(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 687 951 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : **95303857.7**

(51) Int. Cl.[6] : **G03C 5/26,** G03C 7/407

(22) Date of filing : **06.06.95**

(30) Priority : **10.06.94 JP 129157/94**

(43) Date of publication of application :
20.12.95 Bulletin 95/51

(84) Designated Contracting States :
DE FR GB NL

(71) Applicant : **KONICA CORPORATION**
26-2, Nishi-shinjuku 1-chome
Shinjuku-ku
Tokyo 163 (JP)

(72) Inventor : **Deguchi, Takashi**
c/o Konica Corporation,
1 Sakura-machi
Hino-shi, Tokyo (JP)
Inventor : **Tsuchiya, Ichiro**
c/o Konica Corporation,
1 Sakura-machi
Hino-shi, Tokyo (JP)

(74) Representative : **Ellis-Jones, Patrick George Armine**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(54) **Granular or tablet-form color-developing composition**

(57) A solid processing compositon for color-developing a silver halide color photographic material which is in the form of granules or a tablet, the solid processing composition containing an alkali agent and a compound represented by the following formula [P] and having a moisture content of 0.5 to 5.0% by weight,
formula [P]
$HO-(A_1-O)_{\ell 1}-(A_2-O)_{\ell 2}-(A_3-O)_{\ell 3}-H$
where A_1, A_2 and A_3 independently represent an alkylene group.

EP 0 687 951 A1

Field of the Invention

The present invention relates to a granular processing composition and a tablet-form processing composition (hereinafter referred to simply as a solid processing composition as a general term) both for color-developing a silver halide color photographic light-sensitive material.

Background of the Invention

Recently, a method wherein photographic processing chemicals are solidified and added directly to a dissolving tank, or a method wherein processing agents are dissolved in water in advance and are used as a conventional working solution (a starter and a replenisher) as disclosed in Japanese Patent Publication Open to Public Inspection Nos. 119454/1993, 254853/1992 and 197090/1993 (hereinafter referred to as Japanese Patent O.P.I Publication) are under study, for the purpose of solving problems, such as legal restriction for transportation, a problem of handling, mixing of other processing agent caused by the bursting of a container caused by a shock in transportation and reduction of storage space at the user side, all are caused by the fact that photographic processing chemicals are a liquid.

In Japanese Patent O.P.I. Publication No. 61837/1976, on the other hand, there are disclosed a photographic processing tablet-formed composition containing a carbonate and polyethyleneoxide and a method of manufacturing the same. This method, however, proved to have a new problem that the tablet absorbs moisture rapidly and swells because it is anhydrous, when it is subjected to aging storage, though it is dissolved easily in water.

In Japanese Patent O.P.I. Publication No. 254853/1992, on the other hand, there is disclosed a photographic processing agent that is spray granulated polyethyleneoxide. Granules prepared in this method are greatly free from occurrence of fine powder, but it proved to have a new problem that a solid processing composition sticks to another (blocking phenomenon) when the processing agents are stored hermetically for a certain period of time.

In Japanese Patent O.P.I. Publication No. 119450/1993, on the other hand, there is disclosed a tablet whose moisture content is controlled to 0.5 - 10.0 wt%. A tablet made by this method has been improved remarkably in residue rate of a color developing agent, the state of a tablet immediately after it is dropped, and existence of insoluble matters. Even in this method, however, it proved to have new problems that a solid processing composition is swollen or causes blocking.

In Japanese Patent O.P.I. Publication Nos. 142708/1993, 197090/1993, 341468/1993 and 102628/1994, on the other hand, there are disclosed granules wherein a paraphenylenediamine (hereinafter referred to sometimes as p-phenylenediamine) type color developing agent, hydroxylamine derivative and alkali agent are respectively granulated, and average particle size of the granules is controlled within a specific range, or polyethylene glycol and a specific compound are contained. The tablet made through this method has been remarkably improved, as compared with a conventional one, in dissolving property, residue rate of paraphenylenediamine type color developing agent, reduction of occurrence of insoluble matters and strength as well as molding property of the tablet. However, it was proved to have a new problem.

Summary of the Invention

In view of the aforementioned problems, an object of the invention is to provide a granular processing composition and tablet-form processing composition used for color-developing a silver halide color photographic light-sensitive material capable of reducing greatly generation of fine powder caused by hygroscopic swelling of solid processing composition. Another object of the invention is to provide a granular solid processing composition and tablet-form processing composition used for color-developing a silver halide color photographic light-sensitive material wherein sticking of solid processing composition can be reduced greatly in aging storage of the processing compositions.

The objects of the invention mentioned above can be attained by the following constitution.

1. A granular processing composition used for color-developing a silver halide color photographic light-sensitive material containing an alkali agent, wherein the composition contains a compound represented by the following formula [P] is, having a moisture content of 0.5 - 5.0 wt%.

Formula [P] $HO\text{-}(A_1\text{-}O)_{\ell 1}\text{-}(A_2\text{-}O)_{\ell 2}\text{-}(A_3\text{-}O)_{\ell 3}\text{-}H$

In the formula, A_1, A_2 and A_3 each represent a straight chained or branched alkylene group, which may be substituted, and these may be either the same with or different from each other. ℓ_1, ℓ_2 and ℓ_3 each represent 0 or an integer of 1 - 500.

2. The granular solid processing composition used for color-developing a silver halide color photographic

light-sensitive material described in Item 1 above, wherein the aforementioned alkali agent is a carbonate.

3. The granular solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Item 1 or Item 2 above, wherein the content of a compound represented by the Formula [P] for the total weight in the above-mentioned granular solid processing composition is 1.0 - 30.0 wt%.

4. The granular solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Items 1 - 3 above, wherein a compound represented by the Formula [P] is polyethylene glycol.

5. The granular solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Item 4, wherein an average molecular weight of the polyethylene glycol is 2000 - 20000.

6. The granular solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Items 1 - 5 above, wherein the granular solid processing composition is a mixture with a paraphenylenediamine type granule.

7. The granular solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Items 1 - 6 above, wherein 60 wt% or more of the granular solid processing compositions have a particle size within a range of 149 - 1490 μm.

8. A tablet-shaped solid processing composition used for color-developing a silver halide color photographic light-sensitive material containing at least one kind of alkali agent, wherein at least one kind of the compounds represented by the Formula [P] mentioned above is contained and moisture content at 80°C is 0.5 - 5.0wt%.

9. The tablet-shaped solid processing composition used for color-developing a silver halide color photographic light-sensitive material containing at least one kind of alkali agent described in Item 8, wherein the granular solid processing composition which contains the alkali agent and at least one kind of the compounds represented by the Formula [P] and has the moisture content of 0.5 - 5.0 wt% at 80°C is formed into the tablet-shaped solid processing composition.

10. The tablet-shaped solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Item 8 or Item 9 above, wherein the alkali agent is a carbonate.

11. The tablet-shaped solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Items 8 - 10 above, wherein the content of a compound represented by the Formula [P] mentioned above for the total weight in the above-mentioned tablet-shaped solid processing composition is 1.0 - 30.0 wt%.

12. The tablet-shaped solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Items 8 - 11 above, wherein a compound represented by the Formula [P] is polyethylene glycol.

13. The tablet-shaped solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Item 12, wherein an average molecular weight of the polyethylene glycol is 2000 - 20000.

14. The tablet-shaped solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Items 8 - 13 above, wherein the tablet-shaped solid processing composition is obtained by compression-molding a mixture of paraphenylenediamine type granule and the alkali agent.

15. The tablet-shaped solid processing composition used for color-developing a silver halide color photographic light-sensitive material described in Items 8 - 14 above, wherein the tablet-shaped solid processing composition is obtained by compression-molding solid processing compositions in which 60 wt% or more of the tablet-shaped solid processing compositions containing the alkali agent have a particle size within a range of 149 - 1490 μm.

Detailed explanations of the invention.

Inventors of the present invention found out, through experiments, the following facts with respect to an alkali agent-containing solid processing composition for color-developing a silver halide color photographic light-sensitive material.

It was found that unless a compound represented by the Formula [P] is contained in the solid processing composition for color-developing a silver halide color photographic light-sensitive material containing alkali agents of the invention, the solid processing composition swells suddenly on moisture sorption, resulting in occurrence of fine powder.

Even when a compound represented by Formula [P] is contained in the solid processing composition, unless the moisture content is controlled in the scaled up production, there happened problems of instability that fine powder was generated and blocking was caused, although sufficient performances as a solid processing

composition were obtained in some cases. Further, in a test model of storage at high temperature for transportation, there was sometimes observed a problem of instability.

After intensive studies on this point, the inventors of the invention found out that it is possible to provide a solid processing composition which are stable even in the scaled up production if the moisture content of the solid processing composition at 80°C is controlled to be within a range of 0.5 - 5.0 wt%.

When the moisture content (wt%) is less than 0.5 wt%, a solid processing composition having no problem immediately after production thereof show, in aging storage, such a problem that the solid processing composition retaining no moisture swells rapidly when they absorb moisture, resulting in production of fine powder.

When the moisture content exceeded 5.0 wt%, there was caused another problem that a solid processing composition retaining moisture stuck to another solid processing composition in storage at high temperature.

The reason why the moisture content is measured is that the stability of solid processing composition in temperature is important for the following reasons, though the stability in humidity is also important. When solid processing composition are transported by sea after shipment, temperature and humidity are not controlled normally during the transportation and actual measured temperature of 45 - 50°C is observed. In this case, it is very difficult to control the temperature though the humidity can be controlled by moistureproofing agents or the like. After making studies on this point, it was found out that solid processing composition extremely improved in temperature stability can be obtained even in the case of scaled up production, if the moisture content of the solid processing composition is controlled within a range of 0.5 - 5.0 wt%, provided that the moisture content (wt%) is calculated under the condition that all of the reduction in weight in heating at 80°C for 1 hour is regarded as moisture.

A solid processing composition of the invention contains at least one of alkali agents and at least one of the compounds represented by the Formula [P], and when this solid processing composition is granular, it is made through granulation after the alkali agent and the compound are mixed. Even when a part of granules contains alkali agent and another part of the granules contains only a compound represented by the Formula [P], such granules are also included in the invention. A tablet-formed solid processing composition may be made either through compression molding after powdery solid materials are mixed or through compression molding after the step of mixing and granulation. From the viewpoint of storage stability, a tablet-shaped solid processing composition made through compression molding after the step of granulation is preferable. The mixture in the invention is one made through mixing or compression molding after alkali agents and paraphenylenediamine compounds are respectively granulated separately, for example, an alkali agent, paraphenylenediamine type color developing agent and preserving agent (hydroxylamine and/or its derivative) are granulated respectively and then subjected to the mixing and the compression molding.

As a method for manufacturing granular solid processing composition, known methods such as rolling granulation, extrusion granulation, compression granulation, cracking granulation, stirring granulation, moving-bed granulation and spray drying granulation may be used, and from the viewpoint of granule strength of a granular processing composition, the method of stirring granulation is preferable.

As a method for manufacturing a tablet-form solid processing composition, a method employing a well-known compressor may be used. For example, a hydraulic press, a single shot tablet-molding machine, a rotary tablet-molding machine and a briquetting machine may be used. Though a tablet-form solid processing composition can take any shape, a cylindrical one is preferable from the viewpoint of productivity and ease of handling. When the tablet-form solid processing composition is cylindrical in shape, a tablet whose ratio of its diameter to its thickness is within a range of 1.0 - 6.0 is preferable and a tablet with that ratio of 2.0 - 4.0 is more preferable from the viewpoint of prevention of occurrence of powder caused by vibration during transportation. While the diameter of a tablet can take any value, depending on the purpose of application, its range of 5 - 50 mm is preferable and that of 7 - 30 mm is more preferable from the viewpoint of productivity.

In the invention, the moisture content of a solid processing composition which is within a range of 0.5 - 5.0 wt% is satisfactory, but from the viewpoint of effects of the invention, the range of 0.8 - 3.5 wt% is preferable. In addition, for controlling the moisture content to be within the range of the invention, the method to granulate by the use of a solvent, namely the wet type granulating method is preferable. In the case of the wet granulation, a solvent is added to raw materials of powder for granulation, and a solvent used in this case includes a polar solvent such as alcohol, acetone, acetonitrile and water, and a mixture thereof may also be used. From the viewpoint of explosion-proof, water is used more preferably. It is preferable that an added amount of the above-mentioned solvent to raw materials is 1 - 10 wt% and that of 2 - 6 wt% is more preferable. When the added amount is less than 1 wt%, granulation can not be conducted sufficiently, while when it exceeds 10 wt%, there sometimes happen that not only drying time is extended but also raw materials are deteriorated in the course of granulation and drying.

Moisture content (at 80°C) in the invention is a value based on all of reduced weight, which is calculated as moisture after drying the material for one hour at 80°C by used of a commercially-available electronic mois-

ture meter. Measurement is conducted, using a sample of about 10 g, under the conditions of atmospheric pressure, temperature of 25 - 30°C and relative humidity of 40 - 45%. Alternatively, the moisture content of the invention is calculated by using the following equation:

$$\text{Percent moisture content} = (w_0 - w)/w_0 \times 100$$

where w_0 and w are a weight of a material before and after being dried at 80°C for one hour, respectively.

A particle size in the invention is a value obtained by measuring particle sizes after sieving them by the use of a sieve specified in the Japanese Industrial Standards. From the viewpoint of preventing the fluctuation before and after the storage, it is preferable that 60 wt% or more of particles have the particle size within the range of 149 - 1490 μm. It is more preferable that 70 wt% or more of particles have the particle size within the range of 149 - 1490 μm.

Next, compounds represented by Formula [P] in the invention will be explained concretely as follows.

$$HO\text{-}(A_1\text{-}O)_{\ell 1}\text{-}(A_2\text{-}O)_{\ell 2}\text{-}(A_3\text{-}O)_{\ell 3}\text{-}H$$

In the formula, A_1, A_2 and A_3 each represent a straight chained or branched alkylene group, which may be substituted and these may be either the same or different.

As a substituent, there may be given a hydroxy group, a carboxy group, a sulfonyl group, an alkoxy group, a carbamoyle group and a sulfamoyle group. Preferably, A_1, A_2 and A_3 are each an unsubstituted alkylene group. More preferably A_1, A_2 and A_3 each are $-CH_2CH_2-$ or $-CH(CH_3)-CH_2-$.

ℓ_1, ℓ_2 and ℓ_3 each represent 0 or integers of 1 - 500, provided that the total number thereof is equal to or larger than 5 ($\ell_1 + \ell_2 + \ell_3 \geqq 5$)

Among the foregoing, preferably, at least one of ℓ_1, ℓ_2 and ℓ_3 is 15 or more and more preferably, at least one of ℓ_1, ℓ_2 and ℓ_3 is 20 or more.

When a compound represented by Formula [P] in the invention is a copolymer wherein two kinds of monomers A and B are copolymerized, those having configurations shown below are also included.

-A-B-A-B-A-B-A-B-A-B-

-A-A-B-A-B-B-A-A-A-B-A-A-B-B-A-

-A-A-A-A-A-A-B-B-B-B-B-B-A-A-A-A-A-

Among those copolymers is preferable a block polymer (nonionic polymer of a Pluronic type) of ethylene glycol and propylene glycol represented by the following Formula [P'].

Formula [P'] $HO\text{-}(CH_2CH_2\text{-}O)_{\ell 4}\text{-}[CH(CH_3)CH_2\text{-}O]_{\ell 5}\text{-}(CH_2CH_2\text{-}O)_{\ell 6}\text{-}H$

In the formula, ℓ_4, ℓ_5 and ℓ_6 are the same as those defined in ℓ_1, ℓ_2 and ℓ_3 in the aforementioned Formula [P].

In a compound represented by Formula [P'] in the invention, it is preferable that the content (wt%) of ethyleneoxide in the total molecular weight is 70 wt% or more, and it is especially preferable that the content is 80 wt% or more.

Concrete compounds represented by Formula [P] and Formula [P'] are further shown below.

Compound, HO-(CH_2-CH_2-O)n"-H	Average molecular weight
P-1	300
P-2	600
P-3	1000
P-4	1500
P-5	2000
P-6	3000
P-7	4000
P-8	6000
P-9	10000
P-10	15000
P-11	20000
P-12	30000

Compound, HO-(CH_2CH_2-O)a'-[$CH(CH_3)$-CH_2-O]b'-(CH_2CH_2-O)c'-H	Content (wt%) of ethyleneoxide in the total molecular weight	Average molecular weight
P'-1	80	8350
P'-2	80	10800
P'-3	50	4600
P'-4	70	6500
P'-5	80	5000
P'-6	50	3500
P'-7	70	7850
P'-8	50	4150

Among compounds represented by Formula [P] and Formula [P'] in the invention, the most preferable is polyethylene glycol (hereinafter referred to sometimes as PEG).

In the case of polyethylene glycol, those having an average molecular weight ranging from 2000 to 20000 are preferable, and especially preferable includes those having an average molecular weight ranging from 3000 to 15000.

The average molecular weight in the invention is a molecular weight determined based on a hydroxyl value.

It is preferable in terms of effects of the invention that a compound represented by the aforementioned Formula [P] is contained in an amount of 1 - 30 wt% per unit weight of solid processing composition of the invention, and 3 - 20 wt% is more preferable. Further, compounds represented by the Formula [P] may be used independently or in combination of two or more kinds.

Next, an alkali agent will be explained as follows.

An alkali agent in the invention is a compound which shows alkalinity of pH of 8 or more in an aqueous

solution thereof. Preferable concrete examples include sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, tripotassium phosphate, , disodium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium hydroxide, potassium hydroxide, and lithium hydroxide. From the moisture-proof viewpoint, sodium carbonate, potassium carbonate sodium bicarbonate, sodium borate and trisodium phosphate are preferable. Among them, a carbonate is especially preferable in the invention.

As a p-phenylenediamine compound in the invention, those having a water-solubilizing group are used preferably because they offer the effects of the invention superbly and they cause less occurrence of fog.

Compared with a paraphenylenediamine compound having no water-solubilizing group such as N,N-diethyl-p-phenylenediamine and others, a p-phenylenediamine compound having a water-solubilizing group not only has an advantage that a light-sensitive material is not contaminated thereby and a rash is not caused even when it sticks to the skin, but also attains efficiently an object of the invention when it is combined with a color developing solution of the invention.

As the above-mentioned water-solubilizing group, those wherein an amino group or a benzene nucleus of p-phenylenediamine compound has at least one are given, and a practical preferable water-solubilizing group includes the following.

$-(CH_2)_n-CH_2OH$,
$-(CH_2)_m-NHSO_2-(CH_2)_nCH_3$,
$-(CH_2)_m-O-(CH_2)_n-CH_3$,
$-(CH_2CH_2O)_nC_mH_{2m+1}$

(m and n represent integers of not less than 0),

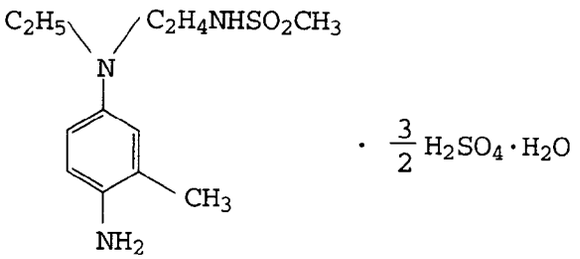
-COOH group,

and

$-SO_3H$

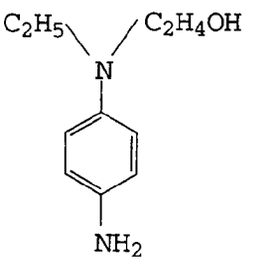
As an exemplified compound of p-phenylenediamine compound used preferably in the invention, there may be given following compounds to which, however, the invention is not limited.

(C-1)



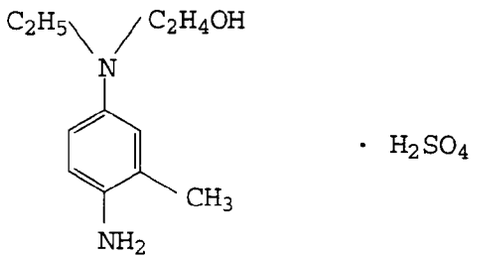
$\cdot \frac{3}{2} H_2SO_4 \cdot H_2O$

(C-2)

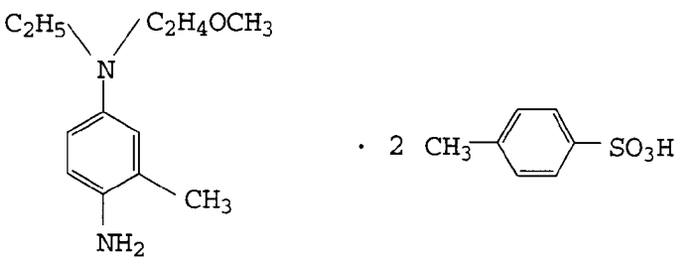


$\cdot H_2SO_4$

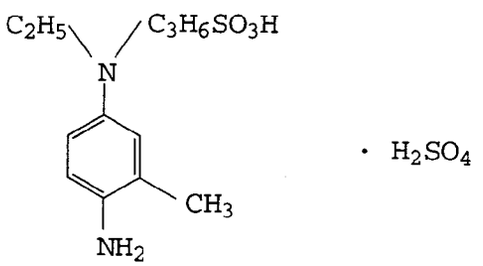
(C-3)



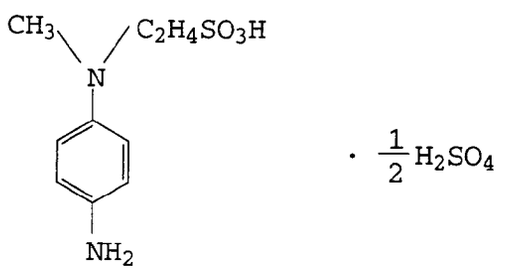
(C-4)



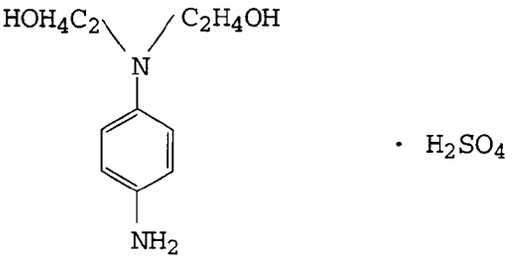
(C-5)



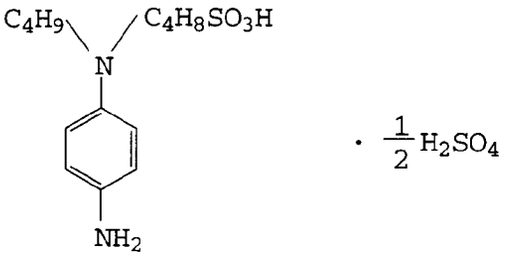
(C-6)



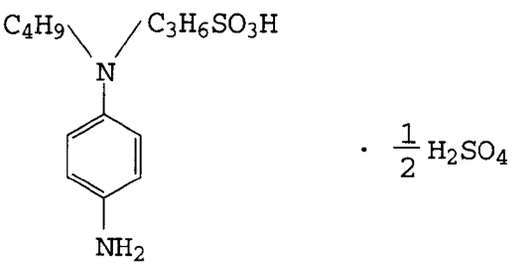
(C-7)



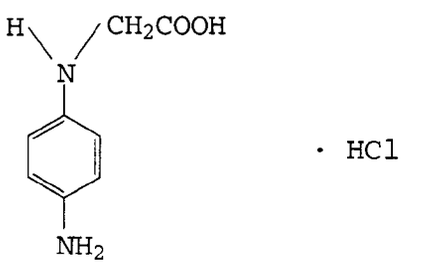
(C-8)



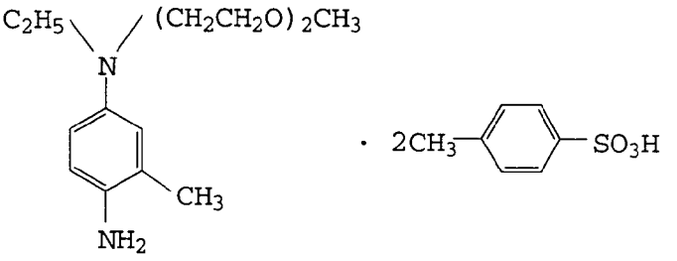
(C-9)



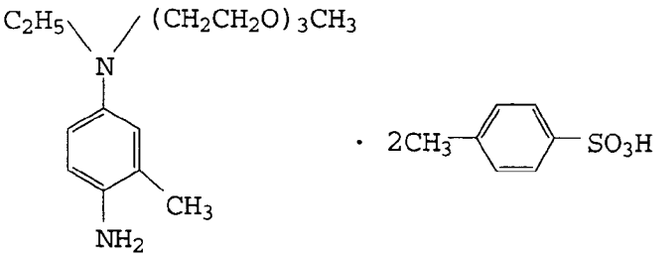
(C-10)



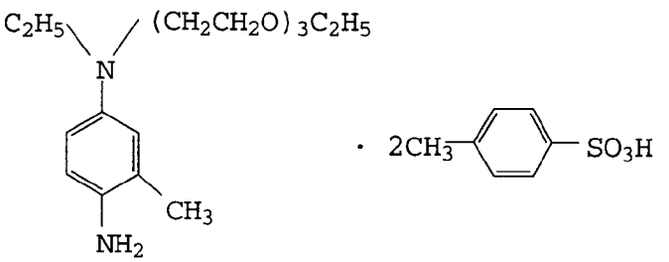
(C-11)



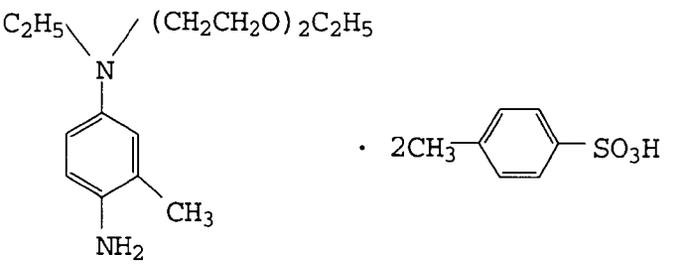
(C-12)



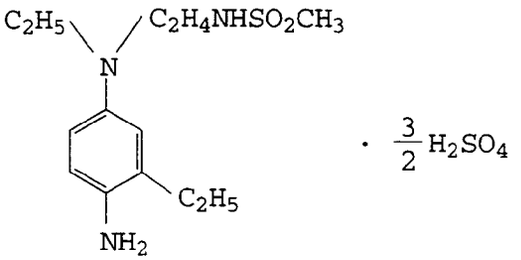
(C-13)



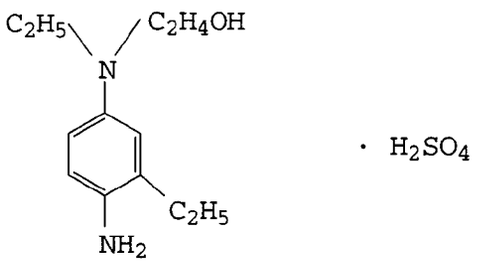
(C-14)



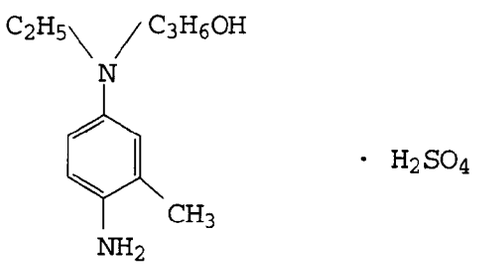
(C-15)



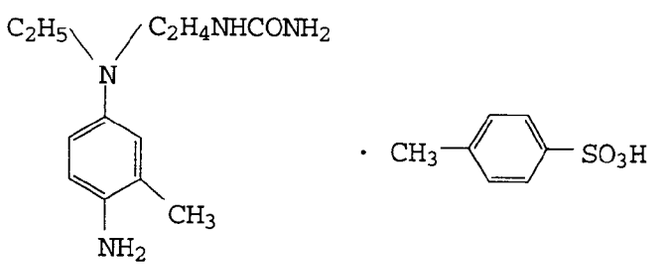
(C-16)



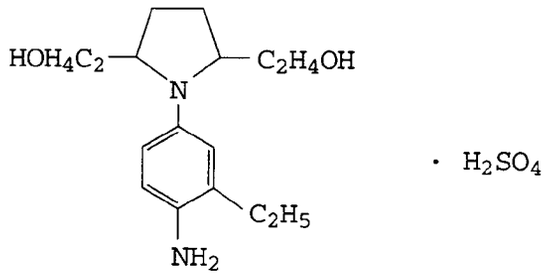
(C-17)



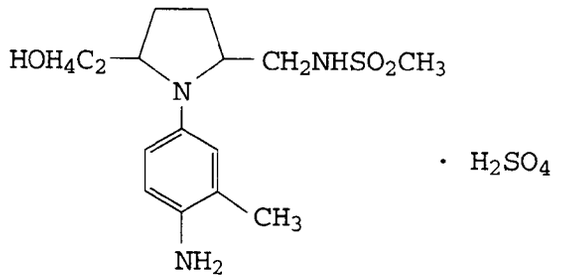
(C-18)



(C-19)



(C-20)

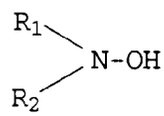


The aforementioned color developing agent is used usually in a form of a salt such as a hydrochloride, a sulfate and a p-toluenesulfonate salt.

In the invention, more advantageous effects can be displayed when the color developing agent of the invention contains a compound represented by Formula [A] shown below.

Namely, there are provided effects that when solidified, storage stability of a solid processing composition such in a form of granule or a tablet is improved compared with other compounds, and in addition, strength of the solid processing composition can be maintained. Further, it is stable in photographic performance and it causes less fog on the unexposed portion.

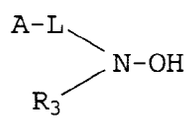
Formula [A]



In the formula, R_1 and R_2 independently represent a hydrogen atom and a substituted or unsubstituted alkyl group.

With regard to the compound represented by the aforesaid Formula [A] of the invention, those represented further by the following Formula [A'] are preferable from the viewpoint of the invention.

Formula [A']



In the formula [A'], L represents a substituted or unsubstituted and straight-chained or branched alkylene group having carbons of 1 - 10, preferably of 1 - 5. For example, methylene, ethylene, trimethylene and propylene are given, and as a substituent, a carboxyl group, a sulphone group, a phosphone group, a phosphinic

acid agroup, a hydroxy group, a cyano group and an ammonio group which may be substituted by an alkyl group having 1 - 5 carbon atoms are given.

A represents a carboxyl group, a sulfone group, a phosphone group, a phosphinic acid residue, a hydroxy group, a cyano group, an alkoxy group, an amino group which may have an alkyl group having 1 to 5 carbon atoms, an ammonio group which may have an alkyl group having 1 to 5 carbon atoms, a carbamoyl group which may have an alkyl group having 1 to 5 carbon atoms, a sulfamoyl group which may have an alkyl group having 1 to 5 carbon atoms and a substituted or unsubstituted alkylsulfonyl group.

The example of A-L- represents carboxymethyl, carboxyethyl, carboxypropyl, sulfoethyl, sulfopropyl, sulfobutyl, phosphonomethyl, phosphonoethyl, methoxyethyl, cyanoethyl and hydroxyethyl.

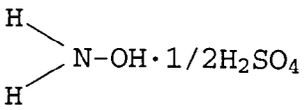
R_3 represents a hydrogen atom, a substituted or unsubstituted, straight chained or branched alkyl group having 1 to 10 carbon atoms. The substituent includes a carboxyl group, a sulfo group, a phosphone group, a phosphonic acid residue, a hydroxy group, a cyano group, an alkoxy group, a carbamoyl group and an ammonio group which may have an alkyl group having 1 to about 5 carbon atoms, provided that L and R may combine to form a ring. These compounds are used as an isolated amine and also as a salt such as a hydrochloride, a sulfate, an oxalate, a p-toluenesulfonate, an alkali metal salt and an ammonium salt.

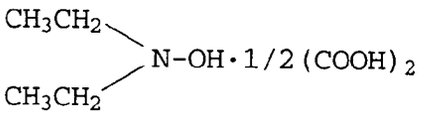
The exemplified compound represented by Formula [A] of the invention will be given below, but is not limited thereto.

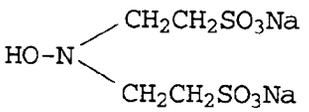
	R_1	R_2
A-1	-H	-H
A-2	-H	$-CH_3$
A-3	$-CH_3$	$-CH_3$
A-4	-H	$-C_2H_5$
A-5	$-CH_3$	$-C_2H_5$
A-6	$-C_2H_5$	$-C_2H_5$
A-7	$-C_3H_7$(n)	$-C_3H_7$(n)
A-8	$-C_3H_7$(i)	$-C_3H_7$(i)
A-9	$-C_4H_9$(n)	$-C_4H_9$(n)
A-10	$-C_4H_9$(i)	$-C_4H_9$(i)
A-11	$-C_4H_9$(t)	$-C_4H_9$(t)
A-12	$-CH_3$	$-CH_2CH_2COOH$
A-13	$-CH_3$	$-CH_2CH_2SO_3H$
A-14	$-CH_3$	$-CH_2COOH$
A-15	$-CH_3$	$-CH_2CH_2PO_3H_2$
A-16	-H	$-CH_2CH_2SO_3H$
A-17	$-CH_2CH_2COOH$	$-CH_2CH_2COOH$
A-18	$-CH_2CH_2SO_3H$	$-CH_2CH_2SO_3H$
A-19	$-CH_2COOH$	$-CH_2COOH$
A-20	$-CH_2CH_2PO_3H_2$	$-CH_2CH_2PO_3H_2$
A-21	$-CH_2CH_2OH$	$-CH_2CH_2OH$
A-22	$-CH_3$	$-CH_2CH_2CONH_2$
A-23	$-CH_2CH_2CONH_2$	$-CH_2CH_2CONH_2$
A-24	$-CH_3$	$-CH_2CH_2OCH_3$
A-25	$-CH_2CH_2OCH_3$	$-CH_2CH_2OCH_3$
A-26	$-CH_3$	$-CH_2CH_2OH$
A-27	$-CH_2CH(CH_3)COOH$	$-CH_2CH(CH_3)COOH$
A-28	$-CH_2CH_2CN$	$-CH_2CH_2CN$

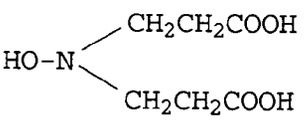
Incidentally, compounds A-12 - A-20 and A-27 can be used in a form of an alkali metal salt (sodium salt, potassium salt and lithium salt).

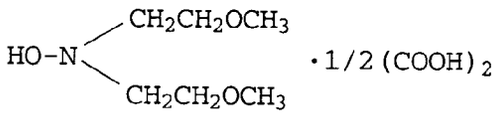
Preferable compounds among those mentioned above are the following compounds.









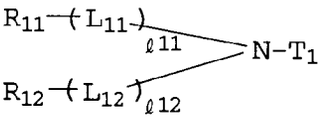


It is preferable in terms of prevention of dispersion caused in production that a sulfite, a bisulfite or a metabisulfite is added to the solid processing composition of the invention. Concrete examples of the aforementioned sulfite, bisulfite, metabisulfite include sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite and potassium metabisulfite. Preferable one includes sodium sulfite and potassium sulfite, and these compounds can be used in an arbitrary form of an anhydrous salt and hydrous salt. In the case of the hydrous salt, however, the one wherein water is not isolated at 50°C or less is especially preferable in terms of the effects of the invention.

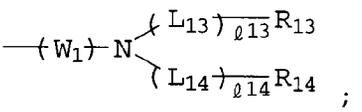
It is possible to add a halide to the solid processing composition of the invention from the viewpoint of prevention of fog. As a halide, there may be given potassium chloride, sodium chloride, potassium bromide, sodium bromide, potassium iodide and sodium iodide.

The solid processing composition of the invention may contain a chelating agent represented by the following Formula [I].

Formula [I]

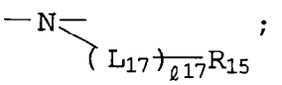


In the formula, T_1 represents a hydrogen atom, a hydroxy group, a carboxy group, a sulfo group, a carbamoyl group, a phosphono group, a phosphone group, a sulfamoyl group, a substituted or unsubstituted alkyl group, an alkoxy group, an alkylsulfonamide group, an alkylthio group, an acylamino group,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



;

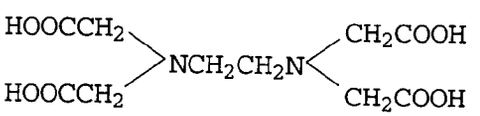
W_1 represents a substituted or unsubstituted alkylene group, an arylene group, an alkenyl group, a cycloalkylene group, an aralkylene group or $-(L_{15}-X)_{\ell 15}-(L_{16})_{\ell 16}-$; X represents -O-, -S-, a divalent heterocycle or



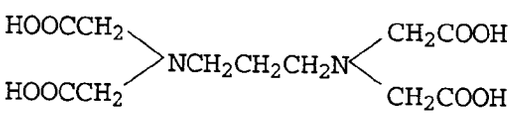
;

R_{11} through R_{15} 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 sulfonamide group, an acylamino group and a hydroxam acid group, provided that at least one of R_{11} through R_{15} represents a carboxy group; L_{11} through L_{17} represent a substituted or unsubstituted alkylene group, arylene group, alkenyl group, cycloalkylene group or aralkylene group; and ℓ_{11} through ℓ_{17} independently represent an integer of 0 to 6, provided that ℓ_{15} and ℓ_{16} are not 0 concurrently.

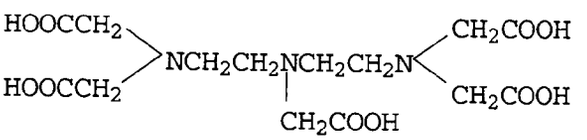
(I-1)



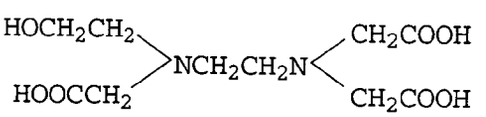
(I-2)



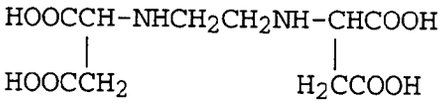
(I-3)



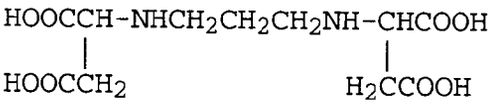
(I-4)



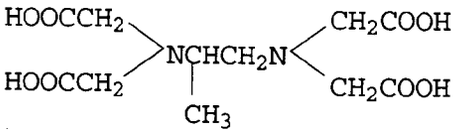
(I-5)



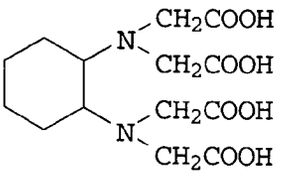
(I-6)



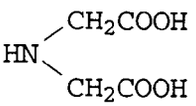
(I-7)



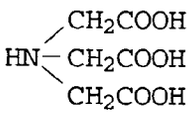
(I-8)



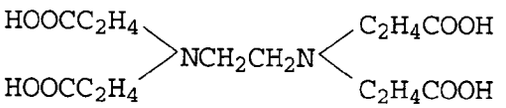
(I-9)



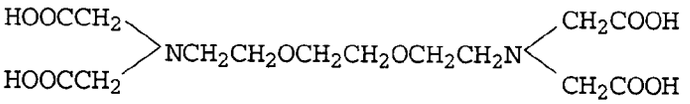
(I-10)



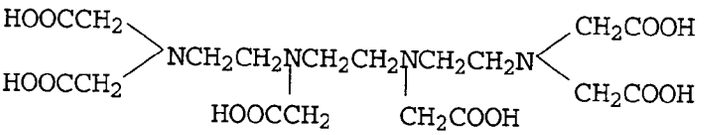
(I-11)



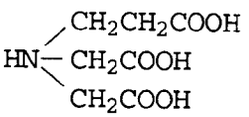
(I-12)



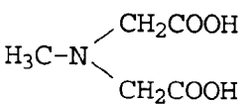
(I-13)



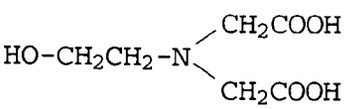
(I-14)



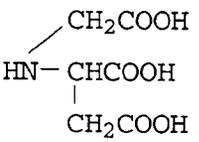
(I-15)



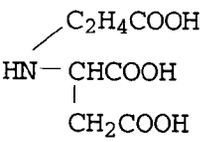
(I-16)



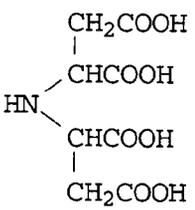
(I-17)



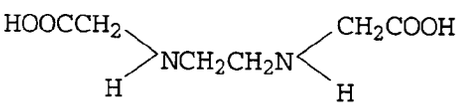
(I-18)



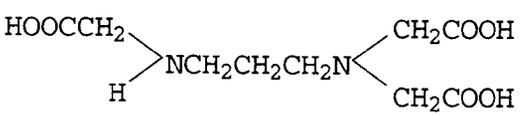
(I-19)



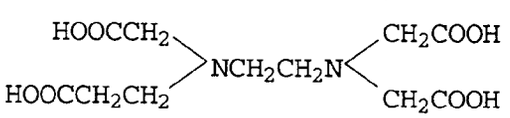
(I-20)



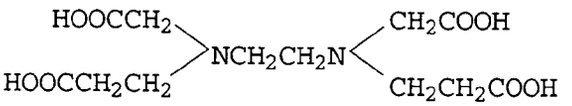
(I-21)



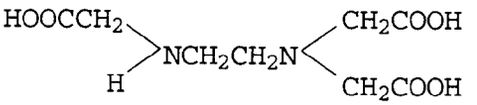
(I-22)



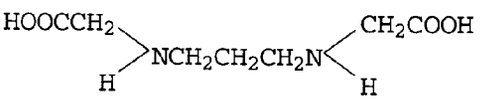
(I-23)



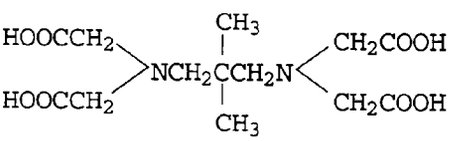
(I-24)



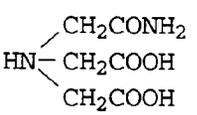
(I-25)



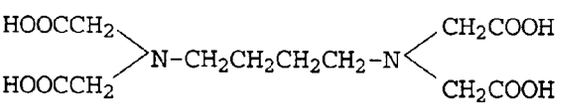
(I-26)



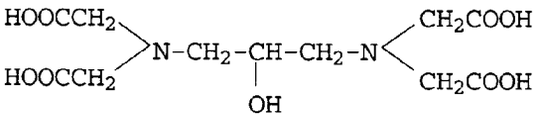
(I-27)



(I-28)



(I-29)



Exemplified compounds of the aforesaid chelating agent that improves the effects of the invention include (I-1) - (I-8), (I-12), (I-14) - (I-20), (I-22), (I-23) and (I-27). Among those, the preferable includes (I-1), (I-2), (I-3), (I-5), (I-6), (I-12), (I-14), (I-15) and (I-17). These compounds can be used in a form of a free acid, sodium salt and potassium salt. An especially preferable compound is sodium salt.

The saccharides in the invention refer to monosaccharides or polysaccharides in which monosaccharides are combined with each other through a glycosid bond including a derivative thereof or a decomposition product thereof.

Monosaccharides refer to as a polyhydroxy aldehyde, polyhydroxy ketone and their derivatives such as reduction derivatives, oxidation derivatives, deoxy-derivatives, amino-derivatives or thio-derivatives. Most of them are represented by the general formula $C_{n'}(H_2O)m'$. The monosaccharide in the invention includes a compound derived from saccharide skeleton represented by the above formula. The preferable is a sugar alcohol 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, 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 including a derivative thereof in the invention will be shown below.

(Exemplified compounds)

B-(1) glycelaldehyde
B-(2) dihydroxyacetone (including a dimer)
B-(3) D-erythrulose
B-(4) L-erythrulose
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-lixose
B-(14) L-lixose
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-quinobose
B-(37) digitalose
B-(38) Digitoxose
B-(39) Cymalose
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-galactosamine
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-glucuronic acid
B-(64) L-glucuronic acid
B-(65) N-acetyl-D-glucosamine
B-(66) Glycerin
B-(67) D-threitol
B-(68) L-threitol
B-(69) meso-Erithorit (produced by Mitsubishi Kasei Shokuhin Co. Ltd., Erythritol)
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

Of these compounds, B-(66) through (83) are preferably used, and B-(69) and B-(74) through (83) are more preferably used.

Examples of polysaccharides and their decomposition products 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) agalose
C-(18) amylose
C-(19) sucrose
C-(20) agarobiose
C-(21) Methylcellulose
C-(22) Dimethylcellulose
C-(23) Trimethylcellulose
C-(24) Ethylcellulose
C-(25) Diethylcellulose
C-(26) Triethylcellulose
C-(27) Carboxymethylcellulose
C-(28) Carboxyethylcellulose
C-(29) Aminoethylcellulose
C-(30) Hydroxymethylcellulose
C-(31) Hydroxyethylcellulose
C-(32) Hydroxypropylcellulose
C-(33) Hydroxypropylmethylcellulose
C-(34) Hydroxypropylmethylcelluloseacetatesuccinate
C-(35) carboxymethylhydroxyethylcellulose
C-(36) α-dextrin
C-(37) β-dextrin
C-(38) γ-dextrin
C-(39) δ-dextrin
C-(40) ε-dextrin
C-(41) α-limit-dextrin
C-(42) β-limit-dextrin
C-(43) Phospherylase limit dextrim
C-(44) Soluble starch
C-(45) Thin-boling starch
C-(46) White dextrin
C-(47) Yellow dextrin
C-(48) British gumm
C-(49) α-cyclodextrin
C-(50) β-cyclodextrin
C-(51) γ-cyclodextrin
C-(52) Hydroxypropyl-α-cyclodextrin
C-(53) Hydroxypropyl-β-cyclodextrin
C-(54) Hydroxypropyl-γ-cyclodextrin
C-(55) Maltodextrin

Of these compounds, C-(21) through (55) are preferably used, and compounds, C-(36) through (55) are more preferably used. The weight average molecular weight of dextrins used in the invention may be any, but

it is preferably 10 through 10000.

Saccharides exist widely in the nature, and are commercially available. The derivatives can be readily prepared by reduction, oxidation or dehydration reactions. The starch compounds available on the market include Pineflow, Pine-dex series, Max 100, Glistar P, TK-16, MPD, H-PDX and Stuco-dex produced by Matsutani Kagaku Co., Ltd. or Oil Q series produced by Nihon Yushi Co., Ltd.

Examples

The invention will be explained in detail as follows, referring to examples to which the invention is not limited.

Example 1

Preparation of samples of granular solid processing composition

Operation (1 - 1)

Alkali agent (Compound described on Table 1)	13000 g
Compound represented by Formula [P], as described in Table 1	2000 g

Compounds stated above each were crushed by a commercially-available hammer mill to the particle size of 149 μm or less. The resulting crushed compounds were mixed sufficiently by a commercially-available stirring granulating machine, and then water was added thereto for granulation.

The granules thus obtained were dried by a commercially-available moving-bed dryer, while controlling the temperature of hot air to be at 50 - 65°C in the course of drying. In the course of drying and after drying, the granules were subjected to grain-dressing by a commercially-available granulating machine, with the use of a 1.5 mm-mesh screen.

An added amount of water and drying time both for the granulation were adjusted appropriately so that the moisture content described in Table 1 may be obtained.

In the manner stated above, granule samples (1-1) - (1-26) were prepared.

Experiment (1-1)

The granular samples (1-1) - (1-26) thus prepared were vibrated for one minute by a micro-type electromagnetic vibration screening machine (Model M-100) by the use of a screen with 100 μm-mesh. After fine powder is removed completely, samples weighing 50 g on the screen were put in an opened laboratory dish to prepare two each for various samples, which were stored for three hours in the environmental chamber where the temperature was 25°C and relative humidity was 45%. After the storage, the granular samples were screened again by the screen with 100 μm-mesh under the above-mentioned conditions, to test the occurrence of powder after storage.

Following criteria were used for evaluation.

⓪⓪: None of the two samples passed through the screen.

⓪: Only one sample passed through the screen, and occurrence of fine powder was observed. However, an amount of fine powder was very small and it did not fly up, causing no problem.

○: Both samples passed through the screen. However, an amount of fine powder was very small and it did not fly up, causing no problem.

×: Both samples passed through the screen, and occurrence of fine powder was caused and its flying up was observed.

Experiment (1-2)

From each of granular samples (1-1) - (1-26) prepared, samples each weighing 100 g were picked up and sealed by aluminum packaging material individually. These were stored for 30 days under the following conditions by use of a small-sized environmental testing machine. Blocking properties of the granular samples after the storage were evaluated.

The results of the evaluation are shown on Table 1.

Following criterias were used for evaluation.

ⓞⓞ: Two samples did not show at all the occurrence of blocking.

ⓞ: Only one sample showed blocking, but it was caused just partially, which was restored soon by fine vibration.

○: Both samples showed blocking, but it was caused just partially, which was restored soon by fine vibration.

×: Both samples showed blocking each taking place on about a half of the total of each sample, and the blocking was not restored by fine vibration.

Samples ranked X, when they are supplied at a constant amount, cause dispersion, which is a problem.

Temperature change conditions

Temperature was changed to be 60°C → 20°C → 60°C at a cycle of 16 hours Incidentally, conditions for temperature to rise and fall was 5°C/1 hour.

Table 1

Sample No.	Alkali agent	Compounds represented by Formula [P]	Moisture content (wt%)	Occurrence of fine powder	Blocking	Remarks
1-1	Potassium carbonate	PEG Average molecular weight 300	2.0	○	○	Inv.
1-2	Potassium carbonate	PEG Average molecular weight 600	2.0	○	○	Inv.
1-3	Potassium carbonate	PEG Average molecular weight 1500	2.0	○	○	Inv.
1-4	Potassium carbonate	PEG Average molecular weight 2000	2.0	○	◎	Inv.
1-5	Potassium carbonate	PEG Average molecular weight 3000	2.0	◎◎	◎◎	Inv.
1-6	Potassium carbonate	PEG Average molecular weight 6000	2.0	◎◎	◎◎	Inv.
1-7	Potassium carbonate	PEG Average molecular weight 10000	2.0	◎◎	◎◎	Inv.
1-8	Potassium carbonate	PEG Average molecular weight 15000	2.0	◎◎	◎◎	Inv.
1-9	Potassium carbonate	PEG Average molecular weight 20000	2.0	◎	◎◎	Inv.
1-10	Potassium carbonate	PEG Average molecular weight 30000	2.0	○	◎◎	Inv.
1-11	Potassium carbonate	Pluronic A*1	2.0	○	◎◎	Inv.
1-12	Potassium carbonate	Pluronic B*2	2.0	○	◎	Inv.
1-13	Potassium carbonate	Pluronic C*3	2.0	○	◎◎	Inv.
1-14	Sodium carbonate	PEG Average molecular weight 6000	2.0	◎◎	◎◎	Inv.
1-15	Trisodium-phosphate	PEG Average molecular weight 6000	2.0	○	◎◎	Inv.
1-16	Potassium carbonate	PEG Average molecular weight 6000	0.3	×	◎◎	Comp.
1-17	Potassium carbonate	PEG Average molecular weight 6000	0.5	○	◎◎	Inv.
1-18	Potassium carbonate	PEG Average molecular weight 6000	0.8	◎	◎◎	Inv.
1-19	Potassium carbonate	PEG Average molecular weight 6000	1.0	◎◎	◎◎	Inv.
1-20	Potassium carbonate	PEG Average molecular weight 6000	1.5	◎◎	◎◎	Inv.

Table 1 (continued)

Sample No.	Alkali agent	Compounds represented by Formula [P]	Moisture content (wt%)	Occurrence of fine powder	Blocking	Remarks
1-21	Potassium carbonate	PEG Average molecular weight 6000	3.0	◎◎	◎	Inv.
1-22	Potassium carbonate	PEG Average molecular weight 6000	3.5	◎	◎	Inv.
1-23	Potassium carbonate	PEG Average molecular weight 6000	4.0	◎	○	Inv.
1-24	Potassium carbonate	PEG Average molecular weight 6000	5.0	◎	○	Inv.
1-25	Potassium carbonate	PEG Average molecular weight 6000	6.0	◎	×	Comp.
1-26	Potassium carbonate	-	2.0	×	◎	Comp.

Inv.: Invention Comp.: Comparative

*1 Blockpolymer of ethyleneoxide and propyleneoxide; ethyleneoxide content, 80 wt%; average molecular weight 8350

*2 Blockpolymer of ethyleneoxide and propyleneoxide; ethyleneoxide content, 50 wt%; average molecular weight 4150

*3 Blockpolymer of ethyleneoxide and propyleneoxide; ethyleneoxide content, 70 wt%; average molecular weight 6500

As is apparent from Table 1, it is understood that when a compound represented by Formula [P] and an alkali agent are contained in a granular solid processing composition of the invention and the moisture content is controlled to be 0.5 - 5.0 wt%, it is possible to provide a granular solid processing composition wherein occurrence of fine powder after moisture absorption and blocking tendency in hermetical storage are greatly reduced.

Effects of the invention were remarkably exhibited when an alkali agent is a carbonate and a compound represented by Formula [P] is polyethyleneglycol having an average molecular weight of 2000 - 20000. Though the moisture content that ranges from 0.5 wt% to 5.0 wt% is satisfactory in the invention, it was found that more effects of the invention were obtained when the moisture content is within the range of 0.8 - 3.5 wt%.

Example 2

Operation (2-1)

Preparation of granular solid processing composition samples

Potassium carbonate	10000 g
Sodium sulfite	1400 g
Pentasodium diethylenetriaminepentaacetate	600 g
Polyethyleneglycol #6000 (made by Nihon Yushi Co., Ltd.)	added amount in Table 2
Sodium paratoluenesulfonate	2000 g
D-mannitol	1000 g

Each of the above-mentioned compounds was crushed and granulated in the same manner as in Example 1. In this case, an amount of water added was 4 wt% of the total weight used for granulation, and granules thus obtained were dried until the moisture content showed 1.5 - 2.0 wt%.

The resulting granules were subjected to grain-dressing in a similar manner to Example 1.

The samples thus obtained were defined to be granular samples (2-1) - (2-11).

Operation (2-2)

Potassium carbonate	7000 g
Sodium sulfite	100 g
Pentasodium diethylenetriaminepentaacetate	700 g
Polyethyleneglycol #4000 (made by Nihon Yushi Co., Ltd.)	added amount in Table 2
D-mannitol	1200 g
Sodium paratoluenesulfonate	3000 g
Lithium hydroxide monohydrate	800 g

Granular samples (2-12) - (2-22) were prepared from the above-mentioned compounds through the same manner as in Operation (2-1).

Experiment (2-1)

Evaluation was made for the samples in the same manner as in Experiments (1-1) and (1-2).

Table 2 shows the results of the experiments.

Table 2

Sample No.	Added amount (wt%) of compound represented by Formula [P] per composition	Occurrence of fine powder	Blocking	Remarks
2-1	0	×	◎	Comparative
2-2	0.5	○	◎	Invention
2-3	1.0	◎	◎	Invention
2-4	3.0	◎	◎◎	Invention
2-5	5.0	◎◎	◎◎	Invention
2-6	10.0	◎◎	◎◎	Invention
2-7	15.0	◎◎	◎◎	Invention
2-8	20.0	◎◎	◎◎	Invention
2-9	25.0	◎◎	◎	Invention
2-10	30.0	◎◎	◎	Invention
2-11	35.0	◎◎	○	Invention
2-12	0	×	◎	Comparative
2-13	0.5	○	◎	Invention
2-14	1.0	◎	◎	Invention
2-15	3.0	◎	◎◎	Invention
2-16	5.0	◎◎	◎◎	Invention
2-17	10.0	◎◎	◎◎	Invention
2-18	15.0	◎◎	◎◎	Invention
2-19	20.0	◎◎	◎◎	Invention
2-20	25.0	◎◎	◎	Invention
2-21	30.0	◎◎	◎	Invention
2-22	35.0	◎◎	○	Invention

As is apparent from Table 2, it is understood that addition of polyethyleneglycol in an amount of 1.0 - 30 wt% per unit weight to the granular solid processing composition of the invention is preferable in terms of the effects of the invention, and an addition amount of 3.0 - 20.0 wt% is more preferable.

Example 3

Operation (3-1)

4-amino-3-methyl-N-ethyl-β-(hydroxy)ethyl-aniline sulfate granule (CD-4) (produced by Konica Chemical Co., Ltd.)	1700 g

The above-mentioned granules were subjected to grain size-dressing by a grain size-selecting machine, and classified by the use of a screen to control them within a range of particle size from 149 to 1490 μm. This

was defined to be Granule (A).

Operation (3-2)

4-amino-3-methyl-N-ethyl-N-[-β-(methane-sulphoneamide)ethyl]aniline 3/2 sulfate monohydrate granules (CD-3) (produced by Konica Chemical Co., Ltd.)	3000 g

The above-mentioned compounds were sieved and classified in the same manner as in Operation (3-1), and this was denoted as Granule (B).

Operation (3-3)

Hydroxylamine sulfate	1000 g
Potassium bromide	100 g
Disodium pyrocatechol-3,5-disulfonic acid monohydrate	50 g
Pineflow (maltodextrin)	100 g

The above compounds were crushed by a commercially-available hammer mill to the particle size of 149 μm or less.

These crushed compounds were mixed sufficiently by a commercially-available stirring and granulating machine, and then water was added thereto for granulation.

An amount of water added in this case was 3 wt% of the total weight of the crushed compounds. These granules were dried by a commercially-available moving-bed dryer until the moisture content (at 80°C) showed 1.5 - 2.0 wt% while controlling the temperature of hot air for drying at 50 - 60°C. The granules were size-selected by a commercially-available grain size-dressing machine during the course of drying and after drying, and then classified by the use of a screen to control the particle size of the granules within a range of 149 - 1490 μm.

These granules were defined to be Granule (C).

Operation (3-4)

Bis(sulphoethyl)hydroxylamine disodiumsalt	1000 g
Tinopal SFP (produced by Ciba Geigy Co., Ltd.)	3000 g
Sodium paratoluenesulfonate	500 g
D-mannitol	500 g

The above-mentioned compounds were crushed, granulated, dried and size-selected under the same conditions as in Operation (3-3), and then were fractionated. These granules were defined to be Granule (D).

Operation (3-5)

Potassium carbonate	10000 g
Sodium sulfite	1400 g
Pentasodium diethylenetriaminepentaacetate	600 g
Polyethyleneglycol #6000 (produced by Nihon Yushi Co., Ltd.)	1300 g
Sodium paratoluenesulfonate	2000 g
D-mannitol	2000 g

The above-mentioned compounds were crushed, granulated, dried and size-selected under the same conditions as in Operation (2-1). In this case, the screen for size-selecting was changed and the compounds were classified by the use of a screen so that the particle size was controlled to that shown on Table 3. These granules were defined to be Granule (E).

Operation (3-6)

Potassium carbonate	7000 g
Sodium sulfite	100 g
Pentasodium diethylenetriaminepentaacetate	700 g
Polyethyleneglycol #4000 (produced by Nihon Yushi Co., Ltd.)	1000 g
D-mannitol	2000 g
Paratoluenesulfonicacid sodium salt	3000 g
Lithium hydroxide monohydrate	800 g

The above-mentioned compounds were crushed, granulated, dried, size-selected and classified in the same manner as in Operation (3-5) so that the particle size was controlled to that shown on Table 3. These granules were defined to be Granule (F).

Experiment (3-1)

The mixture of granules described on Table 3 was put in a commercially-available cross-rotary mixing machine for sufficient mixing. After that, 1 kg of the mixture was picked up to be stored under the same conditions as in Experiment (1-1).

Granular samples (3-1) - (3-12) among the mixture mentioned above each weighing 10 g were picked up 10 times for the determination of paraphenylenediamine compound to evaluate the fluctuation thereof.

The aforementioned granular samples after being stored were mixed again by the mixing machine. The samples after mixing each weighing 10 g were picked up 10 times for the test of fluctuation of solid processing composition through determination of paraphenylenediamine compound.

Evaluation criteria

ⓞⓞ: All samples are within a fluctuation range of ±3%.
ⓞ: All samples are within a range of ±5%.
○: Not less than 7 pcs are within a range of ±5% and the rest are within a range of ±10%.
×: Not less than 5 pcs are within a range of +5% and some of the rest exceed ±10%.
However, when some of them exceed ±10%, processing is adversely affected, which is not allowed.

Experiment (3-2)

Some 20 g of the mixture prepared by mixing combined granules at the rate described on Table 3 was picked up and put in an opened laboratory dish, then stored for 60 minutes under the conditions of temperature

at 25°C and relative humidity at 45%. After that, the granular samples (3-1) - (3-12) after being stored were sealed with aluminum packaging materials and stored for 30 days in a small-sized environmental testing equipment having the same condition of temperature change as in Experiment (1-2). The granular samples after being stored were subjected to evaluation of coloring.

Evaluation criteria

⊚: Blackened portion was not observed.
○: Tiny blackened portions were observed partially at several locations, each being in a shape of a spot.
×: Most portions were blackened.

Table 3 shows the results of the evaluation.

Table 3

Sample No.	Granules			Moisture content (%)	Fluctuation		Coloring	Remarks
					Fresh sample	Stored sample		
3-1	(A)	(C)	(E) 50*	2.0	○	○	○	Inv.
3-2	(A)	(C)	(E) 60*	2.0	○	○	⊚	Inv.
3-3	(A)	(C)	(E) 70*	2.0	⊚	⊚	⊚	Inv.
3-4	(A)	(C)	(E) 80*	2.0	⊚⊚	⊚⊚	⊚	Inv.
3-5	(A)	(C)	(E) 80*	0.3	⊚⊚	×	×	Comp.
3-6	(A)	(C)	(E) 80*	6.0	⊚⊚	×	×	Comp.
3-7	(B)	(D)	(F) 50*	2.0	○	○	○	Inv.
3-8	(B)	(D)	(F) 60*	2.0	○	○	⊚	Inv.
3-9	(B)	(D)	(F) 70*	2.0	⊚	⊚	⊚	Inv.
3-10	(B)	(D)	(F) 80*	2.0	⊚⊚	⊚⊚	⊚	Inv.
3-11	(B)	(D)	(F) 80*	0.3	⊚⊚	×	×	Comp.
3-12	(B)	(D)	(F) 80*	6.0	⊚⊚	×	×	Comp.

* Percentage (wt%) of granules (E) or (F) having a size of 149 - 1490 μm

As is apparent from Table 3, when a paraphenylenediamine compound is mixed with the granular solid processing composition of the invention, it is possible to provide a granular solid processing composition wherein coloring and composition fluctuation of after storage are greatly reduced. Further, it is understood that when 70 wt% or more of solid processing composition is accounted for by granules having a particle size of 149 - 1490 μm, the fluctuation before storage can also be reduced.

Example 4

Preparation of tablet-shaped solid processing composition samples

Operation (4-1)

Granular samples were prepared in the same manner as in Example 1. To the granular solid processing composition thus prepared, sodium myristoyl-N-methyl-β-alanine crushed to the particle size of 100 μm or less

was added in an amount of 0.5 wt% of the total weight of the solid processing composition, and then they were mixed for 3 minutes by a commercially-available cross-rotary mixing machine. The mixed granules were subjected to continuous tablet-molding on the modified rotary tableting machine, Clean Pressed Correct 18K made by Kikusui Manufacturing Co., Ltd. Tablets were prepared under conditions that a diameter of a tablet was 15 mm, weight of a tablet, 1.5 g and pressure for compression, 1400 kg/cm^2 (Samples 4-1 through 4-26).

Operation (4-2)

Alkali agent (compound described on Table 5)	13000 g

The compounds were each crushed to the particle size of 149 μm or less by a commercially-available hammer mill. These crushed compounds were granulated in a commercially-available stirring and granulating machine by adding water thereto.

The granules thus obtained were dried by a commercially-available moving-bed drying machine while controlling the temperature of hot air for drying to be at 50 - 65°C. The granules were size-selected by a commercially-available size-selecting machine by the use of a 1.5 mm screen during the course of drying and after drying. Further, an amount of water added for granulation and a drying time were adjusted appropriately so that moisture content shown on Table 5 may be obtained.

2000 g of a compound (described on Table 5) represented by Formula [P] and crushed to the particle size of 149 μm or less was added to the granules mentioned above, and they were mixed for 10 minutes in a commercially-available cross-rotary mixing machine. Then, sodium myristoyl-N-methyl-β alanine crushed to the particle size of 100 μm or less was added to the above-mentioned mixture in an amount of 0.5 wt% of the total weight of the solid processing composition, and mixing was further conducted for 3 minutes. The mixture was subjected to continuous tablet-molding in the same manner as in Operation (4-1). Thus, tablet-shaped Samples (4-27) - (4-37) were prepared.

In the manner mentioned above, tablet-shaped Sample (4-1) - (4-37) were prepared.

Experiment (4-1)

The tablet-shaped samples thus prepared were put in an opened laboratory dish so that two each for respective samples were prepared. They were stored for 3 hours in an environmental chamber where temperature and relative humidity were maintained at 25°C and 45% respectively. Each sample after storage was vibrated for 1 minute by a micro-type electromagnetic vibrator (Model M-100) with a screen with 100 μm-mesh, and occurrence of fine powder after storage was tested.

Evaluation conditions for the above test were the same as those in Experiment (1-1).

Experiment (4-2)

Two each of the respective tablet-shaped samples thus prepared were superposed and packed in the same manner as in Experiment (1-2), and they were stored. The above-mentioned tablet-shaped samples after storage was evaluated with respect to stickiness thereof.

Tables 4 and 5 show the results of the evaluation.

Evaluation criteria

ⓞⓞ: Sticking was not observed at all.
ⓞ: When lifting tablets, sticking between tablets was slightly felt, but no sticking was observed.
○: When lifting tablets, sticking between tablets took place. However, they were easily separated by slight vibration.
×: There occurred sticking between tablets which were not separated by slight vibration.

Table 4

Sample No.	Granular sample used	Alkali agents	Compounds represented by Formula [P]	Moisture content (wt%)	Occurrence of fine powder	Sticking	Remarks
4-1	1-1	Potassium carbonate	PEG Average molecular weight 300	2.0	○	○	Inv.
4-2	1-2	Potassium carbonate	PEG Average molecular weight 600	2.0	○	○	Inv.
4-3	1-3	Potassium carbonate	PEG Average molecular weight 1500	2.0	○	○	Inv.
4-4	1-4	Potassium carbonate	PEG Average molecular weight 2000	2.0	○	◎	Inv.
4-5	1-5	Potassium carbonate	PEG Average molecular weight 3000	2.0	◎◎	◎◎	Inv.
4-6	1-6	Potassium carbonate	PEG Average molecular weight 6000	2.0	◎◎	◎◎	Inv.
4-7	1-7	Potassium carbonate	PEG Average molecular weight 10000	2.0	◎◎	◎◎	Inv.
4-8	1-8	Potassium carbonate	PEG Average molecular weight 15000	2.0	◎◎	◎◎	Inv.
4-9	1-9	Potassium carbonate	PEG Average molecular weight 20000	2.0	◎	◎◎	Inv.
4-10	1-10	Potassium carbonate	PEG Average molecular weight 30000	2.0	○	◎◎	Inv.
4-11	1-11	Potassium carbonate	Pluronic A*1	2.0	○	◎◎	Inv.
4-12	1-12	Potassium carbonate	Pluronic B*2	2.0	○	◎	Inv.
4-13	1-13	Potassium carbonate	Pluronic C*3	2.0	○	◎◎	Inv.
4-14	1-14	Sodium carbonate	PEG Average molecular weight 6000	2.0	◎◎	◎◎	Inv.
4-15	1-15	Trisodium-phosphate	PEG Average molecular weight 6000	2.0	○	◎◎	Inv.
4-16	1-16	Potassium carbonate	PEG Average molecular weight 6000	0.3	×	◎◎	Comp.

*1 Block copolymer of ethyleneoxide and propyleneoxide, ethyleneoxide content 80 wt% average molecular weight 8350

*2 Block copolymer of ethyleneoxide and propyleneoxide, ethyleneoxide content 50 wt% average molecular weight 4150

*3 Block copolymer of ethyleneoxide and propyleneoxide, ethyleneoxide content 70 wt% average molecular weight 6500

Table 4 (continued)

Sample No.	Granular sample used	Alkali agents	Compounds represented by Formula [P]	Moisture content (wt%)	Occurrence of fine powder	Sticking	Remarks
4-17	1-17	Potassium carbonate	PEG Average molecular weight 6000	0.5	○	◎◎	Inv.
4-18	1-18	Potassium carbonate	PEG Average molecular weight 6000	0.8	◎	◎◎	Inv.
4-19	1-19	Potassium carbonate	PEG Average molecular weight 6000	1.0	◎◎	◎◎	Inv.
4-20	1-20	Potassium carbonate	PEG Average molecular weight 6000	1.5	◎◎	◎◎	Inv.
4-21	1-21	Potassium carbonate	PEG Average molecular weight 6000	3.0	◎◎	◎	Inv.
4-22	1-22	Potassium carbonate	PEG Average molecular weight 6000	3.5	◎	◎	Inv.
4-23	1-23	Potassium carbonate	PEG Average molecular weight 6000	4.0	◎	○	Inv.
4-24	1-24	Potassium carbonate	PEG Average molecular weight 6000	5.0	◎	○	Inv.
4-25	1-25	Potassium carbonate	PEG Average molecular weight 6000	6.0	◎	×	Comp.
4-26	1-26	Potassium carbonate	-	2.0	×	◎	Comp.

Table 5

Sample No.	Granular sample used	Alkali agents	Compounds represented by Formula [P]	Moisture content (wt%)	Occurrence of fine powder	Sticking	Remarks
4-27	-	Potassium carbonate	PEG Average molecular weight 6000	0.3	×	◎	Comp.
4-28	-	Potassium carbonate	PEG Average molecular weight 6000	0.5	○	◎	Inv.
4-29	-	Potassium carbonate	PEG Average molecular weight 6000	0.8	○	◎	Inv.
4-30	-	Potassium carbonate	PEG Average molecular weight 6000	1.0	◎	◎	Inv.
4-31	-	Potassium carbonate	PEG Average molecular weight 6000	1.5	◎	◎	Inv.
4-32	-	Potassium carbonate	PEG Average molecular weight 6000	2.0	◎	◎	Inv.
4-33	-	Potassium carbonate	PEG Average molecular weight 6000	3.0	◎	◎	Inv.
4-34	-	Potassium carbonate	PEG Average molecular weight 6000	3.5	○	○	Inv.
4-35	-	Potassium carbonate	PEG Average molecular weight 6000	4.0	○	○	Inv.
4-36	-	Potassium carbonate	PEG Average molecular weight 6000	5.0	○	○	Inv.
4-37	-	Potassium carbonate	PEG Average molecular weight 6000	6.0	×	×	Comp.

Inv.: Invention Comp.: Comparative

As is apparent from Tables 4 and 5, it is understood that when a compound represented by Formula [P] and an alkali agent are contained in a tablet-shaped solid processing composition of the invention and the moisture content is controlled to be 0.5 - 5.0 wt%, it is possible to provide a tablet-shaped solid processing composition wherein occurrence of fine powder after moisture absorption and sticking of tablet-shaped solid processing compositions in hermetical storage are greatly reduced. In addition, it is understood that more effects of the invention are displayed by tablet-shaped samples prepared by mixing an alkali agent and a compound represented by Formula [P] and using the granular samples.

Further, when an alkali agent is a carbonate and a compound represented by Formula [P] is polyethyleneglycol having an average molecular weight of 2000 - 20000, more effects of the invention are exhibited.

The moisture content that is within 0.5 - 5.0 wt% is satisfactory, but when it is within 0.8 - 3.5 wt%, more effects of the invention can be exhibited.

Example 5

Preparation of tablet-shaped solid processing composition

Operation (5-1)

Granular samples were prepared in the same manner as in Example 2.

From the granular samples, tablet-shaped Samples (5-1) - (5-22) were prepared in the same manner as in Example 4.

Samples were prepared under the condition that a diameter of a tablet was 20 mm, weight of a tablet, 2.6

g and pressure for compression, 1400 kg/cm^2.

Experiment (5-1)

In the same manner as in Experiments (4-1) and (4-2), samples were evaluated with respect to occurrence of fine powder and sticking, provided that the method and criteria of the evaluation were the same as those in Example 4.

Table 6 shows the results of the evaluation.

Table 6

Sample No.	Granular sample used	Added amount (wt%) of compound represented by Formula [P]	Occurrence of fine powder	Sticking	Remarks
5-1	2-1	0	×	◎	Comparative
5-2	2-2	0.5	○	◎	Invention
5-3	2-3	1.0	◎	◎	Invention
5-4	2-4	3.0	◎	◎◎	Invention
5-5	2-5	5.0	◎◎	◎◎	Invention
5-6	2-6	10.0	◎◎	◎◎	Invention
5-7	2-7	15.0	◎◎	◎◎	Invention
5-8	2-8	20.0	◎◎	◎◎	Invention
5-9	2-9	25.0	◎◎	◎	Invention
5-10	2-10	30.0	◎◎	◎	Invention
5-11	2-11	35.0	◎◎	○	Invention
5-12	2-12	0	×	◎	Comparative
5-13	2-13	0.5	○	◎	Invention
5-14	2-14	1.0	◎	◎	Invention
5-15	2-15	3.0	◎	◎◎	Invention
5-16	2-16	5.0	◎◎	◎◎	Invention
5-17	2-17	10.0	◎◎	◎◎	Invention
5-18	2-18	15.0	◎◎	◎◎	Invention
5-19	2-19	20.0	◎◎	◎◎	Invention
5-20	2-20	25.0	◎◎	◎	Invention
5-21	2-21	30.0	◎◎	◎	Invention
5-22	2-22	35.0	◎◎	○	Invention

As is apparent from Table 6, it is understood that it is preferable in terms of effects of the invention that polyethyleneglycol is added in an amount of 1.0 - 30 wt% per unit weight, and 3.0 - 20.0 wt% is more preferable.

Example 6

Operation (6-1)

Granules (A), (C) and (E) were prepared in the same manner as in Example 3.

Granules (A), (C) and (E) were mixed for 10 minutes by a commercially-available cross-rotary mixing machine, then sodium myristoyl-N-metyl-β-alanine was added thereto in an amount of 0.5 wt% of the total weight of the mixture to be mixed for another 3 minutes, and thereby tablet-shaped samples (6-1) - (6-6) were prepared in the same manner as in Example 4. In the conditions for preparation in this case, a diameter of a tablet was 30 mm, weight of a tablet was 12.0 g and pressure for compression was 1400 kg/cm^2.

Operation (6-2)

Granules (B), (D) and (F) were subjected to mixing and compression-molding under the same conditions for preparation as in Operation (6-1), and thereby tablet-shaped samples (6-7) - (6-12) were prepared.

Experiment (6-1)

In the same manner as in Experiment (3-2), the tablet-shaped solid processing composition was evaluated with respect to coloring thereof.

Table 7 shows the results of the evaluation.

Experiment (6-2)

From an average value (average of 10 pcs) of compression breaking strength of the prepared tablet-shaped solid processing composition before storage (S_0) and that after the storage (S) under the same conditions as in Experiment (6-1), the rate of reduction between before and after the storage was calculated ((S_0-S)/S_0×100).

The results thereof are shown on Table 7, wherein, those showing the reduction of 10% or more are not acceptable because they are broken by shock.

Table 7

Sample No.	Granular sample used	Coloring	Reduction of compression breaking strength (%)	Remarks
6-1	3-1	○	5.3	Invention
6-2	3-2	◎	5.8	Invention
6-3	3-3	◎	2.7	Invention
6-4	3-4	◎	0.9	Invention
6-5	3-5	×	25.3	Comparative
6-6	3-6	×	4.2	Comparative
6-7	3-7	○	5.6	Invention
6-8	3-8	◎	4.9	Invention
6-9	3-9	◎	2.4	Invention
6-10	3-10	◎	1.1	Invention
6-11	3-11	×	24.8	Comparative
6-12	3-12	×	3.8	Comparative

As is apparent from Table 7, it is understood that when a tablet-shaped solid processing composition of the invention is mixed with paraphenylenediamine compound, it is possible to provide a tablet-shaped solid processing composition improved in coloring. It is further understood that when 70 wt% or more of the processing composition is accounted for by the particle size within a range of 149 - 1490 μm, hardness reduction after storage can also be greatly reduced.

Claims

1. A solid processing compositon for color-developing a silver halide color photographic material wherein said solid processing composition is in the form of granules or a tablet, said solid processing composition containing an alkali agent and a compound represented by the following formula [P] and having a moisture content of 0.5 to 5.0% based on weight, the moisture content being a value based on all of the reduced weight of the composition after drying the composition for one hour at 80°C,

formula [P] $HO\text{-}(A_1\text{-}O)_{\ell 1}\text{-}(A_2\text{-}O)_{\ell 2}\text{-}(A_3\text{-}O)_{\ell 3}\text{-}H$

wherein A_1, A_2 and A_3 independently represent an alkylene group; and ℓ_1, ℓ_2 and ℓ_3 is independently an integer of 0 to 500.

2. The solid processing composition of claim 1, wherein said alkali agent is a carbonate.

3. The solid processing composition of claim 1, wherein said compound represented by formula [P] is contained in an amount of 1.0 to 30.0% based on weight.

4. The solid processing composition of claim 3, wherein said compound represented by formula [P] is polyethylene glycol.

5. The solid processing composition of claim 4, wherein said polyethylene glycol has an average molecular weight of 2000 to 20000.

6. The solid processing composition of claim 1, wherein said solid processing composition is mixed with a granulated p-phenylenediamine compound to form a mixture.

7. The solid processing composition of claim 1, wherein said solid processing composition is in the form of granules, at least 60% by weight of said solid processing composition having a particle size of 149 to 1490 μm.

8. The solid processing composition of claim 1, wherein said solid processing composition is in the form of a tablet and is prepared by pressure-molding said solid processing composition which is in the form of granules containing the alkali agent and the compound represented by formuls [P] and having a moisture content of 0.5 to 5.0% based on weight to form a tablet.

9. The solid processing composition of claim 1, wherein said solid processing composition is in the form of a tablet and is prepared by a process of comprising the steps of;

mixing a granulated p-phenylenediamine compound with the solid processing composition which is in the form of granules containing the alkali agent and the compound represented by formula [P] and having a moisture content of 0.5 to 5.0% based on weight to form a mixture and

compression-molding the mixture to prepare the tablet.

10. The solid processing composition of claim 9, wherein at least 60% by weight of said solid processing composition which is in the form of granules has a particle size of 149 to 1490 μm.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 3857

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)
P,X	EP-A-0 640 872 (KONICA CORPORATION) * Example 1 ; see especially operation (iii) and Tablets A,B,C * * page 18, line 24 - line 42 * * Table 1, experiments with hygroscopic properties G and F * * Table 2, experiment 2-6 * * Example 3; see especially Tablets 1 and 5 * * Table 3, experiments 3-1 , 3-2, 3-9, 3-10 * * Example 4, Table 4 *	1-10	G03C5/26 G03C7/407
Y	US-A-5 258 268 (K.H REUTER ET AL) * column 1, line 50 - column 2, line 12 * * column 2, line 42 - line 51; claim 1 *	1-10	
D,Y	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 *	1-10	
Y	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 *	1-10	
A	EP-A-0 534 227 (KONICA CORPORATION) * Table 1, samples 6,7 * * page 6, line 1 - line 17 *	1,2,4	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
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
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)