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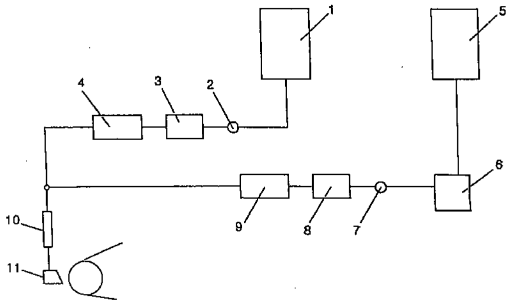
(54) Process for manufacturing photographic materials

(57) A process for manufacturing a photographic material by coating continuously a running support with a silver halide emulsion containing hydrophobic photographic additives, which comprises continuously dispersing a hydrophilic colloidal dispersion of the hydrophobic photographic additives by a dynamic mixing-dispersing means; thereafter adding the hydrophilic colloidal dispersion to the silver halide emulsion and mixing both of them; and starting coating immediately after that, whereby coarse particles formed by stagnation aging from the hydrophilic colloidal dispersion of the hydrophobic photographic additives disappear to develop no coating defect.



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Description

FIELD OF THE INVENTION

The present invention relates to a process for manufacturing photographic materials, and particularly to a process for adding a hydrophilic colloidal dispersion of hydrophobic photographic additives to a silver halide emulsion and mixing both of them immediately before coating.

BACKGROUND OF THE INVENTION

In general, hydrophobic photographic additives have hitherto been dispersed into hydrophilic colloidal aqueous solutions by an oil-in-water dispersing method. In the oil-in-water dispersing method, the hydrophobic photographic additives are dissolved with the aid of heat in a single solvent of either a high boiling organic solvent having a boiling point of 175°C or higher or a low boiling organic solvent usually having a boiling point of 120°C or lower, or in a mixed solvent consisting of both the high and low boiling organic solvents, and thereafter, the resulting solution is finely dispersed into a hydrophilic colloidal aqueous solution of gelatin or the like in the presence of an emulsifying agent such as a surfactant.

The fine dispersion thus prepared is not stable. During aging storage, growth of particles takes place to increase an average particle size, causing deterioration in photographic properties, or coarse particles are formed or crystallization of the hydrophobic additives proceeds to frequently develop spot-like defects on coated surfaces.

Various attempts have been made to correct this disadvantage. For example, improvements in emulsifying agents described in JP-A-60-168141 (The term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-B-59-31689 (The term "JP-B" as used herein means an "examined Japanese patent publication"), etc.; improvements in dispersing processes described in JP-A-57-53227, JP-A-55-129136, etc.; and improvements in high boiling solvents described in JP-B-58-25260, JP-A-56-19049, etc. were attempted to stabilize the fine dispersion, but these attempts failed to bring about the adequate effects.

Further, JP-A-63-296046 discloses that dispersions of couplers having particular structure are mixed with silver halide emulsions immediately before coating to correct the coating defect.

Although this method helps to avoid instabilizing the fine dispersion owing to stagnation aging after mixing a dispersed coupler with a silver halide emulsion, the issue of stabilization against stagnation aging remains unsolved as to the dispersion itself before contact with the silver halide emulsion or as to the dispersion itself of additives unmiscible with the silver halide emulsion.

In the system of adding a dispersion of hydrophobic additives such as couplers to a silver halide emulsion immediately before coating, manufacturing lines for small amounts and many kinds of products make it advantageous in cost to store the hydrophobic additives in the dispersion state. Such storage results in prolonged stagnation aging of said dispersion itself before mixing, and as a result, particles are similarly aggregated into coarse particles, which are brought as such in the mixing and coating steps to develop spot-like defects on coated surfaces.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for manufacturing photographic materials, in which coarse particles formed by stagnation aging from a hydrophilic colloidal dispersion of hydrophobic photographic additives disappear to develop no coating defect.

In a process for manufacturing photographic materials in which a silver halide emulsion containing hydrophobic photographic additives is continuously applied to a running support, this object of the present invention can have been achieved by developing a process which comprises continuously dispersing a hydrophobic colloidal dispersion of said hydrophobic photographic additives by a dynamic mixing-dispersing means; adding the hydrophilic colloidal dispersion thus dispersed to a silver halide emulsion and mixing both of them; and starting coating immediately after that.

Further, the above-mentioned object can have been more effectively attained by defoaming the hydrophilic colloidal dispersion prepared by the dynamic mixing-dispersing means passing through a defoamer, followed by addition to and mixing with the silver halide emulsion.

Furthermore, the above-mentioned object can have been achieved with more striking effect by mixing the hydrophilic colloidal dispersion with the silver halide emulsion by use of a static mixer.

BRIEF DESCRIPTION OF THE DRAWING

The attached FIGURE shows an outline of the process for manufacturing photographic materials of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is illustrated below with reference to Figure in detail.

In Figure, a coating solution other than a dispersion of hydrophobic photographic additives is fed with the aid of transfer apparatus 2 from feeder 1 to applicator 11 through filter 3 and defoamer 4 to defoam the coating solution.

The dispersion of hydrophobic photographic additives is continuously fed from feeder 5 (which may be used also as a preparing apparatus for said dispersion) to dynamic mixing dispersing apparatus 6. Dynamic mixing dispersing apparatus 6 includes a flow-through pipe and a rotator for mixing and dispersing. The clearance between the rotator and the inner wall of dynamic mixing dispersing apparatus 6 is preferably 1 mm or less, and particularly preferably 0.8 mm or less, and the peripheral speed of the rotator is from 3 to 20 m/second, and particularly preferably from 5 to 15 m/second. Any of commercially available mixing dispersing apparatuses of an in-line type can be employed as dynamic mixing dispersing apparatus 6.

Dynamic mixing dispersing apparatus 6 is employed to pulverize coarse particles having diameters of 10 μm or more, and nevertheless, does not substantially have an effect on particles having diameters of 1 μm or less which occupy an overwhelming majority.

The dispersion which is given pulverizing energy by the rotator of dynamic mixing dispersing apparatus 6 may come to contain fine bubbles in some cases. It is a matter of course that the coating solution contaminated with the bubbles develops pinhole-like defects. Said dispersion is therefore fed to defoamer 9 through filter 8 with the aid of transfer apparatus 7.

Defoamer 9 for the dispersion may be either the same in type as defoamer 4 for the solution other than said dispersion or a defoamer of a different type. In the manufacture of photographic materials, a ultrasonic defoamer can be employed as described in JP-A-52-119576, JP-A-53-76164 and JP-A-59-156405. To prevent the dispersion from deterioration due to stagnation aging and to effectively remove the bubbles formed in dynamic mixing dispersion apparatus 6, a closed-type ultrasonic defoamer is preferably employed under pressure.

The dispersion which is passed through defoamer 9 is joined with the solution containing other components in a pipeline as shown in Figure, and both the liquids joined are continuously mixed in mixer 10. The mixing is performed by use of static mixer 10 to prevent the mixture from formation of fresh bubbles and from deterioration due to stagnation aging, and the resulting mixture is rapidly fed to applicator 11.

Any of well-known multistage mixing elements of a type inserted into a transfer pipeline can be employed as static mixer 10. Although shapes of the elements are not particularly limited, elements described in S.J. Chen, et al., Static Mixing Handbook, Sogokagaku Kenkyusho (1973) or J.B. Gray, Turbulent Radial Mixing in Pipes, Academic Press, "Mixing vol. 3" (1986) can be preferably employed.

In the present invention, the timing of passing of the hydrophilic colloidal dispersion of said hydrophobic additives through dynamic mixing dispersing apparatus 6 varies depending upon rates of formation of coarse particles having diameters of 10 μm or more, the rates of formation being determined by ratios of the hydrophobic additives. However, this timing is within approximately 3 hours before coating, preferably within 1 hour, and more preferably within 30 minutes.

Although the timing of passing of the above-mentioned dispersion through defoamer 9 for the dispersion also varies depending upon the rates of formation of coarse particles having diameters of 10 μm or more, the timing is within approximately 1 hour before coating, preferably within 30 minutes, and more preferably within 10 minutes.

Further, although the timing of passing of the above-mentioned dispersion through static mixer 10 to mix it with the solution of other components varies depending upon rates of formation of coarse particles growing in the whole coating solution, the timing is within approximately 30 minutes before coating, preferably within 10 minutes, and more preferably within 2 minutes. It is preferred that all the apparatus employed in the present invention are thermally insulated, and the temperatures thereof usually range from 32 to 60°C, and particularly preferably from 35 to 50°C.

In the present invention, the hydrophobic photographic additives are photographic materials such as color couplers or other hydrophobic additives including high boiling oils and hydrophobic polymers.

The color couplers herein mean compounds which can form dyes by coupling with the oxidation products of aromatic primary amine developing agents. Typical examples of useful color couplers include naphthol or phenol type compounds, pyrazolone or pyrazoloazole type compounds, and chain-closed or heterocyclic ketomethylene compounds. Examples of these cyan, magenta and yellow couplers usable in the present invention are described in Research Disclosure, 17643 (December, 1978), Item VII-D and patent specifications cited in ibid., 18717 (November, 1979).

It is preferred that color couplers incorporated in the photographic materials are made nondiffusive by introducing ballasting groups into the color couplers or forming polymers from them. Two equivalent couplers substituted by coupling releasing groups are preferred to four equivalent couplers in which hydrogen atoms occupy the coupling active sites thereof, because the amounts of coated silver can be saved.

Further, couplers from which dyes having moderate diffusibility are formed, color nonforming couplers, DIR couplers from which development inhibitors are released accompanied by the coupling reaction, and couplers from which development accelerators are released can also be employed.

Typical yellow couplers usable in the present invention are oil protected acylacetamide type couplers. Examples of these couplers are described in U.S. Patents 2,407,210, 2,875,057, 3,265,506, etc. In the present invention, use of two equivalent yellow couplers is preferred, and examples thereof include oxygen atom-releasing type yellow couplers described in U.S. Patents 3,408,194, 3,447,928, 3,933,501, 4,022,620, etc. and nitrogen atom-releasing type yellow couplers described in JP-B-58-10739, U.S. Patents 4,401,752 and 4,326,024, Research Disclosure, 18053 (April, 1979), British Patent 1,425,020, West German Patent (OLS) Nos. 2,219,917, 2,261,361, 2,329,587, and 2,433,812, etc.

α-Pivaloylacetanilide type couplers are excellent in fastness, particularly light fastness, of dyes formed from the couplers, and on the other hand, α-benzoylacetanilide type couplers produce dyes having high color densities.

Magenta couplers usable in the present invention are of an oil protected indazolone type, a cyanoacetyl type, a 5-pyrazolone type, and a pyrazoloazole type such as pyrazolotriazoles. The magenta couplers of the last two types are preferably used. In view of the hues and color densities of formed dyes, 5-pyrazolone type couplers substituted by arylamino groups or acylamino groups at the 3-position are preferred, and typical examples thereof are described in U.S. Patents 2,311,082, 2,343,703, 2,600,788, 2,908,573, 3,062,653, 3,152,896, 3,936,015, etc. Releasing groups of two equivalent 5-pyrazolone type couplers used particularly preferably are nitrogen atom-releasing groups described in U.S. Patent 4,310,619 and arylthio groups described in U.S. Patent 4,351,897. Dyes having high color densities are obtained from 5-pyrazolone type couplers containing ballasting groups described in European Patent 73636.

Examples of the pyrazoloazole type couplers include pyrazolobenzimidazoles described in U.S. Patent 3,061,432, and preferably, pyrazolo[5,1-c][1,2,4]triazoles described in U.S. Patent 3,725,067, pyrazolotetrazoles described in Research Disclosure (June, 1984) and JP-A-60-33552, and pyrazolopyrazoles described in Research Disclosure (June, 1984) and JP-A-60-43659. Because of weak yellow sub-absorption and light fastness of formed dyes, imidazo[1,2-b]pyrazoles described in U.S. Patent 4,500,630 are preferred and pyrazolo[1,5-b][1,2,4]triazoles are particularly preferred.

Cyan couplers usable in the present invention are oil protected naphthol type and phenol type couplers, and typical examples thereof include naphthol type couplers described in U.S. Patent 2,474,293, and preferably, oxygen atom-releasing type two equivalent naphthol type couplers described in U.S. Patents 4,052,212, 4,146,396, 4,228,233, and 4,296,200. Examples of the phenol type couplers are described in U.S. Patents 2,369,929, 2,801,171, 2,895,826, etc. Cyan couplers exhibiting resistance to moisture and temperature are preferably employed in the present invention, and typical examples thereof include phenol type cyan couplers having alkyl groups with two or more carbon atoms at the meta position of the phenol nuclei as described in U.S. Patent 3,772,002; 2,5-diacylamino-substituted phenol type couplers described in U.S. Patents 2,772,162, 3,758,308, 4,126,396, 4,334,011, and 4,327,173, West German Patent (OLS) No. 3,329,729, European Patent 121,365, etc.; and phenol type couplers having phenylureido groups at the 2-position and acylamino groups at the 5-position as described in U.S. Patents 3,446,622, 4,333,999, 4,451,559, 4,427,767, etc. Naphthol type cyan couplers substituted by sulfonamido groups, amido groups, or the like at the 5-position as described in JP-A-60-237448, JP-A-61-153640 and JP-A-61-145557 form color images excellent in fastness to be preferably used in the present invention.

To correct unnecessary absorption which dyes formed from magenta and cyan couplers have in the short wavelength region, it is preferred that colored couplers are simultaneously used for color negative photographic materials for shooting. Typical examples of the colored couplers include yellow colored magenta couplers described in U.S. Patent 4,163,670, JP-B-57-39413, etc. and magenta colored cyan couplers described in U.S. Patents 4,004,929 and 4,138,258, British Patent 1,146,368, etc.

Couplers from which moderately diffusive dyes are formed can be used together with the couplers described above to improve granularity. Examples of such "blur" couplers are described in U.S. Patent 4,366,237 and British Patent 2,125,570 as to magenta couplers and in European Patent 96,570 and West German Patent (OLS) 3,234,533 as to yellow, magenta, or cyan couplers.

Dye formation couplers and the above-mentioned particular couplers may be converted into polymers of not less than dimer. Typical examples of such polymerized dye formation couplers are described in U.S. Patents 3,451,820 and 4,080,211, Examples of polymerized magenta couplers are described in British Patent 2,102,173, U.S. Patent 4,367,282, JP-A-61-232455 and JP-A-62-054260.

To meet characteristics required by the photographic materials, two or more kinds of various couplers used in the present invention can be simultaneously involved in a single photosensitive layer, or one kind of them can also be introduced into two or more layers.

Further, DIR couplers which are functional couplers can also be used. Examples of the DIR couplers include couplers from which heterocyclic mercapto type development inhibitors are released as described in U.S. Patent 3,227,554, etc.; couplers from which benzotriazole derivatives are released as development inhibitors as described in JP-B-58-9942; the so-called color nonforming DIR couplers as described in JP-A-51-16141; couplers in which, after releasing, the formation of nitrogen-containing heterocyclic development inhibitors is released accompanying decomposition of methylol as described in JP-A-52-90932; couplers in which, after releasing, the formation of development inhibitors is released accompanying an intramolecular nucleophilic reaction as described in U.S. Patent 4,248,962 and JP-A-57-56837; couplers in which, after releasing, development inhibitors are released by electron transfer through conjugated systems as described in JP-A-56-114946, JP-A-57-154234, JP-A-57-188035, JP-A-58-98728, JP-A-58-209736, JP-A-58-209737, JP-A-58-209738, JP-A-58-209739, JP-A-58-209740, etc.; couplers from which diffusive development inhibitors are formed, which lose development inhibiting ability thereof in developing solution as described in JP-A-57-151944, JP-A-58-217932, etc.; couplers from which reactive compounds are released followed by forming development inhibitors by reaction in membranes on development or by losing development inhibiting ability thereof as described in JP-A-60-182438, JP-A-60-184248, etc. Of the above-mentioned DIR couplers, DIR couplers used more preferably in relation to the present invention are of the type losing development inhibiting ability in developing solution as represented by couplers described in JP-A-57-151944; the timing type as represented by couplers described in U.S. Patent 4,248,962 and JP-A-57-154234; and the reactive type as represented by couplers described in Japanese Patent Application No. 59-39653, and particularly preferred DIR couplers are the DIR couplers of the type which loses the development inhibiting ability in developing solution as described in JP-A-57-151944, JP-A-58-217932, JP-A-60-218645, JP-A-60-225156, JP-A-60-233650, etc. and the DIR couplers of the reactive type described in JP-A-60-184248.

Compounds from which nucleating agents, development accelerators, or their precursors (Hereinafter these compounds are referred to as the "development accelerators or the like") are released only in image portions on development can be used as hydrophobic photographic additives. Typical examples of such compounds are described in British Patents 2,097,140 and 2,131,188, and include DAR couplers, that is, couplers from which development inhibitors or the like are released by a coupling reaction with the oxidation products of aromatic primary amine developing agents.

It is preferred that the development inhibitors or the like which are released from DAR couplers contain adsorbing groups toward silver halides, and examples of such DAR couplers are described in JP-A-59-157638 and JP-A-59-170840. DAR couplers from which N-acyl-substituted hydrazines containing monocyclic or ring-condensed heterocycles as the adsorbing groups are released together with sulfur atoms or nitrogen atoms at coupling active sites of the photographic couplers are particularly preferably employed, and examples of such DAR couplers are described in JP-A-60-128446.

Compounds containing development accelerator moieties in the coupler residues as described in JP-A-60-37556 and compounds from which the development accelerators or the like are released by the redox reaction with developing agents as described in JP-A-60-107029 can also be used in the manufacture of the photographic materials of the present invention.

In the present invention, hydrophobic photographic additives which may be used as color antifoggants or color mixing preventives include hydroquinone derivatives, aminophenol derivatives, amines, gallic acid derivatives, catechol derivatives, ascorbic acid derivatives, color nonforming couplers, sulfonamidophenol derivatives, etc.

Well-known discoloration preventives can be used as the hydrophobic photographic additives in the present invention. Typical examples of the known discoloration preventives include hindered phenols derived mainly from hydroquinones, 6-hydroxychromans, 5-hydroxycoumarans, spirochromans, p-alkoxyphenols, and bisphenols; and gallic acid derivatives, methylenedioxybenzenes, aminophenols, hindered amines, their ethers prepared by silylation or alkylation of phenolic hydroxyl groups of these compounds, and their ester derivatives. Further, metallic complexes represented by (bissalicylaldoximato)nickel complex and (bis-N,N-dialkyldithiocarbamato)nickel complex can also be used.

Ultraviolet absorbing agents can be added to hydrophilic colloidal layers as the hydrophobic photographic additives in the present invention. Examples thereof include benzo-triazoles substituted by aryl groups as described in U.S. Patents 3,553,794 and 4,236,013, JP-B-51-6540, European Patent 57,160, etc.; butadienes described in U.S. Patents 4,450,229 and 4,195,999; cinnamic acid esters described in U.S. Patents 3,705,805 and 3,707,375; benzophenones described in U.S. Patent 3,215,530 and British Patent 1,321,355; and polymeric compounds containing ultraviolet absorbing residues as described in U.S. Patents 3,761,272 and 4,431,726. Typical examples of ultraviolet absorbers described in U.S. Patents 3,499,762 and 3,700,455 are described in Research Disclosure, 24239 (June, 1984), etc.

Oil-soluble dyes as described in U.S. Patent 4,420,555 may be added as the hydrophobic photographic additives.

To disperse the above-mentioned hydrophobic photographic additives, high boiling organic solvents (oils), hydrophobic polymers, polymer latexes, or the like may be added as oil-drop forming substances.

Typical examples of the high boiling organic solvents are described in U.S. Patents 2,272,191 and 2,322,027, JP-A-54-31728, JP-A-54-118246, etc. (The above refers to phthalates); JP-A-53-1520, JP-A-55-36869, U.S. Patents 3,676,137, 4,217,410, 4,278,757, 4,326,022, 4,353,979, etc. (The above refers to phosphates and phosphonates); U.S. Patent 4,080,209 (referring to benzoates); U.S. Patents 2,533,514, 4,106,940, 4,127,413, etc. (The above refers to amides); JP-A-51-27922, JP-A-53-13414, JP-A-53-130028, U.S. Patent 2,835,579, etc. (The above refers to alcohols and phenols); JP-A-51-26037, JP-A-51-27921, JP-A-51-149028, JP-A-52-34715, JP-A-53-1521, JP-A-53-64333, JP-A-56-114940, U.S. Patents 3,748,141, 3,779,765, 4,004,928, 4,430,421, 4,430,422, etc. (The above refers to aliphatic carboxylic acid esters); JP-A-58-105147 (referring to anilines); JP-A-50-62632, JP-A-54-99432, U.S. Patent 3,912,515, etc. (The above refers to hydrocarbons); and in addition, JP-A-53-146622, U.S. Patents 3,689,271, 3,700,454, 3,764,336, 3,765,897, 4,075,022, and 4,239,851, West German Patent (OLS) 2,410,914, etc. The high boiling organic solvents can also be used as mixtures of two or more kinds thereof, and for example, combinations of phthalates with phosphates are described in U.S. Patent 4,327,175.

Polymers described in JP-A-51-59943, JP-B-51-39853, JP-B-56-126830, U.S. Patents 2,272,163 and 4,201,589, etc. can also be used as oil-drop forming substances.

Oil drops can be formed from these hydrophobic photographic additives by various known dispersing methods. Typical examples of the dispersing methods include a solid dispersing method, an alkali dispersing method, preferably a latex dispersing method, and more preferably an oil-in-water dispersing method. In the oil-in-water dispersing method, the hydrophobic photographic additives are dissolved in a single solvent of either a high boiling organic solvent or a low boiling organic solvent, the so-called co-solvent, or in a mixed solvent consisting of both the high and low boiling organic solvents, and the resulting solution is finely dispersed into an aqueous medium such as water or an aqueous solution of gelatin in the presence of a surfactant. Examples of the high boiling organic solvents are described in U.S. Patent 2,322,027, etc. The dispersion may accompany phase inversion, and when a co-solvent is used, the co-solvent may be separated by distillation, or removed or reduced by water washing with noodle or ultrafiltration, as needed, and the resulting dispersion may be used for coating.

To disperse these oil-drop forming compounds into an aqueous medium, emulsifying dispersing machines such as colloid mills, supersonic emulsifiers, high-pressure type dispersing machines (for example, dispersing machines called homogenizers, homomixers, dissolvers, etc.) are used.

Modified types of these general dispersing machines as described in JP-B-52-11221, JP-A-61-293537, etc. can also be used for the same purpose.

A method in which a phase inversion process is utilized as disclosed in JP-A-55-129136 and JP-A-57-78038 and a method in which a contrived method of addition is used as described in JP-A-57-53227 and JP-A-57-94746 can also be introduced.

Although gelatin is generally used as the hydrophilic colloid in the present invention, various synthetic hydrophilic polymeric substances can also be used as other hydrophilic colloids than gelatin. Examples of the synthetic hydrophilic polymeric substances include proteins such as gelatin derivatives, graft polymers of gelatin with other polymers, albumin, or casein; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose, or cellulose sulfates; sugar derivatives such as sodium alginate or starch derivatives; homopolymers or copolymers of polyvinyl alcohol, partial acetals of polyvinyl alcohol, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole, polyvinylpyrazole, etc.

In addition to general-purpose lime-treated gelatin, acid-treated gelatin, enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, No. 16, p. 30 (1966), or hydrolyzates of gelatin can be used as gelatin. It is possible to use gelatin which is subjected to various ion exchange treatments.

For the manufacture of the photographic materials in the present invention, various kinds of surfactants are used as coating aids, antistatic agents, sliding property improvers, emulsifying dispersing agents, blocking preventives, and photographic property improvers (for example, development acceleration, sensitization, and hard gradation enhancement). Typical coating aids are described, for example, in B.M. Deryagin and S.M. Levi, Theory of Film Coating, The Focal Press, 1964, pp. 159-164, U.S. Patents 4,242,444 and 4,547,459, JP-A-55-116799, JP-A-60-209732, etc. Typical antistatic agents are described in Swiss Patent 506093, British Patent 1,417,915, JP-A-57-146248, JP-A-58-208743, JP-A-61-143750, and Research Disclosure, 23815, and a good many of these compounds simultaneously have the effects that blocking preventives or sliding property improvers have. The surfactants described above as coating aids can be used also as the emulsifying dispersing agents, and in addition, compounds described in JP-B-48-9979, JP-A-50-66230, JP-51-129229, JP-A-53-138726, JP-A-54-99416, JP-A-55-153933, etc. also are representative of the emulsifying dispersing agents. Typical photographic property improvers are described in Kenichi Eda, Kaimenkasseizai Kenkyu-2, II Shashinkogyo eno Ohyo (Research on Surfactants-2, II Application to Photographic Technology), Saiwaishobo, 1963, pp. 384-391.

All these compounds described above are only typical examples of the respective agents, and it is possible to add commercially available surfactants in accordance with purposes. The surfactants used in the present invention are not limited to the above-mentioned examples.

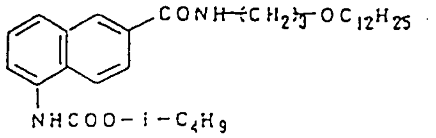
Coating systems to be applied to the manufacture of the photographic materials in the present invention are not particularly limited, and any of coating methods used usually for the manufacture of photographic materials, which include slide bead coating, extrusion coating, and curtain coating, can be effectively used.

EXAMPLE

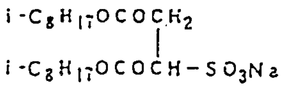
An example is given below to more clearly illustrate the effect of the present invention.

A solution was prepared by dissolving with the aid of heat 200 g of a cyan coupler represented by the following formula C-1 and 50 g of a cyan coupler represented by the following formula C-2 (The above couplers are hydrophobic additives), and 4 g of a surfactant represented by the following formula W-1 in 1 liter of ethyl acetate at 70°C, and mixed with 7 kg of a 7 wt% aqueous solution of gelatin. The resulting mixture was thereafter dispersed by use of a high speed impeller type dispersing apparatus to prepare a hydrophilic colloid solution.

C-1

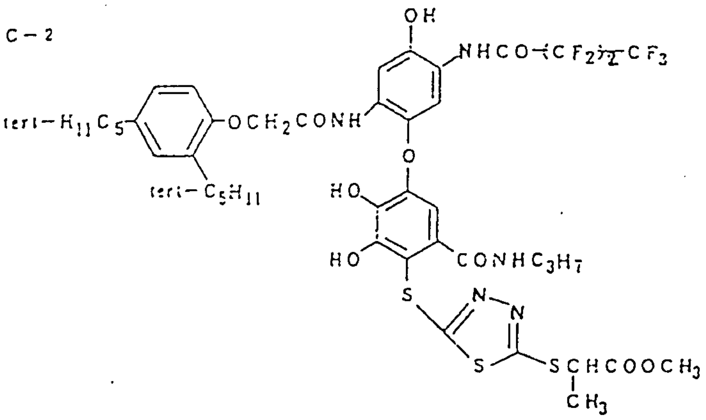


W-1



$$\begin{array}{l} i\text{-}C_8H_{17}OCOCH_2 \\ \qquad\qquad\;| \\ i\text{-}C_8H_{17}OCOCH-SO_3Na \end{array}$$

C-2



This hydrophilic colloidal solution was allowed to stand at 40°C for 48 hours with slowly stirring in a vessel equipped with propeller type impeller, and added to a silver halide emulsion by use of a unit constituted of the apparatuses corresponding to the present invention as shown in Figure.

A milder dispersing machine manufactured by Ebara Corp. was employed as the dynamic mixer, and an in-line mixer manufactured by Sulzer Ltd. in Switzerland as the static mixer.

Samples were collected at all the stages of the process, allowed to stand at 40°C for 1 hour, and spread on slides to count coarse particles having diameters of 20 µm or more with the aid of a light microscope.

Increases in number of coarse particles were checked at all the stages to evaluate variation due to aging. Results are shown in Table 1.

TABLE 1

In Hydrophilic Colloidal Solutions	Numbers of Coarse Particles (/ml)
Immediately after Preparation	0.3
After 48-Hour Storage	5.2
After Addition of Silver halide Emulsions	
Mixing alone by Static Mixer	2.9
Mixing by Both Dynamic and Static Mixers	0.3

The results reveal that, in the present invention, the number of aggregated oil drops or coarse particles which have been contained in the hydrophilic colloidal dispersion of the hydrophobic photographic additives since the preparation thereof is sharply decreased (and in addition, bubbles formed by that are rapidly and continuously removed), and heat improvement on coated surfaces which would be expected from the addition of the additives immediately before coating can be greatly achieved.

It should be understood that the foregoing relates to only a preferred embodiment of the invention, and that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purposes of the disclosure, which do not constitute departures from the spirit and scope of the invention.

Claims

1. A process for manufacturing a photographic material by continuously coating a running support with a silver halide emulsion containing a hydrophobic photographic additive, which comprises continuously dispersing a hydrophilic colloidal dispersion of the hydrophobic photographic additive by a dynamic mixing-dispersing means; adding thereafter the hydrophilic colloidal dispersion to the silver halide emulsion and mixing both of them; and starting coating immediately after that.

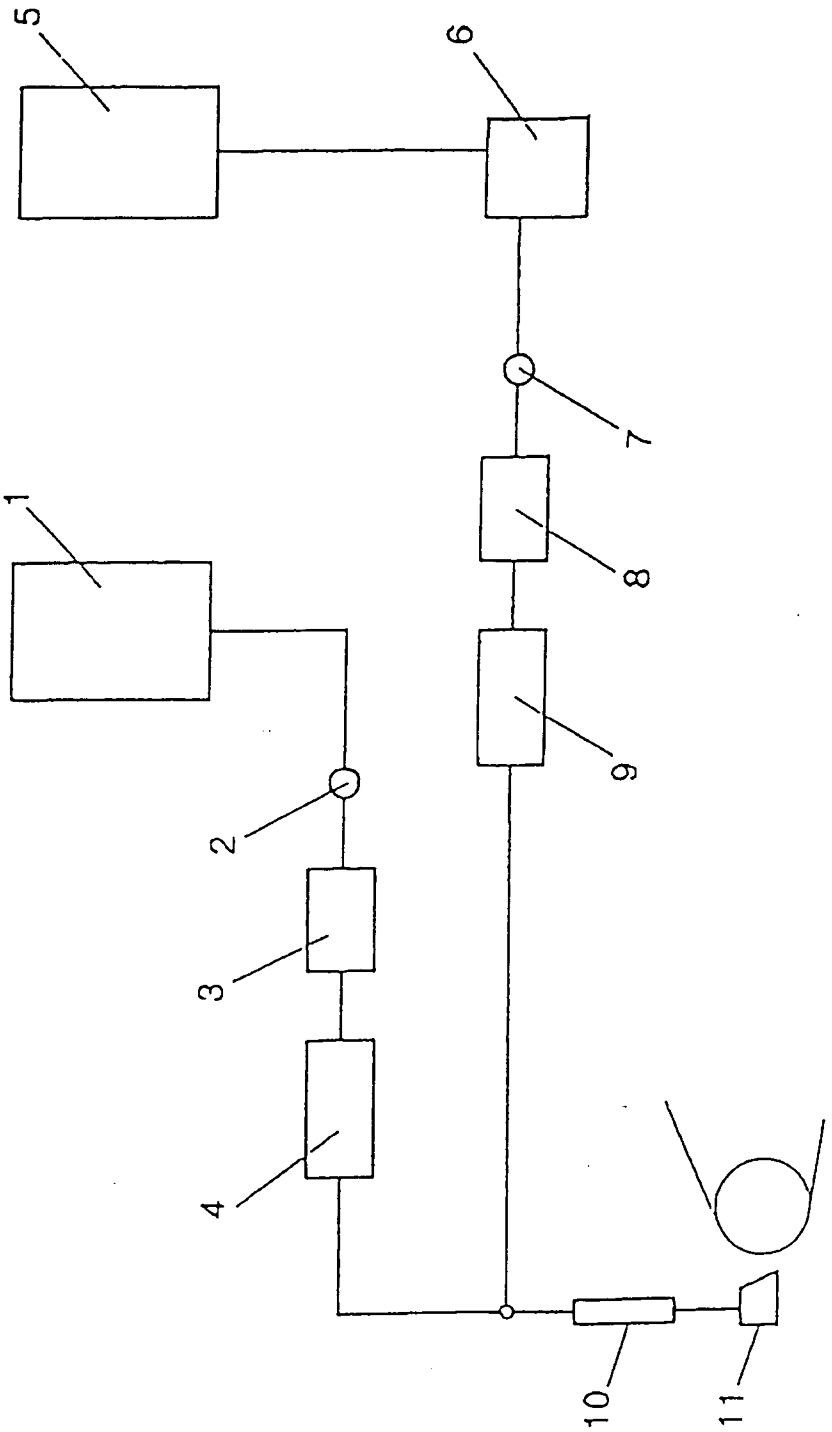
2. A process for manufacturing a photographic material as claimed in claim 1, wherein the hydrophilic colloidal dispersion prepared by the dynamic mixing-dispersing means is continuously defoamed by passing through a defoamer, followed by addition to and mixing with the silver halide emulsion.

3. A process for manufacturing a photographic material as claimed in claim 1, wherein mixing of the hydrophilic colloidal dispersion with the silver halide emulsion is performed by use of a static mixer.

4. A process for manufacturing a photographic material as claimed in claim 2, wherein mixing of the hydrophilic colloidal dispersion with the silver halide emulsion is performed by use of a static mixer.

5. A process for manufacturing a photographic material as claimed in claim 2, wherein the coating is started within 3 hours after the mixing of said hydrophilic colloidal dispersion and said silver halide emulsion.

6. A process for manufacturing a photographic material as claimed in claim 5, wherein said dispersion and said mixing are executed under the temperature from 32°C to 60°C.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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 6762

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 604 934 (EASTMAN KODAK CO) 6 July 1994 * page 5, line 14 - line 35; figure 3 * ---	1	G03C1/015 G03C1/74 G03C1/025
A	EP-A-0 573 938 (EASTMAN KODAK CO) 15 December 1993 * example 1 * ---	1	
D,A	US-A-4 419 441 (NITTEL FRITZ ET AL) 6 December 1983 * claims 1-9 * * column 1, line 13 - line 48 * ---	1,6	
A	GB-A-2 056 292 (FUJI PHOTO FILM CO LTD) 18 March 1981 * examples 1,2 * ---	2,6	
A	GB-A-1 501 515 (AGFA GEVAERT AG) 15 February 1978 * page 1, line 11 - line 68 * * page 2, line 116 - page 3, line 46 * * page 4, line 62 - line 75 * * page 4, line 123 - page 5, line 10 * * page 6, line 12 - line 22 * -----	3-6	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	21 January 1997	Lindner, T

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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