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(54) Solid processing composition for silver halide color photographic light-sensitive materials and processing method for the same.

(57) A solid processing composition for a silver halide color photographic light-sensitive material is disclosed, the composition comprising a color developing composition containing lithium hydroxide.

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Field of the Invention

This invention relates to a processing composition for a silver halide color photographic light-sensitive material and particularly to a solid processing composition suitable for preserving the environment of the earth and excellent in aging preservability; and to a method of processing a silver halide color photographic light-sensitive material in which the processing composition is used.

Background of the Invention

In a process for color developing a silver halide color photographic light-sensitive material, silver halide exposed to light is reduced to be silver and, at the same time, an oxidized aromatic primary amine developing agent is reacted with a coupler so as to form a dye. In the course thereof, a halogen ion produced by reducing silver halide is eluted and then accumlated in a developer solution. On the other hand, the color developing agent is consumed or brought out with the photographic light-sensitive material, so that a concentration of the developing agent is getting lowered. Therefore, in a method of processing a silver halide photographic light-sensitive material in series through an automatic processor, it is required to provide a means for keeping a concentration of a developer component constant within a specific range so as to avoid any possible finished development quality variation which may be produced by concentration variation of the developer component. As for such a means as mentioned above, it has been usual to take a method of replenishing the developer with a replenisher to compensate a component in shortage and dilute any unnecessary increased component. When such a replenisher as mentioned above is replenished, a large quantity of a waste solution already used (that is so-called an overflow solution) are produced and they are discarded. This fact has raised a serious economical and environmental problem.

For reducing the above-mentioned overflow, there have been a proposal for adding a regenerator to an overflow so as to use it again as replenisher, and another proposal for replenishing a concentrated solution in a small amount. Among these proposals, a system for regenerating an overflow has such a disadvantage that an extra space for a stock tank and so forth is required and, in addition, that the operations become complicated for a photofinisher. In recent years, particularly, this system can hardly be introduced into a small-scaled photofinisher (so-called a mini-lab.) where an on-site processing service is carried out. On the other hand, another system for replenishing a concentrated replenisher in a small amount may be suitable particularly for a small-scaled photofinisher, because this system is of the space-saving type without requiring any extra device. However, this system still has some disadvantages as follows.

When preparing a concentrated replenisher, there has been a certain limitation to carry out a small amount replenishment, because a color developing agent is low in solubility. Further, a conventional color developing composition has been required to be supplied after separating it into plural parts so that the components of the developing composition can be avoided from a chemical reaction with each other, because the necessary components thereof have been supplied in the state of an aqueous solution. When preparing a replenisher, a work has been required to add the parts of the replenisher one after another and then to dissolve them together. Therefore, after a replenisher is once prepared, it cannot be preserved for a long period, because a chemical reaction gradually occurs and the replenisher is then deteriorated. Particularly when trying to make a small amount replenishment, not only an unpreferable chemical reaction is accelerated because the component concentration in the replenisher is made higher, but also there may be such a danger that a photographic processing characteristic variation may be produced by the deterioration of the replenisher, because an amount of the replenisher consumed becomes small and the preservation period thereof is accordingly prolonged.

There has been another disadvantage that not only a transportation cost is increased, but also a wide space is required for storage, because a conventional processing composition is made in the form of an aqueous solution and is then filled in a plastic bottle or the like. Further another serious problem has also been raised on how to discard an empty plastic bottle after it is used up. In Europe, for example, it has been the actual situations where a strong legislative movement has become active, for example, a plastics should be recycled or prohibited from the use, or a decomposable plastics is obliged to be used.

For solving the above-mentioned problems, it has been considered that a processing composition is solidified and is then replenished. In relation to the consideration, Japanese Patent Publication Open to Public Inspection (hereinafter abbreviated to JP OPI Publication) No. 2-109042/1990 discloses a granulated color developing composition and JP OPI Publication No. 51-61837/1976 discloses a tablet type processing composition, However, when trying to achieve a small amount replenishment in a method such as mentioned above, the other new problems have been raised. To be concrete, when making a replenishment smaller in amount, it is required to add a color developing agent to be consumed and an alkali capable of neutralizing a developer and keeping a high pH value in an amount much more than it used to be added. In recent years, there has

been an increasing demand for making a processing time shorter. And, for performing a rapid process, it has also been required to make a color developing agent higher in concentration and pH value. However, potassium carbonate having so far been used for an alkali is not enough to keep a pH suitable for a small-amount replenishment or for a rapid process, so that such a strong alkali as potassium hydroxide has been required to use. It was, however, found out that potassium hydroxide is very high in deliquescence and requires a peculiar drying condition for preparing a solid type developing composition, and that, even when a solid type developing composition finished as a product is moisture-resistibly packed, there is a disadvantage to use up the product at once. It was also found that, even when a fixer or a stabilizer is solidified, such an alkali having a high deliquescence as mentioned above is disadvantageous to be used.

There was still another problem. When a granule or tablet solid processing composition whose main component is potassium carbonate is prepared, the strength of the resulting solid processing composition was not sufficient. For example, if the hardness of the tablet was insufficient, the tablet was sometimes cracked or broken off due to shock when being dropped or vibrated during transportation.

Brief Description of the Drawings

Fig. 1 illustrates a schematic perspective view showing an example of processing composition supplying means in a peal-open system; and

Fig. 2 illustrates an example of processing composition supplying means in a system for cutting a series of packages into two parts.

Summary of the Invention

It is accordingly an object of the invention to provide a processing composition for a silver halide color photographic light-sensitive material, that has the following features, and to provide a method of processing a silver halide color photographic light-sensitive material, in which the above-mentioned processing composition is used.

First, the environment of the earth can clearly be preserved by reducing a waste liquid and saving a plastic bottle packaging material;

Second, the processing composition is excellent in aging preservability, and particularly excellent in handling property such as fluidity or strength; and

Third, when processing a light-sensitive material in series, the light-sensitive material can be performed rapidly and the photographic characteristics of the light-sensitive material can be maintained safely.

The present inventors have so studied as to solve the above-mentioned problems and have found that the above-mentioned objects can be achieved by any one of the following constitutions (1) through (9).

(1) A solid processing composition for a silver halide color photographic light-sensitive material, in which lithium hydroxide is contained;

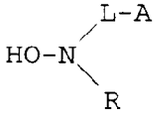
(2) A solid processing composition for a silver halide color photographic light-sensitive material as mentioned in (1) above, in which the solid type processing composition is in a tablet or granule form;

(3) A solid processing composition for a silver halide color photographic light-sensitive material as mentioned in (2) above, in which the tablet is obtained by compressing and molding particles.

(4) A solid processing composition for a silver halide color photographic light-sensitive material as mentioned in (1) through (3) above, in which the solid type processing composition is a color developing composition containing a p-phenylenediamine color developing agent;

(5) A solid processing composition for a silver halide color photographic light-sensitive material as mentioned in (1) through (4) above, in which the solid type processing composition is a color developing composition and contains at least one of the compounds represented by the following Formula [A].

Formula [A]

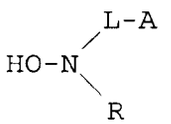


wherein L represents an alkylene group; A represents a carboxyl group, a sulfo group, a phosphono group, a phosphinic acid residual group, a hydroxy group, an amino group, an ammonio group, a carbamoyl group or a sulfamoyl group; and R represents a hydrogen atom or an alkyl group;

(6) A solid processing composition for a silver halide color photographic light-sensitive material as mentioned in (4), in which the color developing composition comprises a mixture of a granule containing lithium hydroxide and a granule containing a p-phenylenediamine type color developing agent.

(7) A solid processing composition for a silver halide color photographic light-sensitive material as mentioned in (6), in which the mixture further comprises a granule containing a compound represented by the following Formula (A):

Formula [A]



wherein L represents an alkylene group; A represents a carboxyl group, a sulfo group, a phosphono group, a phosphinic acid group, a hydroxy group, an amino group, an ammonio group, a carbamoyl group or a sulfamoyl group; and R represents a hydrogen atom or an alkyl group.

(8) A solid processing composition for a silver halide color photographic light-sensitive material as mentioned in (2), in which the tablet was prepared by tabulating a mixture of a granule containing lithium hydroxide and a granule containing a p-phenylenediamine type color developing agent.

(9) A method of processing a silver halide color photographic light-sensitive material using the above described solid processing composition.

Detailed Description of the Invention

Now, the invention will be detailed below.

Lithium hydroxide of the invention may also be either an anhydride or a hydrate thereof.

The granulated composition of the invention means a granule that is prepared by applying a granulation process to powder and has a granule size within the range of 50 to 5000μm.

A tablet composition of the invention means those prepared by compression-molding a powder to take a specific configuration, or those prepared by granulating a powder once and then by compression-molding the granule to take a specific configuration.

Among the above-mentioned solid processing compositions, a tablet composition can preferably be used from the viewpoint of more remarkably displaying the effects of the invention.

A method of preparing a preferable tablet composition includes, for example, a method in which a powder solid processing composition is granulated and is then subjected to a tableting process. When making use of this method, the resulting tablet composition can be improved on solubility and preservability more than a solid processing composition prepared simply by mixing up the components of a solid processing composition and then by tableting it in a tableting process. As the result, the resulting composition can have such an advantage that the photographic characteristics thereof can be stabilized.

A granulating method for forming a granule includes, for example, any well-known method such as a convoluting granulation method, an extruding granulation method, a compressing granulation method, a pulverizing granulation method, a stirring granulation method, a fluidized-bedding granulation method, and a spray-drying granulation method. The average granule size of the resulting granules is within the range of, preferably, 100 to 800μm and, more preferably, 200 to 750μm. If the average granule size is smaller than 100μm or larger than 800μm, the components of the granule lack the uniformity so as to cause a so-called segregation unpreferably when the granules are mixed up and then compressed.

Also, it is preferable when not less than 60% of the whole resulting granule have a granule-size distribution within the deviation range of ±100 to 150μm.

For compressing the resulting granules, any well-known compressor may be used, such as a hydraulic press, a single tableting machine, a rotary tableting machine and a briquetting machine. A solid type processing composition prepared in a compression process can take any configuration. However, a processing composition of a cylindrical type that is a so-called tablet type is preferable to be used, from the viewpoints of a productivity and a handling efficiency.

It is more preferable when a component such as an alkali, a reducer, an oxidizer or a preservative is separately granulated in the course of carrying out a granulation, because the foregoing effect can remarkably be displayed. Particularly, a color developing composition is preferable to be granulated separately from an alkali.

From the viewpoints of the solubility of a solid processing composition and the effect of the invention, the

bulk density of a solid processing composition is preferably within the range of 1.0 g/cm^3 to 2.5 g/cm^3 when the processing composition is of a tablet type. If the bulk density thereof is not less than 1.0 g/cm^3, it is preferable from the viewpoint of the strength of the resulting solid and, if the bulk density is not more than 2.5 g/cm^3, it is preferable from the viewpoint of the solubility of the resulting solid. When the resulting solid processing composition is of a granule or powder type, the bulk density thereof is preferably within the range of 0.40 to 0.95 g/cm^3.

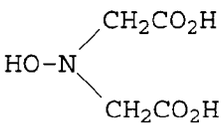
When processing a silver halide color photographic light-sensitive material in series by making use of a solid processing composition of the invention, an amount replenished is preferably not more than 150 ml per m^2 of the light-sensitive material and particularly not more than 100 ml. The term, "an amount replenished", herein stated also include an amount of water supplied (i.e., a water-replenished amount) when a solid type color developing composition and water for dissolving it are separately replenished. Further, when a time required for carrying out a color development is not longer than 30 seconds, the effect of the invention can more remarkably be displayed.

Now, the compounds represented by Formula [A] will be detailed.

In the formula, L represents a straight-chain or branched-chain alkylene group having 1 to 10 carbon atoms which may have a substituent and, among them, one having 1 to 5 carbon atoms is preferred. To be more concrete, the preferable example thereof includes a methylene group, an ethylene group, a trimethylene group and a propylene group. The substituent thereof includes, for example, a carboxy group, a sulfo group, a phosphono group, a phosphinic acid residual group, a hydroxy group, an alkyl-substitutable ammonio group and, among them, the preferable example thereof includes a carboxy group, a sulfo group, a phosphono group and a hydroxy group; A represents a carboxy group, a sulfo group, a phosphono group, a phosphinic acid residual group, a hydroxy group, an alkyl-substitutable amino group, an alkyl-substitutable ammonio group (preferably having 1 to 5 carbon atoms), an alkyl-substitutable carbamoyl group (preferably having 1 to 5 carbon atoms) or an alkyl-substitutable sulfamoyl group (preferably having 1 to 5 carbon atoms) and, among them, the preferable example thereof includes a carboxy group, a sulfo group, a hydroxy group, a phosphono group and an alkyl-substitutable carbamoyl group. The example of -L-A includes, preferably, a carboxymethyl group, a carboxyethyl group, a carboxypropyl group, a sulfoethyl group, a sulfopropyl group, a sulfobutyl group, a phosphonomethyl group, a phosphonoethyl group and a hydroxyethyl group and, among them, the particularly preferable example thereof includes a carboxymethyl group, a carboxyethyl group, a sulfoethyl group, a sulfopropyl group, a phosphonomethyl group and a phosphonoethyl group; and R represents a hydrogen atom, a straight-chain or the branched-chain alkyl group having 1 to 10 carbon atoms, which may have a substituent and, among them, one having 1 to 5 carbon atoms is preferred. The substituent thereof includes, for example, a carboxy group, a sulfo group, a phosphono group, a sulfinic acid residual group, a hydroxy group, an alkyl-substitutable amino group, an alkyl-substitutable ammonio group, an alkyl-substitutable carbamoyl group, an alkyl-substitutable sulfamoyl group, a substitutable alkylsulfonyl group, an acylamino group, an alkylsulfonylamino group, an arylsulfonylamino group, an alkoxycarbonyl group, an alkyl-substitutable amino group, an arylsulfonyl group, a nitro group, a cyano group and a halogen atom, provided that there may be two or more substituents. The preferable example thereof represented by R includes a hydrogen atom, a methyl group, an ethyl group, a propyl group, a carboxymethyl group, a carboxyethyl group, a carboxypropyl group, a sulfoethyl group, a sulfopropyl group, a sulfobutyl group, a phosphonomethyl group, a phosphonoethyl group and a hydroxyethyl group and, among them, the particularly preferable example thereof includes a hydrogen atom, a carboxymethyl group, a carboxyethyl group, a sulfoethyl group, a sulfopropyl group, a phosphonomethyl group and a phosphonoethyl group, provided that L and R may also be coupled to each other so as to form a ring.

Next, among the compounds represented by Formula [A], some typical examples thereof will be given below. However, the invention shall not be limited to the compounds given below.

(1)



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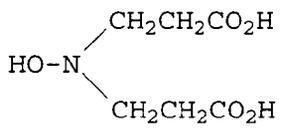

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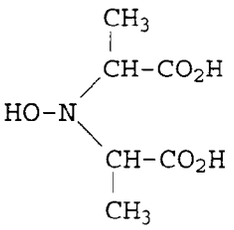

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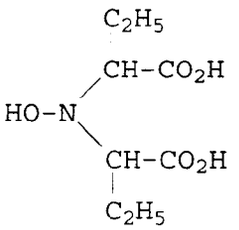

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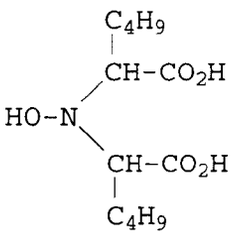

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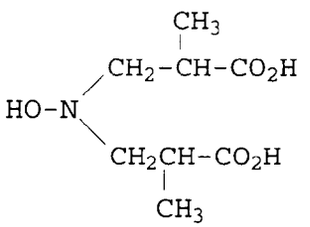

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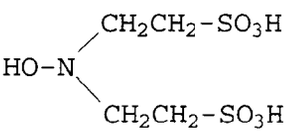

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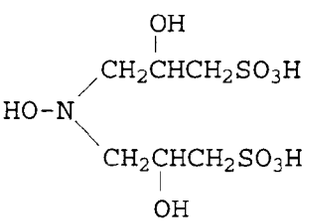

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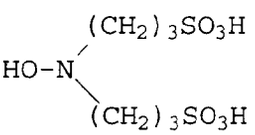

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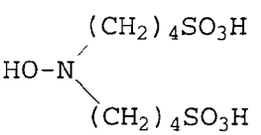

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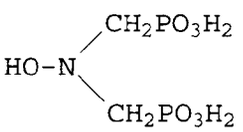

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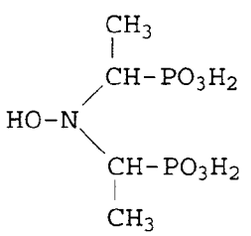

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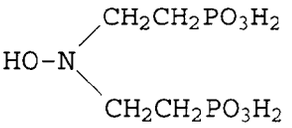

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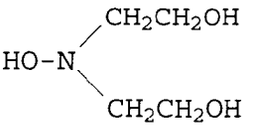

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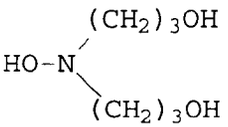

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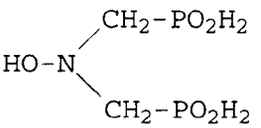

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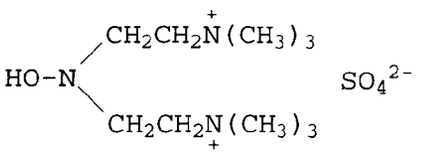

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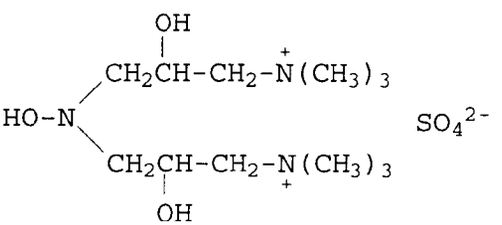

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(20) HO-NH-$CH_2CH_2CO_2H$

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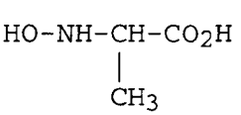

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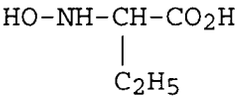

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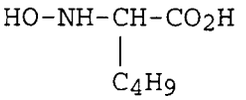

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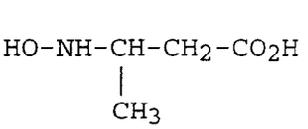

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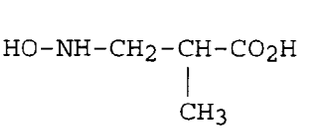

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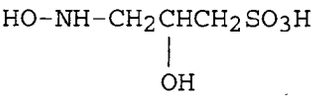

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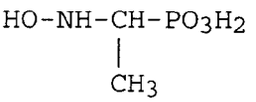
(29) $HO\text{-}NH\text{-}(CH_2)_4SO_3H$

(30) $HO\text{-}NH\text{-}CH_2PO_3H_2$

(31)



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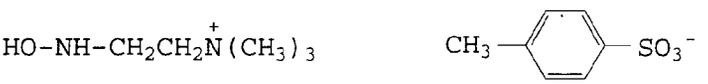
(33) $HO\text{-}NH\text{-}CH_2CH_2OH$

(34) $HO\text{-}NH\text{-}(CH_3)_3OH$

(35) $HO\text{-}NH\text{-}CH_2\text{-}PO_3H_2$

(36)



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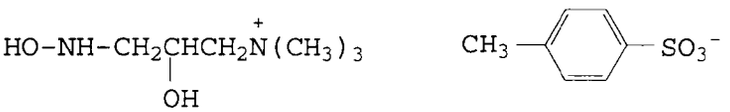

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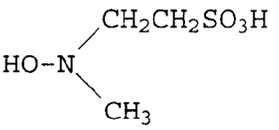

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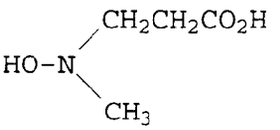

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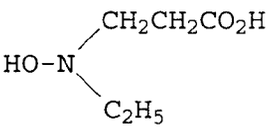

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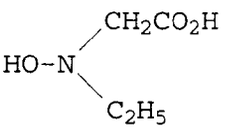

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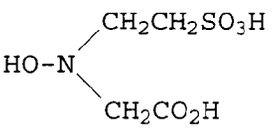

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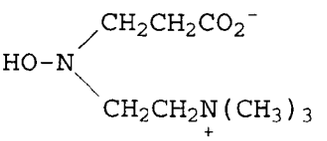

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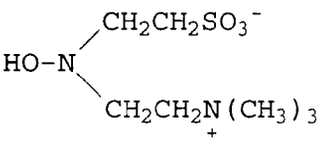

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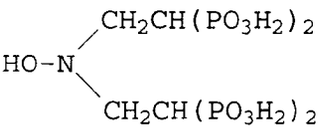
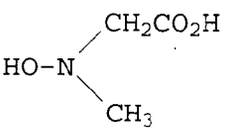


(46) $HONHCH_2CH(PO_3H_2)_2$

(47)



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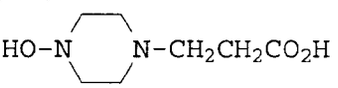

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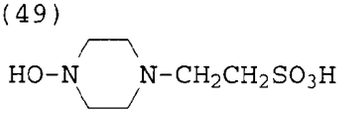

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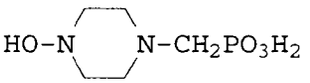

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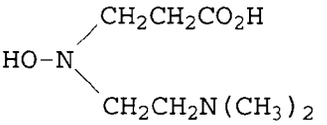

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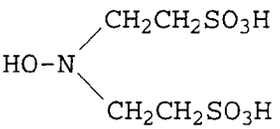

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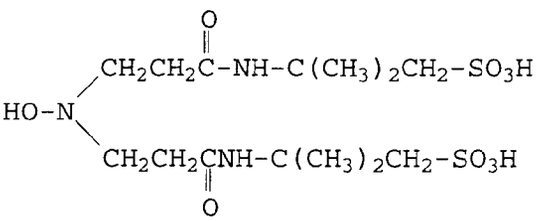

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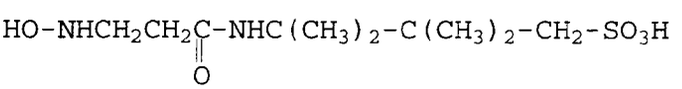

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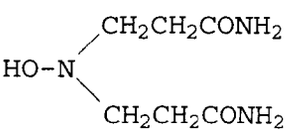


Among the compounds, a particularly preferable compound includes, for example, those of (2), (7), (14), (38), (39), (40) and (55). The compound may be used in the form of an alkali-metal salt or an ammonium salt.

The compounds represented by Formula [A] can be synthesized by making an alkylating reaction (such as a nucleophilic substituting reaction, an adduct reaction and a Mannich reaction) with a hydroxylamine readily available on the market. The synthesization thereof can be performed with reference to the synthesization procedures described in, for example, West German Patent Publication "Inorganica Chimica Acta", 93, (1984), pp. 101-108, and so forth.

The solid processing composition of the invention may consist of a single unit comprising in admixture the total components for processing a silver halide color photographic light-sensitive material or separate units comprising one or more components which are readily reactive with each other. Between the two cases, however, the single unit is preferable from the viewpoint of the handling convenience and working efficiency. In

this case, the two compounds readily chemically reactive with each other are also allowed to take a layer-shaped configuration in which one of the compounds is partitioned off from the other by a different compound inert with the above-mentioned two compounds or by a film or the like.

For example, the conventional developer replenisher consists of three units, i.e., a color developing agent unit, a preserver unit and an alkali agent unit in view of storage stability. The present invention provides the solid processing composition consisting of a single unit in the solid form which contains all the components, and has good storage stability. Further, the single unit has an advantage in that it requires only one supplying means.

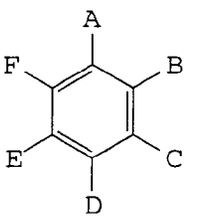
When the solid color developing composition of the invention consists of a single unit, it is preferable to contain anhydrous lithium hydroxide therein. Particularly when a solid type color developing composition contains such a deliquescent substance as potassium carbonate or such an acidic substance as an aminopolycarboxylic acid or a salt of a paraphenylenediamine type color developing agent, a moisture absorption and an internal reaction can be inhibited and thereby the effect of the invention can more remarkably be displayed by making use of anhydrous lithium hydroxide as an alkalizer to make it coexistent therein.

The solid color developing composition of the invention preferably contains an aromatic sulfonic acid or salt thereof which inhibits an internal chemical reaction.

The nomenclature, "an aromatic sulfonic acid or a salt thereof' used herein means a compound in which a sulfonate is directly bonded to an unsaturated conjugate ring showing an aromaticity, provided that a sulfonic acid group thereof or the sulfonate may comprise either one or more of them and the ring showing an aromaticity may contain a hetero atom or any substituent. A single compound may have plural rings showing an aromaticity or may be a polymer. The sulfonates include, for example, an alkali metal salt such as a salt of lithium, sodium or potassium, or an ammonium salt.

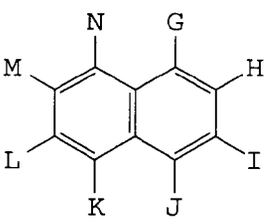
The aromatic sulfonic acid or salt thereof preferably applicable to the invention include, for example, the compound represented by the following Formula [1] or [2].

Formula [1]



wherein at least one of A through F represents a sulfonic acid group or a sulfonate and the others represent each a hydrogen atom, a halogen atom, an alkyl group or an alkenyl group.

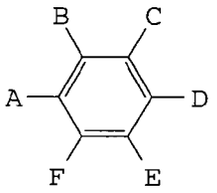
Formula [2]



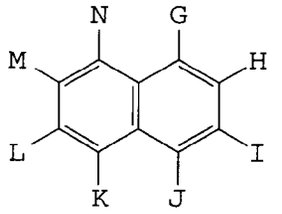
wherein at least one of G through N represents a sulfonic acid group or a sulfonate and the others represent each a hydrogen atom, a halogen atom, an alkyl group or an alkenyl group.

In the above-given Formula [1] or [2], the alkyl or alkenyl group represented by A through F or G through N is preferable to have 1 to 10 carbon atoms, provided that the carbon chain thereof may be either straight-chained or side-chained.

Now, some typical examples of the compounds represented by Formula [1] or [2] will be given below. However, the invention shall not be limited thereto. The every exemplified compound will be given in the form of a sodium salt. However, a part or the whole of them may also be either a sulfonic acid salt or a salt of others.



Exemplified compound No.	A	B	C	D	E	F
1-1	H	H	H	$-SO_3Na$	H	H
1-2	$-CH_3$	H	H	$-SO_3Na$	H	H
1-3	H	$-CH_3$	H	$-SO_3Na$	H	H
1-4	H	H	$-CH_3$	$-SO_3Na$	H	H
1-5	$-CH_2CH_3$	H	H	$-SO_3Na$	H	H
1-6	$-CH_2CH_2CH_3$	H	H	$-SO_3Na$	H	H
1-7	$-CHCH_3$ | CH_3	H	H	$-SO_3Na$	H	H
1-8	$-C(CH_3)_3$	H	H	$-SO_3Na$	H	H
1-9	$-CH=CH_2$	H	H	$-SO_3Na$	H	H
1-10	$-CH=CHCH_3$	H	H	$-SO_3Na$	H	H
1-11	$-C=CH_2$ | CH_3	H	H	$-SO_3Na$	H	H
1-12	-Cl	H	H	$-SO_3Na$	H	H
1-13	-Br	H	H	$-SO_3Na$	H	H
1-14	$-CH_3$	H	$-CH_3$	$-SO_3Na$	H	H
1-15	$-CH_3$	H	H	$-CH_3$	$-SO_3Na$	H
1-16	-Cl	H	$-CH_3$	$-SO_3Na$	H	H
1-17	$-CH_3$	H	-Cl	$-SO_3Na$	H	H
1-18	H	H	$-SO_3Na$	H	$-SO_3Na$	H
1-19	$-SO_3Na$	H	H	$-SO_3Na$	H	H
1-20	$-CH_3$	H	$-SO_3Na$	H	$-SO_3Na$	H



Exemplified compound No.	G	H	I	J	K	L	M	N
2-1	$-SO_3Na$	H	H	H	H	H	H	H
2-2	H	$-SO_3Na$	H	H	H	H	H	H
2-3	H	$-SO_3Na$	H	H	H	$-CH_3$	H	H
2-4	$-SO_3Na$	H	H	H	$-SO_3Na$	H	H	H
2-5	H	$-SO_3Na$	H	H	H	$-SO_3Na$	H	H
2-6	H	H	$-SO_3Na$	H	H	$-SO_3Na$	H	H
2-7	H	$-SO_3Na$	H	$-SO_3Na$	H	H	H	H
2-8	$-SO_3Na$	H	$-SO_3Na$	H	H	$-SO_3Na$	H	H
2-9	$-CH_3$	H	$-SO_3Na$	H	H	$-SO_3Na$	H	H
2-10	-Cl	H	$-SO_3Na$	H	H	$-SO_3Na$	H	H
2-11	H	$-SO_3Na$	H	H	H	$-SO_3Na$	H	-Cl
2-12	H	H	$-SO_3Na$	H	H	-Cl	H	H

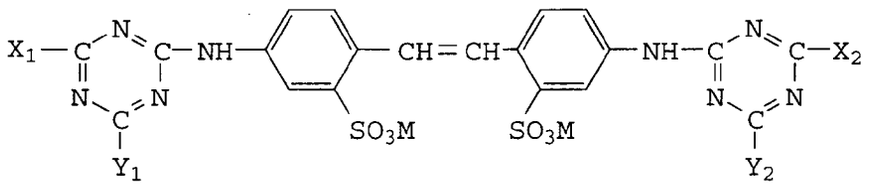
Among the compounds given above, exemplified compound (1-2), (1-14), (2-6) or (2-8) is preferably used. It is also preferable to use the compounds in the form of an alkali metal salt and particularly in the form of a sodium salt.

It is similarly preferable to contain polyethylene glycol in a solid color developing composition as a compound capable of effectively inhibiting an internal chemical reaction. The average molecular weight of the above-mentioned polyethylene glycol applicable to the invention is preferably 300 to 50,000 and more preferably, 2,000 to 20,000. When polyethylene glycol is in the form of a liquid, it is preferable to be added in the course of granulating a solid composition. This compound can more remarkably display the effect of the invention when used together with the foregoing aromatic sulfonic acid or salt thereof.

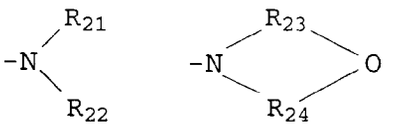
A color developing agent applicable to the solid color developing composition the invention is preferable to contain a paraphenylenediamine type color developing agent. The typical exemplified compounds of the color developing agent preferably applicable to the invention include, for example, compounds (C-1) through (C-16) given in JP OPI Publication No. 4-86741/1992, pp. 26-31, compounds (1) through (8) given in JP OPI Publication No. 61-289350/1986, and compounds (1) through (26) given in JP OPI Publication No. 3-246543/1991, pp.6-9. Among these compounds, the particularly preferable include compounds (C-1) and (C-3) given in JP Application No. 2-203169/1990, Exemplified Compounds (2) given in JP OPI Publication No. 61-289350/1986 and Exemplified Compound (1) given in JP OPI Publication No. 3-246543/1991.

From the viewpoint of displaying the effect of the invention, it is preferable that the color developing composition or the developing composition of the invention contain each a triazinyl stilbene type fluorescent whitening agent. Such a fluorescent whitening agent as mentioned above includes, preferably, a compound represented by the following Formula [E].

Formula [E]



wherein X_1, X_2, Y_1 and Y_2 represent each a hydroxyl group a halogen atom such as those of chlorine, bromine and so forth, an alkyl group, an aryl group,



or OR_{25}, in which R_{21} and R_{22} represent each a hydrogen atom, an alkyl group (including a substituent thereof) or an aryl group (including a substituent thereof), R_{23} and R_{24} represent each an alkylene group (including a substituent thereof), R_{25} represents a hydrogen atom, an alkyl group (including a substituent thereof) or an aryl group (including a substituent thereof), and M represents a cation.

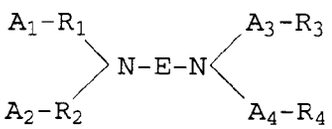
The groups in Formula [E] and the substituents thereof are each synonymous with those described in JP OPI Publication No. 4-118649/1992, the 8th line from the bottom of p. 62 to the 3rd line from the bottom of p. 64. The typical compounds thereof include, for example, E-1 to E-45 given in ibid., pp. 65-67. Among them, E-4, E-24, E-34, E-35, E-36, E-37 and E-41 may preferably be used. These compounds are each added in an amount within the range of, preferably, 0.2 to 10 g per liter of a color developing solution and, particularly, 0.4 to 5 g.

Further, an auxiliary developing composition can also be used together with a developing agent. The well-known auxiliary developing compositions include, for example, N-methyl-p-aminophenol hexasulfate (that is so-called Metol), phenidone, N,N-diethyl-p-aminophenol hydrochloride and N,N,N',N'-tetramethyl-p-phenylenediamine hydrochloride. Usually, they are each added preferably in an amount within the range of 0.01 to 1.0 g per liter.

Besides the above, a variety of additives such as an antistaining agent, an antisludging agent and an interlayer-effect accelerating agent may also be used therein.

From the viewpoint of effectively achieving the object of the invention, it is preferable that a color developing composition and a black-and-white developing composition are each contain a chelating agent represented by the following Formula [K] and the exemplified compounds thereof K-1 through K-22, which are given in JP OPI Publication No. 4-118649/1992, the 9th line from the bottom of p. 69 to p. 75.

Formula [K]



wherein E represents an alkylene group, a cycloalkylene group, a phenylene group (each may have a substituent), $-R_5OR_5-$, $-R_5OR_5OR_5-$ or $-R_5ZR_5-$; R_1 through R_5 represent each an alkylene group (including a substituent); Z represents $=N-R_5-A_5$ or $=N-A_5$; A_1 through A_5 represent each a hydrogen atom, a hydroxyl group, $-CO_2M$ group or $-PO_3(M)_2$ group; and M represents a hydrogen atom or an alkali metal atom.

Among the above-given chelating agents, K-2, K-9, K-12, K-13, K-17 and K-19 may preferably be used. In particular, when K-2 and K-9 are added to a color developing solution, the effect of the invention can be more remarkably displayed.

The chelating agent may be added in an amount of 0.1 to 20 g per liter of a color developing solution and more preferably 0.2 to 8 g.

Also, a color developing composition is also allowed to contain such a surfactant as a anionic, cationic, amphoteric or nonionic surfactant.

The solid processing composition applicable to the invention can be embodied by solidifying the whole of an alkali, a color developing agent and a reducing agent in the case of solidifying a color developing composition, or the composition consists of not more than four units and most preferably a single unit in the case of preparing a tablet type processing composition. In the case where a solid type processing composition is prepared by separating it into not less than two units, the resulting plural tablets or granules are preferable to be put in one package.

EXAMPLES

Now, the invention will be detailed concretely with reference to the examples given hereafter. However, the invention shall not be limited thereto.

Example 1

Under the following procedure, alkali particle samples and tablet samples were prepared.

In a bandamu mill available on the market, 120.0 g of Tinopar SFP (produced by Chiba-Geigy), 16.0 g of sodium sulfite, 1400 g of potassium carbonate, 1.4 g of potassium bromide, 100 g of pentasodium diethylenetriamine pentaacetic acid and alkaline agents described in Table 1 were crushed so that the average grain size thereof be 10 μm. In a stirring granulator available on the market, 10 ml of water was added to the above-mentioned fine powder to obtain a granule. Next, the resulting granule was dried in a fluid-bed type drier for 1 hour at 60 °C so that moisture was substantially removed therefrom. Thus, granule samples Nos. 1-1 through 1-10 were prepared. When the average grain size of the samples was measured by means of a screening method using a screen stipulated by JIS, it was in the range of 150 to 1500 μm.

Incidentally, in Procedure (C), the alkaline agent was crushed at the relative humidity of 55 %, the deliquescence of potassium hydroxide and sodium was noticeable. After that, therefore, the crushing was conducted under a relative humidity of 40 % RH. With regard to the alkali of the present invention, there occurred substantially no problem.

One half of the resulting granule prepared in the above-described procedure was compression-tabulated so as to have a filled amount of 5.0 g per tablet by the use of Touch Press Correct Model 1527 HU manufactured by Kikusui Works, which was modified into a tabulating machine. Thus, 100 pieces of each of tablet sample Nos. 1-11 to 1-20 having a diameter of 17 mm were prepared as replenishing color developing compositions for color paper.

The resulting samples were evaluated as follows.

(Evaluation of Deliquescent Property)

A sample of 5.0 g (one piece in the case of a tablet) was put in a sample bottle remaining uncapped and was preserved in a thermostat having a temperature of 30°C and a relative humidity of 40%RH. Three samples were prepared in each procedure and deliquescence of the samples was observed in terms of deformation or moisture adherence.

The evaluation standards will be shown as follows.

××: Deliquescence occurred on the same day (within 6 hours) to start a preservation;
×: Deliquescence occurred on the next day to start a preservation;
Δ: Deliquescence occurred within 3 days after starting a preservation;
○: A deliquescence was produced within one week after starting a preservation; and
◎: A configuration was maintained for not shorter than one week after starting a preservation.

(Measurement of fluidity of granules)

In an envelope made of polyethylene (10 cm x 10 cm) 5.0 g of the sample was placed. The envelope was sealed tightly by means of a heat seal and stored in a temperature-constant room at 60 °C and 40 %RH for 4 weeks. Angle of repose of the sample after being stored was measured.

(Measurement of strength of a tablet)

The hardness of 10 pieces of tablets was measured by means of a speed checker (produced by Okada Seiko Co., Ltd.), and the average value was defined to be degree of strength.

The results are shown in Table 1. LiOH shall represent lithium hydroxide anhydride, unless otherwise men-

tioned.

Table 1

No.	Alkali (Amount added)	Deli-quescence	Angle of repose (degree)	Hardness (Kg)	
1-1	——	△	46		Comparison
1-2	KOH 35g	××	48		Comparison
1-3	KOH 70g	××	50		Comparison
1-4	KOH 140g	××	unmeasurable		Comparison
1-5	NaOH 25g	××	unmeasurable		Comparison
1-6	NaOH 100g	××	unmeasurable		Comparison
1-7	LiOH 15g	△	43		Invention
1-8	LiOH 30g	△	40		Invention
1-9	LiOH 60g	○	39		Invention
1-10	LiOH 120g	○	39		Invention
1-11	——	△		20	Comparison
1-12	KOH 35g	×		20	Comparison
1-13	KOH 70g	××		19	Comparison
1-14	KOH 140g	××		17	Comparison
1-15	NaOH 25g	××		18	Comparison
1-16	NaOH 100g	××		16	Comparison
1-17	LiOH 15g	○		25	Invention
1-18	LiOH 30g	○		30	Invention
1-19	LiOH 60g	○		32	Invention
1-20	LiOH 120g	○		33	Invention

From the above-mentioned table, it can be understood that the alkaline agent of the present invention is not only excellent in deliquescence but also excellent in terms of fluidity after stored for a long time and also excellent in strength of tablets.

Example 2

A solid color developing composition for color paper use was prepared in the following procedures.

1) A tablet for replenishing a color developing composition for color paper use

Procedure (A)

In an air-jet pulverizer was pulverized 1200 g of a developing agent CD-3, 4-amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]ethyl sulfonate to have an average particle size of 10 μm. The resulting fine particles thereof were granulated by spraying 30 ml of water thereto at room temperature for about 5 minutes in

a fluid-bed spray type granulator available on the market and the resulting granules were then dried at 60°C for 8 minutes. Thereafter, the granules were further dried up in a vacuum condition at 40°C for 2 hours, so that the moisture of the granules were almost completely removed.

Procedure (B)

In the same manner as in Procedure (A) was pulverized and granulated, 1200 g of a compound a preservative shown in Table 2, except that 1.0 ml of water is sprayed. After the granulation was completed the granules were dried at 50°C for 10 minutes. Thereafter, the granules were dried up in vacuum condition at 40°C for 2 hours, so that the moisture of the granules were almost completely removed therefrom.

Procedure (C)

Tinopar SFP (manufactured by Ciba-Geigy AG.) of 300 g, 400 g of sodium sulfite, 3500 g of potassium carbonate, 3.0 g of potassium bromide, 250 g of diethylene triamine penta acetic acid penta sodium sult and an alkali shown in Table 2 were pulverized in the same manner as in Procedure (A). Thereafter, the resulting pulverized matters were mixed up by a mixer available on the market. Then, the resulting mixtures were granulated in the same manner as in Procedure (A), except that 150 ml of water were sprayed thereto. After completing the granulation, the granules were dried in a vacuum condition at 40°C for 2 hours, so that the moisture of the granules were almost removed therefrom.

Procedure (D)

The resulting granules prepared in the above-described Procedures (A) through (C) were uniformly mixed up at 25°C for 10 minutes by making use of a mixer in a room maintained not higher than 40%RH.

Procedure (E)

One half of the resulting mixture prepared in the above-described Procedure (D) was compression-tableted so as to have a filled amount of 10.0 g per tablet by making use of Touch Press Correct Model 1527HU manufactured by Kikusui Mfg. Works, which was remodeled into a tableting machine, so that 80 pieces of tablets having a diameter of 30 mm for replenishing a color developing composition for color paper use were prepared.

The resulting samples were evaluated as follows.

(Evaluation of Deliquescent Property)

A sample of 10.0 g (one piece in the case of a tablet) was put in a sample bottle remaining uncapped and was preserved in a thermostat having a temperature of 30°C and a relative humidity of 40%RH. Three samples were prepared in each procedure and deliquescence of the samples was observed in terms of deformation or moisture adherence.

The evaluation standards will be shown as follows.

××: Deliquescence occurred on the same day (within 6 hours) to start a preservation;
×: Deliquescence occurred on the next day to start a preservation;
Δ: Deliquescence occurred within 3 days after starting a preservation;
○: A deliquescence was produced within one week after starting a preservation; and
⓪: A configuration was maintained for not shorter than one week after starting a preservation.

(Measurement of Residual Concentration of Developing Agent)

A sample of 10.0 g (or, one piece in the case of a tablet) was put in a polyethylene-made bag (having a size of 10cm x 10cm) and then tightly sealed by applying heat. The sealed bag was preserved for 3 weeks in a thermostat having a temperature of 50°C. The resulting sample was dissolved in a specific amount of water, and the concentration of the color developing agent remaining in the solution was measured.

Fluidity of granules and strength of tablets were measured in the same manner as in Example 1.

The results thereof will be shown in Table 2, wherein LiOH represents an anhydrous lithium hydroxide, unless otherwise expressly stated.

Table 2

No.	Alkali (Amount added)	Preservative	Sodium p-toluene-sulfonate	PEG 6000	Deli-quescence	Angle of repose (degree)	Residual Concentration of developing agent (%)	
2-1	—	—	—	—	△	48	75	Comparison
2-2	KOH 110g	—	—	—	×	50	71	Comparison
2-3	KOH 350g	—	—	—	××	urmeasurable	65	Comparison
2-4	NaOH 250g	—	—	—	××	urmeasurable	63	Comparison
2-5	KOH 350g	Diethyl hydroxylamine oxalate	—	—	××	urmeasurable	74	Comparison
2-6	NaOH 350g	Diethyl hydroxylamine oxalate	added	added	××	urmeasurable	76	Comparison
2-7	LiOH 30g	—	—	—	△	44	85	Comparison
2-8	LiOH 75g	—	—	—	○	43	84	Invention
2-9	LiOH 150g	—	—	—	○	43	82	Invention
2-10	LiOH 150g	Diethyl hydroxylamine oxalate	—	—	△	44	88	Invention
2-11	LiOH 150g	Exemplified compound (2)	—	—	○	42	90	Invention
2-12	LiOH 150g	Exemplified compound (7) 2Na salt	—	—	◎	38	91	Invention
2-13	LiOH 150g	Exemplified compound (14)	—	—	○	39	90	Invention
2-14	LiOH 150g	Exemplified compound (19)	—	—	○	40	88	Invention
2-15	LiOH 150g	Exemplified compound (7) 2Na salt	added	—	◎	37	92	Invention

Table 2 (continued)

No.	Alkali (Amount added)	Preservative	Sodium p-toluene-sulfonate	PEG 6000	Deli-quescence	Angle of repose (degree)	Residual Concentration of developing agent (%)	
2-16	LiOH 150g	Exemplified compound (7) 2Na salt	—	added	◎	38	93	Invention
2-17	LiOH 150g	Exemplified compound (7) 2Na salt	added	added	◎	36	96	Invention
2-18	—	—	—	—	X	45	77	Comparison
2-19	KOH 110g	—	—	—	XX	40	72	Comparison
2-20	KOH 350g	—	—	—	XX	37	66	Comparison
2-21	NaOH 250g	—	—	—	XX	38	65	Comparison
2-22	KOH 350g	Diethyl hydroxylamine oxalate	—	—	XX	40	74	Comparison
2-23	NaOH 350g	Diethyl hydroxylamine oxalate	added	added	XX	42	75	Comparison
2-24	LiOH 30g	—	—	—	○	50	87	Comparison
2-25	LiOH 75g	—	—	—	○	52	85	Invention
2-26	LiOH 150g	—	—	—	○	53	82	Invention
2-27	LiOH 150g	Diethyl hydroxylamine oxalate	—	—	△	52	90	Invention
2-28	LiOH 150g	Exemplified compound (2)	—	—	○	51	92	Invention
2-29	LiOH 150g	Exemplified compound (7) 2Na salt	—	—	◎	55	92	Invention
2-30	LiOH 150g	Exemplified compound (14)	—	—	◎	54	92	Invention

Table 2 (continued)

No.	Alkali (Amount added)	Preservative	Sodium p-toluene-sulfonate	PEG 6000	Deli-quescence	Angle of repose (degree)	Residual Concentration of developing agent (%)	
2-31	LiOH 150g	Exemplified compound (19)	—	—	◎	53	90	Invention
2-32	LiOH 150g	Exemplified compound (7) 2Na salt	added	—	◎	56	95	Invention
2-33	LiOH 150g	Exemplified compound (7) 2Na salt	—	added	◎	58	96	Invention
2-34	LiOH 150g	Exemplified compound (7) 2Na salt	added	added	◎	60	98	Invention

From Table 2, it was proved that, when making use of lithium hydroxide as an alkali, deliquescence is low and the residual concentration of a color developing agent is also high. The granule shows improved fluidity and the tablet shows improved strength. Further, when making use of a compound represented by Formula (A) as a preservative, more excellent results can be displayed. It was also proved that still more excellent results can further be displayed when sodium p-toluene sulfonate as an aromatic sulfonate or polyethylene glycol

is used.

When comparing a tablet to a granule mixture, it was proved that the effects of the invention can be more remarkable in the case of a tablet. Also, from the viewpoint of the operability for preparing a composition and the prevention of scattering fine powder, the preferable shape of the composition is of the tablet type.

Example 3

Each of the granules prepared in the same manner as in Procedure (A), (B) or (C) of Example 2 was tableted in the same manner as in Procedure (E), so that three kinds of tablets were prepared separately. Disodium salt of Exemplified Compound (7) was used as a preservative and the compound shown in Table 2 (in an amount of 0.94 mols/kg) was used as an alkali. The weight of each tablet was set to be 0.45 g for (A), 0.45 g for (B) and 1.60 g for (C).

The same one-part tablet comprising a mixture of (A), (B) and (C) as those prepared in Example 2 was also prepared.

On the resulting samples, deliquescence evaluation and measurement of residual concentration of a developing agent were carried out in the same manner as in Example 2. The three kinds of tablets were put in one sample bottle and in one polyethylene bag, so that they were preserved and then evaluated. The results thereof will be shown in Table 3.

Table 3

No.	Tablet by part	Alkali	Deliquescence	Residual concentration of developing agent	Remarks
2-1	ABC in 3-parts	LiOH	◎	93%	Invention
2-2	ABC in 1-part	LiOH	○	89%	Invention
2-3	ABC in 3-parts	$LiOH \cdot H_2O$	○	91%	Invention
2-4	ABC in 1-part	$LiOH \cdot H_2O$	△	82%	Invention
2-5	ABC in 3-parts	KOH	×	75%	Comparison
2-6	ABC in 1-part	KOH	××	66%	Comparison

As shown in Table 3, a solid color developing composition is more preferable when the color developing agent and an alkali are separated into plural units than when put into one unit, from the viewpoints of deliquescence and prevention of a developing agent oxidation. However, when they are put into one part from the viewpoint of easy handling, deterioration can be inhibited by making use of anhydrous lithium hydroxide.

Example 4

A tablet for processing a color paper was prepared in the following procedures.

1) Tablet for replenishing a color developing composition for color paper use

Procedure (A)

In a bandamu-mill was pulverized up 1200 g of developing agent CD-3, 4-amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]ethyl sulfonate to have an average particle size of 10 μm. The resulting fine particles thereof were granulated by adding 50 ml of water thereto at room temperature for about 7 minutes in a stirring granulator available on the market. Thereafter, the granules were dried up at 40°C for 2 hours in a fluid-bed type drier, so that the moisture of the granules were almost completely removed therefrom. The resulting granules thereby prepared and 150 g of polyethylene glycol 6000 were uniformly mixed up for 10 minutes by making use of a mixer in a thermo-hydrostatic room at 25°C and not higher than 40%RH. Then, 4 g of sodium N-lauroylalanine was added and mixed together by taking 3 minutes. Thereafter, the resulting mixture was com-

pression-tableted by varying the filled amount per tablet as shown in Table 3, by making use of a tableting machine, a remodeled Tough Press Correct Model 1527HU manufactured by Kikusui Mfg. Works, so that Tablet (A) for replenishing a color developing composition for color paper use was prepared.

Procedure (B)

Disodium disulfoethyl hydroxylamine of 1200 g was pulverized and granulated in the same manner as in Procedure (A), except that water was added in an amount of 60 ml. After completing the granulation, the resulting granules were dried up at 50°C for 30 minutes, so that the moisture of the granules were almost completely removed therefrom. Then, 4 g of sodium N-lauroylalanine was added to the resulting granules and mixed up together by making use of a mixer for 3 minutes in a thermo-hydrostatic room at 25°C and not higher than 40%RH. The resulting mixture was compression-tableted to have a filled amount of 1.0 g per tablet by making use of a tableting machine, a remodeled Tough-Pressed-Collect Model 1527HU manufactured by Kikusui Mfg. Works, so that 1,000 pieces of tablet B for replenishing a color developing composition for color paper use was prepared.

Procedure (C)

Tinopar SFP (manufactured by Ciba-Geigy AG.) of 300 g, 37 g of sodium sulfite, 3 g of potassium bromide, 250 g of diethylene triamine pentaacetic acid, 2800 g of sodium p-toluene sulfonate, an alkali shown in Table 3, 106 g of mannitol were pulverized in the same manner as in Procedure (A). Thereafter, the resulting pulverized matters were uniformly mixed up by a mixer available on the market. Then, granulation was carried out in the same manner as in Procedure (A), except that 150 ml of water was added. After completing the granulation, the granules were dried up at 60°C for 30 minutes, so that the moisture of the granules were almost removed therefrom. Then, 4 g of sodium N-lauroylalanine was added to the resulting granules and mixed up together by making use of a mixer for 3 minutes in a thermo-hydrostatic room at 25°C and not higher than 40%RH. The resulting mixture was compression-tableted to have a filled amount of 3.2 g per tablet by making use of a tableting machine obtained by modifying Tough Press Correct Model 1527HU manufactured by Kikusui Mfg. Works, so that 1,000 pieces of tablet C for replenishing a color developing composition for color paper use was prepared.

Procedure (D)

Potassium carbonate of 3,500 g was pulverized and then granulated in the same manner as in Procedure (A). Water was added in an amount of 150 ml and the granulation was made. Thereafter, the resulting granules were dried up at 700°C for 30 minutes, so that the moisture of the granules were almost completely removed therefrom.

The resulting granules thereby prepared and 150 g of polyethylene glycol 6000 were uniformly mixed up for 10 minutes by making use of a mixer in a thermo-hydrostatic room at 25°C and not higher than 40%RH. Then, 4 g of sodium N-lauroylalanine was added and mixed together by taking 3 minutes. Thereafter, the resulting mixture was compression-tableted to have a filled amount of 3.0 g per tablet as shown in Table 3, by making use of a tableting machine obtained by modifying Tough Press Correct Model 1527HU manufactured by Kikusui Mfg. Works, so that 1,000 pieces of Tablet D for replenishing a color developing composition for color paper use was prepared.

2) Tablet for replenishing a bleach-fixing composition for color paper use

Procedure (E)

Ferric ammonium ethylenediamine tetraacetate of 1250 g, ethylenediamine tetraacetic acid of 25 g, maleic acid of 250 g and Pineflow (manufactured by Matsutani Chemical Co.) of 46 g were pulverized and granulated in the same manner as in Procedure (C), except that 80 ml of water was added. After completing the granulation, the granules were dried at 60°C for 2 hours so that the moisture thereof was almost completely removed therefrom. Sodium N-lauroylsarcosine of 20 g was added to the resulting granules and they were then mixed up in a thermo-hydrostatic room at 25°C and not higher than 40%RH by making use of a mixer for 3 minutes. The resulting mixture was then compression-tableted so as to have a filled amount of 4.3 g per tablet by making use of a tableting machine obtained by modifying Tough Press Correct Model 1527HU manufactured by Kikusui Mfg. Works, so that 340 pieces of Tablet A for replenishing a bleach-fixing composition for color paper use was

prepared.

Procedure (F)

Ammonium thiosulfate of 1640 g, sodium sulfite of 750 g, potassium bromide of 40 g, p-toluene sulfinic acid of 50 g and Pineflow of 55g were pulverized and granulated in the same manner as in Procedure (C), except that 100 ml of water was added. After completing the granulation, the resulting granules were dried at 60°C for 120 minutes, so that the moisture of the granules were almost completely removed therefrom. Sodium N-lauroyl sarcosine of 20 g was added to the resulting granules and they were mixed up in a thermo-hydrostat room at 25°C and not higher than 40%RH by making use of a mixer for 3 minutes. The resulting mixture was then compression-tableted so as to have a filled amount of 3.35 g per tablet by making use of a tableting machine obtained by modifying Tough Press Correct Model 1527HU manufactured by Kikusui Mfg. Works, so that 720 pieces of Tablet B for replenishing a bleach-fixing composition for color paper use was prepared.

3) Tablet for replenishing a stabilizing composition for color paper use

Procedure (G)

Sodium carbonate monohydrate of 10 g, disodium 1-hydroxyethane-1,1-disulfonate of 200 g, Tinopar SFP of 150 g, sodium sulfite of 300 g, zinc sulfate heptahydrate of 200 g, disodium ethylenediamine tetraacetate of 150 g, ammonium sulfate of 200 g, o-phenylphenol of 10 g and Pineflow of 25 g were pulverized and granulated in the same manner as in Procedure (C), except that 60 ml of water was added. After completing the granulation, the granules were dried at 70°C for 60 minutes, so that the moisture of the granules were almost completely removed therefrom. Sodium N-lauroyl sarcosine of 10 g was added to the resulting granules and they were mixed up in a thermo-hydrostat room at 25°C and not higher than 40%RH by making use of a mixer for 3 minutes. The resulting mixture was then compression-tableted so as to have a filled amount of 3.14 g per tablet by making use of a tableting machine obtained by modifying Tough Press Correct Model 1527HU manufactured by Kikusui Mfg. Works, so that 360 pieces of Tablet for replenishing a stabilizing composition for color paper use was prepared.

[Color Paper Processing Steps]

The method of the invention of processing a light-sensitive material using an automatic processor will be explained below.

A tablet supplying function, a liquid level detecting function, and a water supplying function were provided to a Konica Color Paper Type QA Processor Model CL-PP-718, and the following processing experiments were carried out. As for the tablet supplying function, liquid level detecting function, water supplying function and so forth, the devices shown in Figs. 3 and 5 illustrated in JP OPI Publication No. 5-119454/1993 were used. The devices thereof shown in the figures are detailed in the same application, pp. 44-53. The standard processing conditions of the processor were as follows.

Processing step	Temperature	Time
Color developing	39±0.3°C	22sec.
Bleach-fixing	35±1.0°C	22sec.
Stabilizing-1	33±3.0°C	20sec.
Stabilizing-2	33±3.0°C	20sec.
Stabilizing-3	33±3.0°C	20sec.
Drying	72±5.0°C	40sec.

A stabilizer was replenished to the 3rd tank (for stabilizing step-3) and the overflow was made flowed into the 2nd tank (for stabilizing step-2) and then into the 1st tank (for stabilizing step-1) in this order, that is so-called a cascade system.

The processing solutions for an automatic processor was prepared in the following procedures.

(1) Color developing tank solution (in 23.0 liters)

To an automatic color developing tank, 18 liters of warm water being kept at 35°C was added. Thereto, 177 pieces of each of tablets A through D for replenishing a color developing solution for color paper use were added and then dissolved. Thereafter, 23 pieces of starter having the following chemical formula, which had separately been tableted as a starter component, were added and then dissolved. After completing the dissolution, warm water was added up to the marked line of the tank, so that a tank solution was completed.

Color developing starter for color paper use (per liter)	
Potassium chloride	See Table 3
Potassium hydrogen carbonate	4.8 g
Potassium carbonate	2.1 g

(2) Bleach-fixing solution (in 23.0 liters)

To a bleach-fixing tank of an automatic processor, 15 liters of water was added and then 852 pieces of tablet A for replenishing a bleach-fixing solution for color paper use and 1704 pieces of tablet B with the same purpose were added and then dissolved, respectively. After completing the dissolution, warm water was added up to the marked line of the tank, so that a tank solution was completed.

(3) Stabilizing solution (15 liters each to the 1st to the 3rd tanks)

In each of the 1st, 2nd and 3rd stabilizing tanks of the automatic processor, 60 pieces of the tablet for replenishing a stabilizing solution for color paper use were dissolved in 12 liters of warm water being kept at 35°C. Thereafter, warm water was added up to the marked line of the tank, so that a tank solution was completed.

While the automatic processor was being made thermostatic, 20 pieces of each tablet for replenishing already prepared in the example, were set in a replenishing tablet supplying device provided to the automatic processor. When one m^2 of color paper was processed, one of each of tablets A through D for replenishing a color developing solution, one piece of tablet A and 2 pieces of tablet B each for replenishing a bleach-fixing solution, and one piece of tablet for replenishing a stabilizing solution, were supplied. At the same time, replenishing warm water was so set as to be supplied in an amount shown in Table 3 to the color developing tank, in an amount of 42 ml to the bleach-fixing tank and in an amount of 247 ml to the stabilizing tank, by the warm water supplying device.

Konica Color QA Paper, Type A5, manufactured by Konica Corp. was used as a light-sensitive material subject to the tests. After imagewise exposing the light-sensitive material to light in an ordinary method, and then the exposed light-sensitive material was running processed in the foregoing processing steps. The running process was continuously carried out until a replenishment amount was twice the capacity of the color developing tank, which refers to 2R. The quantity of the light-sensitive materials processed per day was 0.05R.

A wedgewise exposed light-sensitive material was processed when starting the running process and when completing the running process, and the density of the processed light-sensitive materials was measured. Each maximum density (Dmax) in blue, green and red was also measured. On 20 pieces each of the tablets set to the replenishing tablet supplying device of the automatic processor, the observation was made on how the tablet shape varied until tablet C for replenishing a color developing solution was used up. The results thereof will be shown in Table 4.

Table 4

No.	Water replenishment (ml/m²)	Amt. of Tablet A (g)	Alkali content of Tablet C; ( )=Amt. added (g)	Amt.of KCl added when starting (g/l)	When starting			When completing			Variation of tablet shape (*)	Remarks
					Blue	Green	Red	Blue	Green	Red		
3-1	162	1.65	KOH (23)	2.5	3.10	2.46	1.98	3.00	2.34	1.90	Δ	Comparison
3-2	147	1.53	KOH (26)	3.3	3.11	2.45	1.99	2.88	2.20	1.75	×	Comparison
3-3	127	1.37	KOH (30)	4.0	3.09	2.47	1.98	2.87	2.18	1.71	×	Comparison
3-4	101	1.16	KOH (38)	5.4	3.10	2.46	1.97	2.83	2.17	1.70	×	Comparison
3-5	96	1.12	KOH (41)	5.7	3.09	2.46	1.98	2.75	2.03	1.58	××	Comparison
3-6	81	1.00	KOH (48)	7.0	3.09	2.45	1.98	2.73	2.01	1.55	××	Comparison
3-7	162	1.65	LiOH (10)	2.5	3.11	2.47	1.99	3.09	2.45	1.97	○	Invention
3-8	147	1.53	LiOH (11)	3.3	3.10	2.46	1.97	3.07	2.43	1.95	○	Invention
3-9	127	1.37	LiOH (13)	4.0	3.11	2.48	1.97	3.08	2.44	1.95	○	Invention
3-10	101	1.16	LiOH (16)	5.4	3.10	2.46	1.97	3.08	2.43	1.94	○	Invention
3-11	96	1.12	LiOH (18)	5.7	3.10	2.47	1.98	3.07	2.44	1.95	○	Invention
3-12	81	1.00	LiOH (20)	7.0	3.11	2.47	1.98	3.08	2.44	1.94	○	Invention

* ○: No shape varied
Δ: Moisture adhered to tablet surface
×: Tablet surface deliquesced
××: Tablet almost completely deliquesced

From the results shown in Table 3, it was proved that the effects of the invention could remarkably be displayed on the prevention of the variation of the tablet shape and the processing stability when water was replenished to a color developing tank in an amount of not more than 150 ml per m² of a light-sensitive material,

and that a greater effect can also be displayed when water was replenished in an amount of not more than 100 ml per m^2 of a light-sensitive material.

Example 5

In the same manner as in Example 4, each tablet was prepared and was then running processed; provided, the time required for carrying out the color developing step was varied as shown in Table 5, and, the filled amount of tablet A for replenishing a color developing composition and the alkali contained in tablet C were each varied as shown in Table 5.

Also, the color developing agent contained in tablet A and the preservative contained in tablet B were each varied as shown in Table 5. Further, the amount of water replenished to a color developing tank was set to be 81 ml per m^2 of a light-sensitive material and 7.0 g of potassium chloride was added as a starter when starting a running process.

The evaluations were made in the same manner as in Example 4 by observing both of the maximum color densities obtained when starting a running process and when completing the same process, and the variation of the tablet shape. The results thereof will be shown in Tables 5 and 6.

Table 5

No.	Color developing time	Color developing agent	Amt. of tablet A filled (g)	Alkali content of tablet C: ( )= Amt.contained (g)	Preservative contained in tablet B
4-1	45"	CD-3	0.81	KOH (25)	Exemplified compound (7)
4-2	35"	CD-3	0.86	KOH (32)	Exemplified compound (7)
4-3	27"	CD-3	0.94	KOH (44)	Exemplified compound (7)
4-4	22"	CD-3	1.00	KOH (48)	Exemplified compound (7)
4-5	45"	CD-3	0.81	LiOH (11)	Exemplified compound (7)
4-6	35"	CD-3	0.86	LiOH (14)	Exemplified compound (7)
4-7	27"	CD-3	0.94	LiOH (19)	Exemplified compound (7)
4-8	22"	CD-3	1.00	LiOH (20)	Exemplified compound (7)
4-9	22"	CD-3	1.00	LiOH (20)	Exemplified compound (1)
4-10	22"	CD-3	1.00	LiOH (20)	Exemplified compound (2)
4-11	22"	CD-3	1.00	LiOH (20)	*1 DEHA oxalate
4-12	22"	*2	1.00	LiOH (20)	Exemplified compound (7)

*1 Diethylhydroxyamine oxalate

*2 2-amino-3-methyl-N-ethyl-N-(3-hydroxypropyl)aniline sulfate

Table 6

No.	When starting			When completing			Variation of tablet shape	Remarks
	Blue	Green	Red	Blue	Green	Red		
4-1	3.10	2.46	1.98	2.99	2.34	1.87	×	Comparison
4-2	3.11	2.47	1.99	2.96	2.33	1.85	×	Comparison
4-3	3.10	2.47	1.98	2.74	2.03	1.57	××	Comparison
4-4	3.09	2.45	1.98	2.73	2.01	1.55	××	Comparison
4-5	3.10	2.46	1.97	3.09	2.45	1.95	○	Invention
4-6	3.10	2.46	1.97	3.08	2.45	1.94	○	Invention
4-7	3.11	2.47	1.97	3.08	2.45	1.95	○	Invention
4-8	3.11	2.47	1.98	3.08	2.44	1.95	○	Invention
4-9	3.10	2.46	1.98	3.06	2.42	1.94	○	Invention
4-10	3.09	2.46	1.97	3.07	2.43	1.94	○	Invention
4-11	3.09	2.46	1.97	3.02	2.39	1.90	○	Invention
4-12	3.11	2.48	1.99	3.11	2.47	1.98	○	Invention

*1 Diethylhydroxyamine oxalate
*2 2-amino-3-methyl-N-ethyl-N-(3-hydroxypropyl)aniline sulfate

From the results shown in Tables 5 and 6, it was proved that, when the processing time for the color developing step was not longer than 30 seconds, the effects of the invention could remarkably be displayed on the processing stability and the prevention of the variation of tablet configuration, that, when a compound represented by Formula [A] was used, the processing stability can more be improved, and that, when 4-amino-3-methyl-N-ethyl-N-(3-hydroxypropyl)aniline sulfate was used as a color developing agent, the processing stability could be somewhat more improved than in the case of using CD-3.

Example 6

A tablet for processing a color negative film was prepared in the following procedures.

1) Tablet for replenishing a color developing composition for color negative film use

Procedure (1)

In a bandamu mill available on the market, 3750.0 g of potassium carbonate, 580.0 g of sodium sulfite, 1.4 g of potassium bromide, 240.0 g of pentasodium diethylene-triamine pentaacetic acid, 500.0 g of sodium p-toluene sulfonate and an alkaline agent described in Table 7 were crushed so that the average grain size thereof be 10 μm. In a stirring granulator available on the market, 500.0 g of PEG 6000, 800.0 g of mannitol and 160 ml of water were added to the above-mentioned fine powder and granulated for 7 minutes to obtain a granule. Next, the resulting granule was dried in a fluid-bed type drier available on the market for 120 minutes at 70 °C so that moisture was substantially removed therefrom.

Procedure (2)

Hydroxylamine sulfate of 360.0, 40.0 g 0f potassium bromide and 20.0 g of pyrocatechol-3,5-disodiumsulfonate were crushed in the same manner as in above Procedure (1). Then, 20.0 g of Pineflow (manufactured by Matsutani Chemical Co.) and 3.5 ml of water were added to the above-mentioned fine powder, mixed and granulated for 7 minutes to obtain a granule. The resulting granule was dried for 60 minutes at 60 °C so that

moisture was substantially removed therefrom.

Procedure (3)

Color developing agent, CD-3 (4-amino-3-methyl-N-ethyl-β-(hydroxy)ethylaniline sulfate) of 650.0 g was crushed in the same manner as in above Procedure (1). Then, 10 ml of water were added to the above-mentioned fine powder, mixed and granulated for 7 minutes to obtain a granule. The resulting granule was dried for 2 hours at 40 °C so that moisture was substantially removed therefrom.

Procedure (4)

In a cross-rotary mixing machine available on the market were mixed the granules prepared in the above procedures (1) to (3) and 40.0 g of sodium lauryl sulfonate for about 7 minutes at a room temperature. The resulting mixture was tabulated by using a rotary tabulating machine (Clean Press Correct H18 manufactured by Kikusui Mfg. Works). Thus, 600 pieces of tablets each having a diameter of 25 mm and a weight of 10.0 g were obtained as replenishing color developing compositions for color negative film use.

The above-obtained tablet sample Nos. 6-1 to 6-10 were evaluated in the same manner as in Example 2. The results are shown in Table 7.

Table 7

No.	Alkali (Amount added)	Deli-quescence	Hardness (Kg)	Residual Concentration of CD-4	
6-1	——	△	38	82	Comparison
6-2	KOH (60g)	××	37	80	Comparison
6-3	KOH 120g	××	35	78	Comparison
6-4	KOH 170g	××	30	77	Comparison
6-5	NaOH 120g	××	34	89	Comparison
6-6	LiOH 60g	○	45	93	Invention
6-7	LiOH 120g	◎	52	95	Invention
6-8	LiOH 170g	◎	53	95	Invention

As is apparent from table 7, the tablet of the invention show improved deliquescence and hardness.

Example 7

A tablet for processing a color negative film was prepared in the following procedures.

1) Tablet for replenishing a color developing composition for color negative film use

Procedure (1)

In a bandamu mill available on the market, 150 g of a developing agent CD-4, [that is 4-amino-3-methyl-N-ethyl-β-(hydroxy)ethylaniline sulfate], was pulverized to have an average particle size of 10 μm. In a stirring type granulator available on the market, the resulting fine powder was granulated by adding 10 ml of water at room temperature for about 7 minutes and was then dried by a fluid-bed type drier at 40°C for 2 hours, so that the moisture of the granules was almost completely removed therefrom. To the resulting granules, 0.3 g of sodium N-lauroylalanine and 1.9 g of polyethylene glycol 6000 were added. The mixture thereof was then uniformly mixed up for 10 minutes by making use of a mixer in a thermo-hydrostatic room at 25°C and not higher than 40%RH. Next, the resulting mixture was compression-tableted to have an amount filled of 1.1 g per tablet

by making use of a tableting machine obtained by modifying Tough Press Correct 1527HU manufactured by Kikusui Mfg. Works, so that 126 pieces of tablet A for replenishing a color developing composition for color negative film use were prepared.

Procedure (2)

After pulverizing 69.4 g of hydroxylamine sulfate and 4 g of Pineflow (manufactured by Matsutani Chemical Co.) in the same manner as in Procedure (1), they were mixed up and granulated. An amount of water added was set to be 3.5 ml and, after completing the granulation, the granules were dried at 60°C for 30 minutes, so that the moisture of the granules were almost completely removed therefrom. To the resulting granules, 0.3 g of sodium N-lauroylalanine was added. The mixture thereof was further mixed up for 3 minutes by making use of a mixer in a thermo-hydrostatic room at 25°C and not higher than 40%RH. Next, the resulting mixture was compression-tableted to have an amount filled of 0.56 g per tablet by making use of a tableting machine in the same manner as in Procedure (1), so that 120 pieces of tablet B for replenishing a color developing composition for color negative film use were prepared.

Procedure (3)

Diethylenetriamine pentaacetic acid of 20 g, disodium 1-hydroxyethane-1,1-diphosphonate of 15 g, potassium sulfite of 72.8 g, potassium carbonate of 375 g, anhydrous lithium hydroxide of 3 g, sodium bromide of 3.7 g and mannitol of 22 g were pulverized in the same manner as in Procedure (1) and mixed up together. Thereto 40 ml of water was added, so that the resulting mixture was granulated. After completing the granulation, the granules were dried up at 70°C for 60 minutes, so that the moisture of the granules was almost completely removed therefrom. To the resulting granules, 2 g of sodium N-lauroylalanine was added. The mixture thereof was mixed up for 3 minutes by making use of a mixer in a thermo-hydrostatic room at 25°C and not higher than 40%RH. Next, the resulting mixture was compression-tableted to have an amount filled of 3.9 g per tablet by making use of a tableting machine in the same manner as in Procedure (1), so that 120 pieces of tablet C for replenishing a color developing composition for color negative film use were prepared.

2) Tablet for replenishing a bleaching solution for color negative film use

Procedure (4)

Ferric ammonium 1,3-propanediamine tetraacetate monohydrate of 175 g, 1,3-propanediamine tetraacetic acid of 2 g and Pineflow (manufactured by Matsutani Chemical Co.) of 17 g were pulverized in the same manner as in Procedure (1) and then mixed up together. Thereto, water was added in an amount of 8 ml, so that the resulting mixture was granulated. After completing the granulation, the granules were dried at 60°C for 30 minutes, so that the moisture of the granules was almost completely removed therefrom.

Procedure (5)

Succinic acid of 133 g, ammonium bromide of 200 g and Pineflow of 10.2 g were pulverized, mixed up and then granulated. Thereto, water was added in an amount of 17 ml, so as to be granulated. After completing the granulation, the granules were dried up at 70°C for 60 minutes, so that the moisture of the granules were almost completely removed therefrom.

Procedure (6)

Potassium nitrate of 66.7 g, potassium hydrogen carbonate of 60 g and mannitol of 8 g were pulverized, mixed up and then granulated in the same manner as in Procedure (1). Thereto, water was added in an amount of 13 ml, so that they were granulated. After completing the granulation, the granules were dried up at 60°C for 60 minutes, so that the moisture of the granules were almost completely removed therefrom.

Procedure (7)

The granules prepared in the above-mentioned Procedures (4) through (6) were uniformly mixed up together for 10 minutes by making use of a mixer in a thermo-hydrostatic room at 25°C and not higher than 40%RH. To the resulting mixed granules, 6 g of sodium N-lauroylsarcosine was added and then mixed up for

3 minutes. The resulting mixture was compression-tableted to have a filled amount of 6.78 g per tablet by making use of a tableting machine obtained by modifying Tough Press Correct 1527HU manufactured by Kikusui Mfg. Works, so that 80 pieces of tablet for replenishing a bleaching solution for color negative film use were prepared.

3) Tablet for replenishing a fixing solution for color negative film use

Procedure (8)

Ammonium thiosulfate of 2500 g, sodium sulfite of 150 g, disodium ethylenediamine tetraacetate of 20 g and Pineflow (manufactured by Matsutani Chemical Co.) of 65 g were pulverized, mixed up and then granulated in the same manner as in Procedure (1). Thereto, water was added in an amount of 50 ml, so that they were granulated. After completing the granulation, the granules were dried up at 60°C for 120 minutes, so that the moisture of the granules were almost completely removed therefrom.

Procedure (9)

The granules prepared in the above-mentioned Procedure (8) and 13 g of sodium N-lauroylsarcosine were mixed up by making use of a mixer in a thermo-hydrostatic room at 25°C and not higher than 40%RH. The resulting mixture was then compression-tableted to have a filled amount of 9.3 g per tablet by making use of a tableting machine obtained by modifying Tough Press Correct 1527HU manufactured by Kikusui Mfg. Works, so that 280 pieces of tablet for replenishing a fixing solution for color negative film use were prepared.

4) Tablet for replenishing a stabilizing solution for color negative film use

Procedure (10)

m-Hydroxybenzaldehyde of 150 g, sodium laurylsulfate of 20 g, disodium ethylenediaminetetraacetate of 60 g, the alkali indicated in Table 6, and Pineflow of 10 g were pulverized, mixed up and then granulated in the same manner as in Procedure (1). Thereto, water was added in an amount of 10 ml, so that they were granulated. After completing the granulation, the granules were dried up at 50°C for 2 hours, so that the moisture of the granules were almost completely removed therefrom.

Procedure (11)

The granules prepared in the above-mentioned Procedure (10) were compression-tableted to have a filled amount of 0.48 g per tablet by making use of a tableting machine obtained by modifying Tough Press Correct 1527HU manufactured by Kikusui Mfg. Works in a thermo-hydrostatic room at 25°C and not higher than 40%RH, so that 280 pieces of tablet for replenishing a stabilizing solution for color negative film use were prepared.

The above-mentioned procedures were repeated, so that the tablets in number necessary for trying the following experiments were prepared.

[Color negative film processing step]

Now the descriptions will be made on the light-sensitive material processing steps in which an automatic processor of the invention is used.

A Konica Color Negative Film Processor Model CL-KP-50QA was so modified as to be provided with a tablet supplying function, a liquid level detecting function, a warm water supplying function and so forth. The following processing experiments were carried out by making use of the above-mentioned automatic processor.

The standard processing conditions for the automatic processor were as follows.

Processing step	Temperature	Time
Color developing	38±0.3°C	3min.15sec.
Bleaching	38±1.0°C	45sec.
Fixing-1	38±1.0°C	45sec.
Fixing-2	38±1.0°C	45sec.
Stabilizing-1	38±3.0°C	20sec.
Stabilizing-2	38±3.0°C	20sec.
Stabilizing-3	38±3.0°C	20sec.
Drying	60°C	60sec.

The stabilizing solution was replenished to the 3rd tank (for stabilizing step-3) and the overflow therefrom was flowed into the 2nd tank (for stabilizing step-2) and then to the 1st tank (for stabilizing step-1); and the fixing solution was replenished to the 2nd tank (for fixing step-2) and the overflow therefrom was flowed into the 1st tank (for fixing step-1) and then to the 1st tank (for stabilizing step-l); that is so-called a cascade system.

Processing solutions applicable to the automatic processor were prepared in the following procedures.

(1) Color developing tank solution (in 21.0 liters)

To an automatic color developing tank, 15 liters of warm water being kept at 35°C was added. Thereto, 118 pieces each of tablets A and B and 236 pieces of tablet C each for replenishing a color developing solution for color negative film use were added and then dissolved, respectively. Thereafter, 21 pieces of starter tablet having the following composition, which had separately been tableted as a starter component, were added and then dissolved. After completing the dissolution, warm water was added up to the marked line of the tank, so that a tank solution was completed.

Color developing starter for color negative film use (per liter)

Sodium bromide	0.8 g
Sodium iodide	2.0 mg
Sodium hydrogen carbonate	3.0 g
Potassium carbonate	0.5 g

(2) Bleaching solution (in 5.0 liters)

To the bleaching tank of the automatic processor, 3.0 liters of warm water being kept at 35°C was added and 350 pieces of tablet for replenishing a bleaching solution for color negative film use, which were prepared in the same manner as in the example, were added and dissolved. Thereafter, 5 pieces of starter tablet having the following composition, which had separately been tableted as a starter component, were added and dissolved. After completing the dissolution, warm water was added up to the marked line of the tank, so that a

tank solution was prepared.

Bleaching starter for color negative film use (per liter)	
Potassium bromide	10.0 g
Sodium hydrogen carbonate	1.5 g
Potassium carbonate	3.5 g

(3) Fixing solution (in 4.5 liters each for the 1st and 2nd tanks)

In each of the 1st and 2nd fixing tanks of the automatic processor 136 pieces of the tablet for replenishing a fixing solution for color negative film use were dissolved in 3.0 liters of warm water being kept at 35°C, respectively. Thereafter, warm water was added up to the marked line of the tank, so that a tank solution was completed.

(4) Stabilizing solution (in 3.2 liters each for the 1st to the 3rd tanks)

In each of the 1st, 2nd and 3rd stabilizing tanks of the automatic processor 20 pieces of the tablet for replenishing a stabilizing solution for color negative film were dissolved in 3.0 liters of warm water being kept at 35°C, respectively. Thereafter, warm water was added up to the marked line of the tank, so that a tank solution was completed.

While the automatic processor was being kept thermostatic, 20 pieces each of the tablets already prepared for replenishing the respective solutions were set in a tableted replenisher supplying device provided to the automatic processor. When 8 rolls of 135-size/24-exposure film were processed, one piece of tablet A, one piece of tablet B and two pieces of tablet C for replenishing a color developing solution, 4 pieces of tablet for replenishing a bleaching solution, 8 pieces of tablet for replenishing a fixing solution and one piece of tablet for replenishing a stabilizing solution, were supplied to the tablet supplying device. At the same time, replenishing warm water was so set as to be supplied in an amount of 154.4 ml to the color developing tank, 27.2 ml to the bleaching tank, 204.8 ml to the fixing tank and 320 ml to the stabilizing tank, from a warm water supplying device, respectively.

A color negative film, Konica Color Super DD 100 manufactured by Konica Corp., was exposed imagewise to light and processed in the foregoing processing steps. After completing the process, the stains produced on the rear surface of the processed film were evaluated. The deliquescence of the tablet for replenishing a stabilizing solution was also evaluated in the same manner as in Example 1. The results thereof will be shown in Table 7.

Table 7

No.	Alkali (Amt. added)	Stain on rear surface	Deliquescence	Remarks
1	K_2CO_3 (200g)	×	××	Comparison
2	$LiOH \cdot H_2O$ (65g)	○	◎	Invention

Evaluation standard of stains produced on a rear surface:

× : White unevenness produced;

Δ : Slight unevenness produced; and

○ : Almost no stain produced.

Evaluation standard of deliquescence:

The same as in Example 2.

From Table 7, it was proved that, when making use of an alkali of the invention, the stains produced on the rear surface of a processed film could be reduced and deliquescence thereof could also be improved. In

particular, it was proved that, when making use of lithium hydroxide, the effects of the invention could remarkably be displayed.

Example 8

Each of the tablets was prepared in the same manner as in Example 4. One of each of tablets A, B, C and D for replenishing a color developing composition, total 4 tablets, were packed as one package. A series of 20 fractionized packages were packaged in a 4-side sealing system by making use of a peal-open type packaging material. Further, one of tablet A and 2 pieces of tablet B for replenishing a bleach-fixing composition, total 3 tablets, were packed as one package and a series of 20 packages were packaged in the same manner as in the case of the tablets for replenishing a color developing composition.

One piece of tablet for replenishing a stabilizing composition were packed as one package and then packaged in the same manner as mentioned above.

The peal-open packaging material was prepared by making use of a Tocello CMPSO11C as a sealant film and then laminating the sealant film on a non-stretched polypropylene film surface of a non-stretched polypropylene film/a stretched polypropylene film.

The prepared peal-open film and a non-stretched polypropylene film/a stretched polypropylene film were heat-sealed together in a manner that the above-mentioned tablet was packed between them.

A running experiment was carried out under the same conditions as in No.3-12 shown in the foregoing Table 4, provided, that the tablet supplying means was changed into the following device so that a package could be opened immediately before replenishing a tablet.

Water-supplying device and so forth were arranged in the same as in Example 4, that is, based upon those described in JP Application No. 4-111502/1992.

Fig. 1 illustrates a perspective view showing an example of solid processing composition supplying devices 140 of the invention, wherein the solid processing composition was supplied to a processing tank by pealing off a package containing the solid type processing composition.

The leading edge of a 4-side sealed package containing a solid type processing composition was attached to take-up spool 142 serving as a fixing means through roller 141. When a subject light-sensitive material was processed, it was detected by a processed quantity information detecting means. When reaching a specific processed quantity, a signal is sent from a processing composition supply controlling means, so that the motor of take-up spool 142, that was also serving as a processing composition supplying means, was rotated by receiving the signal. Thereby a package containing a solid type processing composition is moved forward to a specific length, so that the necessary solid type processing composition in number could be put in a processing tank. Any means for moving a package may be used, for example, a means for detecting a notch provided in advance to a package, another means for detecting a printed pattern, and a further means for detecting a processing composition contained in a package. In short, such a means for moving a package as mentioned above is to be capable of precisely detecting necessary solid type processing compositions in number and moving them through roller 141 or take-up spool 142. Roller 141 was provided for the purpose of fixing or positioning a package and, thereby, a package is pealed off by two take-up spools and necessary solid type processing composition in number could be put in a processing tank.

Figs. 2(a) and 2(b) illustrate each a system for dividing and cutting a series of packages into two parts.

Wherein, when a subject light-sensitive material was processed, it was detected by a processed quantity information detecting means. When reaching a specific processed quantity, a signal was sent from a processing composition supplying means to transport rollers 502. At the same time when transport rollers 502 were rotated, ceramic or stainless steel-made circular edge 301 was rotated to cut the lower part of a series of packages 603 into 2 parts, so that solid type processing composition 10 could be put into a processing tank. When cutting a series of packages into 2 parts, the packages were spread out toward the both sides of suction guide 202 by a suction so that solid type processing composition could readily be dropped. Empty package 603 containing no solid type processing composition 10 was moved out of the position by transport rollers 401 when making the next solid processing composition 10 ready to be dropped and was then scrapped in package container 101.

In any one of the processing composition supplying means, it was proved that the same excellent photographic characteristics as in No. 3-12 shown in Table 4 of Example 4 can be obtained, and that these means were advantageous from the viewpoints of the preservability and handling convenience of a solid tablet processing composition.

The above-mentioned processing composition supplying means can be applied to those of not only a solid tablet type but also a powder or granule type.

Claims

1. A solid processing composition for a silver halide color photographic light-sensitive material, wherein the composition comprises lithium hydroxide.

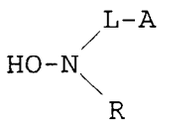
2. The solid processing composition of claim 1, comprising anhydrous lithium hydroxide.

3. The solid processing composition of claim 1, wherein said composition is in a form of a tablet or granule.

4. The solid processing composition of claim 1, wherein said composition is a color developing composition comprising a p-phenylenediamine type color developing agent.

5. The solid processing composition of claim 4, wherein said color developing composition further comprises a compound represented by the following Formula (A) :

Formula [A]



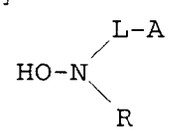
wherein L represents an alkylene group; A represents a carboxyl group, a sulfo group, a phosphono group, a phosphinic acid group, a hydroxy group, an amino group, an ammonio group, a carbamoyl group or a sulfamoyl group; and R represents a hydrogen atom or an alkyl group.

6. The solid processing composition of claim 5, wherein said color developing composition further comprises an aromatic sulfonic acid or salt thereof.

7. The solid processing composition of claim 4, wherein said color developing composition comprises a mixture of a granule containing lithium hydroxide and a granule containing a p-phenylenediamine type color developing agent.

8. The solid processing composition of claim 7, wherein the mixture further comprises a granule containing a compound represented by the following Formula (A) :

Formula [A]



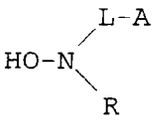
wherein L represents an alkylene group; A represents a carboxyl group, a sulfo group, a phosphono group, a phosphinic acid group, a hydroxy group, an amino group, an ammonio group, a carbamoyl group or a sulfamoyl group; and R represents a hydrogen atom or an alkyl group.

9. The solid processing composition of claim 4, wherein said color developing composition is in a form of a tablet.

10. The solid processing composition of claim 9, wherein said tablet is prepared by tabulating a mixture of a granule containing lithium hydroxide and a granule containing a p-phenylenediamine type color developing agent.

11. The solid processing composition of claim 9, wherein said tablet is prepared by tabulating a mixture of a granule containing lithium hydroxide, a granule containing a p-phenylenediamine type color developing agent and a granule containing a compound represented by the following Formula (A) :

Formula [A]



wherein L represents an alkylene group; A represents a carboxyl group, a sulfo group, a phosphono group, a phosphinic acid group, a hydroxy group, an amino group, an ammonio group, a carbamoyl group or a sulfamoyl group; and R represents a hydrogen atom or an alkyl group.

12. A method of processing an exposed silver halide color photographic light-sensitive material comprising the step of;

(a) developing the exposed material with a developer, and

(b) replenishing the developer with a solid color developing composition, said solid color developing composition comprising lithium hydroxide and a p-phenylenediamine type color developing agent.

FIG. 1

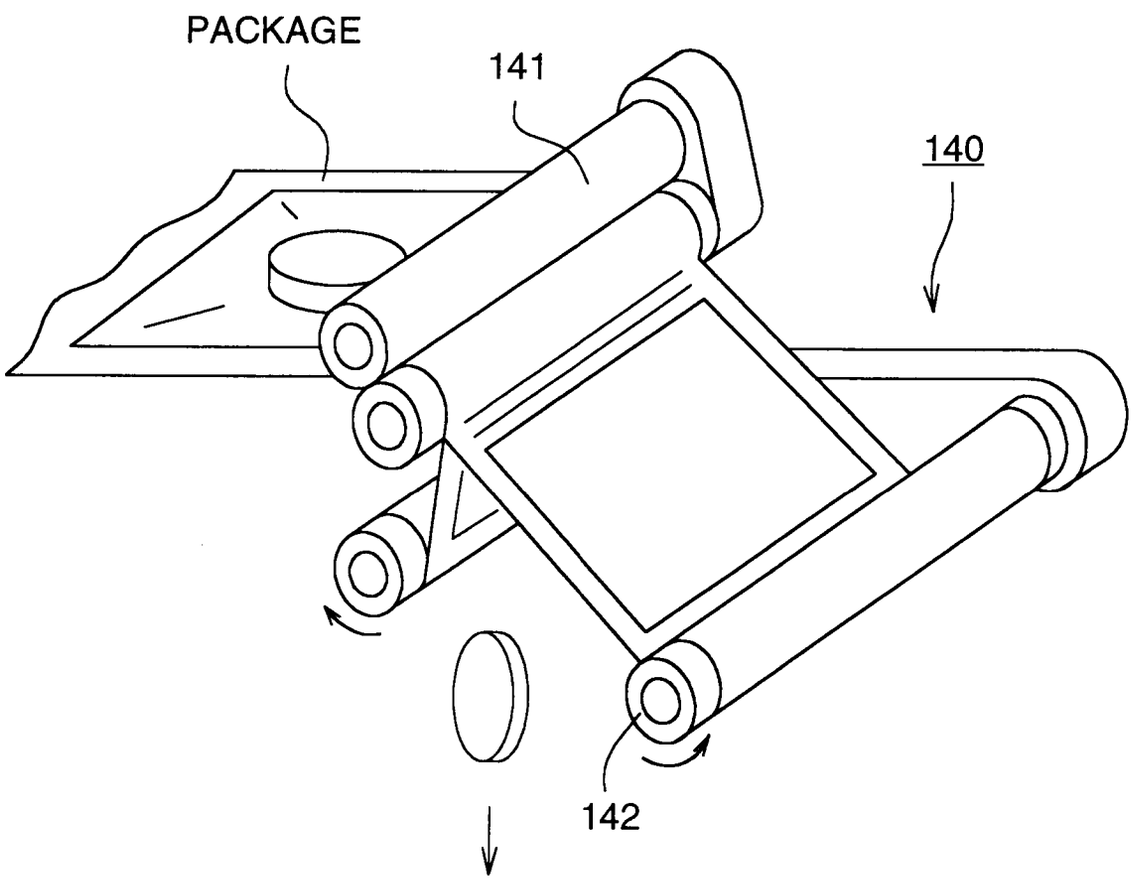


FIG. 2 (A)

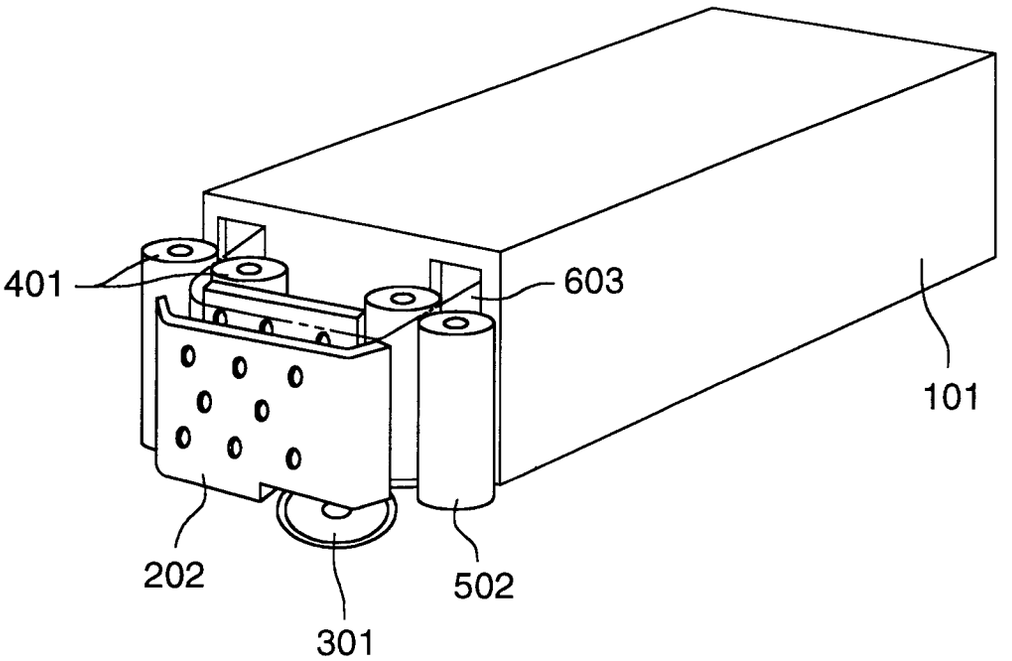


FIG. 2 (B)

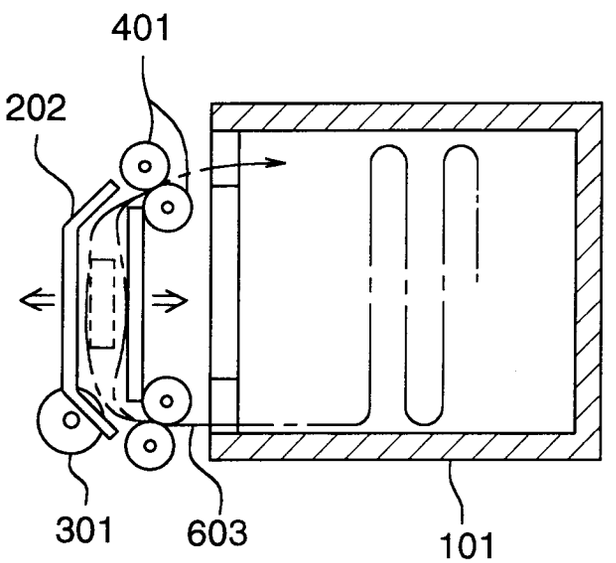
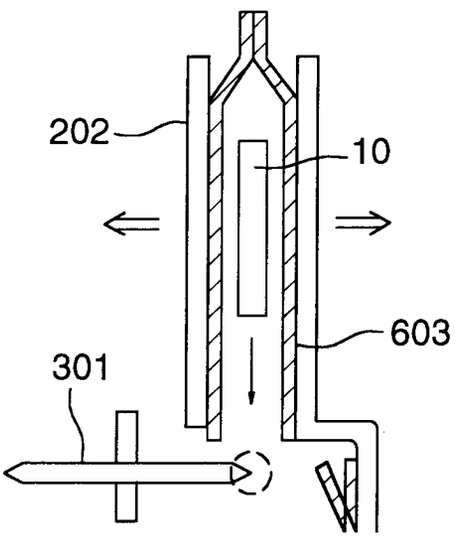


FIG. 2 (C)



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 0373

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	US-A-4 756 996 (POLAROID CORPORATION) 12 July 1988 *See column 5, processing composition A * ---	1-12	G03C7/407 G03C7/44 G03C5/26
A	EP-A-0 358 034 (AGFA-GEVAERT) 14 March 1990 * See claim 1 * & JP-A-2 109 042 (D,A) -----	1-12	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	10 May 1994	Guillemois, F

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
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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