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(54) Developing granule or tablet for silver halide photographic light-sensitive materials and method of manufacturing the same

(57) A method of manufacturing a granular or tablet developing composition for a silver halide photographic light-sensitive material is disclosed which comprises the step of:

granulating a developing agent to prepare first granules comprising the developing agent,

granulating an alkali agent to prepare second granules comprising the alkali agent, and

mixing the first granules and the second granules,

wherein the content in the first granules of granules having a particle size of 1000μm or more (JIS) is not more than 10 weight % based on the total weight of the first granules and the content in the second granules of granules having a particle size of 1000μm or more (JIS) is not more than 10 weight % based on the total weight of the second granules.

EP 0 691 571 A1

Description

FIELD OF THE INVENTION

The invention relates to a solid developing composition for a silver halide photographic light-sensitive material and a manufacturing method thereof, and particularly a solid developing composition having improved storage stability for a silver halide photographic light-sensitive material and a manufacturing method thereof.

BACKGROUND OF THE INVENTION

A developing composition for a silver halide photographic light-sensitive material is usually supplied in the form of plural concentrated solutions (kit) to consumers. Recently, in the color photographic processing industry, small-scaled developing stores, so-called mini-labs, which process a photographic material using a small automatic processor, rapidly increased and the amount of the processing kits used also increased. A processing kit, in which plural concentrated solutions are packaged in plastic bottles of 100 milliliter to 5 liter, is supplied to customers, but the processing kit still requires much storage space. Further, the cost for transport is not low. The discarded plastic bottles increase year by year, causing an environmental problem. The processing kit for developer is usually supplied in plural separate parts. The consumers mix the parts in a specific proportion to prepare developer replenisher, but errors frequently occur during the mixing operations.

Powder photographic processing compositions are considered in order to overcome the above problems. However, the powder compositions produce loose powder when dissolved in water, and operators breathe in loose powder particles, resulting in health hazard. Further, other photographic solutions may be contaminated with the components of the loose powder and there occurs the possibility of other troubles in developing process.

In response to these problems Japanese Patent O.P.I Publication Nos. 2-109042/1990 and 2-109043/1990 disclose a technique of using a granular mixture of photographic processing agents. Patent O.P.I Publication Nos. 5-119454/1993 and 5-113646/1993 disclose a photographic processing system using a granular or tablet processing agent.

The above described techniques can prevent fine powder occurrence of the solid processing agent, but there is a problem particularly in a tablet developing composition that it is difficult to discharge tablets in a cartridge or to quantitatively supply tablets in a supplying device on account of expansion of the tablets during storage. The problem is noticeably displayed particularly when the tablets are transported by ship from Japan to Southeast Asia, the Middle and Near East or Africa in 2 to 4 weeks, during which the temperature difference between day and night is 15-20°C and the humidity difference between day and night is 20-30%.

There is another problem that, when different granular processing agents are mixed to obtain one granular processing composition, the granular processing composition having a desired component content cannot be obtained. This causes a serious problem that continuous photographic processing is impossible. In order to solve this problem, Japanese Patent O.P.I. Publication No. 5-119454/1993 discloses a method of obtaining a solid processing composition having a desired component content by using granular compositions having an average particle size within a specific range. However, this reference does not disclose a tablet developing composition and the method disclosed therein could not sufficiently solve the above problems. Japanese Patent O.P.I. Publication No. 5-142708/1993 discloses a method of mixing granular compositions having an average particle size within a specific range and then tableting the mixture to obtain a solid processing composition. This method prevents an inner reaction of a tablet color developing composition during a long term storage, but is not sufficient to prevent expansion of the tablet.

SUMMARY OF THE INVENTION

Accordingly, an object of the invention is to provide a tablet developing composition having a desired component content ratio and less expansion during storage and a method of manufacturing the same.

DETAILED DESCRIPTION OF THE INVENTION

The above object of the invention can be attained by the following method.

1. A method of manufacturing a solid developing composition for a silver halide photographic light-sensitive material, the method comprising the steps of :

mixing first granules comprising a developing agent and second granules comprising an alkali agent,

wherein the content in each granule of granules having a particle size of 1000μm or more (JIS) is not more than 10 weight % based on the total weight of each granule.

2. The method of manufacturing a solid developing composition for a silver halide photographic light-sensitive material of item 1, wherein the content in each granule of granules having a particle size of 350 to 1000μm is not less than 40 weight %.

3. The method of manufacturing a solid developing composition for a silver halide photographic light-sensitive material of item 1 or 2, wherein the content in each granule of granules having a particle size of 350 to 1000μm is 40 to 74 weight %.

4. The method of manufacturing a solid developing composition for a silver halide photographic light-sensitive material of item 1, 2 or 3, wherein the content in each granule of granules having a particle size of 500 to 1000μm is not less than 40 weight %.

5. The method of manufacturing a solid developing composition for a silver halide photographic light-sensitive material of items 1 through 4, wherein the mixing ratio of the first granules comprising a developing agent and the second granules comprising an alkali agent is 1:1 to 1:20.

6. The method of manufacturing a solid developing composition for a silver halide photographic light-sensitive material of items 1 through 5, wherein the developing agent is a p-phenylenediamine color developing agent.

7. The method of manufacturing a solid developing composition for a silver halide photographic light-sensitive material of items 1 through 6, wherein the alkali agent is an alkali metal carbonate.

8. A tablet developing composition for a silver halide photographic light-sensitive material, wherein the composition is obtained by compression-molding the above described granules.

The invention will be explained below.

The present inventors have made an intensive study, and have solved the above problems by controlling the size of granules containing a photographic component to a specific particle size.

The solid processing composition of the invention refers to a processing composition in the form of granules or tablets. When the solid processing composition of the invention is in the form of granules, it is characterized in that the content of granules having a particle size of 1000μm or more is not more than 10 weight % based on the total weight of the granules. The particle size of the invention, unless otherwise specified, refers to that according to JIS (JAPAN INDUSTRIAL STANDARD), and is measured by using a JIS standard screen. For example, granules having a particle size of 1000μm or more refer to granules remained on a 1000μm (16 mesh) screen after sieving by using the screen. In the invention the content of granules having a particle size of 1000μm or more is preferably not more than 8 weight %, and more preferably not more than 5 weight %.

In the granular composition of the invention the content of granules having a particle size of 350 to 1000μm is preferably not less than 40 weight %, and more preferably not less than 40 to 74 weight % in view of the effects of the invention and discoloration during storage. It is also preferable in view of discoloration during storage that the content of granules having a particle size of 500 to 1000μm is not less than 40 weight %.

The method of adjusting granules to the particle size within the invention includes a well known method such as a method of crushing larger particles using a commercial dresser or a method of sieving using a screen. There are hammer mill type, roll mill type or screen mill type commercial dressers. In the screen mill type dresser, a screen of not more than 1.2 mm is preferably used, and a screen of 0.8 to 1.2 mm is more preferably used.

The granular processing composition of the invention can be obtained by using any of the well-known processes such as the processes of a fluidized-layer granulation, a stirring granulation, a rolling granulation, an extrusion granulation and a compression granulation. The drying weight reduction of the solid composition in the invention is preferably 0.5-5 weight %, and more preferably 0.8-2 weight % in view of the effects of the invention. The drying weight reduction referred to herein is a weight variation amount calculated from the weight reduced, which is measured under circumstances of 25°C and 40%RH after the composition is heated at 50°C to a constant weight which is measured with a commercial electronic moisture meter. In order to obtain the weight reduction within the above described range, a wet granulating method is preferable which is carried out in the presence of a solvent. The solvent used in the wet granulating method is preferably a polar solvent such as alcohol, acetone, acetonitrile or water or a mixture thereof, and more preferably water. The addition amount of the solvent is preferably 1 to 20 weight %, and more preferably 3 to 10 weight % based on the total weight of material used. When the amount of the solvent is less than 1 weight %, the granulation is not completed, and when the amount of the solvent exceeds 20 weight %, the granulation requires a longer time and granule properties are deteriorated during the granulation.

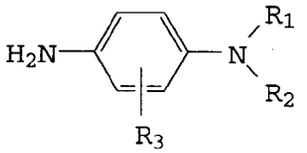
The solid processing tablet in the invention may be in any form according to the intended use, but is preferably in

disk form in view of ease of producibility or processability. The solid processing tablet is produced by well known compressors. The compressors for producing the tablets include a hydraulic press machine, a single tableting machine, a rotary tableting machine and a briqueting machine can be used.

The developing agent of the invention includes a color developing agent and a black-and-white developing agent. The invention is noticeably effected using a p-phenylenediamine color developing agent.

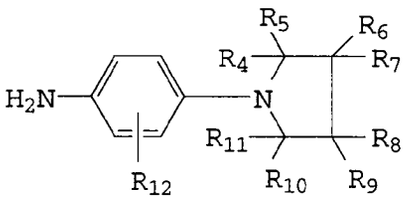
The p-phenylenediamine color developing agent represented by Formula (I) or (II) preferably used in the invention will be shown below.

Formula (I)



wherein R_1 and R_2 may be the same or different, and independently represent a substituted or unsubstituted alkyl group. R_3 represents a hydrogen atom, a halogen atom, an unsubstituted amino group, a hydroxyl group, an alkylamino group, an alkyl group, an alkoxy group, an amido group, a sulfonamide group, an alkoxycarbonylamino group, a ureido group or a sulfamoylamino group.

Formula (II)



wherein wherein R_4 through R_{11} may be the same or different, and independently represent a hydrogen atom, a halogen atom, an unsubstituted amine group, a nitro group, a hydroxyl group, a cyano group, an alkyl group, an alkylamino group, an alkoxy group, an amido group, a sulfonamide group, a carbamoyl group, an alkoxycarbonylamino group, a ureido group, a sulfamoylamino group, a sulfonyl group, a carboxyl group or a sulfo group. R_{12} represents a hydrogen atom, a halogen atom, an unsubstituted amine group, a hydroxyl group, an alkylamino group, an alkyl group, an alkoxy group, an amido group, a sulfonamide group, an alkoxycarbonylamino group, a ureido group or a sulfamoylamino group.

Next, the invention will be explained in detail.

In Formula (I), the alkyl group represented by R_1, R_2 and R_3 includes a straight-chained or branched alkyl group having preferably 1 to 6 carbon atoms, which may have a substituent. The preferable substituent includes an alkenyl group, an alkinyl group, an aryl group, a nitro group, a halogen atom, an unsubstituted amine group, a hydroxyl group, a cyano group, an alkylamino group, an alkoxy group, an amido group, a sulfonamide group, a carbamoyl group, an alkoxycarbonylamino group, a ureido group, a sulfamoylamino group, a sulfonyl group, a carboxyl group and a sulfo group.

The alkenyl group as the substituent includes a vinyl group and an allyl group, the alkinyl group includes an ethenyl group, the aryl group includes a phenyl group, a tolyl group and a naphthyl group, and the halogen atom includes a fluorine atom, a chlorine atom and a bromine atom.

The alkylamino group includes an alkylamino group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a N,N-dimethylamino, N,N-diethylamino or N-butylamino group. The alkoxy group includes an alkoxy group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a methoxy, ethoxy, 2-methoxyethoxy, 2-hydoxyethoxy, 2-hydoxybutoxy and 2-methanesulfonylethoxy group. The amido group includes an amido group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including an acetoamido, 2-methoxypropionamido and pentanoylamido group.

The sulfonamido group includes a sulfonamido group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a methanesulfonamido and benzenesulfonamido group. The carbamoyl group includes a carbamoyl group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl

group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a carbamoyl, N,N-dimethylcarbamoyl, N-ethylcarbamoyl and N-butylcarbamoyl group. The ureido group includes a ureido group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a ureido, methylureido and N,N-diethylureido group.

The sulfamoylamino group includes a sulfamoylamino group having 0 to 16 carbon atoms, and preferably 0 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a sulfamoylamino, dimethylsulfamoylamino and dipropylsulfamoylamino group. The sulfonyl group includes a sulfonyl group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a methanesulfonyl and methanesulfonyl group.

Next, Formula (II) will be explained in detail.

In Formula (II), R_4 through R_{11} may be the same or different, and independently represent a hydrogen atom, a halogen atom, a hydroxyl group, a cyano group, an alkyl group, an amino group, an alkylamino group, an alkoxy group, an amido group, a sulfonamide group, a carbamoyl group, an alkoxycarbonylamino group, a ureido group, a sulfamoylamino group, a sulfonyl group, a carboxyl group or a sulfo group.

The halogen atom includes a fluorine atom, a chlorine atom and a bromine atom. The alkyl group includes a straight-chained, branched or cyclic alkyl group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a methyl, ethyl, propyl, isopropyl, t-butyl, hydroxymethyl, methanesulfonamidomethyl, 2-hydroxyethyl, 3-hydroxypropyl, benzyl, 2-methanesulfonamidoethyl, 3-methanesulfonamidopropyl, 2-methanesulfonylethyl, 2-methoxyethyl, cyclopentyl, 2-acetoamidoethyl, 2-carboxyethyl, 2-carbamoylethyl, 3-carbamoylpropyl, n-hexyl, 2-hydroxypropyl, 4-hydroxybutyl, 2-carbamoylaminoethyl, 3-carbamoylaminopropyl, 4-carbamoylaminobutyl, 4-carbamoylbutyl, 2-carbamoyl-1-methylethyl and 4-nitrobutyl group.

The alkylamino group includes an alkylamino group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a N,N-dimethylamino, N,N-diethylamino or N-butylamino group. The alkoxy group includes an alkoxy group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a methoxy, ethoxy, 2-methoxyethoxy, 2-hydoxyethoxy, 2-hydoxybutoxy and 2-methanesulfonylethoxy group. The amido group includes an amido group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including an acetoamido, 2-methoxypropionamido and pentanoylamido group.

The sulfonamido group includes a sulfonamido group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a methanesulfonamido and benzenesulfonamido group. The carbamoyl group includes a carbamoyl group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a carbamoyl, N,N-dimethylcarbamoyl, N-ethylcarbamoyl and N-butylcarbamoyl group. The alkoxycarbonylamino group includes an alkoxycarbonylamino group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a methoxycarbonylamino, ethoxycarbonylamino and butoxycarbonylamino group. The ureido group includes a ureido group having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a ureido, methylureido and N,N-diethylureido group.

The sulfamoylmino group includes a sulfamoylmino group having 0 to 16 carbon atoms, and preferably 0 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a sulfamoylmino, dimethylsulfamoylmino and dipropypsulfamoylmino group. The sulfonyl group includes a sulfonyl group

having 1 to 16 carbon atoms, and preferably 1 to 6 carbon atoms, which may have a substituent such as an alkenyl group, an alkinyl group, an aryl group, a hydroxyl group, a nitro group, a cyano group or a halogen atom or a substituent formed with an oxygen, nitrogen, sulfur or carbon atom including a methanesulfonyl and ethanesulfonyl group.

The above color developing agents are usually used in the form of hydrochloride, sulfate or p-toluenesulfonic acid salt.

The example of the color developing agents in the invention will be shown below, but is not limited thereto.

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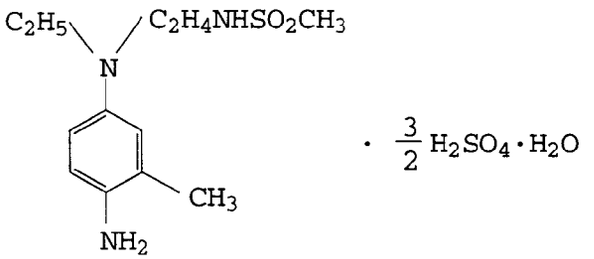

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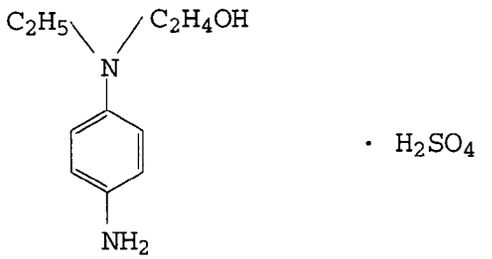

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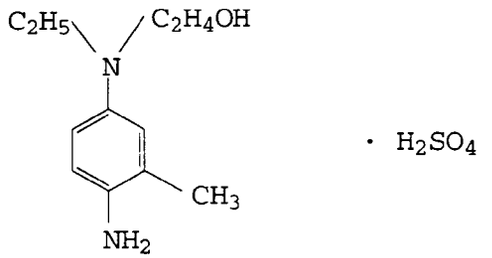

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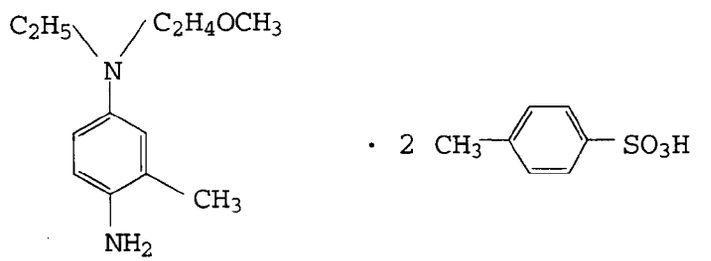

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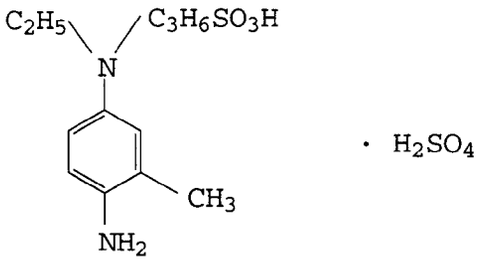

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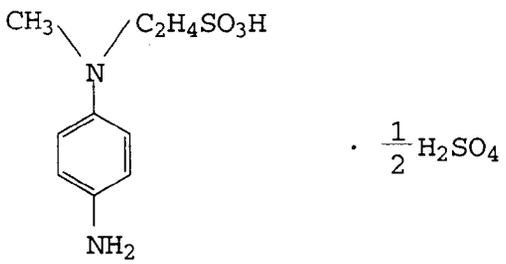

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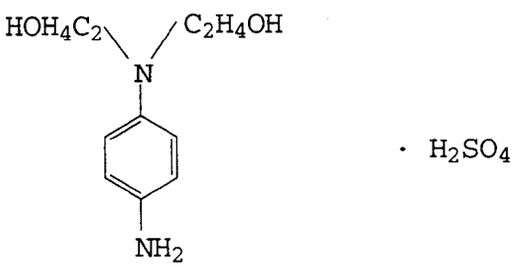

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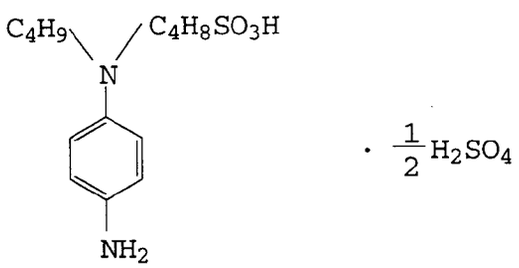

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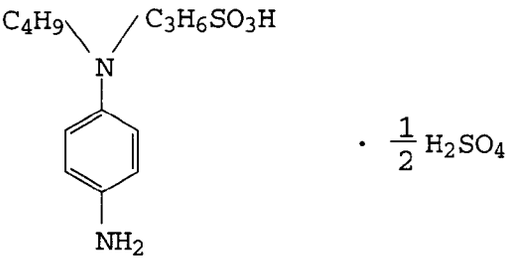

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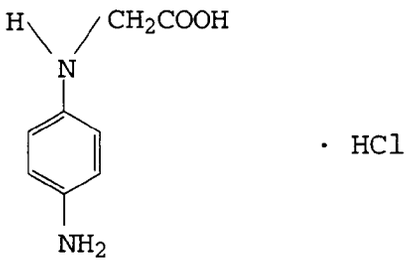

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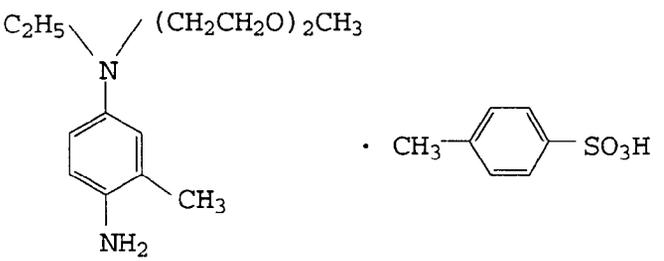

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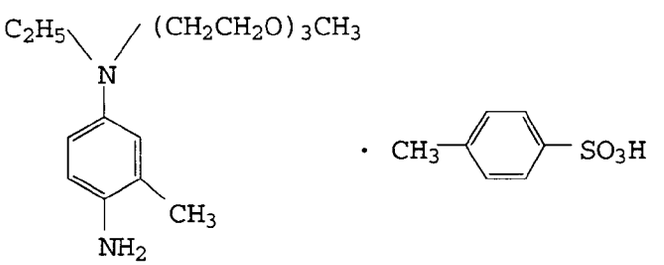

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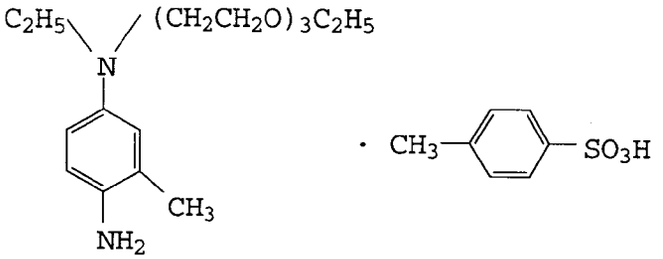

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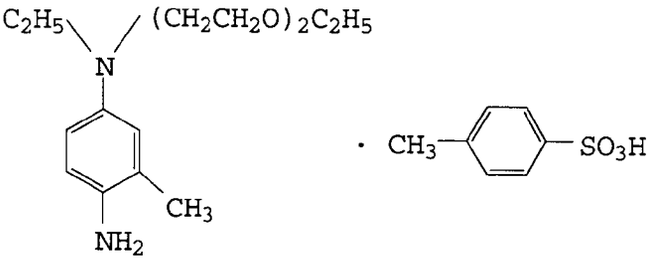

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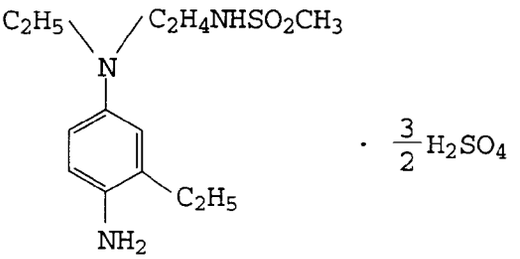

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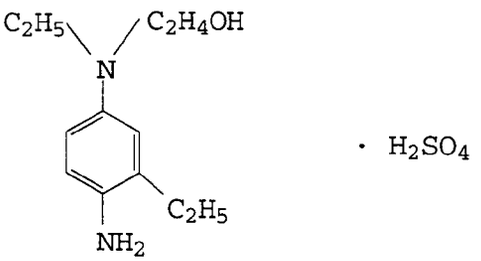

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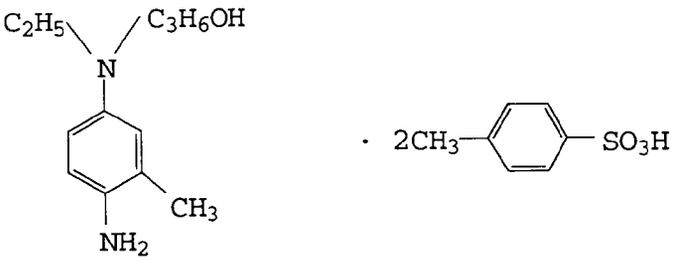

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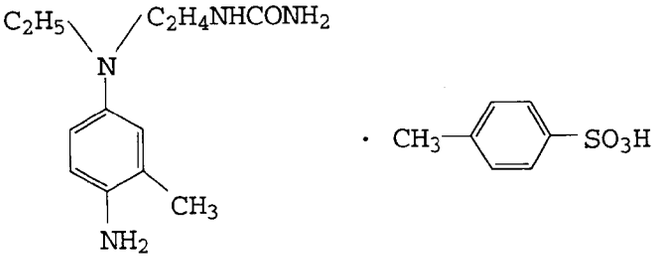

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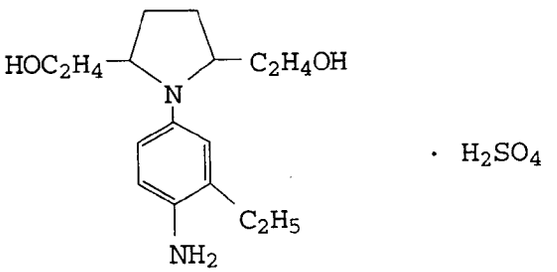
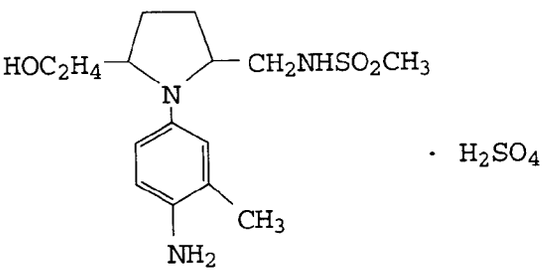


(C-20)



The example of the black-and-white developing agent includes phenidone, hydroquinone, metol, 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone and hydroquinone monosulfonic acid.

The alkali agent of the invention is a compound giving pH 8 or more in its aqueous solution. The preferable example includes sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, tripotassium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfo-salicylate) and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfo-salicylate). Sodium carbonate and sodium bicarbonate are especially preferable.

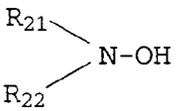
The solid processing composition in the invention may optionally contain a chelating agent, a development accelerating agent, a development inhibitor (halides), a fluorescent brightening agent or a preservative as usually used in the developer.

The preservarive includes a sulfite (sodium sulfite or potassium sulfite), a bisulfite (sodium bisulfite or potassium bisulfite), a metabisulfite (sodium metabisulfite orpotassium metabisulfite) and a hydroxylamine derivative.

The solid developing composition preferably contains a compound represented by Formula (H) or (B). The invention is more effected by the above compound. The solid developing composition containing the above compound shows improved storage stability, strength, stable photographic properties and prevention of fog. It is preferable that the solid processing composition contain a hydroxyamine compound represented by Formula (H). It is more preferable that the granular processing composition containing a developing agent is obtained by mixing the developing agent with the hydroxyamine compound and then granulating the mixture.

When granules containing a compound represented by the following Formula (H) or (B) is prepared separate from granules containing a developing agent, the content in the granules containing the compound of granules having a particle size of not less than 1000 μm is preferably not more than 10 weight %, and the content in the granules containing the compound of granules having a particle size of 350 to 1000 μm is also preferably 40 to 74 weight %.

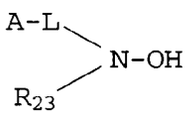
Formula (H)



wherein R_{21} and R_{22} independently represent a hydrogen atom or a substituted or unsubstituted alkyl group.

The compound of the invention represented by Formula (H) is preferably a compound represented by Formula (H') in view of the invention.

Formula (H')



wherein L represents a straight chained or branched, alkylene group having 1 to 10 carbon atoms, which may have a substituent, and preferably 1 to 5 carbon atoms. The example includes a methylene, ethylene, trimethylene and propylene group, and the substituent includes a carboxyl group, a sulfone group, a phosphone group, a phosphinic acid residue, a hydroxy group and an ammonio group which may have an alkyl group having 1 to about 5 carbon atoms.

A represents a carboxyl group, a sulfone group, a phosphone group, a phosphinic acid residue, a hydroxy 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 about 5 carbon atoms and a substituted or unsubstituted alkylsulfonyl group.

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

R_{23} represents a straight chained or branched, alkyl group having 1 to 10 carbon atoms, which may have a substituent. The substituent includes a carboxyl group, a sulfone group, a phosphone group, a phosphinic acid residue, a hydroxy group and an ammonio group which may have an alkyl group having 1 to 5 carbon atoms, provided that R_{23} and L may combine to form a ring.

The exemplified compound of the invention will be given below, but is not limited thereto.

	R_{21}	R_{22}
H-1	-H	-H
A-2	-H	$-CH_3$
A-3	$-CH_3$	$-CH_3$
A-4	-H	$-C_2H_5$
A-5	$-CH_3$	$-C_2H_5$

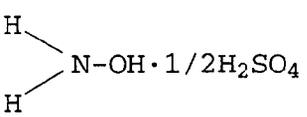
Continuation of the Table on the next page

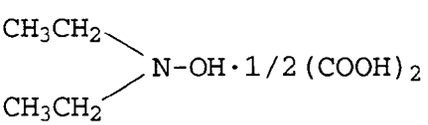
(continued)

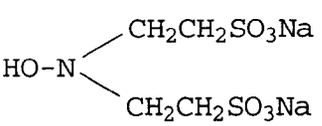
	R_{21}	R_{22}
A-6	$-C_2H_5$	$-C_2H_5$
A-7	$-C_3H_7$	$-C_3H_7$
A-8	$-C_3H_7$ (i)	$-C_3H_7$ (i)
A-9	$-C_4H_9$	$-C_4H_9$
A-10	$-C_4H_9$ (i)	$-C_4H_9$ (i)
A-11	$-C_4H_9$ (t)	$-C_4H_9$ (t)
A-12	$-CH_3$	$-CH_2CH_2COOH$
A-13	$-CH_3$	$-CH_2CH_2SO_3H$
A-14	$-CH_3$	$-CH_2COOH$
A-15	$-CH_3$	$-CH_2CH_2PO_3H_2$
A-16	-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	$-CH_2CH_2CN$	$-CH_2CH_2CN$

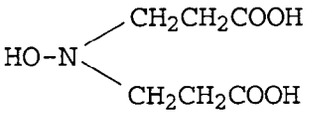
The compounds are usually used in free amine or in the form of hydrochloric acid, sulfate, p-toluenesulfonic acid, oxalic acid, phosphoric acid or acetic acid salt.

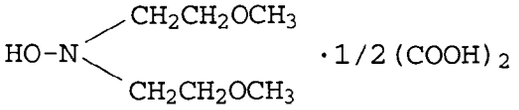
The compounds represented by Fomula (H) or (H') are preferably solids in view of the objects of the invention. Of these, H-1, H-6, H-17, H-18 and H-25 are especially preferable, and the examples will be given below.











Formula (B)

$$R_{11}\text{-}N(\text{-}R_{12})\text{-}N(\text{-}R_{13})\text{-}(R_{15})_n\text{-}R_{14}$$

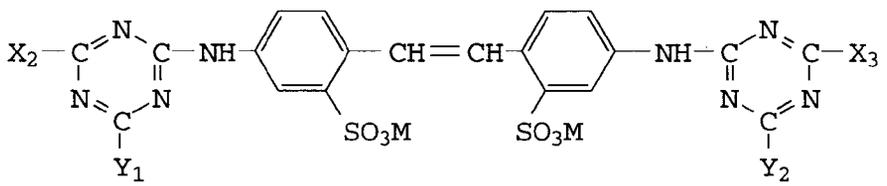
In Formula (B), R_{11}, R_{12} and R_{13} independently represent a substituted or unsubstituted alkyl, aryl or heterocyclic group; R_{14} represents a hydroxy group, a hydroxyamino group or a substituted or unsubstituted alkyl, aryl, heterocyclic, alkoxy, aryloxy, carbamoyl or amino group. The heterocyclic group includes a saturated or unsaturated 5- or 6-membered cyclic group; R_{15} represents a divalent group selected from the group consisting of -CO-, -SO_2- and -C(=NH)-; and n represents 0 or 1, provided that when n is 0, R_{14} represents an alkyl, aryl or heterocyclic group or R_{13} and R_{14} may combine to form a heterocyclic ring.

The preferable example of compounds represented by Formula (B) includes (B-1) through (B-33) on pages 40 to 43 of Japanese Patent O.P.I. Publication No. 4-86741/1992 and (1) through (56) on pages 4 to 6 of Japanese Patent O.P.I. Publication No. 3-33846/1991.

The developing composition of the invention may contain an alkali halide such as potassiun iodide or an organic anti-foggant, a nitrogen-containing heterocyclic compound such as benzotriazole, 6-nitrobenzimidazole, 5-nitroisoindazole, 5-methylbenzotriazole, 5-nitrobenzotriazole, 5-chlorobenzotriazole, 2-thiazolylbenzimidazole, 2-thiazolylmethylbenzimidazole, indazole, hydroxyazaindolidine or adenine.

The developing composition of the invention preferably contain a triadinylstylbene fluorescent brightening agent. The fluorescent brightening agent is preferably a compound represented by the following Formula (E),

Formula (E)



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

or -OR_{25} in which R_{21} and R_{22} independently represent a hydrogen atom, an alkyl group (which may have a substituent), or an aryl group (which may have a substituent), R_{23} and R_{24} independently represent an alkylene group (which may have a substituent), and R_{25} represents a hydrogen atom, an alkyl group (which may have a substituent) or an aryl group (which may have a substituent); and M represents a cation. The groups or substituents thereof in Formula (E) is the same as those described on pages 16 and 17 of Japanese Patent O.P.I. Publication No. 4-118649/1992. The examples of the compounds are preferably compounds represented by [Chemical 8] through [Chemical 16] of Japanese Patent O.P.I. Publication No. 5-119454/1993. These compounds can be synthesized by the conventional method. Of these compounds the compounds especially preferably used are E-4, E-24, E-34, E-35, E-36, E-37 and E-41.

The developing composition of the invention may contain an auxiliary developing agent such as metol, phenidone, N,N-diethyl-p-aminophenol hydrochloride or N,N,N',N''-tetramethyl-p-phenylenediamine hydrochloride, or additives such as an anti-staining agent, an anti-sludging agent and an interlayer accelerating agent.

The color or black-and-white developing composition of the invention preferably contains a chelating agent (especially, exemplified compounds K-1 through K-22) represented by the following Formula (K) which is described on de-

scribed on pages 16 and 17 of Japanese Patent O.P.I. Publication No. 4-118649/1992.

Formula (K)

$$A_1\text{-}R_1\text{-}N(\text{-}R_2\text{-}A_2)\text{-}E\text{-}N(\text{-}R_3\text{-}A_3)\text{-}R_4\text{-}A_4$$

Of these compounds, K-2, K-9, K-12, K-13, K-17 and K-19 are preferable, and K-2 and K-9 are especially preferable.

It is preferable in view of improved fluidity of a granule composition that the solid developing composition of the invention contains at least one selected from compound represented by the following Formula (D).

Formula (D)

$$R_1\text{-}CON(\text{-}R_2)\text{-}L_1\text{-}COOM$$

wherein R_1 represents an alkyl group; R_2 represents a hydrogen atom or an alkyl group having 1 to 5 carbon atoms; L_1 represents an alkylene group having 1 to 5 carbon atoms; and M represents a hydrogen atom, an alkali metal atom or NH_4.

In Formula (D), R_1 represents a straight-chained or branched, substituted or unsubstituted, saturated or unsaturated aliphatic group having preferably 3 to 30 carbon atoms; R_2 represents a hydrogen atom or a straight-chained or branched, substituted or unsubstituted, saturated or unsaturated aliphatic group having 1 to 5 carbon atoms, preferably a hydrogen atom or a methyl, ethyl, propyl, butyl or amyl group and more preferably a methyl group; L_1 represents a straight-chained or branched, substituted or unsubstituted, alkylene or alkenylene group having 1 to 5 carbon atoms, preferably a methylene, ethylene, propylene, butylene, carboxymethylmethylene, carboxymethylethylene or carboxyethylethylene group and more preferably an ethylene group; the substituent includes a carboxymethyl, carboxyethyl, carboxypropyl, carboxybutyl and carboxyamyl group; and M represents a hydrogen atom, an alkali metal atom such as a sodium atom, a potassium atom or a lithium atom or NH_4.

The typical examples of Formula (D) will be shown below, but the invention is not limited thereto.

D-1 $C_5H_{11}\text{-}CON(\text{-}CH_3)\text{-}CH_2CH_2\text{-}COONa$

D-2 $C_7H_{15}\text{-}CON(\text{-}CH_3)\text{-}CH_2CH_2\text{-}COOK$

D-3 $C_9H_{19}\text{-}CON(\text{-}CH_3)\text{-}CH_2CH_2\text{-}COONa$

D-4 $C_{11}H_{23}\text{-}CON(\text{-}CH_3)\text{-}CH_2CH_2\text{-}COONa$

D-5 $C_{13}H_{27}\text{-}CON(\text{-}CH_3)\text{-}CH_2CH_2\text{-}COONa$

D-6 $C_{15}H_{31}\text{-}CON(\text{-}CH_3)\text{-}CH_2CH_2\text{-}COOK$

D-7 $C_{17}H_{35}\text{-}CON(\text{-}CH_3)\text{-}CH_2CH_2\text{-}COOK$

D-8 $C_{19}H_{39}\text{-}CON(\text{-}CH_3)\text{-}CH_2CH_2\text{-}COONa$

D-9 $C_5H_{11}\text{-}CON(\text{-}CH_3)\text{-}CH_2\text{-}COONa$

D-10 $C_7H_{15}\text{-}CON(\text{-}CH_3)\text{-}CH_2\text{-}COONa$

D-11 $C_9H_{19}\text{-}CON(\text{-}CH_3)\text{-}CH_2\text{-}COONa$

D-12 $C_{11}H_{23}\text{-}CON(\text{-}CH_3)\text{-}CH_2\text{-}COONa$

D-13 $C_{13}H_{27}\text{-}CON(\text{-}CH_3)\text{-}CH_2\text{-}COOK$

D-14 $C_{15}H_{31}\text{-}CON(\text{-}CH_3)\text{-}CH_2\text{-}COOK$

D-15 $C_{17}H_{35}\text{-}CON(\text{-}CH_3)\text{-}CH_2\text{-}COONa$

D-16 $C_{19}H_{39}\text{-}CON(\text{-}CH_3)\text{-}CH_2\text{-}COONa$

Of these compounds the preferable are compounds D-5 and D-12.

The content of the above compounds in the tablet composition is 0.1 to 5.0 wt%, and preferably 0.3 to 3.0 wt% based on the total weight of the tablet composition.

The solid processing composition of the invention containing saccharides shows more markedly the effects of the invention. The saccharides in the invention refer to monosaccharides, polysaccharides in which monosaccharides bind through a glycoside bondage or derivatives thereof.

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

Polysaccharides include celluloses, starches or glycogens. The celluloses include derivatives such as cellulose ethers in which all or a part of hydroxy group are etherified, starches include 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 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)	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) D-erythritol

B-(85) L-erythritol

Of these compounds, B-(66) through (85) are preferably used, and B-(74) through (85) are more preferably used. Examples of polysaccharides and their derivatives in the invention will be shown below.

D-(1) Maltose

D-(2) Cellobiose

D-(3) trehalose

D-(4) gentiobiose

D-(5) isomaltose

D-(6) lactose

D-(7) raffinose

D-(8) gentianose

D-(9) stachyose

D-(10) xylan

D-(11) araban

D-(12) Glycogen

D-(13) dextran

D-(14) inulin

D-(15) levan

D-(16) galactan

D-(17) agalose

D-(18) amylose

D-(19) sucrose

D-(20) agarobiose

D-(21) α-dextrin

D-(22) β-dextrin

D-(23) γ-dextrin

D-(24) δ-dextrin

D-(25) ε-dextrin

D-(26) α-cyclodextrin

D-(27) β-cyclodextrin

D-(28) Phospherylase limit dextrim

D-(29) Soluble starch

D-(30) Thin-boling starch

D-(31) White dextrin

D-(32) Yellow dextrin

D-(33) British gum

D-(34) Pineflow (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(35) Pinedex100 (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(36) Pinedex 1 (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(37) Pinedex 2 (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(38) Pinedex 3 (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(39) Pinedex 4 (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(40) Pinedex 6 (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(41) Foodtex (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(42) Max (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(43) Glystar P (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(44) TK-16 (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(45) MPD (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(46) H-PDX (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(47) Stacodex (trade name, produced by Matsutani Kagaku Co., Ltd.)

D-(48) Mabit (trade name, produced by Hayashibara Shoji Co., Ltd.)

D-(49) Pullulan (trade name, produced by Hayashibara Shoji Co., Ltd.)

D-(50) Methylcellulose

D-(51) Dimethylcellulose

D-(52) Trimethylcellulose

D-(53) Ethylcellulose

D-(54) Diethylcellulose

D-(55) Triethylcellulose

D-(56) Carboxymethylcellulose

D-(57) Carboxyethylcellulose

D-(58) Aminoethylcellulose

D-(59) Hydroxymethylcellulose

D-(60) Hydroxyethylcellulose

D-(61) Hydroxypropylcellulose

D-(62) Hydroxypropylmethylcellulose

D-(63) Hydroxypropylmethylcelluloseacetatesuccinate

D-(64) carboxymethylhydroxyethylcellulose

Of these compounds, D-(21) through (64) are preferably used, and compounds, D-(21) through (49) are more preferably used.

The content of the saccharide in the solid color developing composition of the invention is preferably 0.5 to 30 wt%, and more preferably 1.0 to 20 wt%.

EXAMPLES

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

Example 1

A granule color developing composition and a tablet color developing composition were prepared according to the following procedures.

Procedure (1)

In a hammer-mill available on the market 3700.0 g of anhydrous potassium carbonate, 600.0 g of sodium sulfite, 240.0g of pentasodium diethylenetriamine pentaacetate and 500.0g of sodium p-toluenesulfonate were pulverized to a particle size of not more than 149μm. The fine powder was mixed with 800.0g of Pineflow (produced by Matsutani Kagaku Co., Ltd.) and was granulated in a stirring granulator available on the market at room temperature for 7 minutes while adding water thereto. Thereafter, the granules were dried at 70°C using a fluid bed drier available on the market. The dried granules were dressed with a dresser available on the market to have a particle size as shown in Table 1. Thus, granule sample A was obtained.

Procedure (2)

In the same manner as in Procedure (1) were pulverized 630g of a color developing agent CD-4 (4-amino-3-methyl-N-ethyl-β-(hydroxy)ethylaniline sulfate) and 240.0g of bis(sulfoethyl)hydroxylamine disodium salt. The fine powder was mixed with 65g of Pineflow and was granulated at room temperature. Thereafter, the granules were dried at 40°C using a fluid bed drier available on the market. The dried granules were dressed with a dresser available on the market

to have a particle size as shown in Table 1. Thus, granule sample C was obtained.

Procedure (3)

The above obtained granule samples in Procedures (1) and (2) were mixed in an amount as shown in Table 2 at room temperature for 10 minutes through a cross rotary mixer available on the market, and mixed with sodium N-miristoyl β-methylalanine (in an amount of 0.5wt%) for 3 minutes. Thereafter, the resulting mixture granules were continuously tableted making use of a rotary tableting machine to obtain tablets having a diameter of 30 mm, a thickness of 10 mm and a weight of 11.0g. Thus, 600 tablet samples for color developing were obtained from the granule samples.

Procedure (4)

The above granule samples obtained in Procedures (1) and (2) were mixed in an amount as shown in Table 2 for 10 minutes through a cross rotary mixer available on the market. Thus, granule samples for color developing were obtained.

Table 1

	Particles plus 1000μm sieve (wt%)	Particles minus 1000μm sieve and plus 500μm sieve (wt%)	Particles minus 500μm sieve and plus 350μm sieve (wt%)	Particles minus 350μm sieve and plus 149μm sieve (wt%)	Particles minus 149μm sieve (wt%)
A-1	20.6	31.7	16.9	22.3	8.4
A-2	31.4	37.6	16.2	12.8	2.0
A-3	0.0	34.1	37.5	22.8	5.6
A-4	0.5	45.8	22.2	22.6	8.9
C-1	73.5	22.1	3.3	0.7	0.3
C-2	12.6	19.3	23.2	39.4	5.6
C-3	2.2	53.4	21.0	19.8	3.7
C-4	1.0	24.4	37.1	33.9	3.5

The above obtained samples were evaluated according to the following experiments.

Experiment 1: Color developing agent content of the tablet samples

Sixty tablets of each tablet sample were dissolved in pure water. The content of the color developing agent was measured through high speed liquid chromatography and deviation D from the theoretical content was calculated.

Evaluation Criteria were as follows:

◎ : $-3\% < D < +3\%$

○ : $-5\% \leqq D \leqq -3\%$ or $+3\% \leqq D \leqq +5\%$

X : $-30\% < D \leqq -10\%$ or $+10\% \leqq D < +30\%$

XX : $-50\% \leqq D \leqq -30\%$ or $+30\% \leqq D \leqq +50\%$

Experiment 2: Color developing agent content of the granule samples for color developing

In each 1000g of granule sample, 10g were taken from ten different portions of the granule samples and the content of the color developing agent was measured in the same manner as in Experiment 1 through high speed liquid chromatography. The evaluation criteria were the same as in Experiment 1. The results of Experiments 1 and 2 are shown in Table 2 and are identical to each other.

Experiment 3: Expansion degree of the tablet samples

Ten tablets from each tablet sample were placed in an aluminium vapor-deposited polyethylene package, and stored at 40°C and 65%RH for one month. Thereafter, the expansion degree of the tablets was measured and the change was calculated.

Expansion Degree of Tablets (%) = (thickness after storage (mm)- thickness (mm) before storage) × 100 / thickness (mm) before storage

The results are shown in Table 2.

Table 2

Granule Sample A Part (%)	Granule Sample C Part (%)	Deviation of Developing Agent Content of Granule or Tablet Sample	Expansion of Tablet Sample (%)	
A-1 90	C-1 10	××	2.4	Comparative
A-1 90	C-2 10	××	2.3	Comparative
A-1 90	C-3 10	××	2.1	Comparative
A-1 90	C-4 10	××	2.0	Comparative
A-2 90	C-2 10	×	2.0	Comparative
A-3 90	C-1 10	××	2.3	Comparative
A-3 90	C-2 10	×	2.2	Comparative
A-3 90	C-3 10	○	1.0	Invention
A-3 90	C-4 10	○	0.8	Invention
A-4 90	C-4 10	○	0.6	Invention
A-4 95	C-3 5	◎	1.2	Invention
A-4 90	C-3 10	◎	0.8	Invention
A-4 80	C-3 20	◎	0.7	Invention
A-4 60	C-3 40	◎	0.8	Invention
A-4 40	C-3 60	◎	0.7	Invention

As is apparent from Table 2 above, the solid processing composition containing granules having a particle size exceeding 1000μm in an amount of not less than 10 wt% shows greater deviation in the content of a developing agent and greater expansion during storage of tablet samples. On the other hand, the solid processing composition of the invention containing granules having a particle size within the range of the invention shows less deviation in the content of the developing agent and less expansion during storage of tablet samples, giving excellent handling properties.

Example 2

A tablet color developing composition were prepared according to the following procedures.

Procedure (1)

In a hammer-mill available on the market 3700.0 g of anhydrous potassium carbonate, 600.0 g of sodium sulfite, 240.0g of pentasodium diethylenetriamine pentaacetate and 500.0g of sodium p-toluenesulfonate were pulverized to a particle size of not more than 149μm. The fine powder was mixed with 800.0g of Pineflow and was granulated in a stirring granulator available on the market at room temperature for 7 minutes while adding water thereto. Thereafter, the granules were dried at 70°C using a fluid bed drier available on the market. The dried granules were dressed with a dresser available on the market to have a particle size as shown in Table 3. Thus, granule sample A was obtained.

Procedure (2)

In the same manner as in Procedure (1) were pulverized 360.0g of hydroxylamine 1/2 sulfate, 30.0g of potassium bromide, 20.0g of disodium pyrocatechol-3,5-disulfonate and mixed and granulated. Thereafter, the resulting granules were dressed with a dresser to have a particle size as shown in Table 3. Thus, granule sample B was obtained.

In the same manner as in Procedure (1) were pulverized 630g of a color developing agent CD-4 (4-amino-3-methyl-N-ethyl-β-(hydroxy)ethylaniline sulfate) and 240.0g of bis(sulfoethyl)hydroxylamine disodium salt. The fine powder was mixed with 65g of Pineflow and was granulated at room temperature. Thereafter, the granules were dried at 40°C using a fluid bed drier. The dried granules were dressed with a dresser to have a particle size as shown in Table 3. Thus, granule sample C was obtained.

Table 3

	Particles plus 1000μm sieve (wt%)	Particles minus 1000μm sieve and plus 500μm sieve (wt%)	Particles minus 500μm sieve and plus 350μm sieve (wt%)	Particles minus 350μm sieve and plus 149μm sieve (wt%)	Particles minus 149μm sieve (wt%)
A-1	11.4	32.7	35.4	18.3	2.2
A-2	9.5	36.5	38.2	10.4	5.4
B-1	6.1	22.0	18.2	37.7	16.0
C-1	10.9	28.4	26.4	24.3	10.0
C-2	8.8	29.3	35.8	19.4	6.7

Procedure (4)

All the above obtained granule samples in Procedures (1) through (3) were mixed at room temperature for 10 minutes through a cross rotary mixer available on the market, and mixed with sodium N-miristoyl β-methylalanine (in an amount of 0.5wt%) for 3 minutes. Thereafter, the resulting mixture granules were continuously tableted making use of a rotary tableting machine to obtain tablets having a diameter of 30 mm, a thickness of 10 mm and a weight of 11.0g. Thus, 600 tablet samples for color developing were obtained.

The above obtained samples were evaluated in the same manner as in Example 1. The results are shown in Table 4.

Table 4

Granule Sample A	Granule Sample B	Granule Sample C	Deviation of Developing Agent Content of Granule	Expansion of Tablet Sample (%)	
A-1	B-1	C-1	X	1.9	Comparative
A-2	B-1	C-2	○	0.4	Invention

Example 3

The procedures were carried out in the same manner as in Example 2, except that Exemplified Compound C-1, C-15, C-17, C-18 or C-19 was used instead of the color developing agent used in Example 2. The evaluation was out in the same manner as in Example 2. The results were the same as Example 2.

Example 4

A tablet color developing composition were prepared according to the following procedures.

Procedure (A)

In a hammer-mill available on the market were pulverized 1500.0g of a color developing agent CD-3 (4-amino-3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sulfate) and 500g of bis(sulfoethyl)hydroxylamine sodium salt to a

particle size of not more than 149μm. The fine powder was mixed with 150.0g of D-mannitol and granulated at room temperature for about 7 minutes while adding water in a stirring granulator available on the market. Thereafter, the granules were dried at 40°C using a fluid bed drier. The dried granules were dressed with a dresser to have a particle size as shown in Table 5. Thus, granule sample A was obtained.

Procedure (B)

In the same manner as in Procedure (A) were pulverized disodium salt of Exemplified Compound H-18, 400.0g of bis(sulfoethyl)hydroxylamine disodium salt, 1700.0g of sodium p-toluenesulfonate and 300.0g of Tinopar SFP (produced by Ciba-Geigy Co., Ltd.) and granulated while adding water. The resulting granules were dried at 50°C. The dried granules were dressed with a dresser to have a particle size as shown in Table 5. Thus, granule sample B was obtained.

Procedure (C)

In the same manner as in Procedure (A) were pulverized 3300.0 g of potassium carbonate, 37.0g of sodium sulfite, 330.0g of pentasodium diethylenetriamine pentaacetate, 130.0g of sodium p-toluenesulfonate and 340.0g of lithium hydroxide monohydrate. The fine powder was mixed with 800.0g of D-mannitol in a mixer available on the market. The resulting mixture was granulated in the same manner as in Procedure (A). Thereafter, the granules were dried at 60°C. The dried granules were dressed with a dresser to have a particle size as shown in Table 5. Thus, granule sample C was obtained.

Table 5

	Particles plus 1000μm sieve (wt%)	Particles minus 1000μm sieve and plus 500μm sieve (wt%)	Particles minus 500μm sieve and plus 350μm sieve (wt%)	Particles minus 350μm sieve and plus 149μm sieve (wt%)	Particles minus 149μm sieve (wt%)
A-1	9.4	17.3	21.4	42.8	9.1
A-2	9.8	25.3	19.6	34.3	11.0
A-3	7.9	32.4	26.3	28.7	4.7
A-4	6.3	43.8	28.1	15.6	6.2
A-5	3.4	58.3	30.4	6.3	1.6
B-1	7.4	15.3	28.1	38.4	10.8
C-1	8.8	20.4	16.5	40.1	14.2
C-2	7.9	28.2	18.3	35.2	10.4
C-3	7.4	33.1	27.7	20.6	11.2
C-4	4.2	40.1	23.2	21.4	11.1
C-5	2.6	54.1	32.4	8.7	2.1

Procedure (D)

All the above obtained granule samples in Procedures (A) through (C) were mixed with sodium N-miristoyl β-methylalanine (in an amount of 0.5wt%) for 3 minutes. Thereafter, the resulting mixture granules were continuously tableted making use of a rotary tableting machine to obtain tablets having a diameter of 30 mm, a thickness of 10 mm and a weight of 10.5g. Thus, 900 tablet samples for color developing were obtained.

The above obtained granule and tablet samples were evaluated in the same manner as in Example 1 and further evaluated according to the following. The results are shown in Table 6.

Experiment 4

Ten tablets from each tablet sample were packaged in an aluminium vapor-deposited polyethylene package and stored at 45°C and 40%RH for one month. Thereafter, the tablets were observed for coloration.

Δ : The entire surface of the tablet was colored brown.

○ : The side surface of the tablet was colored.

◎ : No coloration was observed.

Table 6

Granule Sample A	Granule Sample B	Granule Sample C	Deviation of Developing Agent Content of Granule	Expansion of Tablet Sample (%)	Coloration
A-1	B-1	C-1	○	1.2	Δ - ○
A-2	B-1	C-2	◎	0.8	○
A-3	B-1	C-3	◎	0.5	○ - ◎
A-4	B-1	C-4	◎	0.4	◎
A-5	B-1	C-5	○	0.4	◎

As is apparent from table 6 above, the composition containing not less than 40wt% of granules having a particle size of 350 to 1000μm shows improved results in deviation of developing agent content and in expansion of tablets. The composition containing not less than 40wt% of granules having a particle size of 500 to 1000μm further prevents coloration during storage in addition to the above effects.

Example 5

A tablet black-and-white developing composition were prepared according to the following procedures.

Procedure (A)

In a bandamu-mill available on the market were pulverized 1500.0g of 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazole and 2300.0g of potassium hydroquinone monosulfate to a particle size of 10μm. The fine powder was mixed with 100.0g of D-mannitol and granulated at room temperature for about 7 minutes while adding water in a stirring granulator available on the market. Thereafter, the granules were dried at 40°C using a fluid bed drier.

Procedure (B)

In the same manner as in Procedure (A) were pulverized 1000.0g of bis(sulfoethyl)hydroxylamine disodium salt, 150.0g of sodium bromide and 0.2g of potassium iodide and mixed with 240.0g of Pineflow (Matsutani Kagaku Co., Ltd.). The mixture was granulated. The resulting granules were dried at 50°C.

Procedure (C)

In the same manner as in Procedure (A) were pulverized 1400.0 g of potassium carbonate, 1100.0 g of potassium bicarbonate, 3700.0g of sodium sulfite, 330.0g of pentasodium diethylenetriamine pentaacetate, 130.0g of amino(trimethylene sulfonic acid sodium salt and 340.0g of lithium hydroxide monohydrate. The fine powder was mixed with 800.0g of mannitol in a mixer available on the market. The resulting mixture was granulated in the same manner as in Procedure (A). Thereafter, the granules were dried at 60°C.

Procedure (D)

All the above obtained granule samples in Procedures (A) through (C) were mixed with sodium N-miristoyl β-methylalanine (in an amount of 0.5wt%) for 3 minutes. Thereafter, the resulting mixture granules were continuously tableted making use of a rotary tableting machine to obtain tablets having a diameter of 15 mm, a thickness of 5 mm and a weight of 1.2g. Thus, 900 tablet samples for color developing replenisher were obtained.

The above obtained granule and tablet samples were evaluated in the same manner as in Example 1. The results

showed 10 % greater expansion than that of tablet samples in Example 4, but the same deviation as that of Example 4 in the developing agent content.

Claims

1. A method of manufacturing a developing composition for a silver halide photographic light-sensitive material, the method comprising the steps of:
granulating a developing agent to prepare first granules comprising the developing agent,
granulating an alkali agent to prepare second granules comprising the alkali agent, and
mixing the first granules and the second granules,
wherein the content in the first granules of granules having a particle size of 1000μm or more (JIS) is not more than 10 weight % based on the total weight of the first granules and the content in the second granules of granules having a particle size of 1000μm or more (JIS) is not more than 10 weight % based on the total weight of the second granules.

2. The method of claim 1, wherein the content in the first and second granules of granules having a particle size of 350 to 1000μm is not less than 40 weight %.

3. The method of claim 1, wherein the content in the first and second granules of granules having a particle size of 350 to 1000μm is 40 to 74 weight %.

4. The method of claim 1, wherein the content in the first or second granules of granules having a particle size of 500 to 1000μm is not less than 40 weight %.

5. The method of claim 1, wherein the mixing ratio of the first granules and the second granules is 1:1 to 1:20.

6. The method of claim 1, wherein the developing agent is a p-phenylenediamine color developing agent.

7. The method of claim 1, wherein the alkali agent is an alkali metal carbonate.

8. The method of claim 1, further comprising the step of compression-molding the first granules and the second granules into a tablet after said mixing step.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 4013

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	JP-A-5 142 708 (KONICA) * abstract * * column 3, line 12 - line 23 * * column 4, line 7 - line 25 * * column 6, line 38 - line 39 * * column 26, line 24 - column 27, line 9 * ---	1-8	G03C5/26
X	EP-A-0 358 034 (AGFA-GEVAERT) * page 3, line 27 - page 4, line 15; claim 3 * -----	1-7	
			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	24 October 1995	Magrizos, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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