional amount of water is removed by applying heat. The water of the complex hydrate of the invention is contained in the above described forms, and the water content of the complex hydrate is represented by the mol ratio of water in the complex hydrate to the complex. The mol ratio is especially preferably 0.3 to 3.5 in the solid composition not containing thiosulfates or thiocyanate and 0.3 to 3.5 in the solid composition containing thiosulfates or thiocyanates, in view of the effects of the invention. The mol ratio of the amino polycarboxylic acid ferric complex hydrate of the invention is obtained by a conventional method such as heat weight analysis, differential thermal analysis, Karl Fischer method or elemental analysis. The content of the amino polycarboxylic acid ferric complex•hydrate in the solid processing composition of the invention is preferably 10 to 70 weight %.

The shape of the amino polycarboxylic acid ferric complex hydrate of the invention is in the form of granules or tablets, and the granules herein referred to include first order particles as powder or secondary order particles obtained by granulating.

In view of the effects of the invention, as for the particle diameter of a granular solid processing composition granules having a particle diameter of less than 149 µm is preferably 30 % by weight or less, more preferably 15 % by weight or less and still more preferably 10 % by weight or less. In order to obtain such granules, the above described granulating procedures may be used. As other methods a bleaching agent and fixing agent crystallized to suitable size from the solution may be used and granules sieved by screening or classifying the crystals may be used. The granules and crystals may be used in combination.

The particle diameter of the invention refers to the diameter measured by a sieve according to JIS, and the above "granules having a particle diameter of less than 149 µm is 30 % or less " means that the weight of the granules minus sieve screened by a sieve having a 149 µm mesh according to JIS is 30 % or less based on the total weight of the granules.

When the solid processing composition of the invention contains an amino polycarboxylic acid ferric complex hydrate and a fixing agent, less contact between an amino polycarboxylic acid ferric complex hydrate as a bleaching agent and a sulfite as a fixing agent is preferable in view of the effects of the invention. In view of the above, at least one of them is preferably granules, since the effects of the invention are markedly displayed. It is more preferable that both agents are granules. This is because of another effect in which fine loose powder is reduced during storage as well as the above mentioned effects.

The drying weight reduction at 50°C of the composition herein referred to is obtained from the weight reduced after the composition is heated at 50°C to the constant weight which is measured with an electronic moisture meter available on the market.

The solid processing composition of the invention is a solid bleaching composition comprising at least one hydrate salt of an amino polycarboxylic acid ferric complex, and it may be a simple mixture of solid materials or a mixture of granules obtained by granulating several powdered solid materials in admixture.

As for the manufacturing method of the above described granules, it is possible to use any of the well-known methods such as a rolling granulation, an extrusion granulation, a compression granulation, a cracking granulation, a stirring granulation, a fluidized-layer granulation and water spray-drying granulation.

The above described solid bleaching composition is compression-molded into tablets, whereby the tablets exhibit the effect of the invention markedly and the effective prevention of fine powder increase during storage.

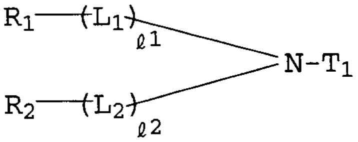
The solid processing tablet is produced by well known compressors. The compressors for producing the tablets include a hydraulic press machine, a single tableting machine, a rotary tableting machine and a bricketing machine can be used. The solid processing tablet may be in any form, but is preferably in the cylindrical form in view of producibility or processability.

The solid processing agent of the invention comprises at least one ferric complex of an amino polycarboxylic acid hydrate, and two or more kinds ferric complexes of the amino polycarboxylic acid hydrates may be used therein.

The ferric complex of an amino polycarboxylic acid is preferably used in the form of an ferric complex of an amino polycarboxylic acid (free acid) represented by the following Formula (I) and the ferric complex is more preferably used in combination with an amino polycarboxylic acid (free acid). It is especially preferable that the ferric complex is used in combination with the same acid as the amino polycarboxylic acid (free acid) constituting the complex. The salt of the ferric complex of an amino polycarboxylic acid such as potassium salt, sodium salt or ammonium salt can be also used. The salt of the amino polycarboxylic acid such as potassium salt or sodium salt can be also used.

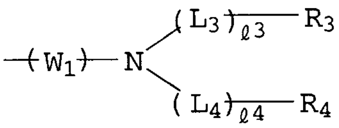
[0029]

Formula (I)



$$\begin{matrix} R_1-(L_1)_{\ell 1} \\ R_2-(L_2)_{\ell 2} \end{matrix} \rangle N-T_1$$

wherein $T_1$ represents a hydrogen atom, a hydroxy group, a carboxy group, a sulfo group, a carbamoyl group, a phosphono group, a phosphon group, a sulfamoyl group, a substituted or unsubstituted alkyl group, an alkoxy group, an alkylsulfonamido group, an alkylthio group, an acylamino group or a hydroxamic acid group, a hydroxyalkyl group or

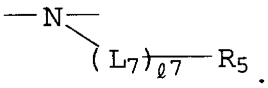


$$-(W_1)-N\langle \begin{matrix} (L_3)_{\ell 3}-R_3 \\ (L_4)_{\ell 4}-R_4 \end{matrix}$$

wherein $W_1$ represents a substituted or unsubstituted alkylene, arylene, alkenylene, cycloalkylene or aralkylene group or

$$-(L_5-X)_{\ell 5}-(L_6)_{\ell 6}-$$

wherein X represents -O-, -S-, a divalent heterocyclic group or

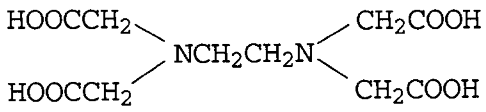


$$\begin{matrix} -N- \\ \quad \backslash (L_7)_{\ell 7}-R_5 \end{matrix}.$$

$R_1$ through $R_5$ independently represent a hydrogen atom, a hydroxy group, a carboxy group, a sulfo group, a carbamoyl group, a phosphono group, a phosphon group, a sulfamoyl group, a sulfonamido group, an acylamino group or a hydroxamic acid group, provided that at least one of $R_1$ through $R_5$ is a carboxy group. $L_1$ through $L_7$ independently represent a substituted or unsubstituted alkylene, arylene, alkenylene, cycloalkylene or aralkylene group; and $\ell_1$ through $\ell_7$ independently represent an integer of 0 to 6, provided that $\ell_5$ through $\ell_6$ are not simultaneously 0.

The example of the amino polycarboxylic acid represented by Formula (I) constituting the ferric complex of an amino polycarboxylic acid hydrate will be shown below.

I-1



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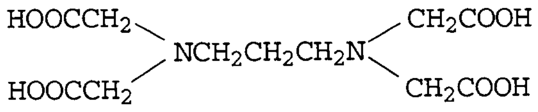

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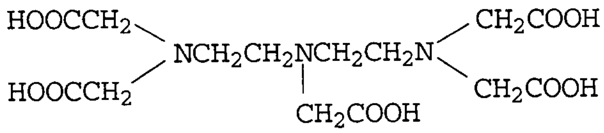

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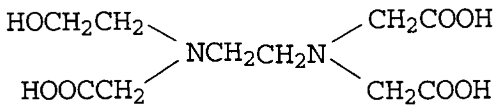

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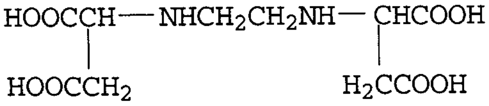
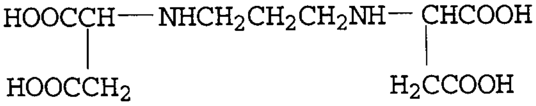


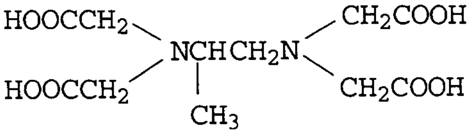
$$\underset{HOOCCH_2}{HOOCCH}-NHCH_2CH_2NH-\underset{H_2CCOOH}{CHCOOH}$$

I-6



$$\underset{HOOCCH_2}{HOOCCH}-NHCH_2CH_2CH_2NH-\underset{H_2CCOOH}{CHCOOH}$$

I-7



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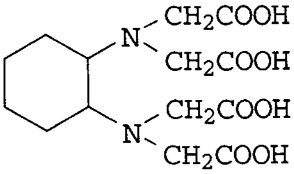

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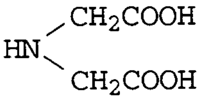

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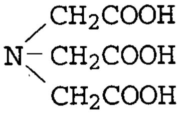

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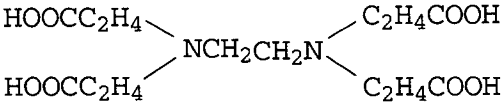

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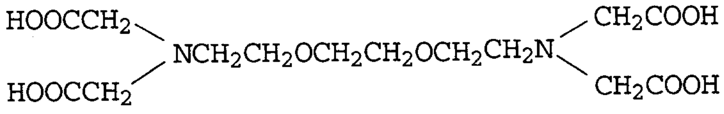

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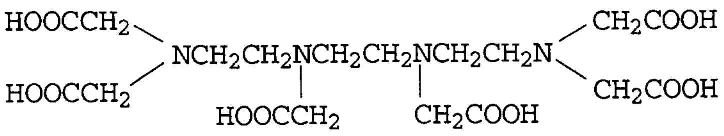

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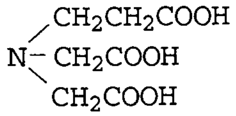

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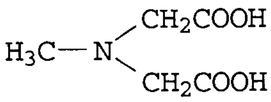

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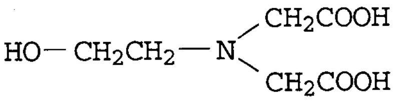

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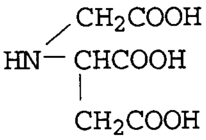

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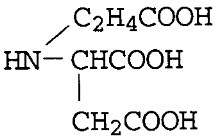

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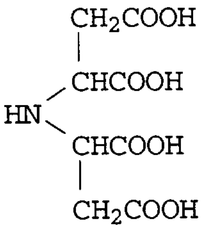

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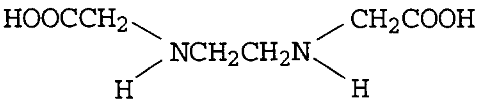

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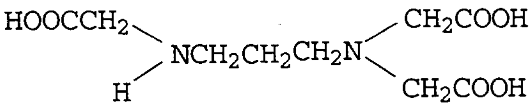

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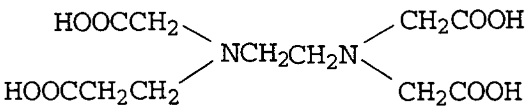

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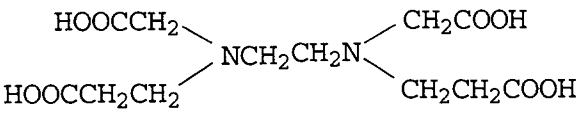
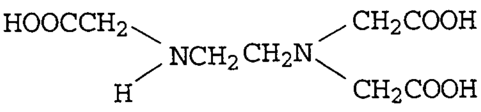


I-24



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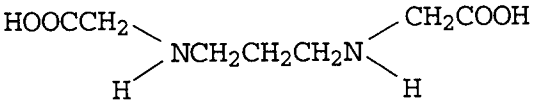

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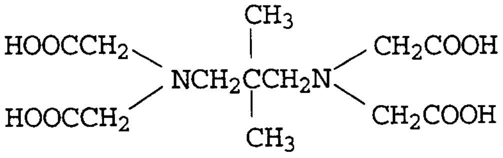

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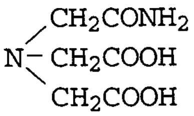

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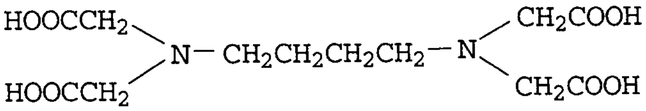
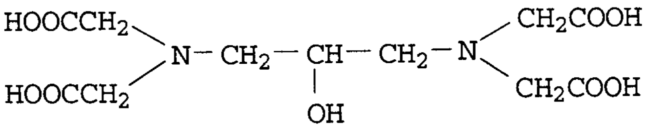


I-29



Among these compounds some have several kinds of isomers since they have asymmetric carbon atom [(1-5), (1-6), (1-7), (1-17) to (1-19)], and the compounds of the invention include any isomers and may be constituted in any content thereof. When an amino polycarboxylic acid has three ligand fields , Fe (III) complex in which the ratio of the acid to Fe (III) is 1:2 is preferable.

As compounds displaying the effects of the invention in the solid composition not containing thiosulfates or thiocyanate, (I-1) through (I-8), (I-12), (I-14) through (I-20), (I-22), (I-23) and (I-27) are preferable, and (I-1)-), (I-2), (I-6), (I-12), (I-14), (I-15) and (I-17) are especially preferable.

In the solid composition containing a fixing agent, compounds (I-1) through (I-9), (I-12), (I-14) through (I-20), (I-22), (I-23) and (I-27) are preferable, and (I-1) through (I-6), (I-9), (I-14) through (I-17) are especially preferable.

The example of the ferric complex of an amino polycarboxylic acid in the invention (exemplified compounds II) and the preferable crystal water content will be shown below, but the invention is not limited thereto.

| Amino polycarboxylic acid Fe(III) complex (Exemplified compound II) | | | Preferable amount of crystal water of amino polycarboxylic acid Fe(III) complex |
|---|---|---|---|
| No. | Amino polycarboxylic acid (Exemplified Compound I) | Cation | Mol of crystal water per mol of the complex |
| II-1 | I-1 | $Na^+$ | 3 |
| II-2 | I-1 | $K^+$ | 2 |
| II-3 | I-1 | $NH_4{}^+$ | 2 |
| II-4 | I-2 | $Na^+$ | 3 |
| II-5 | I-2 | $K^+$ | 1 |
| II-6 | I-2 | $NH_4{}^+$ | 1 |
| II-7 | I-8 | $NH_4{}^+$ | 2 |
| II-8 | I-3 | $K^+$, $H^+$ | 1 |
| II-9 | I-3 | $NH_4{}^+$, $H^+$ | 1 |
| II-10 | I-5 | $Na^+$ | 1 |
| II-11 | I-5 | $K^+$ | 1 |
| II-12 | I-5 | $NH_4{}^+$ | 1 |
| II-13 | I-14 | - | 2 |
| II-14 | I-28 | $K^+$ | 1 |
| II-15 | I-26 | $K^+$ | 1 |
| II-16 | I-10 | - | 1.5 |

For example, Exemplified compound II-1 represents sodium iron (III) ethylenediaminetetraacetate ferric complex trihydrate.

When water-soluble polymers and/or saccharides are used in the solid processing composition in combination, the effects of the invention are displayed more markedly.

The saccharides in the invention refer to monosaccharides or polysaccharides in which monosaccharides bind through a glycoside bondage.

Monosaccharides refer to a single polyhydroxy aldehyde, polyhydroxy ketone or their derivatives such as reduced derivatives, oxidized derivatives, deoxy derivatives, amino derivatives or thio derivatives. Most of them are represented by the general formula $C_nH_{2n}O_n$. The monosaccharides in the invention include derivatives derived from saccharide skeleton represented by the above formula. The preferable are saccharide alcohols having a primary or secondary alcohol group to which an aldehyde or ketone group is reduced.

Polysaccharides include celluloses, starches or glycogens. The celluloses include derivatives such as cellulose ethers in which all or a part of hydroxy group are etherified, starches include dextrins that starches are hydrolyzed to various decomposition compounds or maltose. Celluloses may be in an alkali salt form in view of solubility. Among polysaccharide, celluloses or dextrins are preferably used, and dextrins are more preferably used.

Examples of monosaccharides in the invention will be shown below.

(Exemplified compounds)

| | |
|---|---|
| A-1 | Glycerin |
| A-2 | D-threitol |
| A-3 | L-threitol |
| A-4 | Erithorit |
| A-5 | D-arabitol |

| | |
|---|---|
| A-6 | L-arabitol |
| A-7 | adnite |
| A-8 | xylitol |
| A-9 | D-sorbitol |
| A-10 | L-sorbitol |
| A-11 | D-mannitol |
| A-12 | L-mannitol |
| A-13 | D-iditol |
| A-14 | L-iditol |
| A-15 | D-talitol |
| A-16 | L-talitol |
| A-17 | dulcin |
| A-18 | allodulcitol |
| A-19 | erythritol |

Of these compounds, A-9 through A-19 are preferably used.

Examples of polysaccharides in the invention will be shown below.

| | |
|---|---|
| B-1 | $\alpha$-dextrin |
| B-2 | $\beta$-dextrin |
| B-3 | $\gamma$-dextrin |
| B-4 | $\delta$-dextrin |
| B-5 | $\epsilon$-dextrin |
| B-6 | $\alpha$-limited-dextrin |
| B-7 | $\beta$-limited-dextrin |
| B-8 | phosporylase limited-dextrin |
| B-9 | Soluble starch |
| B-10 | Sizing starch |
| B-11 | White dextrin |
| B-12 | Yellow dextrin |
| B-13 | British gumm |
| B-14 | Pineflow (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-15 | Pinedex 100 (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-16 | Pinedex 1 (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-17 | Pinedex 2 (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-18 | Pinedex 3 (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-19 | Pinedex 4 (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-20 | Pinedex 6 (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-21 | Foodtex 2 (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-22 | Max 1000 (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-23 | Glistar P (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-24 | TK-16 (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-25 | MPD (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-26 | H-PDX (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-27 | Stucodex (trade name, produced by Matsutani Kagakukogyo Co. Ltd.) |
| B-28 | Mabit (trade name, produced by Hayashibara Trading Co., Ltd.) |
| B-29 | Pullulan (trade name, produced by Hayashibara Trading Co., Ltd.) |
| B-30 | Methylcellulose |
| B-31 | Dimethylcellulose |
| B-32 | Trimethylcellulose |
| B-33 | Ethylcellulose |
| B-34 | Diethylcellulose |
| B-35 | Triethylcellulose |
| B-36 | Carboxymethylcellulose |
| B-37 | Carboxyethylcellulose |
| B-38 | Aminoethylcellulose |
| B-39 | Hydroxymethylcellulose |
| B-40 | Hydroxyethymethyllcellulose |
| B-41 | Hydroxypropylcellulose |
| B-42 | Hydroxypropylmethylcellulose |

| | |
|---|---|
| B-43 | Hydroxypropylmethylcelluloseacetatesuccinate |
| B-44 | cabboxymethylhydroxyethylcellulose |

Of these compounds, B-1 through B-28 are preferably used,

Saccharides exist widely in the nature, and are available on the market. The derivatives can be readily prepared by reduction, oxidation or dehydration reactions.

The water-soluble polymer includes a polyethylene glycol, a polypropylene glycol, a block polymer of a polyethylene glycol and a polypropylene glycol (Pluronic type), polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetal, polyvinyl acetate, an aminoalkylmethacrylate copolymer, methacrylic acid-methacrylate copolymer, methacrylic acid-acrylate copolymer, and methacrylic acid betaine type polymer. The polyethylene glycol, polypropylene glycol or Pluronic type polymer has a weight average molecular weight of preferably 500 to 10000 and more preferably 2,000 to 8,000. The preferable polymers will be shown below.

Exemplified compound

| | | |
|---|---|---|
| C-1 | Polyethylene glycol | 600 |
| C-2 | Polyethylene glycol | 1000 |
| C-3 | Polyethylene glycol | 1500 |
| C-4 | Polyethylene glycol | 1540 |
| C-5 | Polyethylene glycol | 2000 |
| C-6 | Polyethylene glycol | 4000 |
| C-7 | Polyethylene glycol | 6000 |
| C-8 | Polyethylene glycol | 10000 |
| C-9 | Polypropylene glycol average molecular weight | 400 |
| C-10 | Polypropylene glycol average molecular weight | 72 |
| C-11 | Polypropylene glycol average molecular weight | 100 |
| C-12 | Polypropylene glycol average molecular weight | 200 |
| C-13 | Polypropylene glycol average molecular weight | 300 |
| C-14 | Pluronic F-68 (Trade name, produced by Asahidenka Kogyo Co., Ltd.) | |
| C-15 | Pluronic F-88 (Trade name, produced by Asahidenka Kogyo Co., Ltd.) | |
| C-16 | Pluronic F-38 (Trade name, produced by Asahidenka Kogyo Co., Ltd.) | |
| C-17 | Pluronic F-77 (Trade name, produced by Asahidenka Kogyo Co., Ltd.) | |
| C-18 | Polyvinyl pyrrolidone K-17 | |
| C-19 | Polyvinyl alcohol average polymerization degree 500 | |
| C-19 | Polyvinyl alcohol average polymerization degree 1000 | |

Of these compounds C-5 through C-7 are especially preferable. These saccharides or water-soluble polymers may be used singly or in combination. The amount used thereof is preferably 0.5 to 30 % by weight, based on the weight of the solid composition of the invention.

In the composition containing not containing thiosulfate or thiocyanate the amount thereof is more preferably 0.5 to 20 % by weight and still more preferably 1.0 to 20 % by weight based on the weight of the solid composition of the invention.

In the composition containing a fixing agent the amount thereof is more preferably 3 to 20 % by weight and still more preferably 5 to 15 % by weight based on the weight of the solid composition of the invention.

On granulating the addition of these compounds enhances the effects of the invention.

When the solid processing composition of the invention is in the form of tablets, the addition of the above described saccharide or water-soluble polymer may be carried out on mixing components in the form of granules, powder or crystal particle before tableting.

The solid processing composition in the invention preferably contains a compound represented by the following Formula [A]

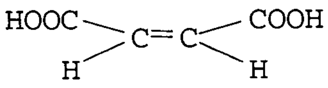
Formula [A] $A(\text{-COOH})_n$

wherein A represents an n valent organic group, n represents an integer of 1 to 6, and M represents an ammonium, an alkali metal (sodium, potassium or lithium) or a hydrogen atom.

In Formula [A] the n valent organic group represented by A includes an alkylene group (such as methylene, ethylene, trimethylene or tetramethylene), an alkenylene group (such as ethenylene), an alkinylene group (such as ethynylene), a cycloalkylene group (such as 1,4-cyclohexanediyl), an arylene group (such as o-phenylene group or p-phenylene), an alkanetriyl group (such as 1,2,3-propanetriyl) or an arylenetriyl group (such as 1,2,4-benzenetriyl). The above n valent organic group includes a group having a substituent (such as a hydroxy group, an alkyl group or a halogen atom). The examples include 1,2-dihydroxyethylene, hydroxyethylene, 2-hydroxy-1,2,3-propanetriyl, methyl-p-phenylene, 1-hydroxy-2-chloroethylene, chloromethylene or chloroethenylene. The preferable compound represented by Formula [A] will be shown below.

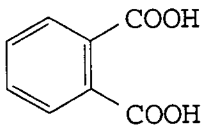
(A-1) $HOOCCH_2C(OH)(COOH)CH_2COOH$
(A-2) $HOOC(CHOH)_2COOH$
(A-3) $HOOCCH_2COOH$
(A-4) $HOOCCH(OH)CH_2COOH$

(A-6)

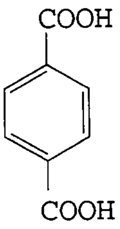


(A-7) $(COOH)_2$

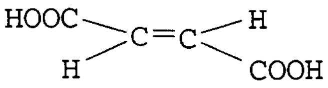
(A-8)



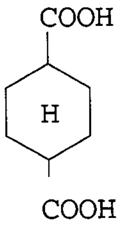
(A-9)



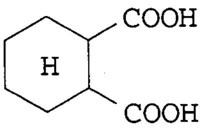
(A-10)



(A-11)



(A-12)

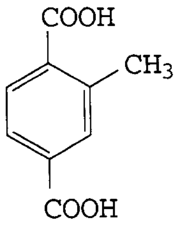


(A-13) $HOOC-(CH_2)_3-COOH$

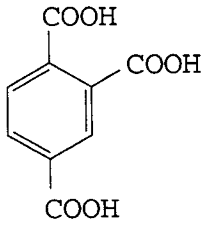
(A-14) $HOOC-(CH_2)_4-COOH$

(A-15) $HOOCC\equiv CCOOH$

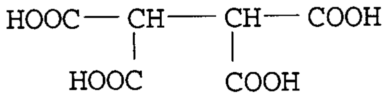
(A-16)



(A-17)

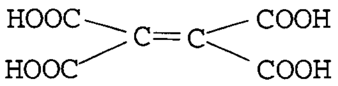


(A-18)



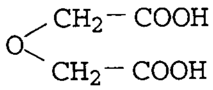
$$HOOC-\underset{\displaystyle HOOC}{\underset{|}{CH}}-\underset{\displaystyle COOH}{\underset{|}{CH}}-COOH$$

(A-19)



(A-20) $HO-CH_2-COOH$

(A-21)



Of these Compounds (A-1), (A-3), (A-4), (A-6), (A-10), (A-13), (A-14), (A-15) and (A-20) are preferable, and (A-1), (A-6), (A-13), (A-14) and (A-20) are especially preferable.

The salt of the above acid includes an ammonium salt, a lithium salt, a sodium salt or a potassium salt, and the sodium salt or potassium salt is preferable in view of storage stability. These organic acids or salts thereof may be used singly or in combination. When the above ferric complex is mixed with the organic acid and/or the salt thereof, granules of the complex may be mixed with granules of the organic acid and/or the salt. However, granules of a mixture of the complex with the organic acid and/or the salt displays the effects of the invention more markedly. Further, the mixture, compression-molded into tablets, gives tablets excellent in the strength.

As the fixing agent in the invention a thiosulfate or a thiocyanate is preferably used, and a thiosulfate is more preferably used. Both agent may be used in combination. The fixing agent is preferably used in the form of sodium, potassium or ammonium salt, and two or more kinds of the salts may be used in combination. The thiosulfate content of the solid processing composition of the invention is preferably 20 to 70 weight %.

In the invention when the thiosulfate is used, a preservative is preferably used, and a sulfite, a bisulfite or metabisulfite is preferable as the preservative. The preservative is preferably used in the form of sodium, potassium or ammonium salt, and two or more kinds of the preservatives may be used in combination. The preservative content of the solid processing composition of the invention is preferably 5 to 30 weight %.

The buffering agent may be optionally used in the solid processing composition of the invention. The buffering agent includes an amino acid (for example, glycine, alanine, aspartic acid, or glutamic acid or salts thereof) or an acetate (for example, sodium acetate, potassium acetate, ammonium acetate, or lithium acetate), and two or more kinds of the compounds may be used in combination.

The solid composition of the invention may contain an alkali halide or an ammonium halide (for example, sodium bromide, potassium bromide, ammonium bromide, sodium chloride, potassium chloride or ammonium chloride).

## EXAMPLES

The invention will be detailed in the following Examples, and is not limited thereto.

Example 1

Procedure (1-1)

| | |
|---|---|
| Succinic acid | 700 g |
| Potassium bromide | 900 g |

In a hammer-mill available on the market the above compounds independently were pulverized to have an average particle size of not more than 50 μm. Using a shelf type dryer 1900 g of Exemplified ferric complex shown in Table 1 were dried to completely remove the crystal water.

The above three kinds of compounds were mixed in a cross rotary mixer available and the mixture was granulated for 8 minutes in a stirring granulator available on the market by spraying 50 ml of polyethylene glycol #600 (produced by Kanto Kagaku Co., Ltd.). The resulting granules were dried at 40 ° C for 3 hours using a fluid-bed type dryer available on the market. Thus, samples (1-1) through (1-5) were obtained.

The drying weight reduction at 50 ° C of the samples was measured. The results are shown in Table 1.

Procedure (1-2)

| | |
|---|---|
| Succinic acid | 700 g |
| Potassium bromide | 900 g |

In the same way as in Procedure (1-1) the above compounds were pulverized and mixed. The resulting mixture was granulated for 8 minutes in a stirring granulator by adding 50 ml of water. The resulting granules were dried at 60 ° C for 4 hours using a fluid-bed type dryer. The resulting granules were mixed with 1900 g of Exemplified ferric complexes shown in Table 1 which were dried to completely remove the crystal water, and granulated for 8 minutes in a stirring granulator available by adding 50 ml of polyethylene glycol #600 (produced by Kanto Kagaku Co., Ltd.). The resulting granules were dried at 40 ° C for 3 hours using a fluid-bed type dryer available on the market. Thus, samples (1-6) through (1-10) were obtained.

The drying weight reduction at 50 ° C of the samples was measured. The results are shown in Table 1.

Procedure (1-5)

| | |
|---|---|
| Ferric complex of Exemplified compound (shown in Table 1) | 1900 g |
| Succinic acid | 700 g |
| Potassium bromide | 900 g |

In the same way as in Procedure (1-1) the above compounds were pulverized and mixed. The resulting mixture was granulated for 8 minutes in a stirring granulator by adding 50 ml of polyethylene glycol #600. The resulting granules were dried at 40 ° C for 3 hours using a fluid-bed type dryer. Thus, samples (1-11) through (1-15) were obtained.

The drying weight reduction at 50 ° C of the samples was measured. The results are shown in Table 1.

Procedure (1-6)

Procedure (1-6) was carried out in the same way as in Procedure (1-5) to obtain granules, except that 100 ml of water was added instead of 50 ml of polyethylene glycol #600. The resulting granules were dried at 60 ° C for 4 hours using a fluid-bed type dryer. Thus, samples (1-16) through (1-20) were obtained.

The drying weight reduction at 50 ° C of the samples was measured. The results are shown in Table 1.

Experiment (1-1)

One hundred and forty-five gram of each of the above obtained samples (1-1) through (1-20) were screened with a 149 µm sieve to obtain granules of not less than 149 µm. One hundred gram of each of the resulting granules were packaged in aluminum packages and tightly sealed. The sealed packages were subjected to a vibration test using a vibration tester BF-UA produced by IDEX Co., Ltd. The resulting granule samples were screened with a 149 µm sieve and evaluated for powder occurrence. The vibration was carried out for 30 minutes under condition of 5-67Hz/210sec. The results are shown in Table 1.

The evaluation criteria are as follows:

| | |
|---|---|
| O : | No problem |
| △ : | Slight powder occurrence but no problem |
| X : | marked powder occurrence |

The samples evaluated X are very low in commercial value.

In the similar manner as in Experiment 1 100 g of each of the resulting granules were packaged in polyethylene packages, tightly sealed and stored at 55 ° C for 7 days. The results are shown in Table 1.

The evaluation criteria are as follows:

| | |
|---|---|
| O : | No adherence of the samples to the packages |
| O-△ : | Slight adherence of the samples to the packages but the adhered readily removed |
| △ : | Slight adherence of the samples to the packages but the adhering powder readily removed when the packages were tapped. |
| X : | Much adherence of the samples to the packages and the adhering powder is not removed when the packages were strongly struck. |

The samples evaluated X are very low in commercial value.

Table 1

| Sample No. | Exemplified Compound II | * Pair ion | Mol ** number of crystal water | Weight reduction at 50 °C | Powder Occurrence | Adherence of Powder | Remarks |
|---|---|---|---|---|---|---|---|
| 1-1 | II-6 | $NH_4^+$ | 0 | 0.04 | X | ○ | Comparative |
| 1-2 | II-5 | $K^+$ | 0 | 0.05 | X | ○ | Comparative |
| 1-3 | II-3 | $NH_4^+$ | 0 | 0.05 | X | ○ | Comparative |
| 1-4 | II-9 | $NH_4^+H^+$ | 0 | 0.04 | X | ○ | Comparative |
| 1-5 | II-11 | $K^+$ | 0 | 0.05 | X | ○ | Comparative |
| 1-6 | II-6 | $NH_4^+$ | 0 | 3.04 | X | ○ | Comparative |
| 1-7 | II-5 | $K^+$ | 0 | 2.98 | X | ○ | Comparative |
| 1-8 | II-3 | $NH_4^+$ | 0 | 3.12 | X | ○ | Comparative |
| 1-9 | II-9 | $NH_4^+H^+$ | 0 | 3.00 | X | ○ | Comparative |
| 1-10 | II-11 | $K^+$ | 0 | 2.95 | X | ○ | Comparative |
| 1-11 | II-6 | $NH_4^+$ | 1 | 0.04 | X | ○ | Comparative |
| 1-12 | II-5 | $K^+$ | 1 | 0.06 | X | ○ | Comparative |
| 1-13 | II-3 | $NH_4^+$ | 2 | 0.03 | X | ○ | Comparative |
| 1-14 | II-9 | $NH_4^+H^+$ | 1 | 0.04 | X | ○ | Comparative |
| 1-15 | II-11 | $K^+$ | 1 | 0.05 | X | ○ | Comparative |
| 1-16 | II-6 | $NH_4^+$ | 1 | 3.03 | ○ | ○ | Invention |
| 1-17 | II-5 | $K^+$ | 1 | 3.12 | ○ | ○ | Invention |
| 1-18 | II-3 | $NH_4^+$ | 2 | 3.06 | ○ | ○ | Invention |
| 1-19 | II-9 | $NH_4^+H^+$ | 1 | 3.21 | ○-△ | ○ | Invention |
| 1-20 | II-11 | $K^+$ | 1 | 3.07 | ○ | ○ | Invention |

* : Pair ion of Exemplified Compound II

**: Mol number of crystal water to Exemplified Compound II in the Exemplified Compound II hydrate.

As is apparent from Table 1, a solid bleaching composition for a silver halide color light-sensitive material less in powder occurrence and in adherence to packages is obtained by using the amino polycarboxylic acid ferric complex hydrate and controlling a weight reduction at 50 °C to be 0.1 to 10.0 % by weight.

Example 2

Procedure (2-1)

| | |
|---|---|
| Exemplified ferric complex (shown in table 2) | 1900 g |
| Free acid of the above complex | 100 g |
| Succinic acid | 700 g |
| Disodium maleate monohydrate | 300 g |
| Adipic acid | 200 g |
| D-Mannitol | 500 g |
| Potassium bromide | 900 g |

In a hammer-mill the above compounds independently were pulverized to have an average particle size of not more than 50 µm and mixed. The resulting mixture was granulated in a stirring granulator by adding 100 ml of water. The resulting granules were dried at 60 °C for 4 hours using a fluid-bed type dryer available on the market. Thus, samples (2-1) through (2-5) were obtained. The drying weight reduction at 50 °C of the samples was measured. The results are shown in Table 2.

Procedure (2-2)

Samples (2-6) through (2-21) were prepared in the same manner as in Procedure (2-1), except that the added amount of water, drying temperature or drying time is suitably changed.

Procedure (2-3)

Sample (2-22) was prepared in the same manner as in Procedure (2-1), except that 1200 g of sodium hydrogen sulfate was added instead of succinic acid, disodium maleate monohydrate and adipic acid. The drying weight reduction at 50 °C of the sample was measured. The results are shown in Table 2.

Experiment (2-1)

The Experiment (2-1) was carried out in the same manner as in Experiment (1-1) or Experiment (1-2). The evaluation is the same as Example 1.

Table 2

| Sample No. | Exemplified Compound II | * Pair ion | Mol ** number of crystal water | Weight reduction at 50°C | Powder Occurrence | Adherence of Powder | Remarks |
|---|---|---|---|---|---|---|---|
| 2-1 | II-6 | $NH_4^+$ | 1 | 3.09 | ○ | ○ | Invention |
| 2-2 | II-5 | $K^+$ | 1 | 2.98 | ○ | ○ | Invention |
| 2-3 | II-3 | $NH_4^+$ | 2 | 3.01 | ○ | ○ | Invention |
| 2-4 | II-9 | $H^+$ | 1 | 3.03 | ○-△ | ○ | Invention |
| 2-5 | II-11 | $K^+$ | 1 | 2.99 | ○ | ○ | Invention |
| 2-6 | II-6 | $NH_4^+$ | 1 | 0.04 | × | ○ | Comparative |
| 2-7 | II-6 | $NH_4^+$ | 1 | 0.12 | △ | ○ | Invention |
| 2-8 | II-6 | $NH_4^+$ | 1 | 0.53 | ○-△ | ○ | Invention |
| 2-9 | II-6 | $NH_4^+$ | 1 | 1.02 | ○ | ○ | Invention |
| 2-10 | II-6 | $NH_4^+$ | 1 | 5.93 | ○ | ○ | Invention |
| 2-11 | II-6 | $NH_4^+$ | 1 | 7.78 | ○ | ○-△ | Invention |
| 2-12 | II-6 | $NH_4^+$ | 1 | 9.89 | ○ | △ | Invention |
| 2-13 | II-6 | $NH_4^+$ | 1 | 12.01 | ○ | × | Comparative |
| 2-14 | II-3 | $NH_4^+$ | 2 | 0.05 | × | ○ | Comparative |
| 2-15 | II-3 | $NH_4^+$ | 2 | 0.13 | △ | ○ | Invention |
| 2-16 | II-3 | $NH_4^+$ | 2 | 0.53 | ○-△ | ○ | Invention |
| 2-17 | II-3 | $NH_4^+$ | 2 | 1.13 | ○ | ○ | Invention |
| 2-18 | II-3 | $NH_4^+$ | 2 | 5.76 | ○ | ○ | Invention |
| 2-19 | II-3 | $NH_4^+$ | 2 | 7.84 | ○ | ○-△ | Invention |
| 2-20 | II-3 | $NH_4^+$ | 2 | 9.94 | ○ | △ | Invention |
| 2-21 | II-3 | $NH_4^+$ | 2 | 12.35 | ○ | × | Comparative |
| 2-22 | II-6 | $NH_4^+$ | 1 | 3.01 | △ | △ | Invention |

* : Pair ion of Exemplified Compound II
**: Mol number of crystal water to Exemplified Compound II in the Exemplified Compound II hydrate.

As is apparent from Table 1, a solid bleaching composition for a silver halide color light-sensitive material less in powder occurrence and in adherence to packages is obtained by using the amino polycarboxylic acid ferric complex hydrate and controlling a weight reduction at 50°C to be 0.1 to 10.0 % by weight. In view of the effects of the invention, the weight reduction at 50°C is preferably 0.5 to 8.0 % by weight, and more preferably 1.0 to 6.0 % by weight.

The solid composition of the invention displays more improved effects by adding a compound represented by Formula [A].

Example 3

Samples were prepared, granulated, dried and evaluated in the same manner as in Example 2, except that ferric complexes (II-5), (II-9), (II-11) or (II-12) was used instead of ferric complex used in sample (2-1). The same results as Example 2 were obtained.

Example 4

Samples (3-1) through (3-11) were prepared in the same manner as in Example 2, except that ferric complexes shown in Table 3 was used and the crystal water was adjusted to be a mol number shown in Table 3. The evaluation was carried out in the same manner as in Example 1. The appearance of the samples was evaluated before and after 10 g of the samples in petri glass were stored at 30 °C and 70%Rh for 4 hours.

The evaluation criteria are as follows:

| | |
|---|---|
| ○ : | No problem |
| △ : | A half of samples are colored. |
| X : | The entire of the samples are colored. |

Table 3

| Sample No. | Exemplified Compound II | * Pair ion | Mol ** number of crystal water | Weight reduction at 50 °C | Powder Occurrence | Adherence of Powder | Appearance after storage | Remarks |
|---|---|---|---|---|---|---|---|---|
| 3-1 | II-6 | $NH_4^+$ | 1 | 0.04 | X | ○ | X | Comparative |
| 3-2 | II-6 | $NH_4^+$ | 1 | 3.08 | ○ | ○ | ○ | Invention |
| 3-3 | II-6 | $NH_4^+$ | 0.2 | 2.98 | ○-△ | ○ | △ | Invention |
| 3-4 | II-6 | $NH_4^+$ | 0.3 | 3.01 | ○ | ○ | ○ | Invention |
| 3-5 | II-6 | $NH_4^+$ | 0.5 | 2.95 | ○ | ○ | ○ | Invention |
| 3-6 | II-6 | $NH_4^+$ | 3.0 | 2.99 | ○ | ○ | ○ | Invention |
| 3-7 | II-6 | $NH_4^+$ | 4.0 | 2.83 | ○ | ○-△ | ○-△ | Invention |
| 3-8 | II-1 | $Na^+$ | 0.2 | 3.01 | △ | ○ | △ | Invention |
| 3-9 | II-1 | $Na^+$ | 0.3 | 3.05 | ○-△ | ○ | ○-△ | Invention |
| 3-10 | II-1 | $Na^+$ | 0.5 | 2.91 | ○ | ○ | ○ | Invention |
| 3-11 | II-1 | $Na^+$ | 1.0 | 3.12 | ○ | ○ | ○ | Invention |
| 3-12 | II-1 | $Na^+$ | 3.0 | 3.05 | ○ | ○ | ○ | Invention |
| 3-13 | II-1 | $Na^+$ | 4.0 | 2.98 | ○ | △ | △ | Invention |
| 3-14 | II-12 | $NH_4^+$ | 0.2 | 3.12 | △ | ○ | △ | Invention |
| 3-15 | II-12 | $NH_4^+$ | 0.3 | 2.87 | ○-△ | ○ | ○ | Invention |
| 3-16 | II-12 | $NH_4^+$ | 0.5 | 2.92 | ○ | ○ | ○ | Invention |
| 3-17 | II-12 | $NH_4^+$ | 1.0 | 2.80 | ○ | ○ | ○ | Invention |
| 3-18 | II-12 | $NH_4^+$ | 3.0 | 3.12 | ○ | ○ | ○ | Invention |
| 3-19 | II-12 | $NH_4^+$ | 4.0 | 3.06 | ○ | △ | △ | Invention |

* : Pair ion of Exemplified Compound II

**: Mol number of crystal water to Exemplified Compound II in the Exemplified Compound II hydrate.

As is apparent from Table 3, a solid bleaching composition for a silver halide color light-sensitive material less in appearance change is obtained by controlling the mol ratio of crystal water to the ferric complex of the amino polycarboxylic acid salt ferric complex hydrate to be 0.3 to 3.0.

## Example 5

Samples (4-1) through (4-14) were prepared in the same manner as in sample (2-1) of Example 2, except that the amount of mannitol shown in Table 4 was used or compounds shown in Table 4 were used instead of D-mannitol. The evaluation was carried out in the same manner as in Example 4. The results are shown in Table 4.

Table 4

| Sample No. | Exemplified Compound II | * Pair ion | Mol number** of crystal water | Binder (weight %) | Weight reduction at 50°C | Powder Occurrence | Adherence of Powder | Appearance after storage |
|---|---|---|---|---|---|---|---|---|
| 4-1 | II-6 | $NH_4^+$ | 1 | None | 3.10 | △ | ○ | △ |
| 4-2 | II-6 | $NH_4^+$ | 1 | D-Mannitol(0.5) | 3.12 | ○-△ | ○ | △ |
| 4-3 | II-6 | $NH_4^+$ | 1 | D-Mannitol(1.0) | 3.04 | ○ | ○ | ○ |
| 4-4 | II-6 | $NH_4^+$ | 1 | D-Mannitol(10.0) | 2.98 | ○ | ○ | ○ |
| 4-5 | II-6 | $NH_4^+$ | 1 | D-Mannitol(20.0) | 2.95 | ○ | ○ | ○ |
| 4-6 | II-6 | $NH_4^+$ | 1 | D-Mannitol(25.0) | 2.88 | ○ | ○-△ | ○ |
| 4-7 | II-6 | $NH_4^+$ | 1 | Pineflow(5.0) (Matsutani Kagaku Kogyo) | 3.12 | ○ | ○ | ○ |
| 4-8 | II-6 | $NH_4^+$ | 1 | Pineflow(10.0) (Matsutani Kagaku Kogyo) | 3.00 | ○ | ○ | ○ |
| 4-9 | II-6 | $NH_4^+$ | 1 | Pinedex#100(5.0) (Matsutani Kagaku Kogyo) | 2.91 | ○ | ○-△ | ○ |
| 4-10 | II-6 | $NH_4^+$ | 1 | Pinedex#100(10.0) (Matsutani Kagaku Kogyo) | 2.83 | ○ | ○-△ | ○ |
| 4-11 | II-6 | $NH_4^+$ | 1 | Hydroxypropyl-cellulose (10.0) | 3.15 | ○ | ○-△ | ○ |
| 4-12 | II-6 | $NH_4^+$ | 1 | β-cyclodextrin(10.0) | 2.97 | ○ | ○ | ○ |
| 4-13 | II-6 | $NH_4^+$ | 1 | Polyethyleneglycol#2000 (0.5) | 3.21 | ○ | ○-△ | ○ |
| 4-14 | II-6 | $NH_4^+$ | 1 | Polyethyleneglycol#2000 (1.0) | 3.06 | ○ | ○-△ | ○ |

* : Pair ion of Exemplified Compound II

**: Mol number of crystal water to Exemplified Compound II in the Exemplified Compound II hydrate.

As is apparent from Table 4, a solid bleaching composition for a silver halide color light-sensitive material adding a binder in an amount of 0.5 to 20 % by weight displays the effects of the invention more effectively.

Example 6

Procedure (6-1)

Sodium N-lauroylsarcosine was added in an amount of 0.5 % by weight to each of samples (2-1) through (2-21) in example 2 and mixed for 3 minutes. The resulting mixture was compression-tableted in an amount of 11 g per tablet making use of a tableting machine in which Clean Press Correct 18K manufactured by Kikusui Mfg. Works was modified to obtain a tablet having a diameter of 30 mm. Thus, tablets for a solid bleaching composition (5-1) through (5-21) were obtained.

Procedure (6-2)

The compounds in Procedure (2-1) of Example 2 were mixed for 10 minutes without granulating and sodium N-lauroylsarcosine was added and mixed for 3 minutes. The resulting mixture was compression-tableted in the same manner as in Procedure (6-1) to have a weight per tablet of 11g and a diameter of 30 mm. Thus, tablet for a solid bleaching composition (5-22) was obtained.

Procedure (6-3)

The tablets for a solid bleaching composition (5-23) through (5-27) were prepared in the same manner as in Procedure (6-1) to have a weight per tablet of 11g and a diameter of 30 mm.

In Table 5 the weight reduction at 50 °C of Samples (5-1) through (5-21) is that of Samples (2-1) through (2-13) (granules) and the reduction at 50 °C of Samples (5-23) through (5-27) is that of Samples (1-1) through (1-5) (granules).

Experiment (6-1)

The evaluation was carried out in the same manner as in Example 1.

Further, Sliding property was measured. Samples were stored for 4 hours under the same condition as Experiment (4-1) of Example 4 and placed on a polyethylene plate at 25 °C and 45%RH. The polyethylene plate was fixed using Static Friction Tester HEIDON-10 (produced by HEIDON Co.) and the angle $\theta$ at which the samples move on the polyethylene plate was measured.

The evaluation criteria are as follows:

○ : The sample slides at not more than 15°.
△ : The sample slides at 15° to 30°.
X : The sample slides at more than 30°.

The results are shown in Tables 5 and 6.

Table 5

| Sample No. | Exemplified Compound II | Pair ion * | Mol number of crystal water ** | Weight reduction at 50°C | Powder Occurrence | Adherence of Powder | Sliding Property | Remarks |
|---|---|---|---|---|---|---|---|---|
| 5-1 | II-6 | $NH_4^+$ | 1 | 3.09 | ○ | ○ | ○ | Invention |
| 5-2 | II-5 | $K^+$ | 1 | 2.98 | ○ | ○ | ○ | Invention |
| 5-3 | II-3 | $NH_4^+$ | 2 | 3.01 | ○ | ○ | ○ | Invention |
| 5-4 | II-9 | $H^+$ | 1 | 3.03 | ○ | ○ | △ | Invention |
| 5-5 | II-11 | $K^+$ | 1 | 2.99 | ○ | ○ | ○ | Invention |
| 5-6 | II-6 | $NH_4^+$ | 1 | 0.04 | × | ○ | △ | Comparative |
| 5-7 | II-6 | $NH_4^+$ | 1 | 0.12 | ○-△ | ○ | △ | Invention |
| 5-8 | II-6 | $NH_4^+$ | 1 | 0.53 | ○ | ○ | △ | Invention |
| 5-9 | II-6 | $NH_4^+$ | 1 | 1.02 | ○ | ○ | ○ | Invention |
| 5-10 | II-6 | $NH_4^+$ | 1 | 5.93 | ○ | ○ | ○ | Invention |
| 5-11 | II-6 | $NH_4^+$ | 1 | 7.78 | ○ | ○ | ○ | Invention |
| 5-12 | II-6 | $NH_4^+$ | 1 | 9.89 | ○ | ○-△ | △ | Invention |
| 5-13 | II-6 | $NH_4^+$ | 1 | 12.01 | ○ | × | × | Comparative |
| 5-14 | II-3 | $NH_4^+$ | 2 | 0.05 | × | ○ | △ | Comparative |
| 5-15 | II-3 | $NH_4^+$ | 2 | 0.13 | ○-△ | ○ | △ | Invention |
| 5-16 | II-3 | $NH_4^+$ | 2 | 0.53 | ○ | ○ | △ | Invention |
| 5-17 | II-3 | $NH_4^+$ | 2 | 1.13 | ○ | ○ | ○ | Invention |
| 5-18 | II-3 | $NH_4^+$ | 2 | 5.76 | ○ | ○ | ○ | Invention |
| 5-19 | II-3 | $NH_4^+$ | 2 | 7.84 | ○ | ○ | ○ | Invention |
| 5-20 | II-3 | $NH_4^+$ | 2 | 9.94 | ○ | ○-△ | △ | Invention |
| 5-21 | II-3 | $NH_4^+$ | 2 | 12.35 | ○ | × | × | Comparative |

* : Pair ion of Exemplified Compound II

**: Mol number of crystal water to Exemplified Compound II in the Exemplified Compound II hydrate.

Table 6

| Sample No. | Exemplified Compound II | * Pair ion | Mol ** number of crystal water | Weight reduction at 50°C | Powder Occurrence | Adherence of Powder | Sliding Property | Remarks |
|---|---|---|---|---|---|---|---|---|
| 5-22 | II-6 | $NH_4^+$ | 1 | 2.85 | △ | ○ | ○ | Invention |
| 5-23 | II-6 | $NH_4^+$ | 0 | 0.04 | X | ○ | X | Comparative |
| 5-24 | II-5 | $K^+$ | 0 | 0.05 | X | ○ | X | Comparative |
| 5-25 | II-3 | $NH_4^+$ | 0 | 0.05 | X | ○ | X | Comparative |
| 5-26 | II-9 | $H^+$ | 0 | 0.04 | X | ○ | X | Comparative |
| 5-27 | II-11 | $K^+$ | 0 | 0.05 | X | ○ | X | Comparative |

* : Pair ion of Exemplified Compound II

**: Mol number of crystal water to Exemplified Compound II in the Exemplified Compound II hydrate.

As is apparent from Tables 5 and 6, a solid bleaching composition for a silver halide color light-sensitive material less in powder occurrence and powder adherence is obtained by compression-tableting a solid composition within the scope of the invention.

Example 7

| A part | |
|---|---|
| Exemplified compound (Fe(III) complex) shown in Table 7 | 1200 g |
| Pineflow (produced by Matsutani Kagaku Co.) | 100 g |

| B part | |
|---|---|
| Ammonium thiosulfate | 1800 g |
| Sodium thiosulfate | 200 g |
| Sodium metabisulfite | 700 g |
| Ethylenediaminetetraacetic acid | 100 g |
| Pineflow (produced by Matsutani Kagaku Co.) | 100 g |

[Preparation of sample (7-3)]

Procedure (7-1)

In a hammer-mill available on the market the compounds of A part independently were pulverized to have an average particle size of not more than 50 µm. The resulting powders were mixed in a cross rotary mixer available on the market at room temperature and the mixture was granulated for 8 minutes in a stirring granulator available on the market by adding 50 ml of polyethylene glycol #600 (produced by Kanto Kagaku Co., Ltd.). The resulting granules were dried at 40°C for 3 hours using a fluid-bed type dryer available on the market. Thus, granules (A7) were obtained.

Procedure (7-2)

In the same manner as in above the compounds of B part independently were pulverized and mixed. The mixture was granulated for 8 minutes in a stirring granulator by adding 70 ml of water. The resulting granules were dried at 60°C for 4 hours using a fluid-bed type dryer. Thus, granules (B7) were obtained.

Procedure (7-3)

The above granules (7A) and (7B) were mixed in a cross rotary mixer available on the market at room temperature to obtain sample (7-3).

[Preparation of samples (7-1), (7-2) and (7-4) through (7-8)]

Procedure (7-4)

Granules having different water content were prepared in the same manner as in Procedure (7-2), except that the added amount of water, drying temperature and drying time were suitably varied. The resulting granules were mixed with granules (A7) in a cross rotary mixer available on the market at room temperature to obtain samples (7-1), (7-2) and (7-4) through (7-8).

[Preparation of samples (7-9) through (7-11)]

Procedure (7-5)

Granules A' were prepared in the same manner as in Procedure (7-1), except that Fe(III) complex having no crystal water was used instead of exemplified Fe(III) complex used in Procedure (7-1). The same procedures as in Procedure (7-4) was carried out, except that granules A' were used instead of granules (A1) to obtain samples (7-9) through (7-11).

[Preparation of samples (7-12) through (7-40)]

Procedure (7-6)

The same procedures as in Procedure (7-4) was carried out, except that exemplified compounds (II-9), (II-11), (II-6) and (II-13) were used instead of exemplified compounds (II-1) to obtain samples (7-12) through (7-22), (7-23) through (7-33), (7-34) through (7-37) and (7-38) through (7-40), respectively.

The drying weight reduction at 50°C of samples (7-1) through (7-40) was measured. The drying weight reduction is obtained by weight reduced after the samples are heated at 50°C in a shelf-type dryer to the constant weight.

Experiment (7-1)

One hundred gram of each of samples (7-1) through (7-40) were packaged in aluminum packages and tightly sealed. The sealed packages were subjected to a vibration test using a vibration tester BF-UA produced by IDEX Co., Ltd. The vibration was carried out for 30 minutes under condition of 5-67Hz/210sec.

The results are shown in Table 7.

The evaluation criteria are as follows:

◎ : Few powder and especially preferable
○ : Slight powder and excellent
X : marked powder occurrence and impermissible

The more the number of ◎ is, the less powder occurrence.

Experiment (7-2), Storage Stability

One hundred gram of each of samples (7-1) through (7-40) were packaged in aluminum packages, tightly sealed and stored at 50°C for 8 days. After that, the samples was dissolved in deionized water. Insoluble matters and the appearance of the solution were observed. The results are shown in Table 7.

The evaluation criteria are as follows:

◎◎ : Transparent, no precipitations and especially preferable
◎ : Slightly turbid, no precipitations and very preferable
○ : A little turbid, no precipitations and preferable
X : Insoluble matters occurrence, turbid and of no commercial value

Samples evaluated X in Experiment (7-1) or (7-2) are of no commercial value.
The results are shown in Table 7.

Table 7

| Sample No. | APC·Fe *1 | | Drying *2 Weight Reduction wt% | Vibration Test | Storage Stability | |
|---|---|---|---|---|---|---|
| | Compound | Crystal *3 Water Mol ratio | | | | |
| 7-1 | II-1 | 3 | 0.04 | × | ◎ | Comparison |
| 7-2 | II-1 | 3 | 0.12 | ○ | ◎ | Invention |
| 7-3 | II-1 | 3 | 0.31 | ◎-○ | ◎ | Invention |
| 7-4 | II-1 | 3 | 0.52 | ◎ | ◎ | Invention |
| 7-5 | II-1 | 3 | 3.02 | ◎ | ◎ | Invention |
| 7-6 | II-1 | 3 | 5.01 | ◎ | ◎-○ | Invention |
| 7-7 | II-1 | 3 | 9.99 | ◎ | ○ | Invention |
| 7-8 | II-1 | 3 | 14.7 | ◎ | × | Comparison |
| 7-9 | II-1 | 0 | 0.04 | × | ◎ | Comparison |
| 7-10 | II-1 | 0 | 1.02 | × | ◎ | Comparison |
| 7-11 | II-1 | 0 | 3.02 | × | ◎ | Comparison |
| 7-12 | II-9 | 1 | 0.03 | × | ◎ | Comparison |
| 7-13 | II-9 | 1 | 0.12 | ○ | ◎ | Invention |
| 7-14 | II-9 | 1 | 0.31 | ◎-○ | ◎ | Invention |
| 7-15 | II-9 | 1 | 0.53 | ◎ | ◎ | Invention |
| 7-16 | II-9 | 1 | 3.03 | ◎ | ◎ | Invention |
| 7-17 | II-9 | 1 | 5.02 | ◎ | ◎ | Invention |
| 7-18 | II-9 | 1 | 9.98 | ◎ | ◎-○ | Invention |
| 7-19 | II-9 | 1 | 15.03 | ◎ | × | Comparison |
| 7-20 | II-9 | 0 | 0.03 | × | ◎ | Comparison |
| 7-21 | II-9 | 0 | 1.02 | × | ◎ | Comparison |
| 7-22 | II-9 | 0 | 3.01 | × | ◎ | Comparison |
| 7-23 | II-11 | 1 | 0.03 | × | ◎ | Comparison |
| 7-24 | II-11 | 1 | 0.12 | ○ | ◎ | Invention |
| 7-25 | II-11 | 1 | 0.31 | ◎-○ | ◎ | Invention |
| 7-26 | II-11 | 1 | 0.53 | ◎ | ◎ | Invention |
| 7-27 | II-11 | 1 | 3.02 | ◎ | ◎ | Invention |
| 7-28 | II-11 | 1 | 5.01 | ◎ | ◎ | Invention |
| 7-29 | II-11 | 1 | 9.92 | ◎ | ◎-○ | Invention |
| 7-30 | II-11 | 1 | 15.02 | ◎ | × | Comparison |
| 7-31 | II-11 | 0 | 0.03 | × | ◎ | Comparison |
| 7-32 | II-11 | 0 | 1.03 | × | ◎ | Comparison |
| 7-33 | II-11 | 0 | 3.02 | × | ◎ | Comparison |
| 7-34 | II-6 | 1 | 0.03 | × | ○ | Comparison |
| 7-35 | II-6 | 1 | 1.02 | ◎ | ○ | Invention |
| 7-36 | II-6 | 0 | 0.05 | × | ◎ | Comparison |
| 7-37 | II-6 | 0 | 1.02 | × | ◎-○ | Comparison |
| 7-38 | II-13 | 2 | 0.03 | × | × | Comparison |
| 7-39 | II-13 | 2 | 1.01 | ◎ | ○ | Invention |
| 7-40 | II-13 | 0 | 1.02 | × | ○ | Comparison |

*1 APC·Fe : Amino polycarboxylic acid Fe(III) complex

*2 the drying weight reduction at 50°C

*3 the ratio of crystal water to APC·Fe (the mole ratio of moisture such as crystal water to Fe)

As is apparent from Table 7, the inventive samples give excellent vibration test results, and excellent storage stability.

Example 8

The experiments and evaluations were carried out in the same manner as in Example 1, except that Exemplified compounds (II-2), (II-3), (II-9), and (II-10) were used instead of Fe(III) complex used in Example 7. The same results as Example 7 were obtained.

Example 9

Samples were prepared as shown below.

| A part | |
|---|---|
| Exemplified compound (Amino polycarboxylic acid Fe(III) complex) shown in Table 8 | 1200 g |
| Ethylenediaminetetraacetic acid | 100 g |
| Pineflow (produced by Matsutani Kagaku Co.) | 100 g |

| B part | |
|---|---|
| Ammonium thiosulfate | 1400 g |
| Sodium thiosulfate | 160 g |
| Sodium metabisulfite | 300 g |
| Sodium sulfite | 300 g |
| Ethylenediaminetetraacetic acid | 200 g |
| Pineflow (produced by Matsutani Kagaku Co.) | 100 g |

Procedure (9-1)

Granules of A part were prepared in the same manner as in Procedure (7-1), except that the mole ratio of the crystal water in the Fe(III) complexes was dried to be as shown in Table 2. Thereafter, procedures were carried out in the same manner as in Example 1 to obtain samples (9-1) through (9-4) and (9-17). Further, Iron (III) complexes (II-9), (II-12) and (II-13) were subjected to the same procedures as above to obtain samples (9-5) through (9-8), (9-9) through (9-12) and (9-13) through (9-16), respectively.

Experiment (9-1)

The above obtained samples were evaluated in the same manner as in Experiments (7-1) and (7-2). The results are shown in Table 8.

Experiment (9-2)

Fine powder occurrence tests under open condition

Samples (9-1) through (9-17) were stored at 25°C and 40%RH for 48 hours under open condition. Thereafter, the fine powder occurrence and the appearance of the samples were observed. The results are shown in Table 8. The evaluation criteria were the same as Experiment 7-1.

Table 8

| Sample No. | APC•Fe | | Drying Weight Reduction wt% | Vibration Test | Storage Stability | Fine Powder Occurrence Under Open Condition | |
|---|---|---|---|---|---|---|---|
| | Exemplified Compound | Crystal Water Mol ratio | | | | | |
| 9-1 | II-1 | 0 | 1.02 | X | ◎ | X | Comparison |
| 9-2 | II-1 | 1.0 | 1.04 | ◎-○ | ◎ | ○ | Invention |
| 9-3 | II-1 | 2.1 | 1.03 | ◎ | ◎ | ◎-○ | Invention |
| 9-4 | II-1 | 3.0 | 1.02 | ◎ | ◎ | ◎ | Invention |
| 9-5 | II-9 | 0 | 0.98 | X | ◎ | X | Comparison |
| 9-6 | II-9 | 0.3 | 1.02 | ◎ | ◎ | ○ | Invention |
| 9-7 | II-9 | 0.5 | 1.01 | ◎ | ◎ | ◎-○ | Invention |
| 9-8 | II-9 | 1.0 | 0.97 | ◎ | ◎ | ◎ | Invention |
| 9-9 | II-12 | 0 | 1.02 | X | ◎ | X | Comparison |
| 9-10 | II-12 | 0.3 | 0.98 | ◎ | ◎ | ○ | Invention |
| 9-11 | II-12 | 0.6 | 1.00 | ◎ | ◎ | ◎-○ | Invention |
| 9-12 | II-12 | 1.0 | 0.97 | ◎ | ◎ | ◎ | Invention |
| 9-13 | II-14 | 0 | 1.02 | X | ◎ | X | Comparison |
| 9-14 | II-14 | 0.4 | 0.99 | ◎-○ | ◎-○ | ○ | Invention |
| 9-15 | II-14 | 0.7 | 1.01 | ◎ | ○ | ◎-○ | Invention |
| 9-16 | II-14 | 1.0 | 0.99 | ◎ | ○ | ◎ | Invention |
| 9-17 | II-1 | 2.1 | 12.3 | ◎ | X | ◎-○ | Comparison |

As is apparent from Table 8, the inventive samples give excellent vibration test results, excellent storage stability and less powder occurrence under open condition.

Example 10

Procedure (10-1)

Sample (7-4) in Example 1 was subjected to screening, and screened with a sieve having a 149 μm mesh (JIS). Thereafter, granules having a particle diameter of not less than 149 μm and granules having a particle diameter of less than 149 μm were mixed so that the weight ratio of the granules having a particle diameter of less than 149 μm was shown in Table 9. Thus, samples (10-1) through (10-6) were obtained. Sample (7-8) was subjected to the same procedures as above to obtain samples (10-7) and (10-8).

Experiment (10-1)

Samples (10-1) through (10-8) were evaluated in the same manner as in Experiments (7-1). The results are shown in Table 9.

Table 9

| Sample No. | APC•Fe | | Weight Ratio* wt% | Vibration Test | Storage Stability | |
|---|---|---|---|---|---|---|
| | Exemplified Compound | Crystal Water Mol ratio | | | | |
| 10-1 | II-1 | 3 | 0 | 1.02 | ◎◎ | Invention |
| 10-2 | II-1 | 3 | 5 | 1.02 | ◎◎ | Invention |
| 10-3 | II-1 | 3 | 10 | 1.02 | ◎◎-◎ | Invention |
| 10-4 | II-1 | 3 | 15 | 1.02 | ◎ | Invention |
| 10-5 | II-1 | 3 | 30 | 1.02 | ◎-○ | Invention |
| 10-6 | II-1 | 3 | 40 | 1.02 | ○ | Invention |
| 10-7 | II-1 | 3 | 0 | 14.7 | X | Comparison |
| 10-8 | II-1 | 3 | 30 | 14.7 | X | Comparison |

* Weight ratio of granules having a particle diameter of less than 149 µm

As is apparent from Table 9, in the inventive samples the less granules having a particle diameter of less than 149 µm, the better storage stability. The ratio is preferably 30 % or less.

Example 11

| A part | |
|---|---|
| Exemplified compound (Fe(III) complex) shown in Tables 10 and 11 | 700 g |
| Maleic acid | 150 g |
| Saccharide or Water-Soluble Polymer | See Tables 10 and 11 |

| B part | |
|---|---|
| Potassium thiosulfate | 1000 g |
| Potassium sulfite | 300 g |
| Potassium metabisulfite | 50 g |
| Ethylenediaminetetraacetic acid | 50 g |
| Saccharide or Water-Soluble Polymer | See Tables 10 and 11 |

Procedure (11-1)

In a hammer-mill available on the market the compounds of A part independently were pulverized to have an average particle size of not more than 50 µm. The resulting powders were mixed in a cross rotary mixer available on the market at room temperature and the mixture was granulated for 8 minutes in a stirring granulator available on the market by adding 50 ml of deionized water. The resulting granules were dried at 40°C for 3 hours using a fluid-bed type dryer available on the market. Thus, granules (A11) were obtained.

Procedure (11-2)

In the same manner as in above the compounds of B part independently were pulverized and mixed. The mixture was granulated for 8 minutes in a stirring granulator by adding 70 ml of water. The resulting granules were dried at 60 ° C for 4 hours using a fluid-bed type dryer. Thus, granules (B11) were obtained.

Procedure (11-3)

The above granules (A11) and (B11) were mixed in a cross rotary mixer available on the market at room temperature for 7 minutes to obtain sample (11-1).

[Preparation of samples (11-2) through (11-20)]

Procedure (11-4)

Procedures were carried out in the same manner as in Procedures (11-1) to (11-3), except that saccharides or water-soluble polymers were varied as shown Tables 10 and 11. Thus, samples (11-2) through (11-20) were obtained.

[Preparation of samples (11-21) through (11-24)]

Procedure (11-5)

| | |
|---|---|
| Exemplified compound (EDTA-Na•$3H_2O$) | 700 g |
| Maleic acid | 150 g |
| Potassium thiosulfate | 1000 g |
| Potassium sulfite | 300 g |
| Potassium metabisulfite | 50 g |
| Ethylenediaminetetraacetic acid | 50 g |
| Saccharide or Water-Soluble Polymer | See Tables 10 and 11 |

In a hammer-mill available on the market the above compounds independently were pulverized to have an average particle size of not more than 50 µm. The resulting powders were mixed in a cross rotary mixer available on the market at room temperature and the mixture was granulated for 8 minutes in a stirring granulator available on the market by adding 500 ml of deionized water. The resulting granules were dried at 40 ° C for 3 hours using a fluid-bed type dryer available on the market. Thus, granules were obtained. The same procedures were carried out varying the amount of saccharides or water-soluble polymers to obtain samples (11-21) through (11-24).

[Preparation of samples (11-25) through (11-32)]

Procedure (11-6)

The same procedures as above were carried, except that amino polycarboxylic acid Fe(III) complexes as shown in Table 11 were used. Thus, samples (11-25) through (11-32) were obtained.

The evaluation was carried out in the same manner as in Example 7. The results are shown in Tables 10 and 11.

Experiment (11-2) Adherence Test to a Package

In the similar manner as in Experiment 7 100 g of each of samples (11-1) through (11-32) were packaged in polyethylene packages, tightly sealed and stored at 55 ° C for 7 days. Thereafter, the packages was uncovered and the samples were dropped from the packages. Then, the adherence of the samples to the packages was observed. The results are shown in Tables 10 and 11.

The evaluation criteria are as follows:

◎ : No adherence of the samples to the packages

○ : Slight adherence of the samples to the packages but the adhered readily removed and preferable

X : Much adherence of the samples to the packages and the adhering powder is not removed when the packages were strongly struck.

The samples evaluated X are very low in commercial value.

Table 10

| Sample No. | APC·Fe | | Saccharides or Water-Soluble Polymers | | | | | Drying Weight Reduction wt% | Powder Occuerrence | Adherence to Packages | Storage Stability |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | A Part | | B Part | | Total Content of A part + B part wt% | | | | |
| | Exemplified Compound | Crystal Water Mol ratio | Exemplified Compound | Content wt% | Exemplified Compound | Content wt% | | | | | |
| 11-1 | II-1 | 3 | B-14 | 0.5 | B-14 | 0.5 | 1 | 1.04 | ○ | ◎ | ○ |
| 11-2 | II-1 | 3 | B-14 | 1 | B-14 | 0 | 1 | 1.03 | ○ | ◎ | ◎ |
| 11-3 | II-1 | 3 | B-14 | 3 | B-14 | 0 | 3 | 1.01 | ◎-○ | ◎ | ◎ |
| 11-4 | II-1 | 3 | B-14 | 5 | B-14 | 0 | 5 | 1.02 | ◎ | ◎ | ◎ |
| 11-5 | II-1 | 3 | B-14 | 10 | B-14 | 0 | 10 | 1.02 | ◎ | ◎ | ◎ |
| 11-6 | II-1 | 3 | B-14 | 15 | B-14 | 0 | 15 | 1.03 | ◎ | ◎ | ◎ |
| 11-7 | II-1 | 3 | B-14 | 30 | B-14 | 0 | 30 | 1.01 | ◎ | ○ | ◎ |
| 11-8 | II-1 | 3 | B-14 | 0 | B-14 | 1 | 1 | 0.99 | ○ | ◎ | ○ |
| 11-9 | II-1 | 3 | B-14 | 0 | B-14 | 5 | 5 | 1.03 | ◎-○ | ◎ | ◎ |
| 11-10 | II-1 | 3 | B-14 | 0 | B-14 | 10 | 10 | 1.02 | ◎-○ | ◎ | ◎ |
| 11-11 | II-1 | 3 | B-14 | 3 | B-14 | 3 | 6 | 0.98 | ◎ | ◎ | ◎ |
| 11-12 | II-1 | 3 | B-14 | 5 | B-14 | 5 | 10 | 1.01 | ◎ | ◎ | ◎ |
| 11-13 | II-1 | 3 | B-18 | 2.5 | B-18 | 2.5 | 5 | 1.00 | ◎ | ◎ | ◎ |
| 11-14 | II-1 | 3 | B-18 | 5 | B-18 | 5 | 10 | 2.00 | ◎ | ◎ | ◎ |
| 11-15 | II-1 | 3 | C-5 | 2.5 | C-5 | 2.5 | 5 | 1.02 | ◎ | ◎ | ◎ |
| 11-16 | II-1 | 3 | C-6 | 3 | C-6 | 3 | 6 | 0.50 | ◎ | ◎ | ◎ |

Table 11

| Sample No. | APC·Fe | | Saccharides or Water-Soluble Polymers | | | | | Drying Weight Reduction | Powder Occuerrence | Adherence to Packages | Storage Stability |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | A Part | | B Part | | Total Content of A part + B part wt% | | | | |
| | Exemplified Compound | Crystal Water Mol ratio | Exemplified Compound | Content wt% | Exemplified Compound | Content wt% | | wt% | | | |
| 11-17 | II-1 | 3.0 | C-1 | 3 | C-1 | 3 | 6 | 1.03 | ◎ | ○ | ◎ |
| 11-18 | II-1 | 3.0 | C-7 | 3 | C-6 | 3 | 6 | 0.60 | ◎ | ◎ | ◎ |
| 11-19 | II-1 | 3.0 | B-2 | 5 | B-2 | 5 | 10 | 0.80 | ◎-○ | ◎-○ | ◎-○ |
| 11-20 | II-1 | 3.0 | A-11 | 5 | A-11 | 5 | 10 | 1.52 | ◎ | ◎-○ | ◎-○ |
| 11-21 | II-1 | 3.0 | B-14 | 3 | - | - | 3 | 1.03 | ○ | ○ | ○ |
| 11-22 | II-1 | 3.0 | B-14 | 5 | - | - | 5 | 1.01 | ○ | ○ | ○ |
| 11-23 | II-1 | 3.0 | B-14 | 10 | - | - | 10 | 0.98 | ○ | ○ | ○ |
| 11-24 | II-1 | 3.0 | B-14 | 15 | - | - | 15 | 1.02 | ◎-○ | ○ | ○ |
| 11-25 | II-12 | 1.0 | B-14 | 3 | B-14 | 3 | 6 | 0.87 | ◎ | ◎ | ◎ |
| 11-26 | II-9 | 1.0 | B-14 | 3 | B-14 | 3 | 6 | 1.02 | ◎ | ◎ | ◎ |
| 11-27 | II-13 | 1.0 | B-14 | 3 | B-14 | 3 | 6 | 1.23 | ◎ | ◎ | ◎-○ |
| 11-28 | II-16 | 1.5 | B-14 | 3 | B-14 | 3 | 6 | 0.98 | ◎-○ | ◎ | ◎ |
| 11-29 | II-6 | 1.0 | B-14 | 3 | B-14 | 3 | 6 | 1.02 | ◎-○ | ◎ | ○ |
| 11-30 | II-3 | 2.0 | B-14 | 3 | B-14 | 3 | 6 | 0.97 | ◎ | ◎ | ◎ |
| 11-31 | II-5 | 1.0 | B-14 | 3 | B-14 | 3 | 6 | 1.13 | ◎ | ◎ | ◎ |
| 11-32 | II-3 | 1.0 | B-14 | 3 | B-14 | 3 | 6 | 0.98 | ○ | ◎ | ◎ |

As is apparent from Tables 10 and 11, the inventive samples using saccharides or water-soluble polymers in an amount of 1 to 30 wt% shows further improved results. Polyethylene glycol of #2000, #4000 or #6000 is preferable in less powder adherence as compared with polyethylene glycol of #600.

Example 12

Procedure (12-1)

Sodium N-lauroylsarcosine was added in an amount of 0.5 % by weight to each of samples (7-1) through (7-11) in Example 7 and mixed for 3 minutes. The resulting mixture was compression-tableted in an amount of 11 g per tablet making use of a tableting machine in which Clean Press Correct 18K manufactured by Kikusui Mfg. Works was modified to obtain a tablet having a diameter of 30 mm. Thus, tablets for a solid bleach-fixing composition (12-1) through (12-11) were obtained.

Procedure (12-2)

In samples (7-1) through (7-11) in Example 7 compounds of A part were mixed for 10 minutes without granulating, and granules of B part (the same as Example 7) and sodium N-lauroylsarcosine was added and mixed for 3 minutes. The resulting mixture was compression-tableted in the same manner as in Procedure (12-1) to have a weight per tablet of 12 g and a diameter of 30 mm. Thus, tablets for a solid bleach-fixing composition (12-12) through (12-22) were obtained.

Procedure (12-3)

The compounds of B part in Example 7 were mixed and exposed to moisture under high humidity to increase the weight and dried. The resulting mixture was mixed with granules of A part in Example 7 and sodium N-lauroylsarcosine was added and mixed for 3 minutes. The resulting mixture was compression-tableted in the same manner as in Procedure (12-1) to have a weight per tablet of 12 g and a diameter of 30 mm. Thus, tablets for a solid bleach-fixing composition (12-23) through (12-28) were obtained.

Procedure (12-4)

The weight increasing compounds of B part obtained in Procedure (12-4) were mixed with compounds of A part for 10 minutes and further mixed with sodium N-lauroylsarcosine for 3 minutes. The resulting mixture was compression-tableted in the same manner as in Procedure (12-1) to have a weight per tablet of 12 g and a diameter of 30 mm. Thus, tablets for a solid bleach-fixing composition (12-29) through (12-33) were obtained.

Procedure (12-5)

The procedures were carried out in the same manner as above, except that Exemplified compound (II-3) was used instead of Exemplified compound (II-1). weight increasing compounds of B part obtained in Procedure Thus, tablets for a solid bleach-fixing composition (12-34) through (12-40) were obtained.

The drying weight reduction at 50 °C of Table 11 was obtained by measuring samples after tableting pulverized with a mortar, but samples before tableting was substantially the same value.

Experiment (12-1)

Five tablets were placed in a tightly sealed polypropylene box, and were subjected to vibration test and evaluated in the same manner as in Experiment (7-1).

Experiment (12-2)

One tablet was placed in an aluminum package and tightly sealed and evaluated in the same manner as in Experiment (7-2).

Experiment (12-3) Tests under open condition

Samples were stored at 25 °C and 40%RH for 48 hours under open condition in the same manner as in Experiment (9-2). Thereafter, the fine powder occurrence and the appearance of the samples were observed. When the samples was taken by a hand, the adherence to the hand was observed.

The evaluation criteria were as follows:

◎◎ : No cracks and no adherence to the hand, especially preferable
◎ : No cracks and slight adherence to the hand, more preferable
○ : Slight cracks and slight adherence to the hand, preferable
X : Big cracks and Much adherence to the hand, not preferable
X X : broken and no initial shape, and cannot be taken by a hand

The samples evaluated X or X X are very low in commercial value.

Experiment (12-4) Rotation Test

Five tablets were placed in an abrasion tester produced by Kayagaki Rikakogyo Co., Ltd. which was modified and subjected to rotation test. The rotated tablets were observed.

The evaluation criteria were as follows:

◎◎ : No change of the appearance, especially preferable
◎ : Slight powder but no defects on the surface
○ : A little powder and slight defects on the surface
X : Much powder and some tablets broken

The results are shown in Table 12.

Table 12

| Sample No. | APC·Fe |  | Drying Weight Reduction | Granuration procedure yes no |  | Vibration test | Storage Stability | Open condition | Rotation test | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
|  | Exemplified Compound | Crystal Water Mol ratio |  | A Part | B Part |  |  |  |  |  |
| 12-1 | II-1 | 3 | 0.04 | Yes | Yes | × | ◎◎ | ○ | × | Comparison |
| 12-2 | II-1 | 3 | 0.12 | Yes | Yes | ○ | ◎◎ | ◎ | ◎ | Invention |
| 12-3 | II-1 | 3 | 0.31 | Yes | Yes | ◎ | ◎◎ | ◎ | ◎◎ | Invention |
| 12-4 | II-1 | 3 | 0.52 | Yes | Yes | ◎◎ | ◎◎ | ◎◎ | ◎◎ | Invention |
| 12-5 | II-1 | 3 | 3.02 | Yes | Yes | ◎◎ | ◎◎ | ◎◎ | ◎◎ | Invention |
| 12-6 | II-1 | 3 | 5.01 | Yes | Yes | ◎◎ | ◎ | ◎◎ | ◎ | Invention |
| 12-7 | II-1 | 3 | 10.02 | Yes | Yes | ◎ | ◎-○ | ◎◎ | ○ | Invention |
| 12-8 | II-1 | 3 | 14.7 | Yes | Yes | ◎ | × | ◎◎ | × | Comparison |
| 12-9 | II-1 | 0 | 0.04 | Yes | Yes | × | ◎ | × | × | Comparison |
| 12-10 | II-1 | 0 | 1.02 | Yes | Yes | × | ◎ | × | × | Comparison |
| 12-11 | II-1 | 0 | 3.02 | Yes | Yes | × | ◎ | × | ○ | Comparison |
| 12-12 | II-1 | 3 | 0.04 | No | Yes | × | ◎ | ○ | × | Comparison |
| 12-13 | II-1 | 3 | 0.12 | No | Yes | ○ | ◎ | ◎-○ | ○ | Invention |
| 12-14 | II-1 | 3 | 0.51 | No | Yes | ◎ | ◎ | ◎ | ◎ | Invention |
| 12-15 | II-1 | 3 | 1.02 | No | Yes | ◎◎ | ◎ | ◎ | ◎ | Invention |
| 12-16 | II-1 | 3 | 3.02 | No | Yes | ◎◎ | ◎ | ◎ | ◎ | Invention |
| 12-17 | II-1 | 3 | 5.01 | No | Yes | ◎◎ | ◎ | ◎ | ◎ | Invention |
| 12-18 | II-1 | 3 | 10.02 | No | Yes | ◎ | ○ | ◎ | ◎ | Invention |
| 12-19 | II-1 | 3 | 14.7 | No | Yes | ◎ | × | ◎ | × | Comparison |
| 12-20 | II-1 | 0 | 0.04 | No | Yes | × | ◎ | × | × | Comparison |
| 12-21 | II-1 | 0 | 1.02 | No | Yes | × | ◎-○ | × | × | Comparison |
| 12-22 | II-1 | 0 | 3.02 | No | Yes | × | ○ | × | × | Comparison |
| 12-23 | II-1 | 3 | 0.04 | Yes | No | × | ◎ | ○ | × | Comparison |
| 12-24 | II-1 | 3 | 0.33 | Yes | No | ○ | ◎ | ○ | ○ | Invention |
| 12-25 | II-1 | 3 | 0.52 | Yes | No | ◎ | ◎ | ◎-○ | ◎-○ | Invention |
| 12-26 | II-1 | 3 | 3.04 | Yes | No | ◎ | ◎ | ◎-○ | ◎-○ | Invention |
| 12-27 | II-1 | 3 | 5.03 | Yes | No | ◎ | ◎-○ | ○ | ○ | Invention |
| 12-28 | II-1 | 3 | 15.02 | Yes | No | ◎ | × | ◎-○ | × | Comparison |
| 12-29 | II-1 | 3 | 0.04 | No | No | × | ◎-○ | ○ | × | Comparison |

Table 12 (continued)

| Sample No. | APC·Fe |  | Drying Weight Reduction | Granuration procedure yes no |  | Vibration test | Storage Stability | Open condition | Rotation test | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|
|  | Exemplified Compound | Crystal Water Mol ratio |  | A Part | B Part |  |  |  |  |  |
| 12-30 | II-1 | 3 | 0.33 | No | No | ○ | ◎-○ | ○ | ○ | Invention |
| 12-31 | II-1 | 3 | 3.04 | No | No | ◎-○ | ○ | ○ | ○ | Invention |
| 12-32 | II-1 | 3 | 5.03 | No | No | ○ | ○ | ○ | ○ | Invention |
| 12-33 | II-1 | 3 | 15.02 | No | No | ○ | × | ◎-○ | × | Comparison |
| 12-34 | II-3 | 2 | 0.04 | Yes | Yes | × | ◎◎ | ○ | × | Comparison |
| 12-35 | II-3 | 2 | 0.12 | Yes | Yes | ○ | ◎◎ | ◎ | ◎ | Invention |
| 12-36 | II-3 | 2 | 0.31 | Yes | Yes | ◎ | ◎◎ | ◎ | ◎◎ | Invention |
| 12-37 | II-3 | 2 | 0.52 | Yes | Yes | ◎◎ | ◎◎ | ◎◎ | ◎◎ | Invention |
| 12-38 | II-3 | 2 | 3.04 | Yes | Yes | ◎◎ | ◎◎ | ◎◎ | ◎◎ | Invention |
| 12-39 | II-3 | 2 | 5.02 | Yes | Yes | ◎◎ | ◎ | ◎◎ | ◎ | Invention |
| 12-40 | II-3 | 2 | 15.02 | Yes | Yes | ○ | × | ◎◎ | × | Comparison |
| 12-41 | II-3 | 0 | 1.03 | Yes | Yes | × | ◎ | ◎◎ | × | Comparison |

As is apparent from Table 12, when the part containing a granulated bleaching agent or a granulated fixing agent is used, the bleach-fixing composition gives more preferable results. The composition shows far more preferable results as compared with one in which a bleaching agent or a fixing agent is granulated separately. Further, the tablets show especially preferable results as compared with Example 7.

Example 13

| A part | |
|---|---|
| Fe(III) complex (Exemplified compound) | 1200 g |
| Saccharide or Water-Soluble Polymer | See Tables 13 to 15 |
| Sodium carbonate monohydrate | 500 g |

| B part | |
|---|---|
| Ammonium thiosulfate | 720 g |
| Sodium thiosulfate | 80 g |
| Sodium metabisulfite | 300 g |
| Ethylenediaminetetraacetic acid | 50 g |
| Saccharide or Water-Soluble Polymer | See Tables 13 to 15 |

| C part | |
|---|---|
| Water-Soluble Polymer | See Tables 13 to 15 |

Procedure (13-1)

In a hammer-mill available on the market the compounds of A part independently were pulverized to have an average particle size of not more than 50 μm. The resulting powders were mixed in a cross rotary mixer available on the market at room temperature and the mixture was granulated for 8 minutes in a stirring granulator available on the market by adding 50 ml of water. The resulting granules were dried at 40 °C for 3 hours using a fluid-bed type dryer available on the market. Thus, granules (A13) were obtained.

Procedure (13-2)

In the same manner as in Procedure (13-1) the compounds of B part independently were pulverized and mixed. The mixture was granulated for 8 minutes in a stirring granulator by adding 50 ml of water. The resulting granules were dried at 55 °C for 4 hours using a fluid-bed type dryer. Thus, granules (B13) were obtained.

Procedure (13-3)

The above granules (A13), (B13) and C part were mixed for 10 minutes and further mixed with a 0.5 wt% sodium N-lauroylsarcosine for 3 minutes. The resulting mixture was compression-tableted in the same manner as in Procedure (12-1) to have a weight per tablet of 12 g and a diameter of 30 mm. Thus, tablets for a solid bleach-fixing composition (13-3).

Procedure (13-4)

Procedures were carried out in the same manner as in procedures (13-1) through (13-3), except that exemplified compounds as shown in Tables 13 and 14 were used. Thus, tablets for a solid bleach-fixing composition (13-1) through (13-48) were obtained. The adding amount of water, drying temperature and drying time were adjusted to give the weight reduction shown in Tables 13 through 15. The weight reduction at 50 °C were measured in the same manner as in Example 12.

Experiment (13-1)

The storage and rotation tests were carried out in the same manner as in Example 12.

Experiment (13-2) Sliding property

One tablet of the samples was placed in an aluminium package and tightly sealed and were stored at 50°C for 2 weeks. The resulting tablets were placed on a polyethylene plate at 25°C and 45%RH. The polyethylene plate was fixed using Static Friction Tester HEIDON-10 (produced by HEIDON Co.) and the angle $\theta$ at which the samples move on the polyethylene plate was measured. Three tablets of each sample were measured.

The evaluation criteria are as follows:

◎◎ : The tablet slides at less than 20°.  
◎ : The tablet slides at 20° to less than 25°.  
○ : The tablet slides at 25° to less than 30°.  
X : The tablet slides at more than 30°.

The tablet sliding at a less angle is more preferable in view of handling. In the Tables two kinds of signs show a different evaluation result in three time measurement.

The results are shown in Tables 13 through 15.

Table 13

| Sample No. | APC·Fe | | Drying Weight Reduction wt% | Saccharides or Water-Soluble Polymers | | | | | | | Storage Stability | Rotation Test | Sliding Test | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | A part | | B part | | C part | | Total Content of A + B + C, wt% | | | | |
| | Exemplified Compounds | Crystal Water Mol ratio | | Exemplified Compounds | Content wt% | Exemplified Compounds | Content wt% | Exemplified Compounds | Content wt% | | | | | |
| 13-1 | II-1 | 3 | 0.04 | B-14 | 3 | B-14 | 3 | C-6 | 5 | 11 | ◎◎ | × | ◎◎ | Comp. |
| 13-2 | II-1 | 3 | 0.11 | B-14 | 3 | B-14 | 3 | C-6 | 5 | 11 | ◎◎ | ◎ | ◎◎ | Inv. |
| 13-3 | II-1 | 3 | 0.50 | B-14 | 3 | B-14 | 3 | C-6 | 5 | 11 | ◎◎ | ◎◎ | ◎◎ | Inv. |
| 13-4 | II-1 | 3 | 3.02 | B-14 | 3 | B-14 | 3 | C-6 | 5 | 11 | ◎◎ | ◎◎ | ◎◎ | Inv. |
| 13-5 | II-1 | 3 | 5.01 | B-14 | 3 | B-14 | 3 | C-6 | 5 | 11 | ◎ | ◎ | ◎ | Inv. |
| 13-6 | II-1 | 3 | 10.03 | B-14 | 3 | B-14 | 3 | C-6 | 5 | 11 | ◎-○ | ○ | ◎ | Inv. |
| 13-7 | II-1 | 3 | 15.01 | B-14 | 3 | B-14 | 3 | C-6 | 5 | 11 | × | × | × | Comp. |
| 13-8 | II-1 | 3 | 1.04 | B-14 | 0.1 | B-14 | 0.1 | C-6 | 0.2 | 0.4 | ◎ | ◎-○ | ◎ | Inv. |
| 13-9 | II-1 | 3 | 1.02 | B-14 | 0.2 | B-14 | 0.3 | C-6 | 0.5 | 1.0 | ◎ | ◎ | ◎ | Inv. |
| 13-10 | II-1 | 3 | 1.03 | B-14 | 1 | B-14 | 1 | C-6 | 1 | 3.0 | ◎◎ | ◎ | ◎◎-◎ | Inv. |
| 13-11 | II-1 | 3 | 0.98 | B-14 | 2 | B-14 | 1 | C-6 | 2 | 5 | ◎◎ | ◎◎ | ◎◎ | Inv. |
| 13-12 | II-1 | 3 | 0.99 | B-14 | 5 | B-14 | 5 | C-6 | 5 | 15 | ◎◎ | ◎◎ | ◎◎ | Inv. |
| 13-13 | II-1 | 3 | 1.02 | B-14 | 7 | B-14 | 7 | C-6 | 7 | 21 | ◎ | ◎ | ◎ | Inv. |
| 13-14 | II-1 | 3 | 1.00 | B-14 | 10 | B-14 | 10 | C-6 | 10 | 30 | ◎ | ◎-○ | ◎-○ | Inv. |
| 13-15 | II-1 | 3 | 1.01 | B-14 | 12 | B-14 | 12 | C-6 | 12 | 36 | ◎ | ○ | ○ | Inv. |
| 13-16 | II-1 | 3 | 0.98 | B-18 | 2 | B-18 | 1 | C-1 | 2 | 5 | ◎◎ | ◎◎ | ○ | Inv. |

Comp.: Comparison Inv.: Invention

Table 14

| Sample No. | APC·Fe | | Drying Weight Reduction wt% | Saccharides or Water-Soluble Polymers | | | | | | | Storage Stability | Rotation Test | Sliding Test | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | A Part | | B Part | | C Part | | Total Content of A + B + C, wt% | | | | |
| | Exemplified Compounds | Crystal Water Mol ratio | | Exemplified Compounds | Content wt% | Exemplified Compounds | Content wt% | Exemplified Compounds | Content wt% | | | | | |
| 13-17 | II-1 | 3 | 1.02 | B-14 | 2 | B-14 | 1 | C-2 | 2 | 5 | ◎◎ | ◎◎ | ○ | Inv. |
| 13-18 | II-1 | 3 | 1.03 | B-14 | 2 | B-14 | 1 | C-4 | 2 | 5 | ◎◎ | ◎◎ | ◎-○ | Inv. |
| 13-19 | II-1 | 3 | 0.99 | B-14 | 2 | B-14 | 1 | C-3 | 2 | 5 | ◎◎ | ◎◎ | ◎◎ | Inv. |
| 13-20 | II-1 | 3 | 1.01 | B-14 | 2 | B-14 | 1 | C-7 | 2 | 5 | ◎◎ | ◎◎ | ◎◎ | Inv. |
| 13-21 | II-1 | 3 | 1.04 | B-14 | 2 | B-14 | 1 | C-8 | 2 | 5 | ○ | ◎◎ | ◎-○ | Inv. |
| 13-22 | II-1 | 3 | 0.98 | B-14 | 2 | B-14 | 1 | C-16 | 2 | 5 | ◎ | ◎◎ | ◎◎ | Inv. |
| 13-23 | II-1 | 3 | 0.97 | B-14 | 2 | B-14 | 1 | C-14 | 2 | 5 | ◎ | ◎◎ | ◎◎ | Inv. |
| 13-24 | II-1 | 3 | 1.03 | C-14 | 2 | C-14 | 2 | C-14 | 1 | 5 | ◎ | ◎◎ | ◎-○ | Inv. |
| 13-25 | II-1 | 3 | 1.04 | B-14 | 15 | B-14 | 15 | C-6 | 5 | 35 | ◎◎ | ◎◎ | ○ | Inv. |
| 13-26 | II-1 | 3 | 1.04 | B-14 | 5 | B-14 | 0 | C-6 | 5 | 10 | ◎ | ◎◎ | ◎ | Inv. |
| 13-27 | II-1 | 3 | 1.04 | B-14 | 0 | B-14 | 5 | C-6 | 5 | 10 | ◎ | ◎ | ◎ | Inv. |
| 13-28 | II-1 | 3 | 1.04 | B-14 | 3 | B-14 | 3 | C-6 | 10 | 16 | ◎ | ◎-○ | ◎ | Inv. |
| 13-29 | II-1 | 3 | 1.04 | B-18 | 4 | B-18 | 4 | C-6 | 5 | 13 | ◎ | ◎◎ | ◎ | Inv. |
| 13-30 | II-1 | 3 | 1.04 | B-2 | 4 | B-2 | 4 | C-6 | 5 | 13 | ◎◎ | ◎◎ | ◎ | Inv. |
| 13-31 | II-1 | 3 | 1.04 | A-11 | 4 | A-11 | 4 | C-5 | 5 | 13 | ◎◎ | ◎ | ◎ | Inv. |

Inv.:Invention

Table 15

| Sample No. | APC·Fe | | Drying Weight Reduction wt% | Saccharides or Water-Soluble Polymers | | | | | | | Storage Stability | Rotation Test | Sliding Test | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | A Part | | B Part | | C Part | | Total Content of A + B + C, wt% | | | | |
| | Exemplified Compounds | Crystal Water Mol ratio | | Exemplified Compounds | Content wt% | Exemplified Compounds | Content wt% | Exemplified Compounds | Content wt% | | | | | |
| 13-32 | II-1 | 3 | 1.04 | A-19 | 4 | A-19 | 4 | C-5 | 5 | 13 | ◎ | ◎ | ◎-○ | Inv. |
| 13-33 | II-1 | 3 | 1.04 | C-6 | 4 | B-14 | 4 | C-5 | 5 | 13 | ◎◎ | ◎ | ◎◎ | Inv. |
| 13-34 | II-1 | 3 | 1.04 | B-14 | 4 | C-6 | 4 | C-5 | 5 | 13 | ◎ | ◎ | ◎◎ | Inv. |
| 13-35 | II-9 | 1 | 1.01 | - | | - | | C-6 | 5 | 5 | ◎◎ | ◎ | ◎ | Inv. |
| 13-36 | II-9 | 1 | 1.01 | B-14 | 4 | B-14 | 4 | C-6 | 5 | 13 | ◎◎ | ◎◎ | ◎◎ | Inv. |
| 13-37 | II-3 | 2 | 1.03 | - | | - | | C-6 | 5 | 5 | ◎◎ | ◎ | ◎ | Inv. |
| 13-38 | II-3 | 2 | 1.02 | B-14 | 4 | B-14 | 4 | C-6 | 5 | 13 | ◎◎ | ◎◎-◎ | ◎◎ | Inv. |
| 13-39 | II-11 | 1 | 1.01 | - | | - | | C-6 | 5 | 5 | ◎◎ | ◎-○ | ◎ | Inv. |
| 13-40 | II-11 | 1 | 1.00 | B-18 | 4 | B-14 | 4 | C-6 | 5 | 13 | ◎◎ | ◎ | ◎◎ | Inv. |
| 13-41 | II-13 | 2 | 1.02 | - | | - | | C-6 | 5 | 5 | ◎-○ | ◎ | ◎ | Inv. |
| 13-42 | II-13 | 2 | 1.01 | B-2 | 4 | B-2 | 4 | C-6 | 5 | 13 | ◎ | ◎ | ◎◎ | Inv. |
| 13-43 | II-12 | 2 | 1.02 | - | | - | | C-6 | 5 | 5 | ◎ | ◎ | ◎ | Inv. |
| 13-44 | II-12 | 2 | 1.02 | B-14 | 4 | B-14 | 4 | C-6 | 5 | 13 | ◎ | ◎ | ◎◎ | Inv. |
| 13-45 | II-5 | 1 | 1.03 | - | | - | | C-6 | 5 | 5 | ◎-○ | ○ | ◎ | Inv. |
| 13-46 | II-5 | 1 | 1.01 | A-19 | 4 | A-19 | 4 | C-6 | 5 | 13 | ◎ | ◎-○ | ◎ | Inv. |
| 13-47 | II-15 | 1 | 1.02 | - | | - | | C-6 | 5 | 5 | ◎ | ◎-○ | ◎-○ | Inv. |
| 13-48 | II-15 | 1 | 1.04 | B-2 | 4 | B-2 | 4 | C-6 | 5 | 13 | ◎ | ◎ | ◎◎-◎ | Inv. |

Inv.:Invention

As is apparent from Tables 13 through 15, the samples of the invention give improved results in view of the effects of the invention, when saccharides or water-soluble polymers are added to each of granules containing a Fe(III) complex and granules containing a sulfite. When saccharides or water-soluble polymers are added to the solid composition as well as to the above granules, further improved results are obtained. Particularly, water soluble polymers having an average molecular weight of 2000 to 8000 gives preferable sliding property.

## Claims

1. A solid processing composition for a silver halide color photographic light-sensitive material, the composition comprising an amino polycarboxylic acid ferric complex hydrate, wherein the drying weight reduction at 50 ° C of the composition is 0.1 to 10.0 % by weight.

2. The solid composition of claim 1, wherein the composition is a solid processing composition for bleaching.

3. The solid composition of claim 2, wherein the mol ratio of crystal water of the ferric complex in the ferric complex hydrate satisfies the following expression:

$$0.3 \leqq \text{crystal water/ ferric complex} \leqq 3.0$$

4. The solid composition of claim 2, wherein the composition further comprises a compound represented by the following Formula (A):

   Formula (A) $A(\text{-COOH})_n$

   wherein A represents an n valent organic group, n represents an integer of 1 to 6, and M represents an ammonium, an alkali metal (sodium, potassium or lithium) or a hydrogen atom.

5. The solid composition of claim 2, wherein the composition further contains at least one selected from a water-soluble polymer and a saccharide.

6. The solid composition of claim 2, wherein the composition further contains at least one selected from a water-soluble polymer and a saccharide in an amount of 0.5 to 20.0 % by weight.

7. The solid composition of claim 2, wherein the composition is compression-molded into tablets.

8. The solid composition of claim 1, further comprising a fixing agent.

9. The solid composition of claim 8, wherein the composition is a solid processing composition for bleach-fixing.

10. The solid composition of claim 9, wherein the composition is in the form of granules and the content of granules having a particle diameter of less than 149 µm is not more than 30 % by weight.

11. The solid bleaching composition of claim 9, wherein the amino polycarboxylic acid ferric complex hydrate is in the form of granules.

12. The solid composition of claim 9, wherein the fixing agent is a thiosulfate.

13. The solid composition of claim 9, wherein all or a part of the fixing agent is in the form of granules.

14. The solid composition of claim 9, wherein the composition further contains at least one selected from a water-soluble polymer and a saccharide in an amount of 1.0 to 30.0 % by weight.

15. The solid composition of claim 9, wherein a composition containing an amino polycarboxylic acid ferric complex hydrate and a fixing agent is compression-molded into tablets.

16. The solid composition of claim 15, wherein the fixing agent is a thiosulfate.

17. The solid composition of claim 15, wherein the amino polycarboxylic acid ferric complex hydrate is in the form of granules.

**18.** The solid composition of claim 15, wherein the fixing agent is in the form of granules.

**19.** The solid composition of claim 15, wherein the amino polycarboxylic acid ferric complex hydrate is in one granules and the fixing agent is in the other granules.

**20.** The solid composition of claim 15, wherein the composition contains at least one selected from a water-soluble polymer and a saccharide in an amount of 1.0 to 30.0 % by weight.

European Patent
Office

# EUROPEAN SEARCH REPORT

Application Number
EP 95101760.7

## 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. 6) |
|---|---|---|---|
| X | <u>EP - A - 0 563 571</u><br>(KONICA CORPORATION)<br>* Claims; page 40, line 32 - page 42, line 48; page 46, line 1 - page 49, line 53 *<br>-- | 1-20 | G 03 C 7/42 |
| X | <u>EP - A - 0 569 852</u><br>(FUJI PHOTO FILM CO., LTD.)<br>* Claims; page 3, line 23; page 3, line 55 - page 4, line 58; page 18, lines 1-7; page 41, lines 1-8 *<br>-- | 1-4,8-13,17-20 | |
| D,A | <u>US - A - 5 053 321</u><br>(KÜHNERT)<br>* Totality *<br>-- | 1,2,5,6,10,11,14 | **TECHNICAL FIELDS SEARCHED (Int. Cl.6)** |
| D,A | <u>EP - A - 0 537 365</u><br>(KONICA CORPORATION)<br>* Pages 30-34, example 1; page 9, lines 16-21; page 20, line 29 - page 24, line 37; claims 2-4 *<br>---- | 1,2,4-9,12-20 | G 03 C |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| VIENNA | 30-05-1995 | SCHÄFER |

CATEGORY OF CITED DOCUMENTS

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