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(54) Black-and-white photographic processing compound.

(57) A black-and-white photographic processing compound comprising polyhydroxybenzene and water-soluble aluminium compound both prepared from grains having the ultimate average diameter of 10 to 500 μm is disclosed. The compound in a solid type is in a powdered, a granulated or a paste form. The average granule size of the compound in a granulated form is 1 mm to 15 mm.

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Field of the Invention

This invention relates to a solid type black-and-white photographic processing compound and particularly to a solid type black-and-white processing compound that does not deteriorate the solubility thereof in storage and the photographic characteristics thereof.

Background of the Invention

Heretofore, processing compound for silver halide photographic light sensitive material use has been used in the forms of a liquid or a powder. In the cases of the liquid forms, they have been used either in their original condition or after the concentrated solution thereof supplied in the form of a kit is diluted with water. In the cases of the powder forms, they have been used after they are dissolved in water.

In the cases of the liquid compounds, they may easily be dissolved, however, they have had the following problems, for example. They contain a considerable amount of water in advance. Therefore, both the volume and weight thereof may become bulky and heavy and, accordingly, the transportation and storage thereof may cost much money and the liquid may be in danger of leaking and, further, the characteristics thereof may be changed in storage.

In the cases of the powder compounds, on the other hand, the powdered compounds are superior in compactness to those of the liquid compounds. However, the powdered compounds are inferior in solubility to those of the liquid compounds. In both cases of the liquid and powdered compounds, the liquid or powder is made adhered to remain on the packaging materials after they are used up, so that the environmental pollution problems may be raised when the waste packaging materials thereof are abandoned.

For solving the above-mentioned problems, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP OPI Publication) No. 3-39735/1991 proposes that powdered processing compound is granulated to serve as a fixing compound and the raw materials thereof are prepared to have a particle size of not larger than 10 μm. As for the concrete examples, a fixing compound for color photographic light sensitive material use and a black-and-white fixing compound not containing a water-soluble aluminium compound are each given in the above-mentioned proposal.

Generally, a water-soluble aluminium compound is used in black-and-white fixing compound for the purpose of hardening the layers of light sensitive materials. In solid type fixing compound each containing a water-soluble aluminium compound, there may be some instances where a hardly soluble substance is produced so that a complete dissolution cannot be made when it is stored for a long time or under the high temperature and humidity conditions, though the reasons are not apparent. Particularly when a water-soluble aluminium compound is so used as to have an average particle size of not larger than 10 μm, it was found that the solubility of the compound is seriously deteriorated in storage, not only in the cases of the powdered compounds, but also in the case of the granulated compounds. In the technological specifications disclosed in the above-given patent publication, it was further found that any practically applicable solid type processing compound cannot be obtained.

For the developing compound as well as for the fixing compound, JP OPI Publication No. 3-109042/1991 proposes that a powdered processing compound is granulated and the raw materials thereof are prepared to have a particle size of not larger than 10 μm. As for the concrete examples, a developing compound for color photographic light sensitive material use is given in the above-mentioned proposal.

In the developing compound each containing a polyhydroxybenzene, which is used in black-and-white photography, it was found that a solid type developing compound is also liable to characteristic deterioration such as the developability deterioration caused in storage by the oxidation-induced deterioration of a polyhydroxybenzene. In the case of making use of a developing compound pulverized into a particle size of not larger than 10 μm, it was also found that the preservability thereof are seriously deteriorated not only in the case of using a powdered developing compound, but also in the cases of using a granulated developing compound. In the technological specifications disclosed in the above-given patent publication, it was further found that any practically applicable solid type processing compound cannot be obtained.

In order to solve the above-mentioned problems, it is an object of the invention to provide a solid type processing compound easy in transportation and storage, excellent in solubility, capable of eliminating the deteriorations of solubility and photographic characteristics in storage, and excellent in environmental aptitude.

Summary of the Invention

The above-mentioned object of the invention can be achieved with the following photographic processing compounds;

a black-and-white photographic developing compound containing a polyhydroxybenzene, that is a solid type black-and-white photographic developing compound characterized in that, among the raw materials thereof, at least the polyhydroxybenzene is prepared in advance to have an average particle size within the range of 10 to 500 μm; and

a black-and-white photographic fixing compound containing a water-soluble aluminium compound, that is a solid type black-and-white photographic fixing compound characterized in that, among the raw materials thereof, at least the aluminium compound is prepared in advance to have an average particle size within the range of 10 to 500 μm.

It is preferred that the above-mentioned developing compound is to contain at least one kind of developing agent selected from the group consisting of a phenidone and a monomethyl-p-amino-phenol sulfate Metols.

Detailed Description of the Invention

Now, the invention will be concretely detailed hereunder.

In the solid type processing compounds applicable to the invention, the expression, "solid type", means common solid-forms including, for example, a powdered form, a granulated form and a paste form, and it may also be any mixed forms thereof.

Next, the methods for dissolving the solid type processing compounds of the invention are similar to the methods for preparing common liquid compounds , wherein the dissolution can be carried out either manually or mechanically and the replenishing tanks may be provided to either the inside of an automatic processor or the outside thereof. Any methods for supplying a processing compound can be used, provided that each component of the processing chemical cannot be scattered. The above-mentioned methods include, for example, a method in which a solid type processing compound is wrapped in a water-soluble high polymer film and the wrapped compound is added as it is, and another method in which a processing compound is packed by paper surface-treated with polyethylene or the like so that any scattering or remaining of powdered compound can be prevented and the packed compound is added into a tank. Taking the solubility of a processing compound to water into consideration, the preferable solid types include a granulated form and a tableted form. However, there are many instances where photographic processing compounds contain a component hardly soluble to water and, in this instance, a hardly soluble substance may sometimes be deposited in a processing solution. To avoid this trouble, it is also allowed to use a method of separately adding a solvent. For preparing granules or tablets, it is preferable to use a popularly applicable granulating aid such as water-, alkali- or acid-soluble high polymers. They include, typically, gelatin, pectin, polyacrylic acid, polyacrylate, polyvinyl alcohol, polyvinyl pyrrolidone, vinylacetate copolymer, polyethylene oxide, sodium carboxymethyl cellulose, hydroxypropyl cellulose, methyl cellulose, alginate, gum arabic, gum traga(ca)nth, methylvinyl ether, maleic anhydride copolymer, polyoxyethylene alkyl ether such as polyoxyethylene ethyl ether and polyoxyethylene stearyl ether, polyoxyethylene alkylphenol ether such as polyoxyethylene octylphenol ether and polyoxyethylene nonylphenol ether, and a combination of 1 or 2 kinds of the water-soluble binders selected from the group consisting of those given in JP Application No. 2-203165/1990.

For increasing the preservability of processing compounds as a kit, it is allowed to enclose the processing compounds in two or more packs in the kit.

The granulation methods applicable to the invention include, for example, a rolling granulation method, an extruding granulation method, a compressing granulation method, a pulverizing granulation method, a stirring granulation method, a spray-dry method, and a dissolving coagulation method. Among these methods, the extruding granulation method and stirring granulation method are particularly preferable.

The sizes and configurations of the granules suitably applicable to the invention are varied to meet the individual objective characteristics. However, in the case of granules, the granule size in sphere equivalent is to be within the range of the order of 0.5 mm to 50 mm and, preferably, 1 mm to 15 mm. The configurations of the granules include, for example, those of the cylindrical, spherical, cubic and rectangular parallelepipedonal shaped. Among the configurations thereof, the spherical or cylindrical shaped are preferable.

The sizes and configurations of the tableted compounds are also varied similarly to the above-mentioned case to meet the various objective characteristics. However, the sizes thereof are preferably within the range of the order of 2 mm to 5 cm. When the solubility is to be increased, it is effective to use a tabular-shaped tablet having a reduced thickness, a tabular-shaped tablet having a reduced thickness of the central portion thereof, a doughnut-shaped tablet having a hollowness in the center and so forth. On the contrary, the sizes thereof may also be made larger for making a dissolution slowly. The sizes can freely be adjusted.

For controlling the solubility, it is also allowed to change the surface conditions (by making the surface flat and smooth or porous, for example).

It is further allowed to take a plurality of configurations for providing various solubilities to a plurality of granules or for matching up the solubilities of raw materials having the different solubilities together. It is still further allowed to use multilayered granules having the different compositions between the surface and the inside thereof.

The polyhydroxybenzene applicable to the invention include, for example, dihydroxybenzenes (such as hydroquinone, chlorohydroquinone, bromohydroquinone, isopropyl hydroquinone, methyl hydroquinone, 2,3-dichlorohydroquinone, 2,5-dimethyl hydroquinone, potassium hydroquinone monosulfonate and sodium hydroquinone monosulfonate), pyrogallol, 3-pyrazolidones (such as 1-phenyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone and 1-phenyl- 4 -dihydroxymethyl-3-pyrazolidone), aminophenols (such as o-aminophenol, p-aminophenol, N-methyl-o-aminophenol, N-methyl-p-aminophenol and 2,4-diaminophenol), 1-aryl-3-aminopyrazolidones (such as 1-(p-hydroxyphenyl)-3-aminopyrazolidone and 1-(p-amino-m-methylphenyl)-3-aminopyrazolidone) and the mixtures thereof.

The color developing agents include, for example, primary aromatic amino developing agents such as phenylenediamines (e.g., 4-amino-N,N-diethyl aniline, 3-methyl-4-amino-N,N-diethyl aniline, 4-amino-N,N-diethyl aniline, 4-amino-N-ethyl-N-β-hydroxyethyl aniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethyl aniline, 3-methyl-4-amino-N-ethyl-N-β-methane sulfonamidoethyl aniline and 4-amino-3-methyl-N-ethyl-N-β-methoxyethyl aniline).

As for the developing agents applicable to the black-and-white developers to be used in the invention, it is preferable to use the combination of dihydroxy benzene ring and a 1-phenyl-3-pyrazolidone, from the viewpoint that the excellent characteristics can be enjoyed. It is the matter of course to further contain a p-aminophenol type developing agent therein, besides the above-mentioned developing agents.

Further besides the above, it is also allowed to use those described in L.F.A. Mason, "Photographic Processing Chemistry" (Focal Press, 1966) pp.226~229, JP OPI Publication No. 48-64933/1973, and so forth. It is preferable to use these developing agents ordinarily in an amount within the range of 0.01 to 1.2 mols per liter.

The sulfite preservatives applicable to the invention include, for example, sodium sulfite, potassium sulfite, lithium sulfite, ammonium sulfite, sodium bisulfite, potassium metabisulfite and sodium formaldehyde bisulfite. The sulfites may be used in an amount of not less than 0.2 mols per liter and, preferably, not less than 0.4 mols per liter. It is also preferable that the upper limit for using the sulfites is up to 2.5 mols per liter.

The pH of the developers applicable to the invention is within the range of preferably 9 to 13 and particularly 10 to 12. The alkalizers applicable to control the pH include, for example, the pH controllers such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, tertiary sodium phosphate and tertiary potassium phosphate.

It is also allowed to use a buffer including, for example, boric acid salts (described in, for example, JP OPI Publication No. 61-28708/1986), saccharose, acetoxime and 5-sulfosalicylic acid (described in, for example, JP OPI Publication No. 60-93439/1985), phosphates and carbonates.

Besides the above-given components, the additives applicable thereto include, for example, a development inhibitor such as sodium bromide, potassium bromide and potassium iodide; an organic solvent such as ethylene glycol, diethylene glycol, triethylene glycol, dimethyl formamide, methyl cellosolve, hexylene glycol, ethanol and methanol; and an antifoggant such as a mercapto type compound, e.g., 1-phenyl-5-mercaptotetrazole and sodium 2-mercaptobenzimidazole-5-sulfonate, an indazole type compound, e.g., 5-nitroindazole, and a benztriazole type compound, e.g., 5-methylbenztriazole. If required, it is further allowed to add a color toner, a surfactant, a defoamer, a water softener and the amino compounds, each described in JP OPI Publication No. 56-106244/1981.

In the developers of the invention, it is allowed to use a silver-stain preventive such as the compounds given in, for example, JP OPI Publication No. 56-24347/1981. In the developers of the invention, it is allowed to use an amino compound such as alkanol amine described in JP OPI Publication No. 56-106244/1981.

It is further allowed to use the amino compounds described in JP OPI Publication No. 56-106244/1981.

As for the typical examples of the water-soluble aluminium compounds applicable to the invention, the halides, phosphates, sulfates and carbonates of aluminium may preferably be included. The double salts of potassium alum or sodium alum may also be used therein. They may be preferably added in an amount within the range of 1.0×10^{-2} to 0.5×10^{-1} mols per liter in terms of aluminium ion content.

The fixing solution prepared of the fixing compound of the invention is to have a pH within the range of 3.8 to 6.0 and, preferably, 4.2 to 5.5.

The fixing compound is preferable to contain a thiosulfate. The thiosulfates are supplied in the solid form. To be more concrete, they are supplied in the form of the salt of lithium, potassium, sodium, ammonium, and they are used after they are dissolved. Among them, it is preferable that they are supplied as a sodium salt or an ammonium salt and then used after they are dissolved. It is further preferable that a fixing solution can be prepared to have a rapid fixing speed by using them after they are supplied as an ammonium salt and dissolved. The concentration of the thiosulfate is within the range of, preferably, 0.1 to 5 mols per liter, further preferably 0.5 to 2 mols per liter and, particularly 0.7 to 1.8 mols per liter.

The fixing compounds contain a sulfite. When a thiosulfate and the sulfite are dissolved to be mixed up together in an aqueous solvent, the concentration of such a sulfite as mentioned above is not more than 0.2 mols per liter and, preferably, not more than 0.1 mols per liter. As for the sulfites, the solid salts of lithium, potassium, sodium or ammonium may be used. They are used by dissolving them with the above-mentioned solid thiosulfates.

It is preferable that the fixing compound contains citric acid, tartaric acid, malic acid and succinic acid and that citric acid, isocitric acid, malic acid, tartaric acid, succinic acid or the optical isomers thereof are contained therein as phenylacetic acids.

The salts thereof preferably applicable thereto include, for example, the salts of lithium, potassium, sodium or ammonium such as, typically, potassium citrate, lithium citrate, sodium citrate, ammonium citrate, lithium hydrogen tartrate, potassium hydrogen tartrate, potassium tartrate, sodium hydrogen tartrate, sodium tartrate, ammonium hydrogen tartrate, ammonium potassium tartrate, sodium potassium tartrate, sodium maliate, ammonium maliate, sodium succinate and ammonium succinate. One or two kinds of them selected from the above-given salts can be used in combination.

The further preferable compounds among them include, for example, citric acid, isocitric acid, malic acid, phenylacetic acid and the salts thereof.

The above-mentioned citric acid, tartaric acid, malic acid and succinic acid are supplied in the solid form and they are used after dissolving them in an aqueous solvent. After they are dissolved in a fixing solution, their content is not less than 0.05 mols per liter and, most preferably, within the range of 0.2 to 0.6 mols per liter.

The fixing compound is also allowed to contain additives such as various acids, salts, a chelating agent, a surfactant, a wetting agent and a fixing accelerator.

The above-mentioned acids include, for example, inorganic acids such as sulfuric acid, hydrochloric acid, nitric acid and boric acid, and organic acids such as formic acid, propionic acid, oxalic acid and malic acid.

The above-mentioned salts include, for example, the lithium salts, potassium salts, sodium salts and ammonium salts of the above-given acids.

The above-mentioned chelating agents include, for example, aminopolycarboxylic acids such as nitrilotriacetic acid and ehtylenediamine tetraacetic acid, and the salts thereof.

The above-mentioned surfactants include, for example, anionic surfactants such as those of sulfates or sulfonates, nonionic surfactants such as those of the polyethylene glycol types or the ester types, and amphoteric surfactants such as those described in JP OPI Publication No. 57-6840/1982 (wherein, the title of the invention is "Fixing Solution for photographic Use").

The above-mentioned wetting agents include, for example, alkanol amine and alkylene glycol.

The above-mentioned fixing accelerators include, for example, the thiourea derivatives described in JP Examined Publication Nos. 45-35754/1970, 58-122535/1983 and 58-122536/1983, alcohol having a triple bond in the molecule thereof, and thioether described in U.S. Patent No. 4,126,459.

Among the above-mentioned additives, the acids such as sulfuric acid, boric acid and aminopolycarboxylic acid and the salts thereof may preferably be used. They may be added preferably in an amount within the range of 0.5 to 20 g per liter.

The developing chemicals and/or fixing chemicals of the invention are preferably prepared of polyhydroxybenzenes and aluminium compounds each having an average particle size within the range of preferably 10 to 200 µm. They are particularly preferable to be solid processing chemicals granulated and formed by making use of polyhydroxybenzenes and aluminium compounds each having an average particle size within the range of, preferably 10 to 200 µm.

The silver halide photographic light sensitive materials applicable with the developing chemicals and/or fixing chemicals of the invention can be prepared in any processes known in the field of the art.

The above-mentioned light sensitive materials include, for example, black-and-white photographic materials such as photographic materials for medical or industrial use, light sensitive materials for photomechanical process use, microphotographic materials, X-ray photographic materials, reversal microphotographic materials, computerized phototype-setting films and paper, negative photographic materials for general picture-taking use and printing paper. Among them, the light sensitive materials for photomechanical process use are preferable and photographic light sensitive materials containing hydrazine derivatives such as those described in JP OPI Publication Nos. 52-18317/1977, 53-95618/1978, 58-173737/1983 and 58-106493/1983 are particularly preferable.

EXAMPLES

Now, referring to the following examples, the advantages of the invention will be illustrated concretely.

EXAMPLE 1

(Preparation of Fixing Chemicals)

Solid fixing chemicals F-1 through F-12 were each prepared as shown in the following Table 1. The average particle sizes of each raw material thereof were prepared by pulverizing the raw materials by a pulverizer or an air-jet mill.

F-1 through F-6 were each prepared as the samples in the following manner. Every part of A, B and C of the raw materials was mixed up and the resulting mixtures were filled up respectively, in the order of A, C and B parts from the top, into the individual moisture-proof containers each made of a polyethylene/A1/paper having a polyethylene-coated inside surface. F-6 through F-12 were each prepared as the samples in the following manner. Water was added in an amount of 12% of the whole amount of the raw materials into each of parts A, B and C. By making use of the resulting mixtures, the granulated solids having an average particle size of 5 mm were each prepared in a fluidized-bed stirring granulation process. After the resulting solids were dried up, each of the parts was mixed together, and the mixtures were sealed respectively in individual moisture containers, in the same manner as in the cases of F-1 through F-6.

Table 1

	Amount used per liter of liquid used	Average particle size (μm)						
		F-1	F-2	F-3	F-4	F-5	F-6	F-7
		F-8	F-9	F-10	F-11	F-12	F-13	F-14
Part A: Ammonium thiosulfate	135 g	800	800	800	800	100	100	5
Sodium sulfite	8 g	100	100	100	100	100	100	5
Part B: Boric acid	7 g	900	900	900	900	50	50	5
Aluminium sulfate·18 H_2O	300 g	800	300	150	50	50	5	5
Part C: Sodium oxalate	5 g	1000	1000	1000	1000	150	150	5
Sodium citrate	2 g	1000	1000	1000	1000	150	150	5
Sodium acetate	20 g	800	800	800	800	150	150	5

(Evaluation of Fixing Compounds)

Fixing compound samples F-1 through F-12 were each allowed to stand as they were, at 50°C for one day, for a substitutive evaluation supposed for a long term storage. After that, they were added into water at ordinary temperature with stirring and the time required to dissolving them up was visually evaluated. The results thereof will be shown in Table 2 given below.

Table 2

	Dissolving time (min)		Remarks
	Immediately after preparation	One day after at 50°C	
F-1	15	16.5	Comparison
F-2	6	7	Invention
F-3	4	4.8	Invention
F-4	3.5	4	Invention
F-5	3	5	Invention
F-6	3	>60	Comparison
F-7	30*	>60*	Comparison
F-8	12	12.5	Comparison
F-9	5	5.5	Invention
F-10	3	4.2	Invention
F-11	2	2.5	Invention
F-12	1	1.5	Invention
F-13	1	30	Comparison
F-14	1	>60	Comparison

* Compound was partly insoluble when being added.

It is apparent from the results shown in Table 2 that the solid fixing compounds of the invention are excellent in solubility and few in solubility deterioration produced in storage. It is also apparent without any exemplification that the solid fixing compounds of the invention are less in volume and weight and more advantageous for transportation and storage, as compared with any concentrated fixing compounds prepared of the same raw materials as those of the solid fixing compounds of the invention. Among those of the invention, F-8 through F-11 do not produce any fixing compound adhesion to any waste packing material containers nor produce any troubles when making disposals of the waste packing material containers.

EXAMPLE 2

(Preparation of Light Sensitive Materials for Evaluation)
(Synthesis of Latex Lx)

A solution was prepared by adding 0.125 Kg of gelatin and 0.05 Kg of ammonium peroxide into 40 liters of water. Thereto, a mixed solution consisting of (a) 4.51 Kg of n-butyl acrylate, (b) 5.49 Kg of styrene and (c) 0.1 Kg of acrylic acid was added while stirring the resulting solution at 80°C and by taking one hour. Thereafter, the resulting mixed solution was stirred for 1.5 hours and, 1.25 Kg of gelatin and 0.005 Kg of ammonium peroxide were then added thereto. After stirring the solution for 1.5 hours to complete the reaction, the remaining monomers were removed by distilling vapor for one hour. After cooling the temperature down to room temperature, the pH was adjusted to be 6.0 by making use of ammonia. The resulting latex solution was finished to be 50.5 Kg by adding water thereto.

In the above-described manner, a monodisperse type latex having an average particle size of 0.25 μm and a Tg of about 0°C could be prepared.

(Preparation of Emulsion A)

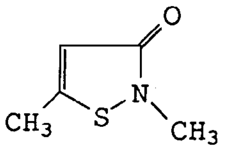
A solution was prepared by adding rhodium hexachloride complex to an aqueous solution of sodium chloride and potassium bromide so that the amount could be $8x10^{-5}$ mols per mol of Ag. The resulting solution and a silver sulfate solution were added at the same time into a gelatin solution while controlling the flow rate. After the resulting solution was desalted, a cubic system, monodisperse silver chlorobromide emulsion having an average grain size of 0.13 M and containing 1 mol% of silver bromide could be prepared.

The resulting emulsion was sulfur-sensitized in an ordinary method and then added with 6-methyl-4-hydroxy-1,3,3a,7-tetrazaindene as a stabilizer. After that, the following additives were added thereto, so that emulsion coating solutions E-1 through E-14 were each prepared. Next, emulsion protective layer coating solution P-0, backing layer coating solution B-0 and backing protective layer coating solution BP-0 were each so prepared as to have the following compositions.

(Preparation of Emulsion Coating Solutions E-1 to E-14)

Compound (a)	1 mg/m^2
NaOH(0.5N)	Adjusted pH to be 5.6
Compound (b)	40 mg/m^2
Compound (c)	30 mg/m^2
Saponin (20%)	0.5 cc/m^2
Sodium dodecylbenzene sulfonate	20 mg/m^2
5-methyl benzotriazole	10 mg/m^2
Compound (d)	2 mg/m^2
Compound (e)	10 mg/m^2
Compound (f)	6 mg/m^2
Latex Lx	An amount given in Table 1
Styrene-maleic acid copolymer, (a thickener)	90 mg/m^2

(a)



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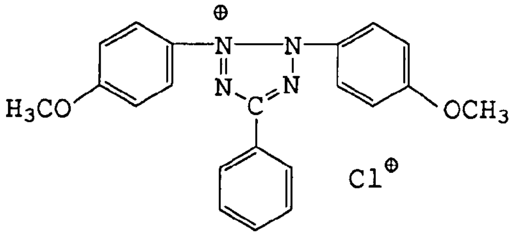

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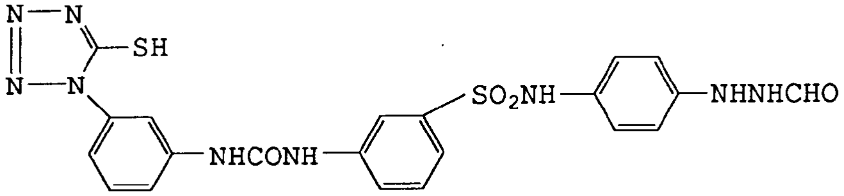

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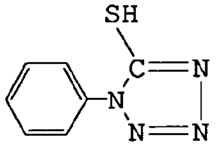

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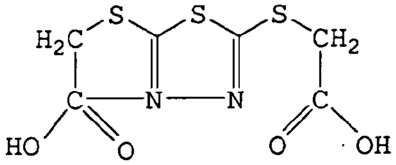

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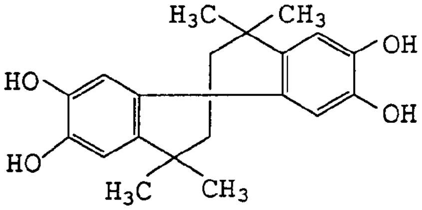


(Emulsion Protective Layer Coating Solution P-0)

Gelatin	0.5 g/m^2
Compound (g) (1%)	25 cc/m^2
Compound (h)	120 mg/m^2
Spherical monodispersed silica (8μ)	20 mg/m^2
Spherical monodispersed silica (3μ)	10 mg/m^2
Compound (i)	100 mg/m^2
Citric acid	Adjusted pH to be 6.0

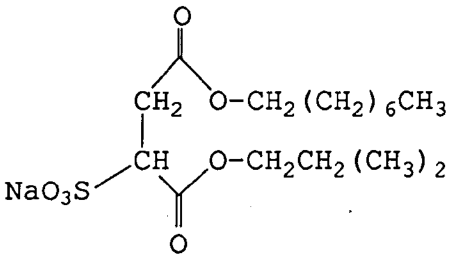
(Backing Layer Coating Solution P-O)

Gelatin	1.0 g/m^2
Compound (j)	100 mg/m^2
Compound (k)	18 mg/m^2
Compound (l)	100 mg/m^2
Saponin (20%)	0.6 cc/m^2
Latex (m)	300 mg/m^2
5-nitroindazole	20 mg/m^2
Styrene-maleic acid copolymer, (a thickener)	45 mg/m^2
Glyoxal	4 mg/m^2
Compound (o)	50 mg/m^2

(Backing Protective Layer Coating Solution BP-O)

Gelatin	0.5 g/m^2
Spherical polymethyl methacrylate (4μ)	25 mg/m^2
Sodium chloride	70 mg/m^2
Glyoxal	22 mg/m^2
Compound (n)	10 mg/m^2

(g)



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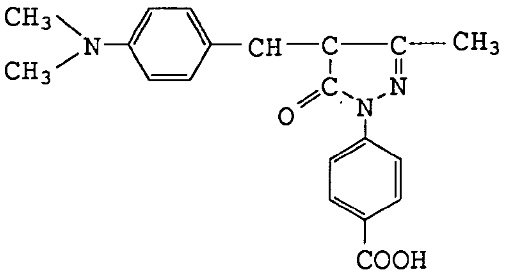
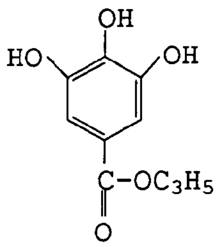
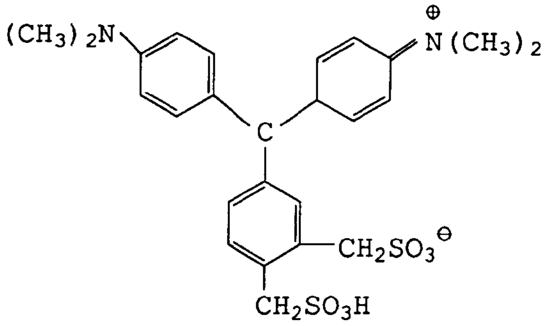


(solid-dispersed dye)

(i)



(j)



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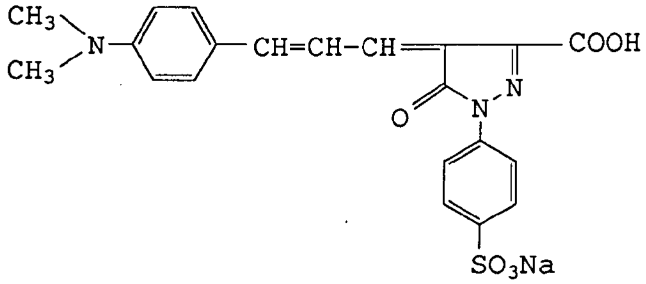

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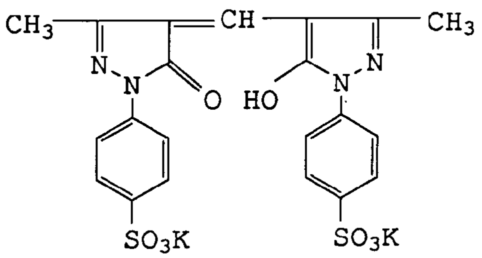
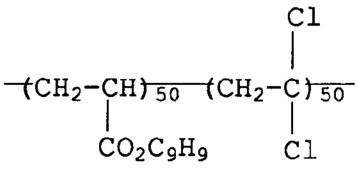
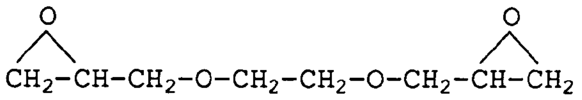


(m)

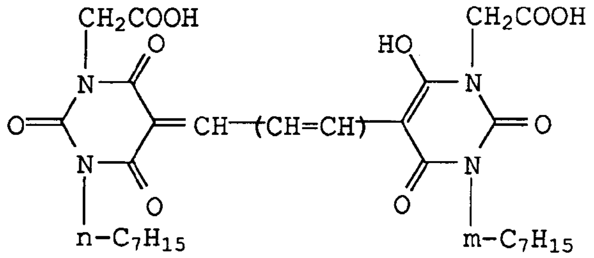


$$-(CH_2-\underset{CO_2C_9H_9}{CH})_{50}-(CH_2-\overset{Cl}{\underset{Cl}{C}})_{50}-$$

(n)

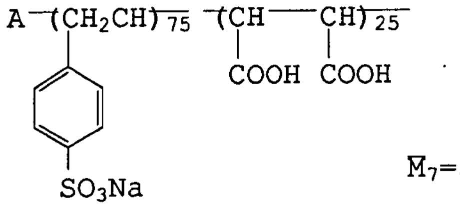


(o)



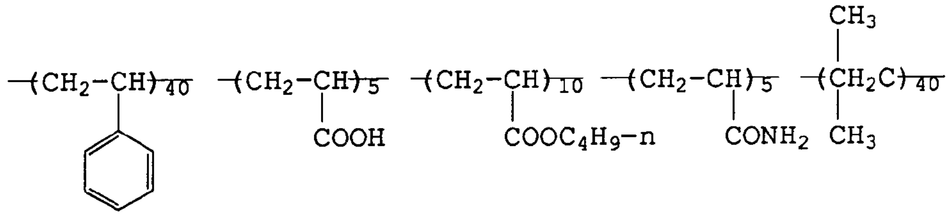
A corona-discharge was applied to a 100μ-thick, subbed polyethylene terephthalate base exemplified in JP OPI Publication No. 59-19941/1984 and, the coating solutions prepared as described above were each coated with the following compositions over the corona-discharged base by making use of a roll-fit coating pan and an air-knife. The drying treatment was carried out for 30 seconds under the parallel flow drying conditions at 90°C and 25 Kcal ($m^2 \cdot hr \cdot °C$) of overall heat-transfer coefficient and another drying treatment was successively carried out for 90 seconds at 140°C. The resulting layer thickness after dried was 1 μ and the specific surface resistance was $1x10^8\Omega$ at 23°C and 55%RH.

Water-soluble polymer	70 g/liter



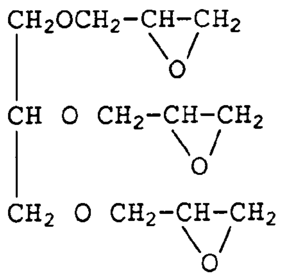
$\bar{M}_7$=5000

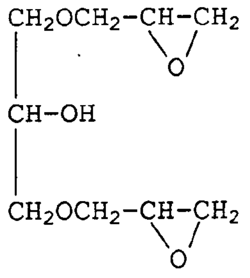
Hydrophobic polymer particle	40 g/liter

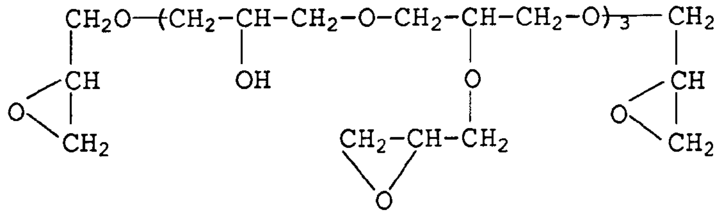


Ammonium sulfate	0.5 g/liter
Polyethylene oxide compound, (having an average molecular weight of 600)	6 g/liter
Hardener	12 g/liter

A mixture of the follwing compounds







Over one of the base surfaces to which the emulsion is to be coated, an emulsion layer and an emulsion protective layer were double-coated simultaneously in this order in a slide-hopper system, while adding a layer hardening solution and keeping the temperature at 35°C. After passing the resulting layer-coated base through a cool-air set zone (at 5°C), a backing layer and a backing protective layer were further coated thereon in the same slide-hopper system while adding a layer hardening solution and the resulting layer-coated base was set by cool-air (at 5°C). At the point of time when passing through each of the set zones, the coating solutions indicated satisfactory setting characteristics. Successively, both sides of the base were dried in a drying zone under the following drying conditions. After both sides of the base were back-coated, the coated base was conveyed without touching it at all, except that it was conveyed by a roller by the time right up to complete the take-up. The coating speed at that time was 100 m/min.

(Drying Conditions)

After completing the above-mentioned setting treatments, the coated base was dried by dry-air at 30°C until the weight ratio of H_2O/gelatin could be 800% and was then dried by dry-air at 35°C (and at 30%RH) until the above-mentioned ratio could be 80 to 200%. After that, the base was still exposed to the wind and, 30 seconds after the point of time when the surface temperature became 34°C (it was regarded as the completion of the drying treatment), it was further dried for one minute by the air at 48°C and 16%RH. At that time, the drying time was required for 50 seconds from the start of the drying to the time when the weight ratio of H_2O/Gelatin was 800%, for 35 seconds from 800% to 200% and for 5 seconds from 200% to the completion of the drying treatment.

The resulting light sensitive material was taken up at 23°C and 15%RH and was then cut apart under the same surrounding conditions.

(Preparation of Developing Chemicals)

Solid developing compounds D1 through D-14 were each prepared as shown in the following Table 3. The average particle sizes of the raw materials were adjusted by pulverizing them by a pulverizer or an air-jet mill.

D1 through D7 were each prepared as the samples in the following manner. Parts A and B of the raw materials were independently mixed up and the resulting mixtures were filled up respectively, in the order of A and B parts from the top, into the individual moisture-proof containers each made of a polyethylene/A1/paper having a polyethylene-coated inside surface. D8 through D-14 were each prepared as the samples in the following manner. Water was added in an amount of 12% of the whole amount of the raw materials into each of parts A and B. By making use of the resulting mixtures, the granulated solids having an average particle size of 3 mm were each prepared in a fluidized-bed stirring granulation process. After the resulting solids were dried up, each of the parts was mixed together, and the mixtures were sealed respectively in individual moisture containers in the same manner as in the cases of D1 through D6.

Table 3

	Amount used per liter of liquid used	Average particle size (µm)						
		D-1	D-2	D-3	D-4	D-5	D-6	D-7
		D-8	D-9	D-10	D-11	D-12	D-13	D-14
Part A: Hydroquinone	135 g	800	800	800	800	100	100	5
1-phenyl-4,4-dimethyl-3-pyrazolidone	8 g	100	100	100	100	100	100	5
Part B: KBr	7 g	900	900	900	900	50	50	5
Disodium ethylenediaminetetraacetate	300 g	800	300	150	50	50	5	5
$KHCO_3$								
K_2SO_3								
* Cyclodextrin clathrate compound								

* Cyclodextrin clathrate compound was prepared by making use of the following raw materials, by dissolving them in 100 ml of water, by homogenizing them at 500 rpm for 10 minutes and then by drying them.

Isoelite (manufactured by Ensuiko-Seito Co.)	5.0 g
KOH	0.5 g
5-nitroindazole	0.15 g
1-phenyl-5-mercaptotetrazole	0.02 g
5-methyl benzotriazole	0.16 g

(Evaluation of Developing Compounds)

Developing compound samples D1 through D12 were each allowed to stand as they were, at 50°C for one day, for a substitutive evaluation supposed for a long term storage. After that, they were added into water at ordinary temperature with stirring and the time required to dissolving them up was visually evaluated.

Films subject to evaluation were each exposed to light through a wedge and were then processed by making use of the above-mentioned developing compounds and fixing compound CFL-871 (manufactured by Konica Corp.) at 28°C for 30 seconds through automatic processor GR-27 (manufactured by Konica Corp.), respectively. The sensitivities obtained were indicated by the reciprocals of the exposure amount for giving a density of 3.5.

The results thereof will be shown in Table 4.

Table 4

	Dissolving time (min)		Specific sensitivity		
	Immediately after preparation	After 1 day, at 50°C	Immediately after preparation	After 1 day, at 50°C	Remarks
F-1	20	21	100	97	Comparison
F-2	7	8	101	97	Invention
F-3	4.5	5.3	101	97	Invention
F-4	4	4.8	100	98	Invention
F-5	3	5	101	97	Invention
F-6	3	6	96	76	Comparison
F-7	5	30	94	70	Comparison
F-8	15	16	99	98	Comparison
F-9	6	6.5	100	99	Invention
F-10	3.8	4.5	101	99	Invention
F-11	3	3.5	100	98	Invention
F-12	2	2.5	101	99	Invention
F-13	2	3	95	83	Comparison
F-14	2	4	94	76	Comparison

It is apparent from the results shown in Table 4 that the solid developing compounds of the invention are excellent in solubility and few in sensitivity deterioration produced in storage. It is also apparent without any exemplification that the solid developing compounds of the invention are less in volume and weight and more advantageous for transportation and storage, as compared with any concentrated developing compounds prepared of the same raw materials as those of the solid developing compounds of the invention. Among those of the invention, D8 through D11 do not cause any fixing compound adhesion to any waste packing material containers nor produce any troubles when making disposals of the waste packing material containers.

According to the invention, solid processing compounds can be provided to be ready for transportation and storage, excellent in solubility in storage, free from any photographic characteristic deterioration and, further, excellent in environmental aptitude.

Claims

1. A black-and-white photographic processing compound comprising:
   a polyhydroxybenzene prepared from grains having an ultimate average diameter of 10 to 500 μm.

2. The black-and-white photographic processing compound of claim 1, further comprising a water-soluble aluminium compound prepared from grains having an ultimate average diameter 10 to 500 μm.

3. The black-and-white photographic processing compound of claim 1, wherein the solid type black-and-white photographic developing compound containing the polyhydroxybenzene is in a powdered, a granulated or a paste form.

4. The black-and-white photographic processing compound of claim 2, wherein the solid type black-and-white photographic fixing compound containing the water-soluble aluminium compound is in a powdered, a granulated or a paste form.

5. The black-and-white photographic processing compound of claim 3, wherein an average granule size in sphere equivalent is 0.5 mm to 50 mm.

6. The balck-and-white photographic processing compound of claim 5, wherein the average granule size is 1 mm to 15 mm.

7. The black-and-white photographic processing compound of claim 4, wherein an average granule size in sphere equivalent is 0.5 mm to 50 mm.

8. The balck-and-white photographic processing compound of claim 7, wherein the average granule size is 1 mm to 15 mm.

9. The balck-and-white photographic processing compound of claim 1, wherein the solid type black-and-white photographic developing compound containing a dihydroxy benzene ring and a 1-phenyl-3-pyrazolidone.

10. A black-and-white photographic processing compound comprising:
a compound having dihydroxy benzene ring and a 1-phenyl-3-pyrazolidone,
and a water-soluble aluminium compound,
both in a granulated form of an average granule size being 1 mm to 15 mm,
and both prepared from grains having an ultimate average diameter 10 to 500 μm.