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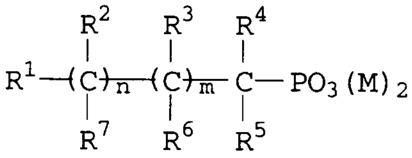
(54) Granular and tablet-shape processing composition for processing a silver halide photographic light-sensitive material

(57) Disclosed is a solid composition for processing a silver halide photographic light-sensitive material comprising a compound represented by Formula I, wherein a decreasing ratio of decreasing weight of said composition after drying at 50 °C to weight of said composition before drying is 0.5 to 10 % by weight of said composition :

Formula [I]



$$R^1 - \left(\overset{R^2}{\underset{R^7}{C}} \right)_n - \left(\overset{R^3}{\underset{R^6}{C}} \right)_m - \overset{R^4}{\underset{R^5}{C}} - PO_3(M)_2$$

wherein R^1 through R^7 independently represent a hydrogen atom, -OH, -COOM, -PO_3M_2, -SO_3M, a substituted or unsubstituted alkyl group having 1 to 6 carbon atoms ; M represents a hydrogen atom or an alkaline metal atom ; and n and m independently represent 0 or 1, provided that n and m are not 0 at the same time.

EP 0 687 950 A1

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FIELD OF THE INVENTION

The present invention relates to a solid photographic processing composition for processing a silver halide photographic light-sensitive material, and more particularly to a granular shape and a tablet shape solid processing composition for processing a silver halide photographic light-sensitive material wherein storage stability has been improved.

BACKGROUND OF THE INVENTION

Recently, in the photographic processing industry, a small-scaled photofinishers so-called a mini-lab has been rapidly increased where a small-sized automatic processor is used and, accordingly, the quantity of processing composition kits used therein has also been increased. The processing composition kits are made of a concentrated liquid. However, the processing composition kits have still needed to have a lot of spaces for storing them, and the transportation cost of the kits can also in no way be slighted. Besides, the quantity of the waste plastic bottles has increased year by year. It is also needed to retrieve and dispose of the waste plastic bottles. A processing composition capable of reducing the quantity of the waste plastics has been demanded, because the waste plastic bottles can hardly be retrieved and disposed.

For solving the above-mentioned problems, the techniques of solidifying a photographic processing agent have been proposed, and for example, it has been considered to pulverize a photographic processing agent and then to supply it. However, a pulverized photographic processing agent has not only such a problem that there is an apprehension for the worker's health, because the fine powder thereof is whirled up in the air when dissolving the composition and he may possibly inhale the flying powder, but also such a problem that a whirling processing composition component is mixed in another photographic processing composition and thereby a trouble is produced in the development process.

Accordingly, the techniques of granulating a photographic processing agent so as to prepare a granular shaped mixture have been described in, for example, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP OPI Publication) Nos. 2-109042/1990 and 2-109043/1990. Besides the above, a photographic processing system in which a solid photographic development processing composition is used, and a solid photographic development processing composition applicable to the photographic system are described in JP OPI Publication Nos. 5-119454/1993, 5-113646/1993 and 5-107696/1993.

Due to the technology of the above-mentioned patented techniques, it is sure that the occurrence of fine powder from a solid processing composition is reduced. However, it is insufficient with this technology only. It was found that, when a solid processing composition containing an organic phosphonic acid type compound is left under the condition of a high humidity for a long time, a phenomenon that a solid processing composition is crumbled occurs. When a solid processing composition described in the aforesaid publication and an automatic processing machine are used for processing, the solid processing composition is crumbled in an accommodating container accommodating the solid processing composition, causing that it is difficult to supply a constant amount or improper supplying occurs. Specifically, when the solid processing composition is transported by sea from Japan to South east Asia, the Middle Near East area and Africa, it takes about 2 to 4 weeks, wherein the difference of temperature between day and night reaches 15 to 20°C and humidity changes by about 20 to 30%RH. In such an occasion, the above-mentioned problem becomes more serious.

In addition, recently, reduction of the number of rolls processed per day and per one mini-lab shop advances due to bristling of mini-lab shops and, low replenishment of processing solution due to the reduction of photo-effluent is accelerated by environmental regulations so that the renewal rate of processing tank solution per day has been lowered. Therefore, improvement of preservability of processing tank solution is demanded.

In a bleaching and fixing step, it is effective to use diethylenetriamine pentaacetic acid ferric complex salt for improving preservability of the above-mentioned processing tank solution. However, since the diffusion property of this diethylenetriamine pentaacetic acid ferric complex salt is small, elution property from a silver halide photographic light-sensitive material is small. Therefore, especially when processing time is short, this diethylenetriamine pentaacetic acid ferric complex salt tends to remain in the light-sensitive material, and yellow stain occures. In order to solve this problem, it is effective to use the above-mentioned organic phosphonic acid compound in a stabilizing processing tank. However, as stated above, the solid processing composition containing the organic phosphonic acid compound crumbles when left at high temperature and high humidity for a long time so that fine powder easily tend to occur, resulting in that it is difficult to supply a certain amount of organic phosphonic acid compound accurately to a stabilizing processing tank. Thus, yellow stain due to the above-mentioned diethylenetriamine pentaacetic acid ferric complex salt is caused.

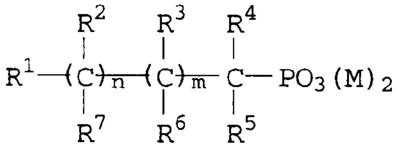
Accordingly, a first object of the present invention is to provide a solid photographic processing composition wherein form change due to storage for a long time is small and handling convenience is secured. A second object of the present invention is to provide a processing method wherein stable processing performance can be maintained without accompanying the occurrence of yellow stain even when diethylenetriamine pentaacetic acid ferric complex salt is used in the bleaching and fixing step.

SUMMARY OF THE INVENTION

The above-mentioned object of the present invention is attained by the following items.

Item 1: A solid composition for processing a silver halide photographic light-sensitive material comprising a compound represented by Formula I, wherein a decreasing ratio of decreasing weight of said composition after drying at 50 °C to weight of said composition before drying is 0.5 to 10 % by weight of said composition:

Formula [I]



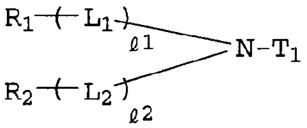
$$R^1-\underset{R^7}{\overset{R^2}{(C)_n}}-\underset{R^6}{\overset{R^3}{(C)_m}}-\underset{R^5}{\overset{R^4}{C}}-PO_3(M)_2$$

wherein R^1 through R^7 independently represent a hydrogen atom, -OH, -COOM, $-PO_3M_2$, $-SO_3M$, a substituted or unsubstituted alkyl group having 1 to 6 carbon atoms; M represents a hydrogen atom or an alkaline metal atom; and n and m independently represent 0 or 1, provided that n and m are not 0 at the same time.

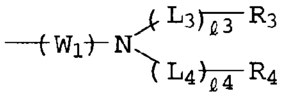
Item 2: The solid composition of item 1, wherein said compound represented by Formula I is contained in an amount of 45 to 90 % by weight of said solid composition.

Item 3: The solid composition of item 1, wherein said composition comprises a compound represented by Formula II:

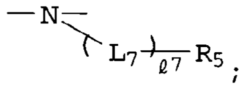
Formula II



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

 ;

W_1 represents a substituted or unsubstituted alkylene group, an arylene group, an alkenylene group, a cycloalkylene group, an aralkylene group or $(L_5\text{-}X)_{\ell 5}(L_6)_{\ell 6}$; X represents -O-, -S-, a divalent heterocyclic group or

 ;

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 phosphone group, a sulfamoyl group, a sulfonamido group, an acylamino group or a hydroxam group, provided that at least one of R_1 through R_5 represents a carboxy group; L_1 through L_7 represent a substituted or unsubstituted alkylene group, arylene group, alkenylene group, cycloalkylene group or aralkylene group; and l_1 through l_7 independently represent an integer of 0 to 6, provided that l_5 and l_6 are not 0 at the same time.

Item 4: The solid composition of item 1, wherein said composition contains a water-soluble polymer or a saccharide.

Item 5: The solid composition of item 4, wherein said saccharide is a sugar alcohol.

Item 6: The solid composition of item 4, wherein said water-soluble polymer is a polyethylene glycol having a number average molecular weight of 1,000 to 20,000.

Item 7: The solid composition of item 1, wherein said solid composition is a granular shape solid composition or a tablet shalpe solid composition.

Item 8: The solid composition of item 7, wherein said tablet shape solid composition is prepared by compression-molding a granular shape solid composition.

Namely, as a result of diligent study, the present inventors discovered that, in a solid processing composition containing an organic phosphonic acid compound, a decreasing ratio in weight of aforesaid solid processing composition noticeably influences the above-mentioned crumbling problem, and they attained the present invention.

In Japanese Patent OPI Publication No. 119450/1993, a technology to control moisture content in a solid processing composition is disclosed. The objects of this technology, however, is to improve initial strength and solubility of the tablet agent. It does not at all disclose the improved results as to the physical property change of the solid processing composition during or after storage which are the object of the present invention. It was very surprising that the physical properties during storage was improved due to decreasing ratio in weight of the solid processing composition after drying of the solid processing composition.

BRIEF EXPLANATION OF DRAWINGS

Fig. 1 is an overall arrangement view of the silver halide photosensitive material processing apparatus.

Fig. 2 is a perspective view of the above silver halide photosensitive material processing apparatus.

Fig. 3 is a sectional view of the automatic processing apparatus of the present invention.

EXPLANATION OF NUMERALS

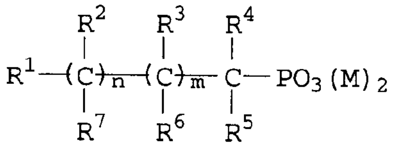
1, 1A, 1B, 1C, 1D and 1E: Processing tank
2, 2A, 2B and 2E: Auxiliary tank
20. Solid processing composition administrating section
30 Solid processing composition replenishing device
31. Throughout information detecting means
32. Throughout supply control means
33. Accomodating container (cartridge)
34. Accommodating container setting means
35. Supplying means
40. Water replenishing means
41. replenishing water tank
42. Bellows pump
43. Inhallation pipe
44. Water supply pipe
45. Replenishing water supply control means
J. Tablet shape solid processing composition
W. Replenishing water

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, the present invention will be explained in detail.

First of all, compounds represented by Formula [I] will be explained.

Formula [I]



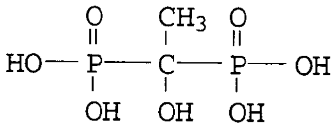
$$R^1\text{---}(\overset{R^2}{\underset{R^7}{C}})_n\text{---}(\overset{R^3}{\underset{R^6}{C}})_m\text{---}\overset{R^4}{\underset{R^5}{C}}\text{---}PO_3(M)_2$$

wherein R^1 through R^7 independently represent a hydrogen atom, -OH, -COOM, $-PO_3M_2$, $-SO_3M$, a substituted or unsubstituted alkyl group having 1 to 6 carbon atoms; M represents a hydrogen atom and an alkaline metal atom; and n and m independently represent 0 or 1, provided that they are not 0 at the same time.

In Formula [I], the number of carbon in aforesaid alkyl group is preferably 1 to 4. The alkyl group may be either straight-chained or branched and may have a substituent. The preferable substituent is -OH, -COOM, $-PO_3M_2$, $-SO_3M$ and $-NR^8R^9$. R^8 and R^9 independently represent a hydrogen atom or an alkyl group having 1 to 3 carbon atoms. M represents a hydrogen atom and an alkaline metal. The preferable is an alkaline metal. n and m independently represent 0 or 1, provided that they are not 0 at the same time. R^1 through R^9 may be the same or different.

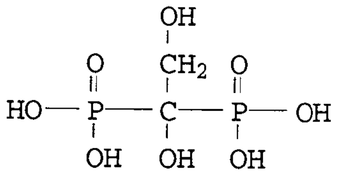
Hereunder, some exemplified compounds preferable to be used as the compounds represented by Formula [I-1] through [I-7] will be given below. However, the present invention shall not be limited thereto.

I-1



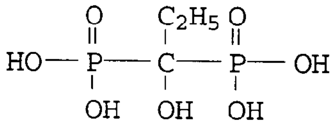
$$HO\text{---}\overset{O}{\underset{OH}{P}}\text{---}\overset{CH_3}{\underset{OH}{C}}\text{---}\overset{O}{\underset{OH}{P}}\text{---}OH$$

I-2



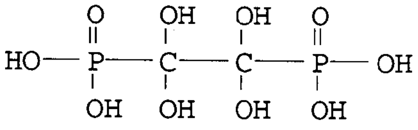
$$HO\text{---}\overset{O}{\underset{OH}{P}}\text{---}\overset{\overset{OH}{CH_2}}{\underset{OH}{C}}\text{---}\overset{O}{\underset{OH}{P}}\text{---}OH$$

I-3



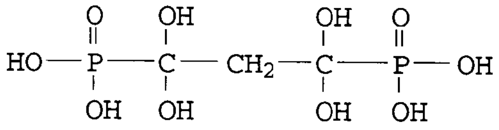
$$HO\text{---}\overset{O}{\underset{OH}{P}}\text{---}\overset{C_2H_5}{\underset{OH}{C}}\text{---}\overset{O}{\underset{OH}{P}}\text{---}OH$$

I-4



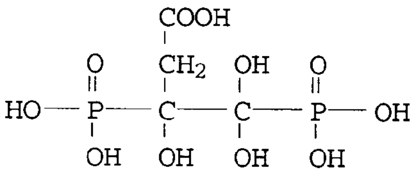
$$HO\text{---}\overset{O}{\underset{OH}{P}}\text{---}\overset{OH}{\underset{OH}{C}}\text{---}\overset{OH}{\underset{OH}{C}}\text{---}\overset{O}{\underset{OH}{P}}\text{---}OH$$

I-5



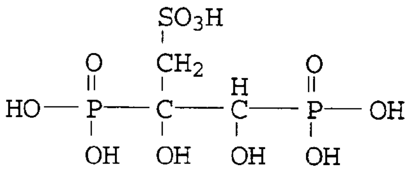
$$HO\text{---}\overset{O}{\underset{OH}{P}}\text{---}\overset{OH}{\underset{OH}{C}}\text{---}CH_2\text{---}\overset{OH}{\underset{OH}{C}}\text{---}\overset{O}{\underset{OH}{P}}\text{---}OH$$

I-6



$$HO\text{---}\overset{O}{\underset{OH}{P}}\text{---}\overset{\overset{COOH}{CH_2}}{\underset{OH}{C}}\text{---}\overset{OH}{\underset{OH}{C}}\text{---}\overset{O}{\underset{OH}{P}}\text{---}OH$$

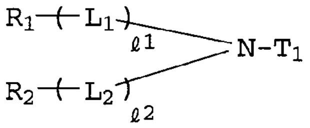
I-7



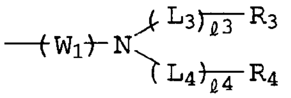
$$HO\text{---}\overset{O}{\underset{OH}{P}}\text{---}\overset{\overset{SO_3H}{CH_2}}{\underset{OH}{C}}\text{---}\overset{H}{\underset{OH}{C}}\text{---}\overset{O}{\underset{OH}{P}}\text{---}OH$$

Next, compounds represented by Formula [II] will be explained.

Formula [II]

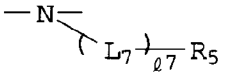


wherein T_1 represents a hydrogen atom, a hydroxy group, a carboxy group, a sulfo group, a carbamoyl group, a phosphono group, a phosphone group, a sulfamoyl group, a substituted or unsubstituted alkyl group, an alkoxy group, an alkylsulfonamido group, an alkylthio group, an acylamino group, a hydroxamic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



;

W_1 represents a substituted or unsubstituted alkylene group, an arylene group, an alkenylene group, a cycloalkylene group, an aralkylene group or $\left(L_5\text{-}X\right)_{\ell 5}\left(L_6\right)_{\ell 6}$; X represents -O-, -S-, a divalent heterocyclic group or



;

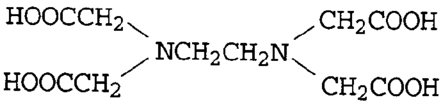
R_1 through R_5 independently represent a hydrogen atom, a hydroxy group, a carboxy group, a sulfo group, a carbamoyl group, a phosphono group, a phosphone group, a sulfamoyl group, a sulfonamido group, an acylamino group and a hydroxam group, provided that at least one of R_1 through R_5 represents a carboxy group;

L_1 through L_7 represent a substituted or unsubstituted alkylene group, arylene group, alkenylene group, cycloalkylene group or aralkylene group; and l_1 through l_7 independently represent an integer of 0 to 6, provided that l_5 and l_6 are not 0 at the same time. Further a salt of a compound represent by Formula II can be employed.

Compound represented by Formula [II] is used as a free acid. In addition, they can be used as a salt of alkaline metal and alkaline earth metal. The alkaline metal salt (sodium salt and potassium salt) is preferable in providing the effects of the present invention more preferably.

Hereunder, practically illustrated compounds represented by Formula [II] of the present invention will be shown below. However, the present invention shall not be limited thereto.

II-1



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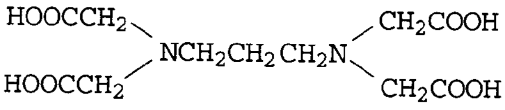

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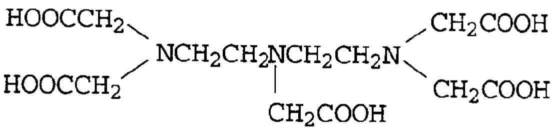

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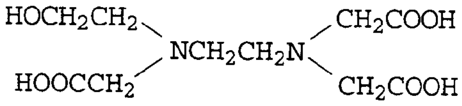

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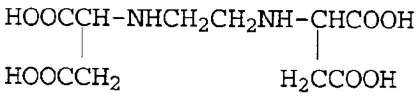

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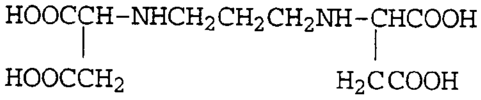

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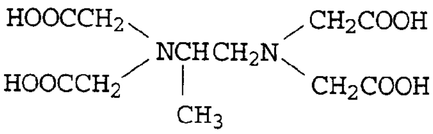

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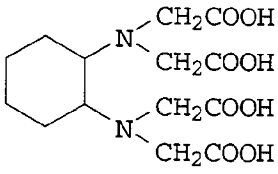

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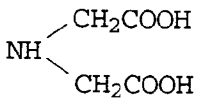

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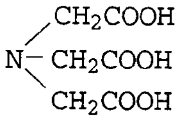

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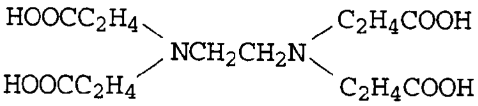

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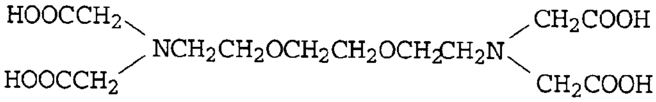

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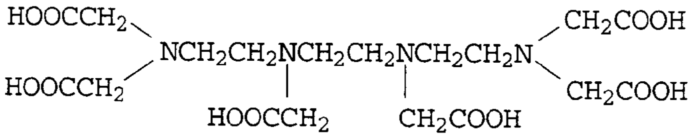

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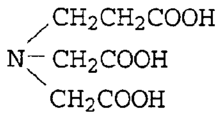

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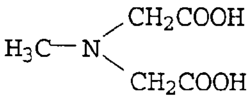

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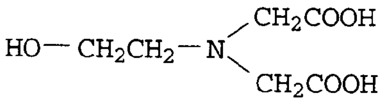

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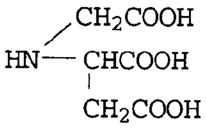
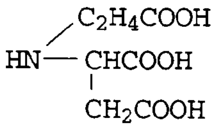
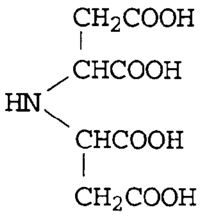


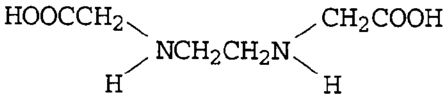
II-18



II-19



II-20



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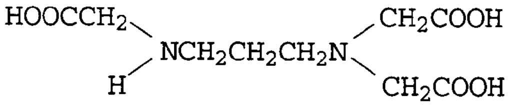

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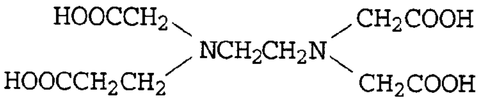

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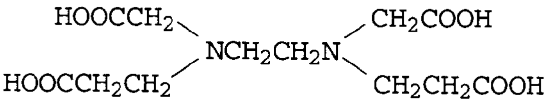

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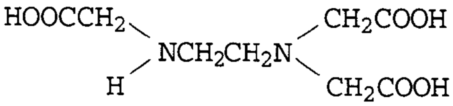

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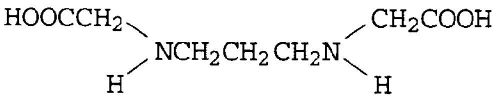

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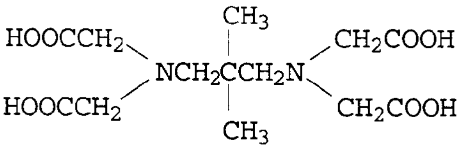

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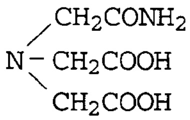

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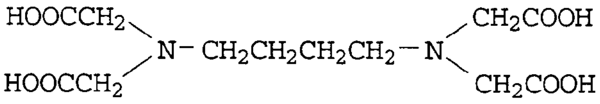
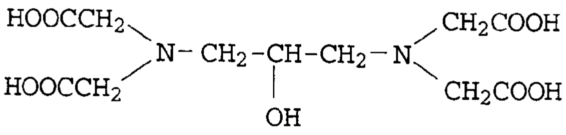


II-29



As compounds providing preferable effects of the present invention, their sodium salts and potassium salts are cited.

The solid processing composition of the present invention means a processing composition in the solid form such as in the granular shape or tablet shape. In the case that a solid processing composition of the invention is granular shape, its average particle size is preferably 100 to 3000 μm, more preferably 150 to 1500 μm and most preferably 300 to 1000 μm. Incidentally, the average particle size referred here is a weight average value obtained by means of a sieving method using a standard sieve of JIS standards. The above-mentioned granular shape processing composition is preferable to be subjected to a granulating step, from the viewpoint of the present invention. When the solid processing composition of the present invention is tablet-shape, it can take an arbitrary form depending upon the state of application. From the viewpoint of productivity and handling convenience, a disc shape is preferable. The tablet-shape processing composition of the present invention can be manufactured by the use of a conventional compressor such as an hydraulic press, a single-shot type tableting machine, a rotary type tableting machine and a briquetting machine.

In the present invention, a decreasing ratio of decreasing weight of a granular shape solid composition after drying at 50 °C to weight of a granular shape solid composition before drying is defined as follows.

A granular shape solid composition is stored in a sealed container under the conditions of a temperature of 25 °C and a Relative humidity of 40 %RH for two days.

About 10 g of a granular shape solid composition is heated in a commercially available infrared moisture meter (FD-600 model) at 50 °C until a weight of a granular shape solid composition has reached a constant weight, and then, a decreasing weight is measured under the conditions, and then, a decreasing ratio of the present invention is calculated from the following equation by using the decreasing weight.

A decreasing ratio (wt%) = $((W_b - W_a)/W_b) \times 100$:

In the equation, W_a is a weight of a granular shape solid composition after drying at 50 °C, and W_b is a weight of a granular shape solid composition before drying.

In the present invention, a decreasing ratio in weight of the solid processing composition is in the range of 0.5 to 10 wt%, preferably 0.8 to 8 wt% and more preferably 1.2 to 6 wt%.

The granular shape processing composition of the present invention can be granulated by the use of a conventional granulation process such as a fluidized-bedding granulation process, a stirring granulation process, a rolling granulation process, an extruding granulation process and a compressing granulation process. In order to control the decreasing ratio within the range of the present invention, so-called wet-type granulation process wherein a solvent is used for granulating is preferable. As a solvent preferably used in the wet-type granulation process, polar solvents such as alcohol, acetone, acetonitrile and water are cited. In addition, their mixtures may be used. From a viewpoint of the present invention, the preferable is water. The preferable added amount of the above-mentioned solvent is 1 to 20 wt/V and more preferably 3 to 10 wt/V to a raw material powder. When it is less than 1 wt/V, sufficient granulating is not conducted. When exceeding 20 wt/V, drying time becomes longer and the raw material may be deteriorated during granulation process.

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

Monosaccharides refer to as a generic term of derivatives in a wide range such as 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 of the invention include derivatives derived from saccharide skeleton represented by the above formula. The preferable are sugar alcohols having a primary or secondary alcohol group to which an aldehyde or ketone group of saccharides is reduced. The especially preferable is a hexitol having 6 carbon atoms.

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, and starches include maltose or dextrins that starches are hydrolyzed to various decomposition compounds. Celluloses may be in an alkali salt form in view of solubility. Among polysaccharides, celluloses or dextrins are preferably used, and dextrins are more preferably used.

Examples of monosaccharides in the invention will be shown below.

(Exemplified compounds)

B-(1) glycelaldehyde
B-(2) dihydroxyacetone (including a dimmer)
B-(3) D-erythrose
B-(4) L-erythrose
B-(5) D-threose
B-(6) L-threose
B-(7) D-ribose
B-(8) L-ribose
B-(9) D-arabinose
B-(10) L-arabinose
B-(11) D-xylose
B-(12) L-xylose
B-(13) D-lyxose
B-(14) L-lyxose
B-(15) D-xylulose
B-(16) L-xylulose
B-(17) D-ribulose
B-(18) L-ribulose

B-(19) 2-deoxy-D-ribose
B-(20) D-allose
B-(21) L-allose
B-(22) D-altrose
B-(23) L-altrose
B-(24) D-glucose
B-(25) L-glucose
B-(26) D-mannose
B-(27) L-mannose
B-(28) D-gulose
B-(29) L-gulose
B-(30) D-idose
B-(31) L-idose
B-(32) D-galactose
B-(33) L-galactose
B-(34) D-talose
B-(35) L-talose
B-(36) D-quinovose
B-(37) digitalose
B-(38) Digitoxose
B-(39) Cymarose
B-(40) D-sorbose
B-(41) L-sorbose
B-(42) D-Tagatose
B-(43) D-fucose
B-(44) L-fucose
B-(45) 2-deoxy-D-glucose
B-(46) D-psicose
B-(47) D-fructose
B-(48) L-fructose
B-(49) D-rhamnose
B-(50) D-glucosamine
B-(51) L-galactosamine
B-(52) D-mannosamine
B-(53) D-glycero-D-galactoheptose
B-(54) D-glycero-D-mannoheptose
B-(55) D-glycero-L-mannoheptose
B-(56) D-glycero-D-guloheptose
B-(57) D-glycero-D-idoheptose
B-(58) D-glycero-L-glucoheptose
B-(59) D-glycero-L-taloheptose
B-(60) D-altroheptulose
B-(61) D-mannoheptulose
B-(62) D-altro-3-heptulose
B-(63) D-glucoronic acid
B-(64) L-glucoronic acid
B-(65) N-acetyl-D-glucosamine
B-(66) Glycerin
B-(67) D-threitol
B-(68) L-threitol
B-(69) Erithorit
B-(70) D-arabitol
B-(71) L-arabitol
B-(72) adnite
B-(73) xylitol
B-(74) D-sorbitol
B-(75) L-sorbitol
B-(76) D-mannitol

B-(77) L-mannitol
B-(78) D-iditol
B-(79) L-iditol
B-(80) D-talitol
B-(81) L-talitol
B-(82) dulcin
B-(83) allodulcitol
B-(84) meso-erithritol

Of these compounds, B-(66) through (83) are preferably used, and B-(74) through (84) are more preferably used.

Examples of polysaccharides and their decomposition compounds in the invention will be shown below.

C-(1) Maltose
C-(2) Cellobiose
C-(3) trehalose
C-(4) gentiobiose
C-(5) isomaltose
C-(6) lactose
C-(7) raffinose
C-(8) gentianose
C-(9) stachyose
C-(10) xylan
C-(11) araban
C-(12) Glycogen
C-(13) dextran
C-(14) inulin
C-(15) levan
C-(16) galactan
C-(17) agarose
C-(18) amylose
C-(19) sucrose
C-(20) agarobiose
C-(21) α-dextrin
C-(22) β-dextrin
C-(23) γ-dextrin
C-(24) δ-dextrin
C-(25) ε-dextrin
C-(26) α-limited-dextrin
C-(27) β-limited-dextrin
C-(28) Phosphorylase-limited-dextrin
C-(29) Soluble starch
C-(30) Sizing starch
C-(31) White dextrin
C-(32) Yellow dextrin
C-(33) British gumm
C-(34) Pineflow (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(35) Pinedex 100 (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(36) Pinedex 1 (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(37) Pinedex 2 (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(38) Pinedex 3 (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(39) Pinedex 4 (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(40) Pinedex 6 (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(41) Foodtex (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(42) Max 1000 (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(43) Glister (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(44) TK-16 (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(45) MPD (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(46) H-PDX (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)
C-(47) Stucodex (Product name, produced by Matsutani Chemical Ind. Co. Ltd.)

C-(48) Mabit (Product name, produced by Hayashibara Trade Ind. Co. Ltd.)
C-(49) Pullulan (Product name, produced by Hayashibara Trade Ind. Co. Ltd.)
C-(50) Methyl cellulose
C-(51) Dimethyl cellulose
C-(52) Trimethyl cellulose
C-(53) Ethyl cellulose
C-(54) Diethyl cellulose
C-(55) Triethyl cellulose
C-(56) Carboxymethyl cellulose
C-(57) Carboxyethyl cellulose
C-(58) Aminoethyl cellulose
C-(59) Hydroxymethyl cellulose
C-(60) Hydroxyethyl cellulose
C-(61) Hydroxypropyl cellulose
C-(62) Hydroxypropylmethyl cellulose
C-(63) Hydroxypropylmethyl cellulose acetate succinate
C-(64) Carboxymethyl hydroxyethyl cellulose

Of these compounds, C-(21) through (64) are preferably used, and compounds, C-(21) through (48) are more preferably used.

The content of the saccharide in the solid processing composition of the invention is preferably 0.5 to 30, and more preferably 1.0 to 20 by weight of the solid processing composition.

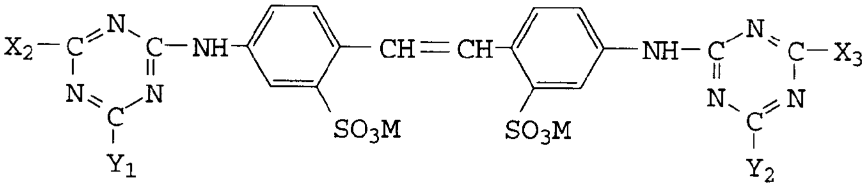
Saccharides exist widely in the nature, and are available on the market. The derivatives can be easily prepared by reduction, oxidation or dehydration reactions.

For the solid processing composition of the present invention, conventional water-soluble polymers can be used. Aforesaid polymers include polyalkylene glycols, polyvinyl pyrrolidones, polyvinyl alcohols and polyacrylic acids. From the viewpoint of the present invention, the preferable are polyethylene glycols, polyvinyl pyrrolidones and polyvinyl alcohol. The more preferable is polyethylene glycols.

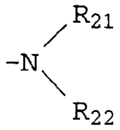
The average molecular weight of polyethylene glycols of the present invention is preferably 600 to 20,000, more preferably 1,000 to 20,000 and most preferably 3,000 to 20,000. The number average molecular weight of polyvinyl alcohols of the present invention is preferably 2,000 to 200,000 and more preferably 3,000 to 100,000. The number average molecular weight of polyvinyl pyrrolidone of the invention is preferably 10,000 to 700,000.

To a stabilizing processing composition used in the present invention, it is preferable to incorporate a triazinylstilbene fluorescent brightening agent from the viewpoint of the effects of the objects of the present invention. As the fluorescent brightening agent, a compound represented by Formula [E] is preferable:

Formula [E]



wherein X_2, X_3, Y_1 and Y_2 independently represent a hydroxyl group, a halogen atom such as chlorine or bromine, an alkyl group, an aryl group,



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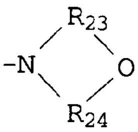


or $-OR_{25}$. Here, R_{21} and R_{22} independently represent a hydrogen atom, an alkyl group (including its substituted group) or an aryl group (including its substituted group), R_{23} and R_{24} represent an alkylene group (including its substituted group), R_{25} represents a hydrogen atom, an alkyl group (including its substituted group) or an aryl group (including its substituted group); M represents a cation, incidentally, details of each group represented by Formula [E] or its substituents are the same as a description in Japanese Patent OPI Publication No. 118649/1992, pp. 16 and 17. Practical examples of compounds represented by Formula [E] are those described in Japanese Patent Application No. 301432/1992, paragraph No. 0159 through 0164. These compounds can be synthesized by a conventional method. Among the above-mentioned illustrated compounds, especially, E-4, E-24, E-34, E-35, E-36, E-37 and E-41 are preferably employed.

In the present invention, when the solid processing composition is a tablet, as a means for supplying the solid processing composition to a processing tank, conventional methods as described in Japanese Utility Publication Open to Public Inspection Nos. 1377783/1988, 97522/1988 and 85732/1989 are cited. Basically, any method is allowed provided that a function to supply the tablet agent to the processing tank is provided. In addition, when the solid processing composition is granule or powder, methods of dropping caused by gravity described in Japanese Utility Model Publication Open to Public Inspection Nos. 81964/1987 and 84151/1988 and Japanese Patent OPI Publication No. 292375/1989 and methods using a screw described in Japanese Utility Publication Nos. 105159/1988 and 195345/1988 are conventional. However, the present invention is not limited thereto.

Any place is allowed for supplying the solid processing composition of the present invention, provided that it is in the processing tank. However, the preferable is a place which is communicated with a processing solution which processes the light-sensitive material and where a processing solution is circulating with aforesaid processing section. In addition, it is preferred that there is a prescribed amount of the circulation of processing section with the processing section so that dissolved component moves to the processing section. It also is preferred that the solid processing composition is supplied into a processing solution whose temperature has been regulated.

An amount of the solid processing composition for one supply is preferably 0.1 g or more from the viewpoint of the effects of the present invention, durability of supplying device and accuracy of the amount supplied. In addition, it is preferred to be 50 g or less from the viewpoint of the effects of the present invention and time for dissolution.

Replenishing water of the present invention means replenishing water supplied to the processing tank in accordance with the volume of light-sensitive material to be processed. The so-called evaporation-replenishing water for replenishing evaporation of moisture from the processing tank is not substantially included thereto. Accordingly, the amount of adding replenishing water in the present invention is the amount of total added amount of moisture supplied to the processing tank minuses the amount of moisture evaporated.

In the present invention, the added amount of replenishing water supplied to a stabilizing processing tank is 50 to 400 ml per 1 m^2 of light-sensitive material. In addition, from the viewpoint of preventing the occurrence of stains and aptitudes to environment, it is preferably 100 to 200 ml.

In addition, in the present invention, it is also possible to make a replenishing water for a bleach-fixing processing tank by letting the tank solution of the first stabilizing processing tank flow into the bleach-fixing tank by means of a pump.

EXAMPLES

Hereunder, practical embodiments of the present invention will be explained referring to examples. However, the present invention shall not be limited thereto.

Example 1

[Preparation of granular samples]

In accordance with the following procedure, granular processing composition samples were prepared.

Illustrated compound I-1 (300 g of 3Na salt and 600 g of sodium carbonate monohydrate) was crushed by the use of a hammer mill available on the market until the average particle size becomes 50 μm. The resulting fine powder was mixed for 10 minutes in a commercially available stirring granulating machine and following this, 85 ml of water was added, granulated for about 10 minutes. Next, the resulting granulated composition was dried by the use of a commercially available fluidized-bed drier. By regulating drying conditions, the decreasing ratio in weight of said composition after drying was regulated as described in Table 1, Thus, granular shape samples 1-1 through 1-9 were prepared.

[Preparation of tablet shape samples]

By the use of the above-mentioned procedure, granulated samples were prepared. To the resulting granule, sodium lauryl sulfate was added by 0.5wt% for mixing 3 minutes. Next, the resulting mixture was compressed and molded by the use of a commercially available hydraulic press to obtain 500 pcs of tablet shape samples 1-10 through 1-18 respectively having a diameter of 17 mm, a thickness of 5.0 mm and weight of 1.7 g.

Next, by the use of solid processing composition samples obtained by the above-mentioned procedure, the following experiments were tried.

Experiment 1: Evaluation of the strength of granular shape samples

40 g of each granular shape sample was poured into a laboratory dish. Under 25°C and 80%RH, the samples were stored for one week. The samples before and after storing were sieved with a sieve shaker for 5 minutes. The weight of fine particle which passed 100 mesh (in accordance with the JIS) was measured.

Experiment 2: Evaluation of the strength of tablet shape samples

10 pcs of tablet shape samples respectively were poured into a laboratory dish, and stored for one week under 25°C and 80%RH. Hardness of each sample before and after storage was measured by the use of a hardness tester (TS-50N, produced by Okada Seiko). The average value was defined as the strength of the tablet shape samples.

Experiment 3: Evaluation of fluidity of granular shape samples

About 200 g of granular shape samples obtained by the above-mentioned procedure was stored in the same conditions as in Experiment 1. By the use of a Miwa-style fluidized surface angle measurer (produced by Tsutsui Rikagaku Kikai Co., Ltd.), the sample containers were rotated at 10 rpm for 2 minutes. Following this, the rotation was stopped. The angle of sample at this time was measured, and it was defined to be a repose angle. The evaluation standard of fluidity is shown as follows.

A: The repose angle is less than 40°.
B: The repose angle is 40° to 45°.
C: The repose angle is 50° or more.
D: Not fluid so that it is impossible to be measured.

When the above-mentioned repose angle is 45° or less, fluidity is judged to be favorable.

Table 1 shows the results.

Table 1

Sample No.	Decreasing ratio (wt%) after drying	Strength before storage	Strength after storage	Fluidity before storage	Fluidity after storage	Remarks
1-1	0.4	18.4 wt%	24.3 wt%	D	D	Comp.
1-2	0.5	10.3 wt%	15.6 wt%	B	B	Inv.
1-3	0.8	9.4 wt%	14.8 wt%	B	B	Inv.
1-4	1.3	8.6 wt%	13.5 wt%	A	A	Inv.
1-5	2.4	8.4 wt%	10.4 wt%	A	A	Inv.
1-6	5.8	8.3 wt%	11.1 wt%	A	A	Inv.
1-7	7.3	8.2 wt%	12.8 wt%	B	A	Inv.
1-8	9.6	7.9 wt%	14.2 wt%	B	B	Inv.
1-9	11.1	7.4 wt%	19.3 wt%	B	D	Comp.
1-10	0.4	5.4 kg	Incapable of measuring *	-	-	Comp.
1-11	0.5	7.8 kg	6.1 kg	-	-	Inv.
1-12	0.8	8.2 kg	6.5 kg	-	-	Inv.
1-13	1.3	8.4 kg	7.0 kg	-	-	Inv.
1-14	2.4	8.7 kg	7.2 kg	-	-	Inv.
1-15	5.8	9.1 kg	7.8 kg	-	-	Inv.
1-16	7.3	9.4 kg	7.6 kg	-	-	Inv.
1-17	9.6	9.6 kg	7.4 kg	-	-	Inv.
1-18	11.1	10.6 kg	Incapable of measuring *	-	-	Comp.

* The tablet was crumbled so that measurement can not be done

As is apparent from the above-mentioned Table 1, it can be understood that the granular shape processing compositions of the present invention are excellent in terms of strength without crumbling after the lapse of time in storage under high humidity so that they are extremely excellent in terms of handling convenience. In addition, it can be understood that the tablet shape processing compositions of the present invention show less deterioration of hardness so that they are excellent in terms of storage stability.

Example 2

In the same procedure as in Example 1 except that the proportion of 3 sodium salt of the illustrated compound I-2 and sodium carbonate monohydrate was changed as shown in Table 2, granular shape samples 2-1 through 2-7 and tablet shape samples 2-8 through 2-14 were prepared. They were subjected to the same experiment as in Example 1.

Table 2 shows the results thereof.

Table 2

Sample No.	wt% of 3 sodium salt of Illustrated compound I-2	Decreasing ratio (wt%) after drying	Strength before storage	Strength after storage	Fluidity before storage	Fluidity after storage
2-1	15	2.4	7.9 wt%	9.1 wt%	B	B
2-2	22	3.1	8.2 wt%	9.2 wt%	B	B
2-3	42	2.6	8.1 wt%	9.7 wt%	A	B
2-4	46	2.8	7.8 wt%	9.6 wt%	A	A
2-5	51	3.3	7.9 wt%	9.9 wt%	A	A
2-6	60	2.9	8.4 wt%	9.8 wt%	A	A
2-7	78	3.0	8.3 wt%	10.1 wt%	A	A
2-8	15	2.4	9.2 kg	7.4 kg	-	-
2-9	22	3.1	9.4 kg	7.3 kg	-	-
2-10	42	2.6	8.8 kg	7.3 kg	-	-
2-11	46	2.8	8.7 kg	7.2 kg	-	-
2-12	51	3.3	8.4 kg	7.1 kg	-	-
2-13	63	2.9	8.3 kg	7.2 kg	-	-
2-14	78	3.0	8.2 kg	7.0 kg	-	-

From the above-mentioned Table 2, it can be understood that the effects of the present invention is provided more noticeably when the compound of the present invention is contained by 45wt% or more.

Example 3

Samples 3-1 through 3-12 wherein the illustrated compounds used in Sample 2-6 of Example 2 were changed to those described in Table 3 were subjected to the same experiment as that in Example 2. Table 3 shows the results thereof.

Table 3

Sample No.	Illustrated compound of Formula [I]	Decreasing ration (wt%) after drying	Strength before storage	Strength after storage
3-1	I-1·3 sodium salt	2.9	7.9 wt%	10.0 wt%
3-2	I-1·4 sodium salt	3.3	7.0 wt%	8.1 wt%
3-3	I-1·3 potassium salt	3.1	7.8 wt%	9.8 wt%
3-4	I-2·4 sodium salt	2.8	8.3 wt%	12.4 wt%
3-5	I-3·3 sodium salt	2.9	9.3 wt%	13.2 wt%
3-6	I-5·4 sodium salt	3.1	8.7 wt%	12.6 wt%
3-7	I-1·3 sodium salt	2.9	8.3 kg	7.2 kg
3-8	I-1·4 sodium salt	3.3	9.3 kg	8.4 kg
3-9	I-1·3 potassium salt	3.1	8.3 kg	7.4 kg
3-10	I-2·4 sodium salt	2.8	7.1 kg	6.4 kg
3-11	I-3·3 sodium salt	2.9	7.3 kg	6.2 kg
3-12	I-5·4 sodium salt	3.1	7.5 kg	6.3 kg

From the above-mentioned Table 3, it can be understood that, of the compounds of the present invention, illustrated compound I-1 provides the effects of the present invention more preferably.

Example 4

[Preparation of granular shape samples]

In accordance with the following procedure, granular shape processing composition samples were prepared.
By the use of a commercially available hammer mil, 3,200 g of illustrated compound I-1·3sodium salt, 150 g of sodium carbonate monohydrate and 1400 g of illustrated compound of Formula [II] (described in Table 4) were crushed until the average particle size becomes 50 µm. This fine powder was mixed for 10 minutes in a commercially available stirring granulating machine. Following this, the resulting mixture was granulated for about 10 minutes by adding water. Next, the resulting granule was dried by the use of a commercially available fluidized-bed drier. By regulating drying conditions, the decreasing ratio (wt%) after drying was regulated as described in Table 4 so that granular shape samples 4-1 through 4-9 were prepared.

[Preparation of tablet shape samples]

By the above-mentioned procedure, granular shape samples were prepared. To the resulting granule, sodium N-lauroyl sarcosinate was added by 0.5 wt% and mixed for 3 minutes. Next, the resulting mixture was compressed-molded by the use of a commercially available hydraulic pressurer to obtain 1000 pcs of tablet shape samples 4-10 through 4-18 respectively each having a diameter of 20 mm, a thickness of 5.0 mm and weight of 4.0 g.

Next, the resulting samples were subjected to an experiment in the same manner as in Example 1. Table 4 shows the results thereof.

Table 4

Sample No.	Illustrated compound of Formula [II]	Decreasing ratio (wt%) after drying	Strength before storage	Strength after storage
4-1	II-1	3.6	6.4 wt%	9.5 wt%
4-2	II-1·2 sodium salt	3.2	6.3 wt%	7.2 wt%
4-3	II-2·2 sodium salt	2.4	6.5 wt%	7.5 wt%
4-4	II-3	3.5	7.1 wt%	9.8 wt%
4-5	II-3·5 sodium salt	2.8	6.2 wt%	7.4 wt%
4-6	II-5·2 sodium salt	3.1	6.8 wt%	7.3 wt%
4-7	II-8	2.9	7.4 wt%	9.2 wt%
4-8	II-14	3.3	7.6 wt%	9.4 wt%
4-9	II-17·1 sodium salt	3.4	6.7 wt%	7.7 wt%
4-10	II-1	3.6	15.4 kg	13.3 kg
4-11	II-1·2 sodium salt	3.2	19.2 kg	18.12
4-12	II-2·2 sodium salt	2.4	18.3 kg	17.1 kg
4-13	II-3	3.5	16.3 kg	14.3 kg
4-14	II-3·5 sodium salt	2.8	18.7 kg	14.1 kg
4-15	II-5·2 sodium salt	3.1	18.9 kg	17.3 kg
4-16	II-8	2.9	14.3 kg	11.1 kg
4-17	II-14	3.3	12.1 kg	9.3 kg
4-18	II-17·1 sodium salt	3.4	17.3 kg	14.4 kg

From the above-mentioned Table 4, it can be understood that, by adding a compound represented by Formula [II] to the solid processing composition of the present invention, initial strength of granular shape processing composition and tablet shape processing composition is further improved so that the effect of the present invention can be obtained more preferably.

Example 5

By the use of 2900.0 g of illustrated compound I-1·4 sodium salt, 450.0 g of sodium carbonate monohydrate, 800.0 g of ethylenediamine tetraacetic acid, 800.0 g of disodium ethylenediamine tetraacetic acid, 70.0 g of o-phenylphenol and 500 g of a saccharide or a water-soluble polymer (described on Table 5), the same procedure as in Example 4 was conducted to obtain granular shape samples 5-1 through 5-9.

In addition, granular shape samples were prepared by the above-mentioned procedure. To the resulting granule, sodium N-lauroyl sarcosinate was added by 0.5wt% and mixed for 3 minutes. Next, the resulting mixture was compressed-molded by the use of a commercially available hydraulic press. Thus, 500 pcs of tablet shape samples 5-10 through 5-18 respectively each having a diameter of 30 mm and weight of 10.0 g were prepared. Next, by the use of samples obtained by the foregoing procedure, an experiment in the same manner as in Example 1 and the following experiment were conducted. Experiment 4: Evaluation of the swelling degree of tablet shape composition

By the use of an aluminum-evaporated polyethylene package, tablet shape samples with 10 pcs respectively were packaged. Following this, they were stored for 1 month at 45 °C and 60%RH. Then, the swelling degree of the tablet was calculated by the following equation:

Swelling degree of tablet (%) = {[Thickness of tablet composition after storage (mm) - Thickness of tablet composition before storage (mm)]}/[Thickness of tablet composition before storage (mm)]} x 100

◎: Swelling degree: less than 1%
○: Swelling degree: 1 to 3 %
Δ: Swelling degree: 5 % or more
×: Incapable of measuring.

Table 5 shows the results thereof.

Table 5

Sample No.	Sugar or water-soluble polymer	Decreasing ratio (wt%) after drying	Strength before storage	Strength after storage	Swelling after storage (%)
5-1	D-sorbitol	2.8	2.5 wt%	2.9 wt%	-
5-2	D-mannitol	3.1	2.2 wt%	3.0 wt%	-
5-3	Lactose	2.9	4.9 wt%	6.3 wt%	-
5-4	Pineflow	2.6	3.3 wt%	4.1 wt%	-
5-5	HPC	3.3	4.6 wt%	5.9 wt%	-
5-6	PVP K-17	3.1	4.3 wt%	5.4 wt%	-
5-7	PEG# 4000	2.4	2.2 wt%	3.3 wt%	-
5-8	PEG# 6000	2.8	2.4 wt%	3.1 wt%	-
5-9	Not added	3.0	6.5 wt%	7.6 wt%	-
5-10	D-sorbitol	2.8	60 kg	58 kg	◎
5-11	D-mannitol	3.1	61 kg	57 kg	◎
5-12	Lactose	2.9	53 kg	45 kg	○
5-13	Pineflow	2.6	52 kg	44 kg	○
5-14	HPC	3.3	48 kg	40 kg	○
5-15	PVP K-17	3.1	49 kg	41 kg	○
5-16	PEG# 4000	2.4	63 kg	61 kg	◎
5-17	PEG# 6000	2.8	65 kg	61 kg	◎
5-18	Not added	3.0	42 kg	36 kg	○

HPC : Hydroxypropyl cellulose
PVP K-17 : Polyvinyl pyrrolidone produced by BASF
PEG$^{\#}$ 4000: Polyethylene glycol produced by Nippon Yushi Co., Ltd.
PEG$^{\#}$ 6000: Polyethylene glycol produced by Nippon Yushi Co., Ltd.

From the above-mentioned Table 5, it can be understood that, by adding a saccharide or a water-soluble polymer to the solid processing composition of the present invention, the effects of the present invention can be obtaine more preferably. Specifically, by the use of sugar alcohol, dextrin and polyethylene glycols, the effects of the present invention becomes noticeable against strength deterioration under high humidity. In addition, swelling of tablet shape composition is prevented under high temperature storage.

Example 6

Granular shape samples were prepared in accordance with the following procedure.

In a commercially available hammer mill, 3700.0 g of anhydrous potassium carbonate, 600.0 g of sodium sulfite, 240.0 g of pentasodium pentaacetic acid diethylene triamine and 200 g of trisodium salt illustrated compound I-1 were crushed until their average particle size becomes 10 µm. To this fine powder, 800.0 g of Mannit was added. The resulting mixture was granulated in a commercially available stirring granulating machine by adding water for about 7 minutes at a room temperature. Following this, the granule was dried by the use of a commercially available fluidized-bed drier at 70°C. Thus, a granular shape sample wherein the decreasing ration (wt%) after drying was 3.2 % was obtained. In addition, by the use of the same granule, the same procedure as in Example was conducted to obtain a tablet shape sample. Next, by the use of the resulting sample, the same experiment as in Example 4 was conducted. As a result, almost the same results as in Sample 5-2 of Example 5 were obtained.

Example 7

By the use of a commercially available hammer mill, 4000 g of tetra sodium salt of illustrated compound I-1, 2000 g of diethylenetriamine pentaacetic acid, 800 g of sodium sulfite, 1000 g of Chinopal SFP (produced by Ciba-Geigy), 800 g of polyethylene glycol #4000 and 70 g of ortho-phenylphenol were crushed to their average particle size of 50 μm. The resulting fine particles were mixed in a commercially-available stirring granulating machine for 10 minutes. Following this, water was added thereto for producing granule. Next, the resulting granule was dried by the use of a commercially available fluidized-bed drier. By regulating drying conditions, the loss on drying was regulated to as described in Table 6 for preparing granule sample. To this granule, sodium N-lauroyl sarcosinate was added by 0.5 wt% for mixing for 3 minutes. Next, the resulting mixture was compression-molded by the use of an hydraulic press to prepare a tablet samples 7-1 through 7-9 each having a diameter of 30 mm, thickness of 10 mm and weight of 8.7 g.

The above-mentioned tablet shape processing composition samples were subjected to evaluation by means of experiments 2 and 4.

Table 6 shows the results thereof.

Table 6

Sample No.	Decreasing ration in weight	Strength before storage (kg)	Strength after storage (kg)	Swelling after storage
7-1	0.4	42	The tablet was crumbled so that measurement was incapable	×
7-2	0.5	55	51	○
7-3	0.8	56	54	○
7-4	1.3	58	57	◎
7-5	2.4	60	58	◎
7-6	5.8	62	59	◎
7-7	7.3	63	59	○
7-8	9.6	65	60	○
7-9	11.1	70	The tablet was crumbled so that measurement was incapable	×

From Table 6, it can be understood that, by controlling the decreasing ratio in weight of the solid processing composition of the present invention in the range of the present invention, strength reduction is small even when it is stored under high humidity environment for a long time and swelling of the tablet can be prevented.

Example 8

An automatic processing apparatus to which the present invention can be applied will be explained with reference to the accompanying drawings. The automatic processing apparatus of this example is a modified NPS818 type automatic processing apparatus manufactured by Konica Co., Ltd. Fig. 1 is a schematic illustration showing the construction of a silver halide photosensitive material processing apparatus (printer processor) in which the automatic processing apparatus A and photographic printer B are integrated.

In Fig. 1, in the left lower portion of the photographic printer B, there is provided a magazine M in which a roll of photographic paper, which is an unexposed silver halide photographic material, is accommodated. The photographic paper is pulled out from the magazine M and conveyed by the feed rollers R1 and cut into a predetermined size by the cutter C. In this way, a sheet of photographic paper can be provided. This sheet of photographic paper is conveyed by the belt conveyance means Be. Then an image of the original O is exposed onto the sheet of photographic paper by a light source and lens L in the exposure section E. The exposed sheet of photographic paper is further conveyed by a plurality of pairs of feed rollers R2, R3 and R4, so that the sheet of photographic paper is introduced into the automatic processing apparatus A. In the automatic processing apparatus A, the sheet of photographic paper is successively conveyed by a roller conveyance means (the reference numeral is not attached to the means) into the color development tank 1A, bleaching and fixing tank 1B and stabilizing tanks (the first stabilizing tank 1C, the second stabilizing tank 1D, and the third stabilizing tank 1E), wherein these 3 tanks substantially compose a processing tank 1. Due to the foregoing, the sheet of exposed photographic paper is subjected to color development, bleaching and fixing processing and stabilizing processing. After the processing has been completed, the sheet of photographic paper is dried by the drying section 5, and then discharged outside of the apparatus.

In this connection, the one-dotted chain line in the drawing shows a conveyance passage of the silver halide photosensitive material. In this example, the photosensitive material is cut into a sheet and introduced into the automatic processing apparatus A, however, a strip-shaped photosensitive material may be introduced into the automatic processing apparatus A in the present invention. In this case, the processing efficiency can be enhanced when an accumulator for temporarily stocking the photosensitive material is provided between the automatic processing apparatus A and photographic printer B. Of course, the automatic processing apparatus A of the present invention may be constructed integrally with the photographic printer B, or alternatively the automatic processing apparatus A of the present invention may be constructed separately from the photographic printer B. Of course, the silver halide photosensitive material processed by the automatic processing apparatus A of the present invention is not limited to the exposed photographic paper, but an exposed negative film may be applied to the automatic processing apparatus A of the present invention. It should be noted that the present invention is not limited to the specific embodiment described above. It is possible to apply the present invention to an automatic processing apparatus substantially composed of 4 tanks of a color developing tank, bleaching tank, fixing tank and stabilizing tank.

The color development tank 1A, the bleaching and fixing tank 1B and the third stabilizing tanks 1E are respectively provided with the solid processing composition supply devices 3A, 3B and 3E for supplying the solid processing composition.

Fig. 2 is a perspective view showing the entire photosensitive material processing apparatus in which the automatic processing apparatus A of the present invention, photographic printer B and sorter C are integrally combined. In Fig. 2, the cover Al of the automatic processing apparatus A is opened upward, and the accommodating container D having solid processing composition is inserted into the attaching section A2 from the left upper to the right lower position in the drawing. After that, they are fixed.

Fig. 3 is a sectional view of the auxiliary tank and processing composition supply means of the color development tank A taken on line I - I in Fig. 1. In this case, the construction of the bleaching and fixing tank 1B and that of the stabilizing tanks (the first stabilizing tank 1C, the second stabilizing tank 1D, and the third stabilizing 1E) are the same as the construction of the color development tank 1A. Therefore, the explanation of the processing tank 1 can be applied to all tanks of the color development tank 1A, the bleaching and fixing tank lb, and the stabilizing tanks (the first stabilizing tank 1C, the second stabilizing tank 1D, and the third stabilizing 1E). In this connection, for enhancing the understanding of the invention, the conveyance means for conveying the photosensitive material is omitted in the drawing. In this example, explanations will be made under the condition that tablet shape solid processing composition are used. The processing tank 1 for processing the photosensitive material is provided with an auxiliary tank 2 and a solid processing composition charging section 20 integrally attached to the outside of the partition wall forming the processing tank 1. The processing tank 1 and the auxiliary tank 2 are separate from each other by the partition wall 21A on which a communication window 21 is formed, so that the processing solution can be communicated through the communication window 21. The auxiliary tank 2 is provided with an enclosure 25 in which the tablets J are received. In this connection, the enclosure 25 is made of material such as a net so that the processing solution can pass through the enclosure 25, however, the tablets J in the form of a solid body can not pass through the enclosure 25 until they are dissolved in the solution.

A cylindrical filter 22 is disposed below the auxiliary tank 2 in such a manner that the cylindrical filter 22 can be replaced. The cylindrical filter 22 removes an undissolved object such as precipitations in the processing solution. A circulation pipe 23 connected with the suction side of a circulation pump 24 (circulation means) is inserted into the filter 22 penetrating through the lower wall of the auxiliary tank 2.

The circulation system includes the circulation pipe 23 forming a circulation passage of the processing solution, and also includes the circulation pump 24, the processing tank 1 and the auxiliary tank 2. One end of the circulation pipe 23 is communicated with the delivery side of the circulation pump 24, and the other end penetrates a lower wall of the processing tank 1, so that the circulation pipe 23 is communicated with the processing tank 1. Due to the foregoing construction, when the circulation pump 24 is operated, the processing solution is sucked from the auxiliary tank 2 and discharged into the processing tank 1, so that the discharged processing solution is mixed with the processing solution in the processing tank 1, and then sent to the auxiliary tank 2. In this way, the processing solution is circulated. In the present invention, the circulating direction of the processing composition is not limited to the direction shown in Fig. 3, but the direction may be reverse to that shown in Fig. 3.

A waste solution pipe 11 is provided for permitting the processing solution in the processing tank 1 to overflow, so the solution level can be maintained constant and an increase in the components conveyed from other tanks into the processing tank 1 can be prevented. Further, an increase in the components oozing out from the photosensitive material can be prevented.

A rod-shaped heater 26T penetrates an upper wall of the auxiliary tank 2, and is dipped in the processing solution in the auxiliary tank 2. The processing solution in the auxiliary tank 2 and processing tank 1 is heated by this heater 26 in accordance with a temperature detected by a thermometer not shown in the drawing arranged in the auxiliary tank 2. In other words, the heater 26T is a temperature regulating means for regulating the temperature of the processing solution in the processing tank 1, so that the temperature can be controlled in an appropriate range, for example, in a range from 20 to 55°C.

A photoelectric sensor to be used as a throughput information detecting means 31 is disposed at an entrance of the automatic processing apparatus A, and detects the throughput of the photosensitive material to be processed. This throughput information detecting means 31 is comprised of a plurality of detecting members that are disposed in a transverse direction. This throughput information detecting means 31 detects the width of photosensitive material, and the result of detection is used for counting the detection time. Since the conveyance speed of photosensitive material is previously set in a mechanical manner, the throughput of photosensitive material, that is, the area of processed photosensitive material can be calculated form the width and time information. An infrared ray sensor, micro switch and ultrasonic sensor capable of detecting the width and conveyance time of photosensitive material can be used for this throughput information detecting means 31. A means for indirectly detecting the area of processed photosensitive material may be used for this throughput information detecting means 31. For example, in the case of the printer processor shown in Fig. 1, a means for detecting an amount of printed photosensitive material may be adopted, or alternatively, a means for detecting an amount of processed photosensitive material, the area of which is predetermined, may be adopted. Concerning the detecting time, in this example, detection is carried out before processing, however, detection may be carried out after processing or while the photosensitive material is being dipped in the processing solution. In these cases, the throughput information detecting means 31 may be disposed at an appropriate position so that detection can be conducted after processing or while the photosensitive material is being processed. It is not necessary to provide the throughput information detecting means 31 for each processing tank 1A, 1B, 1C, 1D, 1E, and it is preferable that one throughput information detecting means 31 is provided for one automatic processing apparatus A. The solid processing composition supply control means 32 receives a signal from the throughput information detecting means 31 so that the supply of the processing composition conducted by the solid processing composition supply means 30T is controlled and further the supply of replenishment water conducted by the replenishment water supply means 40T is controlled.

The solid processing composition replenishing device 30T used for the photosensitive material processing apparatus of the present invention is disposed above the processing tank 1 of the photosensitive material processing apparatus, and comprises an accommodating container 33, accommodating container charging means 34, supply means 35 and drive means 36T, wherein the solid processing composition replenishing device 30T is tightly closed by an upper cover 301. The upper cover 301 is rotatably connected with a main body 101 accommodating the processing tank 1 and auxiliary tank 2, through a support shaft 302 attached to the back of the main body. The upper cover 301 is lifted upward as shown by a one-dotted chain line in the drawing, so that the front and upper portions of the apparatus can be widely opened. In this way, inspection of the solid processing composition replenishing device 30T, and replacement of the filter 22 can be easily conducted.

A skylight 303 is rotatably connected with a portion of the upper surface of the upper cover 301. When the skylight 303 is opened as illustrated by a one-dotted chain line B in the drawing, the accommodating container 33 is attached or replaced.

At a position close to the auxiliary tank 2 in the main body 101 of the photosensitive material processing apparatus, there is provided a replenishment water supply means 40T. The replenishment water supply means 40T includes: a replenishment water tank 41, bellows pump 43, suction pipe 43, and water feed pump 44. Replenishment water W accommodated in the replenishment water tank 41 is sucked by the action of the bellows pump 42 and flows in the suction pipe 43. After that, replenishment water W is extruded by the bellows pump 42 and flows in the water supply pipe 44. In this way, replenishment water W is supplied to an upper portion of the processing solution accommodated in the auxiliary tank 2. A drive motor of the bellows pump 42 is rotated being controlled by the replenishment water supply control means 45, so that replenishment water W is intermittently replenished by the bellows pump 42.

A solid processing composition for processing photographic color paper was made in the following manner.

[1] Solid processing composition (1) for developing photographic color paper was prepared as follows.

OPERATION (1)

In this case, the developing agent of CD-3 is used, that is, 1350.0 g of 4-amino-3-methyl-N-ethyl-[b-(methanesulfonamido)ethyl]aniline sulfate is crushed by a Bandam Mill available on the market so that the average particle size can be 10 mm. To the thus obtained fine powder, 1000.0 g of polyethylene glycol having a number average molecular weight of 6000, is added and mixed uniformly by a mixer available on the market. Next, the mixture is subjected to a granulating machine available on the market for 7 minutes at room temperature while 50 ml of water is added to the mixture. In this way, the granulation is effected. The thus obtained granules are dried by a fluidized-bed dryer for 2 hours at a temperature of 40°C, so that the moisture in the granules is substantially completely removed.

OPERATION (2)

In Operation (2), 400.0 g of disodium salt of bis(sulfoethyl)hydroxylamine, 1700.0 g of p-toluene sulfonic acid sodium salt, and 300.0 g of Chinopal SFP (manufactured by Ciba Geigy Co.) are ground in the same manner as that of Operation (1). The thus obtained mixture is mixed with 240.0 g of Pineflow (manufactured by Matsutani Kagaku Co.) using a mixer available on the market. Next, in the same manner as that of Operation (1), granulation is conducted while 60 ml of water is added. The thus obtained granules are dried for 2 hours at a temperature of 50°C, so that the moisture in the granules is substantially completely removed.

OPERATION (3)

In the same manner as that of Operation (1), 330.0 g of diethylenetriamine pentaacetic acid pentasodium salt, 130.0 g of p-toluene sulfonic acid sodium salt, 37.0 g of sodium sulfite, 340.0 g of lithium hydroxide monohydrate, and 3300.0 g of anhydrous potassium carbonate are crushed in the same manner as that of Operation (1). The thus obtained mixture is mixed with 500.0 g of polyethyleneglycol having a number average molecular weight of 4000, and 600.0 g of mannitol using a mixer available on the market in a room, the humidity of which is adjusted to be not more than 40% RH. Next, in the same manner as that of Operation (1), granulation is conducted while 800 ml of water is added. The thus obtained granules are dried for 30 minutes at a temperature of 60°C, so that the moisture in the granules is substantially completely removed.

OPERATION (4)

All the granules made in Operations (1) to (3) are mixed for 10 minutes using a cross rotary type mixer available on the market at room temperature. To the thus obtained mixture, 50.0 g of N-myristoyl-alanine sodium salt is added and mixed uniformly by a mixer available on the market for 3 minutes. This is defined to be a sample embodiment 1. Then the mixture is subjected to a rotary type tableting machine (Clean Press Correct H18 manufactured by Kikusui Seisakusho Co.), and tablets are made under the condition that the diameter is 30 mm, the thickness is 10 mm, and the amount of charging per one tablet is 10.5 g. In this case, the tablet making force is set at 7 t, and tablets are continuously made. In this way, tablets of the solid processing composition for color development of photographic color paper are made. Thus obtained tablets of the solid processing composition are defined to be sample embodiment 2.

[2] Preparation of a solid processing composition for bleach fixing for color paper

Operation (5)

In the same manner as in Operation (1), 7000.0 g of sodium diethylenetriamine pentaacetic acid ferric and

35 g of D-sorbitol are crushed until an average particle size can be 10 μm. This fine particles are mixed in the same manner as in Operation (1). After 200 ml of water is added and the resulting mixture is granulated, the granulating product is dried with a fluidized-bed drier for 3 hours at 60°C so that moisture in the granulated product is completely removed.

Operation (6)

In the same manner as in Operation (1), 8500 g of ammonium thiosulfate and 1500 g of sodium metabisulfite are crushed. To the resulting products, 180 g of Pine Flow (produced by Matsutani Chemical Co., Ltd.) is added, and mixed in the same manner as in Operation (1). The resulting mixture is granulated in the same manner as in Operation (1) except that 200 mo of water is added. After granulating, the granulated product is dried with a fluidized-bed drier at 60°C for 2 hours so that moisture in the granulated product is completely removed.

Operation (7)

Granulated products obtained by Operations (5) and (6) are mixed in the same manner as in Operation (4). In addition, to the resulting mixture, 800.0 g of polyethylene glycol having a number average molecular weight of 4000, 600 g of potassium carbonate and 97.0 g of sodium N-lauroyl sarcosinate are added. In a room having a temperature of 25°C and a relative humidity of 40%RH or less, the resulting mixture is mixed for 3 minutes by the use of a mixer. This is defined to be Sample embodiment 1. Next, the resulting mixture is tableted by the use of a rotary tableting machine (Tough Press Correct H18 produced by Kikusui Seisakusho), a tablet for replenishing bleach fixing for color paper having a diameter of 30 mm and weight of 11.0 g are prepared. This is defined to be Sample embodiment 2.

[3] Stabilizing solid processing composition for color paper

The same tablet shape processing composition as prepared in Example 7 is used.

By the use of a tablet shape composition (Sample embodiment 2) prepared in Example 7 and by means of an automatic processor shown in the above-mentioned Figs. 1 through 3, a sample described in Japanese patent Publication Open to Public Inspection No. 264550/1992, Example 1 containing silver chloride content of 99.5 mol% is exposed by a conventional method, and then, processed in accordance with the following processing step.

Processing step	Processing temperature	Processing time	Amount of replenishing a tablet	Added amount of replenishing water
Color developing	40.0±0.5°C	Described in table 1	6.5 g/m^2	62 ml/m^2
Bleach-fixing	35.0±1.0°C	22 sec.	13.6 g/m^2	60 ml/m^2
Stabilizing 1	33.0±3.0°C	22 sec.	-	-
Stabilizing 2	33.0±3.0°C	22 sec.	-	-
Stabilizing 3	33.0±3.0°C	22 sec.	0.9 g/m^2	120 ml/m^2
Drying	72.0±5.0°C	50 sec.	-	-

Stabilizing is a counterflow type from 3 to 1. Among the overflow solution in stabilizing 1, 60 ml/m^2 is flowed into a bleach fixing tank as a replenishing water. A tablet is set to a tablet supplying device provided on the automatic processor. Supplying interval is adjusted so that the supplying amount becomes the above-mentioned value. The supplying amount for one time is 2 tablets (21.0 g) for color developing, 2 tablets (22.0 g) for bleach-fixing and 2 tablets (8.7 g) for stabilizing. For meeting the above-mentioned amount, amount of replenishing water is adjusted and processing is conducted. In addition, for the starting solution of each processing tank in the automatic processor, the following formula is used.

[Color developer (per 1 ℓ)]

Sodium sulfite	0.05 g
Pentasodium diethylenetriamine pentaacetic acid	3.0 g
Polyethylene glycol having a number average molecule weight of 4000	10.0 g
Disodium bis(sulfoethyl)hydroxylamine	4.0 g
Chinopal SFP (produced by Chiba-Geigy)	1.0 g
Sodium p-toluenesulfonic acid	30.0 g
Mannitol	6.0 g
Potassium chloride	4.0 g
Pine Flow	3.0 g
Color developing agent: 3-methyl-4-amino-N-ethyl-N-(β-methanesulfonamidoethyl)-aniline sulfate [CD-3]	8.0 g
Potassium carbonate	33.0 g
Lithium hydroxide	3.5 g
Sodium N-myristoyl alanine	0.30 g

[Bleach-fixer (per 1ℓ)]

Sodium diethylenetriamine pentaacetic acid ferric salt	60.0 g
Ammonium thiosulfate	72.0 g
Sodium thiosulfate	8.0 g
Ammonium metabisulfite	7.5 g

pH is adjusted to 6.0 ± 0.5 by the use of potassium carbonate or maleic acid.

[Stabilizer (per 1ℓ)]

Tetrasodium 1-hydroxyethylidene-1,1-diphosphoric acid	4.0 g
Diethylenetriamine pentaacetic acid	2.0 g
Sodium sulfite	0.8 g
Sodium carbonate	0.5 g
o-phenylphenol	0.08 g

pH is adjusted to 8.0 ± 0.5 by the use of potassium carbonate or sulfuric acid.

To the evaporation amount in each processing tank, equivalent amount of water is added whenever occasion arises. In addition, a tablet type processing composition for stabilizing use is stored for one week in accordance with Experiment 2 described in Example 1. By the use of the tablet type processing composition after being stored, running processing is conducted. The running processing is conducted for 2 weeks in terms of color paper 7.5 m^2 per day.

After the running processing, a color paper sample is subjected to wedge light exposure in accordance with a conventional method. Its minimum reflection blue density (Dmin(Y)) is measured by means of an X-rite (produced by Nippon Heihan Kizai Co., Ltd.).

Table 7 shows the results thereof.

Table 7

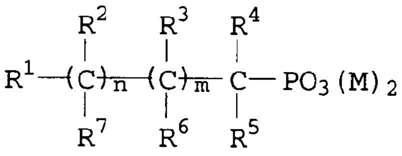
Sample No.	Decreasing ratio (wt%)	Minimum reflection blue-density
8-1	0.4	0.12
8-2	0.5	0.08
8-3	0.8	0.06
8-4	1.3	0.04
8-5	2.4	0.05
8-6	5.8	0.04
8-7	7.3	0.06
8-8	9.6	0.08
8-9	11.1	0.14

As is apparent from Table 7, by controlling a decreasing ratio of decreasing weight of a granular composition after drying at 50 °C of the present invention within the range of the present invention, aforesaid solid processing composition can provide stable processing performance, even using after storage for a long time under high humidity environment.

Claims

1. A solid composition for processing a silver halide photographic light-sensitive material comprising a compound represented by Formula I, wherein a decreasing ratio of decreasing weight of said composition after drying at 50 °C to weight of said composition before drying is 0.5 to 10 % by weight of said composition:

Formula [I]



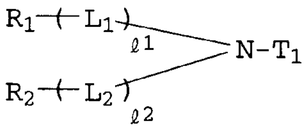
$$R^1\!-\!(\underset{R^7}{\overset{R^2}{C}})_n\!-\!(\underset{R^6}{\overset{R^3}{C}})_m\!-\!\underset{R^5}{\overset{R^4}{C}}\!-\!PO_3(M)_2$$

wherein R^1 through R^7 independently represent a hydrogen atom, -OH, -COOM, $-PO_3M_2$, $-SO_3M$, a substituted or unsubstituted alkyl group having 1 to 6 carbon atoms; M represents a hydrogen atom or an alkaline metal atom; and n and m independently represent 0 or 1, provided that n and m are not 0 at the same time.

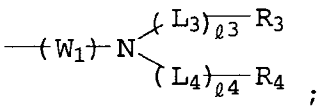
2. The solid composition of claim 1, wherein said compound represented by Formula I is contained in an amount of 45 to 90 % by weight of said solid composition.

3. The solid composition of claim 1, wherein said composition comprises a compound represented by Formula II:

Formula II

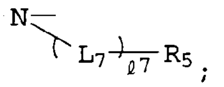


wherein T_1 represents a hydrogen atom, a hydroxy group, a carboxy group, a sulfo group, a carbamoyl group, a phosphono group, a phosphone group, a sulfamoyl group, a substituted or unsubstituted alkyl group, an alkoxy group, an alkylsulfonamido group, an alkylthio group, an acylamino group, a hydroxamic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



$$-(W_1)-N\genfrac{}{}{0pt}{}{\diagup(L_3)_{\ell 3}-R_3}{\diagdown(L_4)_{\ell 4}-R_4}\ ;$$

W_1 represents a substituted or unsubstituted alkylene group, an arylene group, an alkenylene group, a cycloalkylene group, an aralkylene group or $(L_5\text{-}X)_{\ell 5}(L_6)_{\ell 6}$; X represents -O-, -S-, a divalent heterocyclic group or



$$N\genfrac{}{}{0pt}{}{-}{\diagdown(L_7)_{\ell 7}-R_5}\ ;$$

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 phosphone group, a sulfamoyl group, a sulfonamido group, an acylamino group or a hydroxam group, provided that at least one of R_1 through R_5 represents a carboxy group; L_1 through L_7 represent a substituted or unsubstituted alkylene group, arylene group, alkenylene group, cycloalkylene group or aralkylene group; and l_1 through l_7 independently represent an integer of 0 to 6, provided that 15 and 16 are not 0 at the same time.

4. The solid composition of claim 1, wherein said composition contains a water-soluble polymer or a saccharide.

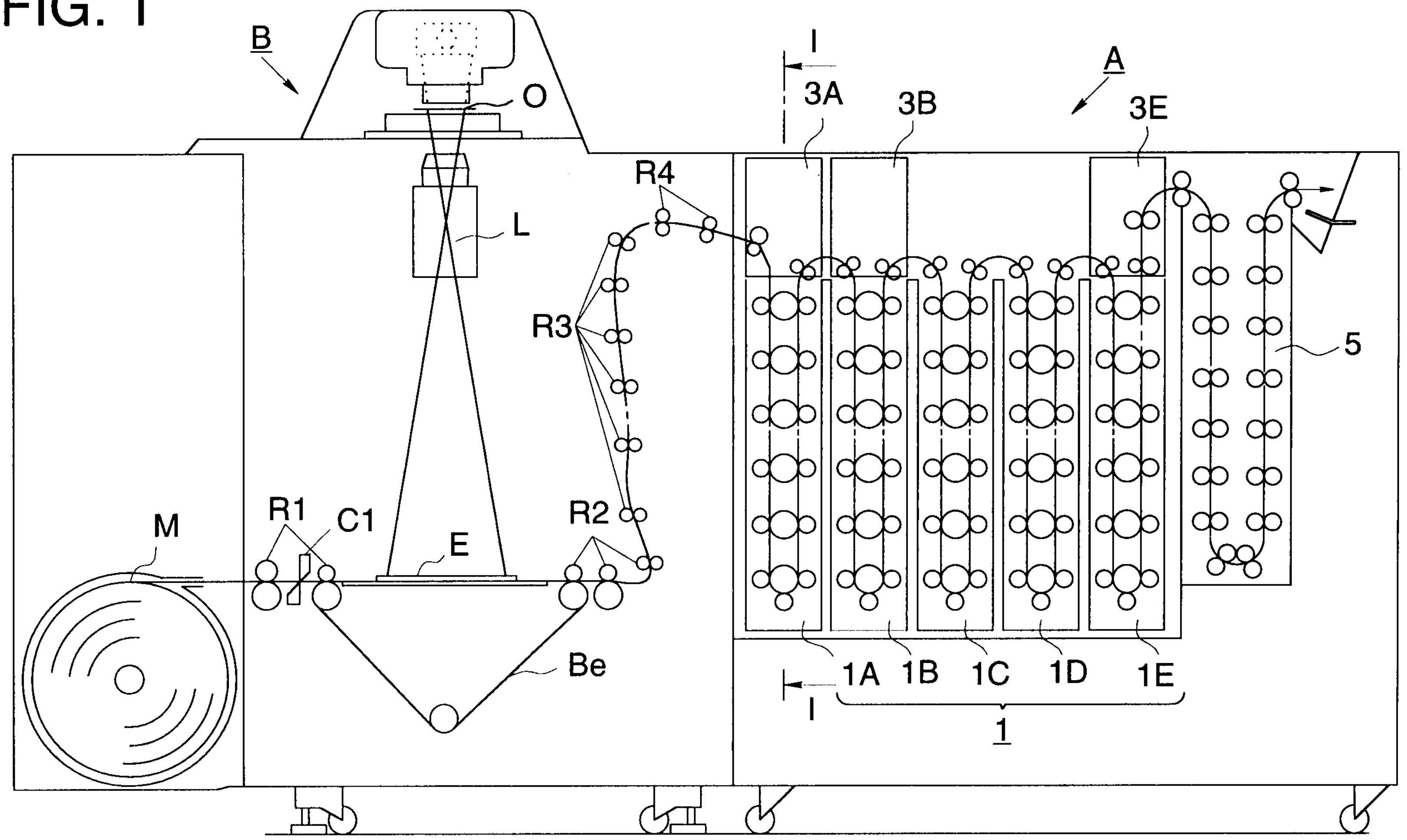
5. The solid composition of claim 4, wherein said saccharide is a sugar alcohol.

6. The solid composition of claim 4, wherein said water-soluble polymer is a polyethylene glycol having a number average molecular weight of 1,000 to 20,000.

7. The solid composition of claim 1, wherein said solid composition is a granular shape solid composition or a tablet shalpe solid composition.

8. The solid composition of claim 7, wherein said tablet shape solid composition is prepared by compression-molding a granular shape solid composition.

FIG. 1



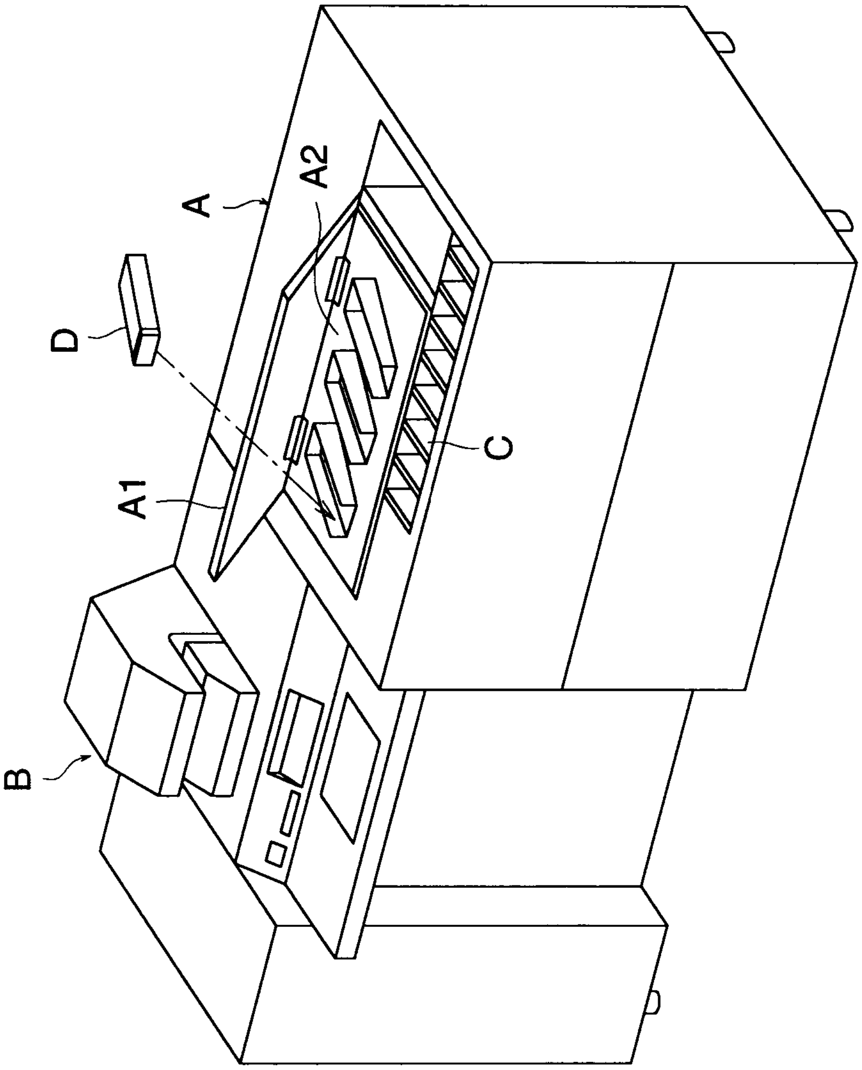
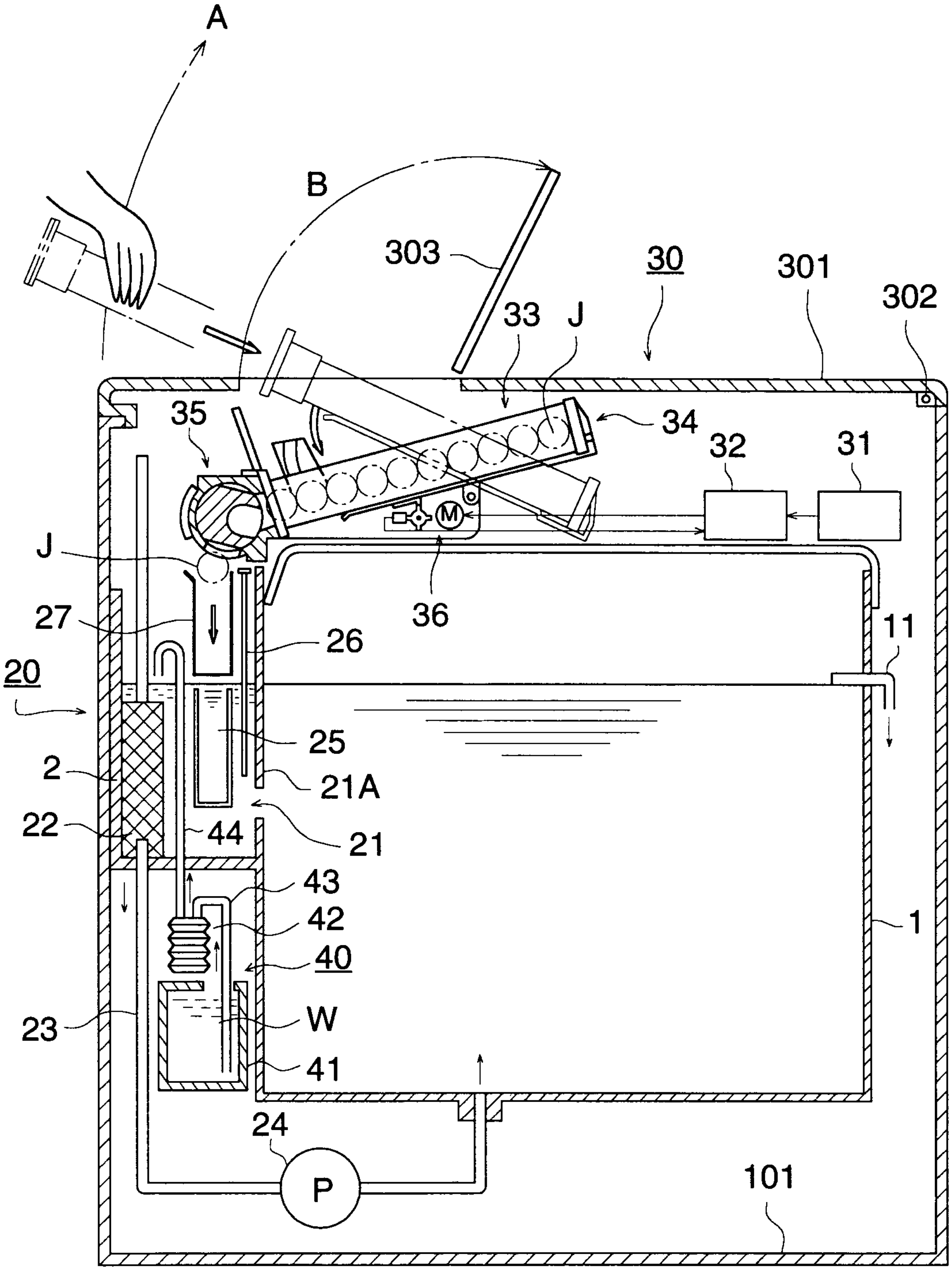


FIG. 2

FIG. 3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EUROPEAN SEARCH REPORT

Application Number
EP 95 30 3582

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)
D,X	DATABASE WPI Section PQ, Week 9324, Derwent Publications Ltd., London, GB; Class P83, AN 93-192311 & JP-A-5 119 450 (KONICA CORPORATION) 18 May 1993 * abstract * ---	1,7,8	G03C5/26
A	DATABASE WPI Section PQ, Week 9321, Derwent Publications Ltd., London, GB; Class P83, AN 93-169857 & JP-A-5 100 370 (KONICA CORPORATION) 23 April 1993 * abstract * ---	1-8	
P,X	EP-A-0 636 930 (KONICA CORPORATION) * page 29, line 25 - line 31 * ---	1,2,6-8	
P,X	EP-A-0 611 989 (KONICA CORPORATION) * page 29, line 17 - line 28 * ---	1-5,7,8	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
P,X	EP-A-0 640 872 (KONICA CORPORATION) * page 27, line 10 - line 21 * -----	1-3,7,8	G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 September 1995	Bolger, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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