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United States Statutory Invention Registration [19]

[11] Reg. Number: **H1016****Hatakeyama et al.**[43] Published: **Jan. 7, 1992****[54] SILVER HALIDE PHOTOSENSITIVE MATERIAL****[75] Inventors:** Akira Hatakeyama; Tomokazu Yasuda; Takashi Naoi; Shigetoshi Ono, all of Kanagawa, Japan**[73] Assignee:** Fuji Photo Film Co., Ltd., Minami-ashigara, Japan**[21] Appl. No.:** 603,507**[22] Filed:** Oct. 26, 1990**[30] Foreign Application Priority Data**

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[51] Int. Cl.⁵ G03C 1/76; G03C 1/005**[52] U.S. Cl.** 430/535; 430/533; 430/534; 430/537; 430/627**[58] Field of Search** 430/533, 534, 537, 627, 430/535**[56] References Cited****U.S. PATENT DOCUMENTS**

4,213,783	7/1980	Cook	430/533
4,495,273	1/1985	Pannocchia	430/534
4,699,869	10/1987	Bayless et al.	430/534
4,714,671	12/1987	Helling et al.	430/627
4,933,267	6/1990	Ishigaki et al.	430/533
4,977,071	12/1990	Kanetake et al.	430/534

Primary Examiner—Robert L. Stoll*Assistant Examiner*—C. Harris*Attorney, Agent, or Firm*—Sughrue, Mion, Zinn, Macpeak & Seas**[57] ABSTRACT**

A silver halide photosensitive material is disclosed, comprising a polyester film support having thereon at least one hydrophilic colloid layer, at least one layer of which is a silver halide emulsion layer and at least one layer of which is a polymer latex-containing hydrophilic colloid layer, said polyester film support having coated on each side thereof a vinylidene chloride copolymer having a weight average molecular weight not more than 45,000, said vinylidene chloride copolymer being a core/shell type latex, said core part containing at least one of each type of repeating unit represented by formulae (I) and (II) and the said shell part contain-

ing at least one of each type of repeating unit represented the formulae (I), (III) and (IV):



wherein A¹ represents a hydrogen atom, a methyl group or a halogen atom, A² represents a substituted or unsubstituted alkyl group or phenyl group, A³ represents a hydrogen atom or a methyl group, A⁴ represents a hydrogen atom, a methyl group or a —CH₂COOM group, A⁵ represents a hydrogen atom, a methyl group or a —COOM group, A⁶ represents a —COOM group or an alkoxy carbonyl group, phenyl group or N-alkylcarbonyl group which is substituted with a —COOM group, and M represents a hydrogen atom or an alkali metal atom.

10 Claims, No Drawings

A statutory invention registration is not a patent. It has the defensive attributes of a patent but does not have the enforceable attributes of a patent. No article or advertisement or the like may use the term patent, or any term suggestive of a patent, when referring to a statutory invention registration. For more specific information on the rights associated with a statutory invention registration see 35 U.S.C. 157.

SILVER HALIDE PHOTOSENSITIVE MATERIAL

FIELD OF THE INVENTION

This invention concerns silver halide photosensitive materials having excellent dimensional stability. Furthermore, the present invention concerns silver halide photosensitive materials comprising a film having improved physical properties, especially with regard to adhesion of the film with the binder.

BACKGROUND OF THE INVENTION

Silver halide photographic materials generally have a layer wherein a hydrophilic colloid such as gelatin, for example, forms a binder on at least one side of a support. Such a hydrophilic colloid layer is disadvantageous in that it is liable to expand and contract in response to changes in humidity and changes in temperature.

The change in dimension of a photosensitive material caused by expansion and contraction of the hydrophilic colloid layer is a very serious disadvantage in the case of a photosensitive material for printing purposes, for example, which is used for the reproduction of screen dot images in multi-color printing or accurate line drawings.

Techniques for obtaining a photosensitive material which exhibits a small variation in dimension, namely, a material having excellent dimensional stability, include techniques wherein the thickness ratio of the hydrophilic colloid layer and the support is specified as disclosed in U.S. Pat. No. 3,201,250, and techniques wherein a polymer latex is included in the hydrophilic colloid layer as disclosed in JP-B-39-4272, JP-B-39-17702, JP-B-43-13482, JP-B-45-5331 and U.S. Pat. Nos. 2,376,005, 2,763,625, 2,772,166, 2,852,386, 2,853,457, 3,397,988, 3,411,911 and 3,411,912. (The term "JP-B" as used herein signifies an "examined Japanese patent publication".) Furthermore, a theoretical discussion regarding the above described techniques is provided by J. Q. Umberger in *Photographic Science and Engineering*, 1957, pages 69-73.

However, the inclusion of a polymer latex in the hydrophilic colloid layer often adversely affects the adhesion of the layer with the substrate, the wear resistance of the film and the film strength in the development processing.

Techniques wherein the above described adverse effects due to the polymer latex are mitigated by using polymers having active methylene groups which react with conventional gelatin film hardening agents are disclosed, for example, in U.S. Pat. Nos. 3,459,790, 3,488,708, 3,554,987, 3,700,456 and 3,939,130, and British Patent 1,491,701. An improvement in dimensional stability to the extent that the film strength and wear resistance in the development processing bath are not lost has been obtained by means of these techniques. However, there is a strong demand for further improvement in dimensional stability in the printing field where multi-color printing and accurate line drawing reproduction is required. Furthermore, a technique for improving dimensional stability of a support wherein both of a polyester film are covered with polyolefin has been proposed in JP-A-60-3627 but this technique is inadequate in practice. (The term "JP-A" as used herein signifies an "unexamined published Japanese patent application".)

Furthermore, methods using hydrazine derivatives for obtaining high contrast photographic characteristics

are disclosed, for example, in U.S. Pat. Nos. 4,224,401, 4,168,977, 4,166,742, 4,311,781, 4,272,606, 4,211,857 and 4,243,739.

High speed photographic characteristics of ultra-high contrast can be obtained using the above noted methods, but the contrast enhancing action of the hydrazine derivatives is inhibited by the use of a large amount of polymer latex for increasing dimensional stability. Furthermore, the amount of a polymer latex which can be used is limited because of the adverse effects which limit the high contrast photographic characteristics, and a satisfactory level of dimensional stability has hitherto not been achieved.

The technique in which the thickness ratio of the hydrophilic colloid layer and the support is specified minimizes the expansion and contraction of the unprocessed film and the processed film due to changes in humidity. However, it is not possible using this technique to improve the dimensional stability before and after the photographic processing (development, fixing, washing and drying). Particularly, the support expands as a result of the uptake of water during development processing and the base does not revert to its original size after the drying process, even over a long period of time such that some expansion remains in practice. Hence, on comparing the dimensions of a film in the unprocessed state with those of the processed film, it is often found that the film is expanded in the processed state. In the industry, this phenomenon is recognized as poor dimensional stability which accompanies processing, and is an especially serious disadvantage for photosensitive materials for printing purposes.

The technique of including a polymer latex in the hydrophilic colloid layer can also reduce the extent of the expansion and contraction which occur with changes in humidity, but the disadvantage described above due to the permeation of processing liquids into the support in the processing operation are not thereby avoided.

A technique using a polyester support which has been covered with a vinylidene chloride copolymer in order to alleviate this problem is proposed in JP-A-64-538. This technique is particularly useful for improving the dimensional stability with respect to processing of photosensitive materials for printing purposes, however, it is difficult to obtain an evenly coated film thickness of the vinylidene chloride-containing copolymer such that coating irregularities tend to occur, and in many cases there is an adverse effect on the adhesion between the support and the binder. An effective solution has still not been found in this regard.

The vinylidene chloride-containing copolymer in JP-A-64-538 contains the vinylidene chloride in an amount of 70 to 99.5 wt % and does not specify a molecular weight and carboxylic acid content, whereas the vinylidene chloride-containing copolymer of the present invention has core-shell type structure, a molecular weight of 45,000 or larger and contains carboxylic group in shell part.

Moreover, powerful shear forces result between the coated surface and the coating machine and at the one-way valves in the coating liquid feed pumps. Polymer condensates are also produced, and these condensates may have an adverse effect on the coated surface condition. Furthermore, the condensates are necessarily removed from the manufacturing equipment.

SUMMARY OF THE INVENTION

A first object of the present invention is to provide a silver halide photosensitive material having excellent dimensional stability with respect to environmental variations and processing.

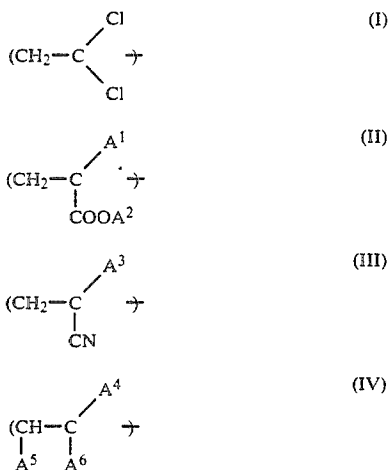
A second object of the present invention is to provide a silver halide photosensitive material having excellent dimensional stability with respect to environmental changes and processing, said photosensitive material also having ultra-high contrast using hydrazine derivatives.

A third object of the present invention is to a silver halide photosensitive material having improved adhesion between the support and the binder, and improved film strength and wear resistance in development processing baths, and having excellent dimensional stability with respect to environmental variations and processing.

A fourth object of the present invention is to provide a silver halide photosensitive material wherein the hydrophilic colloid layer is strongly bonded to the polyester film support.

A fifth object of the present invention is to provide a silver halide photosensitive material wherein the coated film thickness and coated surface condition of the vinylidene chloride-containing copolymer are uniform, and wherein the adhesion between the support and the binder are excellent, and wherein the photosensitive material has excellent dimensional stability with respect to environmental variations and processing.

The above described objectives have been achieved by providing a silver halide photosensitive material comprising a polyester film support having thereon at least one hydrophilic colloid layer, at least one layer of which is a silver halide emulsion layer and at least one layer of which is a polymer latex-containing hydrophilic colloid layer, said polyester film support having coated on each side thereof a vinylidene chloride copolymer having a weight average molecular weight of not more than 45,000, said vinylidene chloride a core/shell type latex, said core part containing at least one of each type of repeating unit represented by the formulae (I) and said shell part containing at least one of each type of repeating unit represented by the formulae (II), (III) and (IV):



wherein A¹ represents a hydrogen atom, a methyl group or a halogen atom, A² represents a substituted or unsub-

stituted alkyl group or phenyl group, A³ represents a hydrogen atom or a methyl group, A⁴ represents a hydrogen atom, a methyl group or a —CH₂COOM group, A⁵ represents a hydrogen atom, a methyl group or a —COOM group, A⁶ represents a —COOM group or an alkoxy carbonyl group, phenyl group or N-alkylcarbamoyl group which is substituted with a —COOM group, and M represents a hydrogen atom or an alkali metal atom.

DETAILED DESCRIPTION OF THE INVENTION

The vinylidene chloride copolymer of the present invention is a copolymer having a weight average molecular weight of not more than 45,000, preferably not more than 40,000 but at least 3,000, and most desirably not more than 35,000 but at least 6,000. The vinylidene chloride copolymer is prepared by combining at least one of each type of monomer component from which the repeating units represented by the formulae (II)–(IV) are derived from with vinylidene chloride. The vinylidene chloride copolymer may also comprise repeating units derived from other monomer components. The weight average molecular weight is that obtained by calculation as polystyrene using the gel permeation chromatography method.

No particular limitation is imposed upon the molecular weight distribution of the vinylidene chloride copolymer of the present invention, and polymers having a mono-disperse molecular weight distribution, a wide molecular weight distribution or a poly-disperse molecular weight distribution can be used.

The core part of the vinylidene copolymer latex of the present invention preferably constitutes from 60 to 95 wt %, and most desirably for from 70 to 90 wt % of the whole of the latex particles, and the shell part preferably accounts for from 5 to 40 wt %, and most desirably for from 10 to 30 wt %, of the whole of the latex particles.

The proportion (w) of repeating units represented by formula (I) in the whole of the vinylidene chloride copolymer core/shell latex particles is from 70 to 98.5 wt %, preferably from 85 to 97 wt %, and most desirably from 88 to 94 wt %.

The proportion (x) of repeating units represented by formula (II) contained in the whole of the latex particles is from 1.0 to 20 wt %, preferably from 2 to 12 wt %, and most desirably from 5 to 10 wt %.

The proportion (y) of repeating units represented by formula (III) contained in the whole of the latex particles is from 0.1 to 5.0 wt %, preferably from 0.3 to 3.5 wt %, and most desirably from 0.5 to 2.5 wt %. The proportion (z) of repeating units represented by formula (IV) contained in the whole of the latex particles is from 0.05 to 3.0 wt %, preferably from 0.1 to 1.5 wt %, and most desirably from 0.1 to 0.8 wt %.

All proportions (X), (Y) and (Z) of the repeating units are based on the latex as a whole.

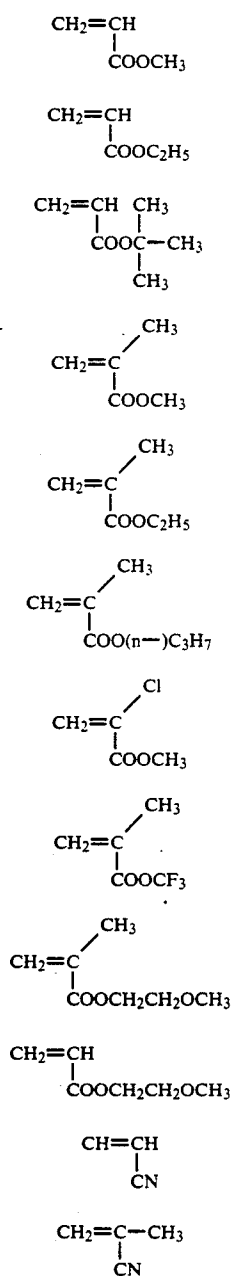
In formulae (II)–(IV), A' is preferably a hydrogen atom, a methyl group or a Cl or an F atom, and it is most desirably a hydrogen atom or a methyl group. A² preferably represents a substituted or unsubstituted alkyl group having from 1 to 6 carbon atoms, and most desirably A² represents an unsubstituted alkyl group having from 1 to 4 carbon atoms. A³ represents a hydrogen atom or a methyl group. A⁴ preferably represents a hydrogen atom, a methyl group or a —CH₂COOH

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group, and most desirably it represents a hydrogen atom or a methyl group. A⁵ preferably represents a hydrogen atom. A⁶ preferably represents a —COOH group or an alkoxycarbonyl group or N-alkylcarbamoyl group which is substituted with a —COOH group, and most desirably A⁶ represents a —COOH group.

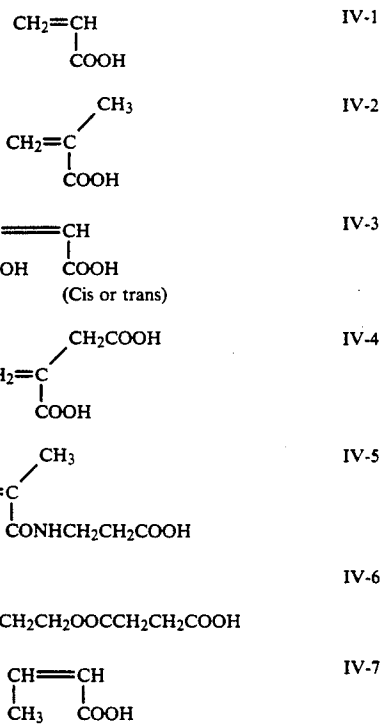
Examples of substituent groups for the substituted alkyl phenyl group represented by A², substituted alkoxy carbonyl group, phenyl group or N-alkylcarbamoyl group represented by A⁶ include alkoxy group (which may be further substituted), halogen atom, nitro group, cyano group, alkyl group (in the case of a substituted phenyl group), carboxamido group, carbamoyl group, sulfonamido group, sulfamoyl group and sulfo group.

Useful examples of monomers from which the repeating units of formulae (II)-(IV) are derived from are indicated below, but the invention is not limited by these examples.



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Additional useful examples of monomers from which the repeating units represented by formula (II) derived from are indicated below:

n-Propyl acetate, isopropyl acrylate, n-butyl acrylate, 3-acryloylpropanesulfonic acid, acetoxyethyl acrylate, phenyl acrylate, 2-methoxy acrylate, 2-ethoxy acrylate, 2-(methoxyethoxy)ethyl acrylate, 2-methanesulfonamidoethyl acrylate, n-butyl methacrylate, tert-butyl methacrylate, cyclohexyl methacrylate, 2-hydroxyethyl methacrylate, 2-ethoxyethyl methacrylate, dimethylethylamino methacrylate.

Other monomers which can be used to prepare the core part of the vinylidene chloride copolymer of the present invention include, for example, crotonic acid esters, vinyl esters, maleic acid di-esters, fumaric acid di-esters, itaconic acid di-esters, acrylamides, methacrylamides, vinyl ethers and styrenes.

Furthermore, monomers from which the repeating units of formulae (III) and (IV) are derived from may be used to prepare the core part, and monomers from which the repeating unit of formula (II) are derived from may be used to prepare the shell part.

Actual examples of these monomers which can be used to prepare the shell part of the vinylidene chloride copolymer include crotonic acid esters, such as butyl crotonate and hexyl crotonate for example, vinyl esters such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl methoxyacetate and vinyl benzoate, maleic acid di-esters such as diethyl maleate, dimethyl maleate and dibutyl maleate, fumaric acid di-esters such as diethyl fumarate, dimethyl fumarate and dibutyl fumarate, itaconic acid di-esters such as diethyl itaconate, dimethyl itaconate and dibutyl itaconate, acrylamides such as acrylamide, methylacrylamide, ethylacrylamide, isopropylacrylamide, n-butylacrylamide, hydroxymethylacrylamide, diacetoneacrylamide, acryloylmorpholine and acrylamido-2-methylpropanesulfonic acid, me-

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thacrylamides such as methylmethacrylamide, ethylmethacrylamide, n-butylmethacrylamide, tert-butylmethacrylamide, 2-methoxyethylmethacrylamide, dimethylmethacrylamide and diethylmethacrylamide, vinyl ethers such as methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, methoxyethyl vinyl ether and dimethylaminoethyl vinyl ether, and styrenes such as styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, isopropylstyrene, butylstyrene, chloromethylstyrene, methoxystyrene, butoxystyrene, acetoxystyrene, chlorostyrene, dichlorostyrene, bromostyrene, vinylbenzoic acid methyl ester, 2-methylstyrene, styrenesulfonic acid, vinylbenzoic acid and trimethylaminomethylstyrene.

Examples of other monomers which can be used to prepare the shell part of the vinylidene chloride copolymer include allyl compounds (for example allyl acetate), vinyl ketones (for example methyl vinyl ketone), vinyl heterocyclic compounds (for example vinylpyrrolidone), unsaturated nitrile compounds (for example acrylonitrile and methacrylonitrile).

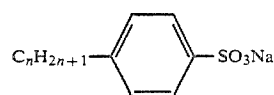
Furthermore, monomers which can be used to prepare both shell and core parts and have groups with bond either directly or via a hardening agent with the binder, for example monomers which have an active methylene group, a (poly)hydroxyphenyl group, a sulfonic acid group, an amino group (which may be substituted with alkyl or phenyl groups), an active ester group, an active halogen atom, an active vinyl group or a precursor thereof, an epoxy group or an ethyleneimino group may also be used to prepare the vinylidene chloride copolymer of the present invention.

The vinylidene copolymers of the present invention can be prepared using emulsion polymerization methods. Emulsion polymerization methods include known techniques and methods of preparation based upon the disclosure of, for example, U.S. Pat. Nos. 4,350,622, 4,401,788, 4,446,273 and 4,535,120, JP-A-61-108650, JP-A-62-256871, JP-A-62-246913, JP-A-62-246912, JP-A-57-139136, JP-A-61-236669, and JP-A-57-137109 can be used. The present invention is realized by means of a vinylidene chloride latex wherein a polymer having excellent adhesion and shear stability is distributed in the shell part and wherein a polymer which imparts barrier properties is distributed in the core part, the vinylidene chloride latex being prepared on the basis of the above noted methods (for example, on the basis of the method described in JP-A-62-256871).

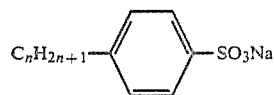
The polymer (shell part) having excellent adhesion, etc., of the present invention is obtained using at least one of each type of monomer from which the repeating units represented by each of formulae (I), (III) and (IV) are derived from, and the polymer (core part) which imparts barrier properties is obtained using at least one of each type of monomer from which the repeating units represented by each of formulae (I) and (II) are derived from.

Any anionic, non-ionic, cationic, betaine or polymeric surfactant, or mixtures thereof, may be used as the emulsifying agent for preparing the vinylidene chloride latex of the present invention, but the use of anionic emulsifying agents is preferred. The use of a surfactant containing at least one type of alkylbenzenesulfonate from among the anionic emulsifying agents is especially desirable, including, for example,

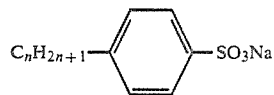
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(where n is a positive integer, average value 11-16),



and $C_nH_{2n+1}SO_3Na$ or a mixture of



and $C_mH_{2m+1}OSO_3Na$ ($m=10, 12, 14, 16$ or 18).

Actual examples of the compounds of the present invention are described below, but the compounds of the present invention are not limited by these examples.

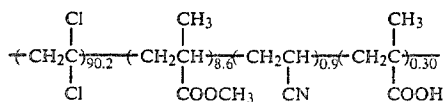
SYNTHESIS EXAMPLE 1

Preparation of Compound 1 of the Present Invention

Water (440 ml), 5 grams of sodium alkylbenzenesulfonate and 0.7 gram of sodium persulfate were introduced into a pressure resistant glass reactor and, after displacing the air with nitrogen, a monomer mixture comprising 39 grams of vinylidene chloride and 4.5 grams of methyl methacrylate was introduced with stirring at a temperature of 50° C. After confirming that the reaction had been completed by a reduction in the internal pressure, a monomer mixture comprising 351 grams of vinylidene chloride and 39 grams of methyl methacrylate was introduced. After confirming that the reaction had been completed by a reduction in the internal pressure, a solution obtained by dissolving 0.15 gram of sodium persulfate and 0.075 gram of sodium sulfite in 25 ml of water was introduced into the reactor. Subsequently, a monomer mixture comprising 60 grams of vinylidene chloride, 5 grams of acrylonitrile and 1.75 grams of methacrylic acid was introduced. After confirming that the reaction had been completed by a reduction in the internal pressure, a 10% aqueous sodium alkylbenzenesulfonate solution was added to obtain the desired latex.

The solid fraction concentration was 50.2%, the average particle size was 148 nm and the weight average molecular weight was 23,600.

It was determined by elemental analysis and NMR spectroscopy that compound 1 of the present invention as prepared above had the structure indicated below.

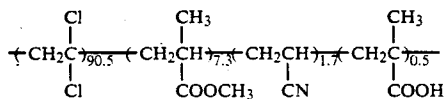


SYNTHESIS EXAMPLE 2

Preparation of Compound 2 of the Present Invention

Water (200 ml), 0.80 gram of sodium hydrogen sulfite and 4.8 gram of sodium alkylbenzenesulfonate (the alkyl group was a mixture with alkyl groups which had 12 carbon atoms as the principal component) were stirred together after displacing the air with nitrogen, 216 grams of vinylidene chloride, 24 grams of methyl methacrylate and an aqueous solution of potassium persulfate (1.9 grams/80 ml) from which the air had been displaced by nitrogen, were added dropwise in a closed system over a period of 12 hours at 55° C. with stirring. After the dropwise addition, the mixture was stirred for an additional period of 3 hours at 55° C. and then 40 more grams of vinylidene chloride, 3 grams of acrylonitrile, 1.5 grams of methacrylic acid and an aqueous solution of potassium persulfate (0.6 gram/20 ml) were added dropwise over a period of 4 hours at 55° C. After the dropwise feeding had been completed, the mixture was stirred for 3 hours at 55° C. and then the unreacted monomer was removed by bubbling nitrogen through the mixture to obtain the desired latex compound.

The solid fraction concentration was 49.8%, the average particle size was 76 nm and the weight average molecular weight was 36,200. Compound 2 of the present invention was determined by elemental analysis and NMR to have the structure indicated below.

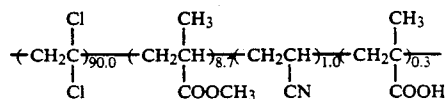


SYNTHESIS EXAMPLE 3

Preparation of Compound 3 of the Present Invention

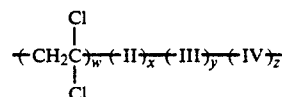
The desired latex was obtained by changing the emulsifying agent in Synthesis Example 1 from sodium alkylbenzenesulfonate to sodium laurylsulfate. The solid fraction concentration was 49.2%, the average particle size was 83 nm and the weight average molecular weight was 31,000.

Compound 3 of the present invention was determined by elemental analysis and NMR to have the structure indicated below.



SYNTHESIS EXAMPLE 4

Compounds 4-20 of the present invention were prepared on the basis of Synthesis Examples 1 and 2 having the structure as indicated in the general formula and Table below.

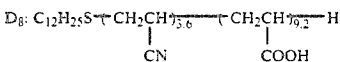
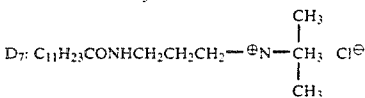
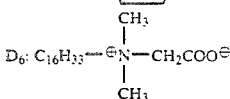
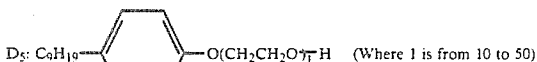
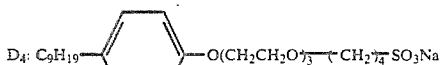


Compound of the invention	II	III	IV	Other monomer components	Based on example of synthesis	Emulsifying agent used	w/x/y/z (wt %)	Solid fraction concentration	Average particle size	Weight average molecular weight
4	II-4	III-2	IV-1	—	1	D ₁	90.1/8.8/0.9/0.2	50.6	132	32100
5	II-4	III-2	IV-2	—	2	D ₁	89.8/8.8/1.1/0.3	48.8	110	40700
6	II-4	III-1	IV-1	—	1	D ₁	91.5/6.8/1.2/0.5	49.2	128	21000
7	II-1	III-1	IV-2	—	2	D ₂	90.3/8.6/0.8/0.3	51.1	105	38500
8	II-1/ II-4 (1/3)	III-1	IV-2	—	1	D ₁	89.7/8.4/1.5/0.4	45.5	88	22200
9	II-4	III-1	IV-1/ IV-2 (1/1)	—	2	D ₂	89.0/8.9/1.8/0.3	49.7	128	18000
10	II-4	III-1	IV-2	—	1	D ₃	90.0/8.7/0.9/0.4	49.6	139	21400
11	II-4	III-1	IV-2	—	2	D ₁ - D ₃ (1/1)	90.2/8.4/1.0/0.4	48.8	97	27600
12	II-4	III-1	IV-4	—	1	D ₁	90.5/8.2/1.1/0.2	38.8	155	33900
13	II-4	III-1	IV-3	—	1	D ₁	90.3/7.6/1.4/0.7	42.6	146	41000
14	II-4	III-1	IV-6	—	1	D ₃	91.3/6.4/1.3/1.0	43.2	101	31600
15	II-4	III-2	IV-2	$\text{CH}_2=\text{C}-\text{CH}_3$ $\text{COOCH}-\text{CH}_2$ O	2	D ₁	90.7/7.2/1.1/0.5/0.5	47.2	83	15800
16	II-2	III-1	IV-2	—	2	D ₄	89.8/7.6/1.1/1.5	45.8	77	34100
17	II-5	III-1	IV-2	—	2	D ₅	89.9/7.3/2.5/0.3	43.6	78	24200

-continued

Compound of the invention	II	III	IV	Other monomer components	Based on example of synthesis	Emulsifying agent used	w/x/y/z (wt %)	Solid fraction concentration	Average particle size	Weight average molecular weight
18	II-3	III-1	IV-2	—	1	D ₆	90.1/7.7/ 1.7/0.5	38.2	115	33900
19	II-6	III-1	IV-2	—	2	D ₇	90.7/6.9/ 1.8/0.6	39.6	82	44000
20	II-9	III-1	IV-2	—	2	D ₈	91.0/6.0/ 1.0/2.0	40.3	85	8900

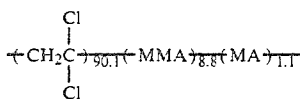
In the Table above:

D₁: Sodium alkylbenzenesulfonateD₂: Sodium laurylsulfonateD₃: C_nH_{2n-1}SO₃Na

SYNTHESIS EXAMPLE 5

Comparative compounds 101-103 were prepared with half the amount of potassium persulfate as employed in Synthesis Examples 1 and 2.

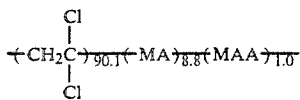
Comparative Compound 101



MMA: methyl methacrylate
MA: methyl acrylate

The solid fraction concentration was 48.9%, the average particle size was 89 nm and the weight average molecular weight was 79,600.

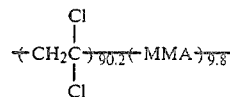
Comparative Compound 102



MAA: methacrylic acid
MA: methyl acrylate

The solid fraction concentration was 45.5%, the average particle size was 78 nm and the weight average molecular weight was 58,800.

Comparative Compound 103



MMA: methyl methacrylate

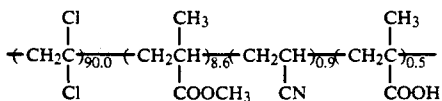
The solid fraction concentration was 48.3%, the average particle size was 83 nm and the weight average molecular weight was 84,000.

SYNTHESIS EXAMPLE 6

Preparation of Comparative Compound 104

Water (200 ml), 2.8 grams of sodium alkylbenzenesulfonate and 0.75 grams of potassium persulfate were introduced into a closed system. The air was displaced by nitrogen, and a monomer mixture comprising 270 grams of vinylidene chloride, 25 grams of methyl methacrylate, 3.0 grams of acrylonitrile, 1.5 grams of IV-2 and an aqueous solution of sodium hydrogen sulfite (0.65 gram/100 ml) from which the air had been displaced by nitrogen, was added dropwise over a period of 16 hours at 50° C. with stirring. After the drip feed had been completed the mixture was stirred for 2 hours at 50° C., the unreacted monomer was removed by bubbling nitrogen through the mixture, and then an additional 2.0 grams of sodium alkylbenzenesulfonate was added to obtain the desired latex.

The solid fraction concentration was 50.8%, the average particle size was 87 nm and the weight average molecular weight was 68,400. Comparative Compound 104 was determined by elemental analysis and NMR to have the structure indicated below.



The generally known coating methods, for example dip coating, air knife coating, curtain coating, roller coating, wire bar coating and gravure coating, or the extrusion coating method in which a hopper is used as disclosed in U.S. Pat. No. 2,681,294, for example, can be used for coating the polyester support with a vinylidene chloride copolymer latex of the present invention.

Compounds well known in the industry as hardening agents can be included in the vinylidene chloride copolymer coating liquids of the present invention. For example, use can be made of the triazine based compounds disclosed, for example, in U.S. Pat. Nos. 3,325,287, 3,288,775 and 3,549,377, and Belgium Patent 6,602,226, the dialdehyde based compounds disclosed, for example, in U.S. Pat. Nos. 3,291,624 and 3,232,764, French Patent 1,543,694 and British Patent 1,270,578, the epoxy based compounds disclosed, for example, in U.S. Pat. No. 3,091,537 and JP-B-49-26580, the vinyl based compounds disclosed in U.S. Pat. No. 3,642,486, the aziridine based compounds disclosed in U.S. Pat. No. 3,392,024, the ethyleneimine based compounds disclosed, for example, in U.S. Pat. No. 3,549,378, and methylol based compounds.

The use of triazine based compounds and dialdehyde compounds, and epoxy based compounds from among these hardening agents is preferred.

The addition amount of the hardening agent is from 0.001 to 30 grams per liter of vinylidene chloride copolymer coating liquid.

The thickness of the coated vinylidene chloride copolymer layer of the present invention is preferably greater than that required to suppress the expansion of the base by the uptake of water during development processing operations. However, if the vinylidene chloride copolymer layer is too thick, it will have an adverse effect on the adhesion of the silver halide emulsion layer.

In view of the above considerations, the thickness of the vinylidene chloride copolymer layer is at least 0.3 μm but not more than 5 μm, and preferably at least 0.5 μm but not more than 2.0 μm. The thickness of the films according to the present invention is defined as in a dry state.

The polyester support of the present invention is a polyester prepared from an aromatic dibasic acid and a glycol as the principal components. Typical dibasic acids include terephthalic acid, isophthalic acid, p-β-oxyethoxybenzoic acid, diphenylsulfone di-carboxylic acid, diphenoxyethane dicarboxylic acid, adipic acid, sebacic acid, azelaic acid, 5-sodium sulfo-isophthalic acid, diphenylene dicarboxylic acid, and 2,6-naphthalene dicarboxylic acid. Typical glycols include ethylene glycol, propylene glycol, butanediol, neopentylene glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, 1,4-bisoxoethoxybenzene, bis-phenol A, diethylene glycol and polyethylene glycol.

Poly(ethylene terephthalate) is the most desirable of the above described polyesters with respect to commercial availability.

No particular limitation is imposed upon the thickness of the polyester support, but a thickness of from about 12-500 μm, and preferably from about 40-200

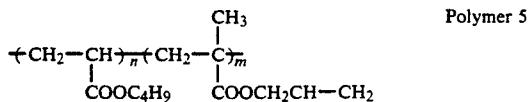
μm, is useful with respect to ease of handling and general applicability. The biaxially extended crystallized polyesters are preferred from with respect to stability and strength, for example. A layer which adheres to the above described polymer layer and the emulsion layer can be established as an subbing layer in order to improve the strength of adhesion between the polymer layer and the emulsion layer (JP-A-51-114120 and 50-131516). Furthermore, the surface of the vinylidene chloride-containing copolymer layer may be subjected to a preliminary corona discharge treatment, ultraviolet irradiation treatment or a flame treatment, for example, in order to further improve the adhesion properties.

The hydrophilic colloid layers of the photosensitive material of the present invention are silver halide emulsion layers, backing layers, protective layers and intermediate layers, for example, and a hydrophilic colloid is contained in these layers. Gelatin is the most desirable hydrophilic colloid. Any of the gelatins, such as lime treated gelatin, acid treated gelatin, enzyme treated gelatin and modified gelatin, for example, which are generally used in the industry can be used, but lime treated gelatin and acid treated gelatin are preferred.

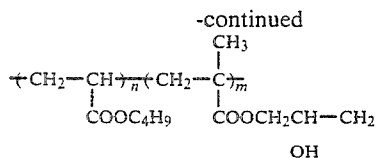
Furthermore, use can be made of proteins such as colloidal albumin and casein, cellulose compounds such as carboxymethylcellulose and hydroxyethylcellulose, sugar derivatives such as starch derivatives, sodium alginate and agar, and synthetic hydrophilic colloids such as poly(vinyl alcohol), poly(N-vinylpyrrolidone) poly(acrylic acid) copolymers, polyacrylamide and derivatives and partial hydrolyzates thereof as well a gelatin. Mixtures of two or more of these colloids can be used, as required.

A polymer latex is contained in at least one hydrophilic colloid layer of the present invention. The preferred polymer latexes are aqueous dispersions of water insoluble polymers having a molecular weight of 1,000 to 1,000,000 preferably 50,000 to 500,000 and an average particle size of from 20 mμ to 700 mμ, and the amount used, in terms of the dry weight ratio with the amount of gelatin used as a binder, is from 0.01 to 1.0, and preferably from 0.1 to 0.8 (JP-A-51-130217).

Preferred examples of polymer latexes are indicated below.



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Polymer 6

5

The polymer latex which the present invention is included in at least one hydrophilic colloid layer. For example, the polymer latex may be contained in a silver halide emulsion layer, a backing layer, a protective layer or an intermediate layer.

The present invention is especially effective for preparing an ultra-high contrast sensitive material containing a hydrazine derivative.

Hydrazine derivative containing ultra-high contrast sensitive materials and methods of image formation employing these materials are disclosed, for example, in U.S. Pat. Nos. 4,224,401, 4,168,977, 4,166,742, 4,241,164 and 4,272,606, JP-A-60-83028, JP-A-60-218642, JP-A-60-258537 and JP-A-61-223738.

When a hydrazine derivative is used in the photographic material of the present invention, the hydrazine derivative is added in an amount of 1×10^{-6} to 5×10^{-2} mol/mol-Ag, preferably 1×10^{-5} to 2×10^{-2} mol/mol-

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Ag into any layer over the support at silver halide emulsion side, such as silver halide emulsion layer, intermediate layer, protective layer, etc., preferably silver halide layer. The hydrazine derivative is preferably a compound represented by the general formula (Q) indicated below.



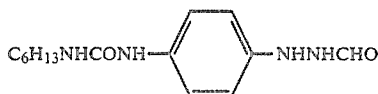
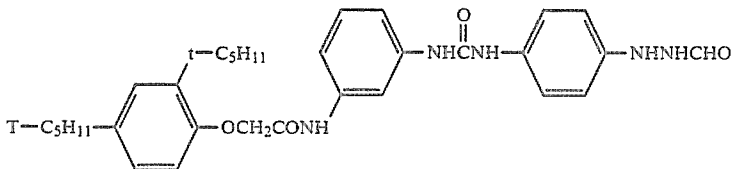
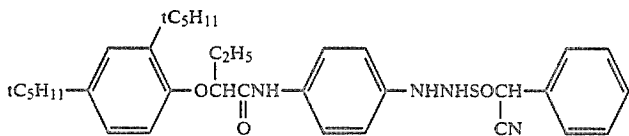
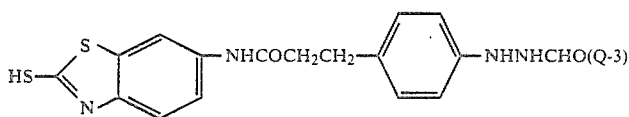
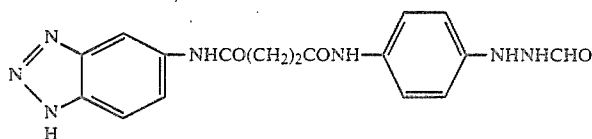
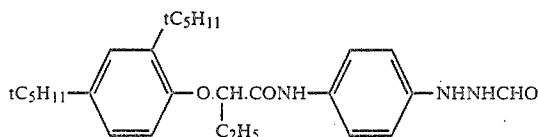
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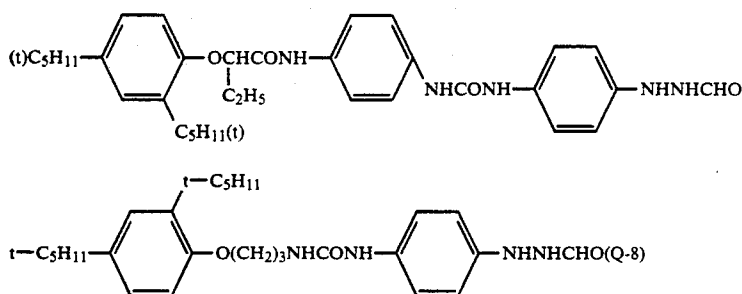
In the formula Q, A'' represents an aliphatic group or an aromatic group and B'' represents a formyl group, an acyl group, an alkyl or aryl sulfonyl group, an alkyl or aryl sulfanyl group, a carbamoyl group, an alkoxy or aryloxy carbonyl group, a sulfenamoyl group, an alkoxy-sulfonyl group, a thioacyl group, a thiocarbamoyl group, a sulfanyl group or a heterocyclic group, and X and Y are either both are hydrogen atoms, or one of X and Y is a hydrogen atom and the other is a substituted or unsubstituted alkylsulfonyl group or a substituted or unsubstituted arylsulfonyl group or a substituted or unsubstituted acyl group.

Useful examples of the hydrazine derivative represented by formula (Q) are indicated below.



-continued

(Q-7)



Moreover, the present invention is effective when the photosensitive material contains a tetrazolium compound and is subjected to high contrast processing using PQ type or MQ type developers which contain comparatively high concentrations of sulfite in which PQ type developers comprises developing agents of pyrazolone and hydroquinone, and MQ type comprises agents of methol and hydroquinone. Methods of image formation using tetrazolium compounds are disclosed, for example, in JP-A-52-18317, JP-A-53-17719 and JP-A-53-17720.

The silver halide emulsion for use in the photosensitive material of the present invention are generally prepared by mixing a solution of a water soluble silver salt (for example silver nitrate) and a solution of a water soluble halogen salt (for example potassium bromide) in the presence of a water soluble polymer solution such as a gelatin solution.

Silver chloride, silver bromide, silver chlorobromide, silver iodobromide and silver chloriodobromide can all be used as the silver halide, and no particular limitation is imposed on the form of the grains or the grain size distribution.

The silver halide emulsion layer can contain photosensitive silver halide, chemical sensitizers, spectral sensitizers, anti-foggants, hydrophilic colloids (especially gelatin), hardening agents such as gelatin hardening agents, surfactants for improving the physical properties of the film, and thickeners, for example. Reference can be made to the disclosures of *Research Disclosure*, Vol. 176, Item 17643 (December 1978), and in JP-A-52-108130, JP-A-52-114328, JP-A-52-121321, JP-A-53-3217 and JP-A-53-44025 in connection with these materials.

The surface protective layer has a thickness of from 0.3 to 3 μm , and preferably from 0.5 to 1.5 μm and contains a hydrophilic binder such as gelatin. The surface protective layer may contain matting agents such as fine particles of poly(methyl methacrylate), colloidal silica and, as required thickeners such as poly(potassium styrenesulfonate), gelatin hardening agents, surfactants, slip agents and UV absorbers, for example.

Examples of useful gelatin hardening agents include chrome salts, aldehydes (for example formaldehyde and glutaraldehyde), N-methylol compounds (for example dimethylolurea), active vinyl compounds (for example, 1,3,5-triacryloyl-hexahydro-s-triazine, bis(vinylsulfonyl)methyl ether, N,N-methylenebis- β -(vinylsulfonyl)propionamide), active halogen compounds (for example, 2,4-dichloro-6-hydroxy-s-triazine), mucohalogen acids (for example, mucochloric acid), N-carbamoylpyridinium salts (for example, (1-morpholinocarbonyl-3-pyridinio)methanesulfonate) and haloamidinium salts (for example, 1-(1-chloro-1-pyridinomethylene)pyrrolidinium 2-naphthalenesulfon-

ate), and these compounds can be used individually or in combination. From among the above described compounds, the use of the active vinyl compounds disclosed in JP-A-53-41220, JP-A-53-57257, JP-A-59-162546 and JP-A-60-80846, and the active halogen compounds disclosed in U.S. Pat. No. 3,325,287 are preferred.

The backing layer is a non-photosensitive layer containing a hydrophilic colloid such as gelatin as a binder. The backing layer may have a single layer structure or a multi-layer structure including intermediate and protective layers, for example.

The thickness of the backing layer is from 0.1 to 10 μm , and as in the silver halide emulsion and surface protective layers the backing layer may contain gelatin hardening agents, surfactants, matting agents, colloidal silica, slip agents, UV absorbers, dyes and thickeners, for example.

The present invention can be applied to a variety of photographic materials which have hydrophilic colloid layers, and generally is useful with photographic materials employing silver halide as the photosensitive component including, for example, photosensitive materials for printing purposes, photosensitive materials for X-ray purposes, general negative photosensitive materials, general reversal photosensitive materials, general positive photosensitive materials and direct positive photosensitive materials. The effect of the present invention is especially pronounced when used in a photosensitive material for printing purposes.

No particular limitation is imposed on the methods of exposing and developing the photosensitive materials of the present invention, and reference can be made to the disclosures of, for example, JP-A-52-108130, JP-A-52-114328 and JP-A-52-121321, and the above noted Research Disclosure in this connection.

In accordance with a preferred embodiment of the present invention, a silver halide photosensitive material having excellent dimensional stability with respect to environmental fluctuations and excellent dimensional stability with respect to processing is obtained by arranging a hydrophilic colloid containing a polymer latex on at least one side of a polyester support, while covering both sides of the support with a vinylidene chloride copolymer comprising a core/shell type latex having an average molecular weight of not more than 45,000.

Furthermore, in accordance with a second preferred embodiment of the present invention, a silver halide photosensitive material having excellent adhesion between the vinylidene chloride copolymer layer and the support and especially between the vinylidene chloride copolymer layer and the adjoining binder layer, is obtained by including repeating unit derived from a mono-

mer having functional groups which bond either directly or via a film hardening agent with the binder in the vinylidene chloride copolymer.

The invention is described in detail below by means of illustrative examples, but the invention is not limited by these examples.

EXAMPLE 1

The under-layer 1 and the under-layer 2 indicated below were both coated in order from the support onto each side of a biaxially extended poly(ethylene terephthalate) support of thickness 100 μm to prepare un-

-continued

(1) Under-layer 1 Formulation

particle size 2.5 μm)	coated weight of 80 mg/m ²
Distilled water	Added to make a total of 100 parts by weight

After adjusting to pH 6 by adding 10% KOH, the coating liquid was coated onto the support to provide a dry film thickness as indicated in Table 1 and dried for 2 minutes at 185° C.

(2) Under-layer 2 Formulation

Gelatin	1 part by weight
Methyl cellulose	0.05 part by weight
$\text{HO}-\left[\begin{array}{c} \text{C} \\ \parallel \\ \text{O} \end{array} \text{---} (\text{CH}_2)_4 \text{---} \begin{array}{c} \text{C} \\ \parallel \\ \text{O} \end{array} \text{---} \text{NH}(\text{CH}_2)_2 \text{---} \text{N} \begin{array}{c} \\ \text{CH}_2 \\ \\ \text{CHOH} \\ \\ \text{CH}_2\text{Cl} \end{array} \text{---} (\text{CH}_2)_2 \text{---} \text{NH} \right]_4 \text{---} \text{HCl}$	0.02 part by weight
C ₁₂ H ₂₅ O(CH ₂ CH ₂ O) ₁₀ H	0.03 part by weight
Distilled water	98.9 parts by weight

dercoated supports 1011-110.

(1) Under-layer 1 Formulation

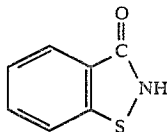
Vinylidene chloride latex (of the type indicated in Table 1)	15 parts by weight
2,4-Dichloro-6-hydroxy-s-triazine, sodium salt	0.15 part by weight
Fine polystyrene particles (average	Added to provide a

This coating liquid was coated to provide a dry film thickness of 0.1 μm and dried for 2 minutes at 170° C. to provide an undercoated support.

The backing layer 1 (electrically conductive layer) and the protective layer 2 were coated in order from the support onto a first side of the undercoated support. The silver halide emulsion layer 1, the silver halide layer 2, the protective layer 2 and the protective layer 3 were coated in order from the support onto the second side of the support to provide samples 101-110.

(1) Backing Layer 1 Formulation (Electrically Conductive Layer)

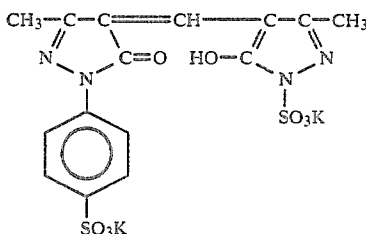
SnO ₂ /Sb (9/1 by weight, average particle size 0.25 μm)	300 mg/m ²
Gelatin	170 mg/m ²
Compound 1	7 mg/m ²



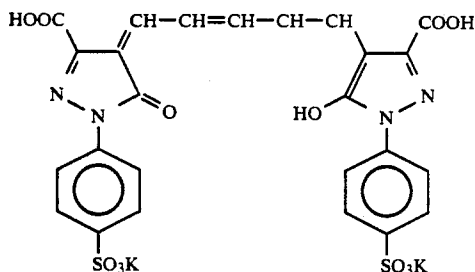
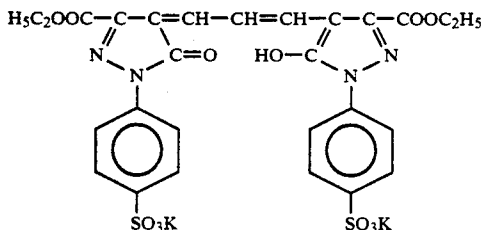
Sodium dodecylbenzenesulfonate	10 mg/m ²
Sodium dihexyl-α-sulfosuccinate	40 mg/m ²
poly(styrenesulfonic acid), sodium salt	9 mg/m ²

(2) Protective Layer 2 Formulation

Gelatin	2.9 mg/m ²
Compound 2	300 mg/m ²



-continued

Compound 3 50 mg/m²Compound 4 50 mg/m²

Compound 1 10 mg/m²
 Sodium dodecylbenzenesulfonate 70 mg/m²
 Sodium dihexyl- α -sulfosuccinate 15 mg/m²
 1,3-Divinylsulfonyl-2-propanol 150 mg/m²
 Ethyl acrylate latex (average particle size 0.05 μ m) 500 mg/m²
 Potassium perfluorooctanesulfonate 10 mg/m²
 Finely powdered silicon dioxide powder (average particle size 3.5 μ m, pore diameter 170 Å , surface area 300 m²/gram) 35 mg/m²

(3) Silver Halide Emulsion

Layer 1 Formulation

Liquid I: Water 300 ml, Gelatin 9 grams
 Liquid II: AgNO₃ 100 grams, Water 400 ml
 Liquid III: NaCl 37 grams, (NH₄)₃RhCl 1.1 mg, Water 400 ml

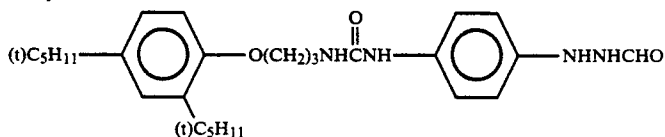
Liquids II and III were added at the same time and at a fixed rate to liquid I, the temperature of which was maintained at 45° C. After removing the soluble salts using a the normal method well known in the industry, gelatin was added to the emulsion and 6-methyl-4-hydroxy-1,3,3a,7-tetra-azaindene was added as a stabilizer. This emulsion was a mono-disperse emulsion of average grain size 0.20 μ m, and the gelatin content was 60 grams per kg of emulsion recovered.

The compounds indicated below were added to the emulsion thus obtained.

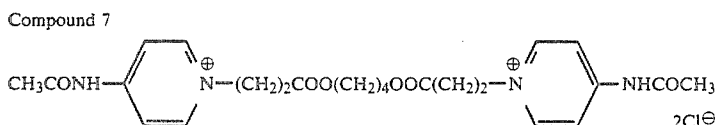
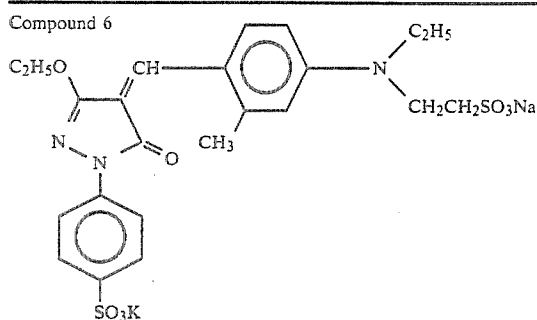
45	Compound 5	6×10^{-3} mol/mol · Ag
	Compound 6	60 mg/m ²
	Compound 7	9 mg/m ²
	Compound 1	10 mg/m ²
	Poly(styrenesulfonic acid), sodium salt	50 mg/m ²
	N-Oleoyl-N-methyltaurine, sodium salt	40 mg/m ²
50	1,2-Bis(vinylsulfonylacetamido)ethane	70 mg/m ²
	1-Phenyl-5-mercaptotetrazole	3 mg/m ²
	Ethyl acrylate latex (average particle size 0.05 μ m)	0.46 g/m ²

55 The coating liquid thus obtained was coated to provide a coated silver weight of 2.0 g/m².

Compound 5



-continued



(4) Silver Halide Emulsion Layer 2 Formulation

Liquid I:	Water 300 ml, Gelatin 9 grams
Liquid II:	AgNO ₃ 100 grams, Water 400 ml
Liquid III:	NaCl 37 grams, (NH ₄) ₃ RhCl 2.2 mg, Water 400 ml

An emulsion was prepared by adding liquids II and III at the same time to liquid I using the same procedure as for the emulsion of formulation (3). This emulsion was a mono-disperse emulsion of average grain size 0.20 μ m.

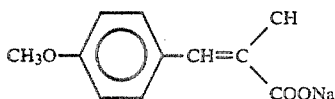
The compounds and emulsified dispersion of a hydrazine derivative indicated below were added to the emulsion obtained.

Emulsified dispersion of hydrazine derivative	5×10^{-3} mol/mol · Ag
Compound 6	(as Compound 5) 60 mg/m ²
Compound 7	9 mg/m ²
Compound 1	10 mg/m ²
Poly(styrenesulfonic acid), sodium salt	50 mg/m ²
N-Oleoyl-N-methyltaurine, sodium salt	40 mg/m ²
1,2-Bis(vinylsulfonylacetamido)ethane	80 mg/m ²
1-Phenyl-5-mercaptotetrazole	3 mg/m ²
Ethyl acrylate latex (average particle size 0.05 μ m)	0.40 g/m ²

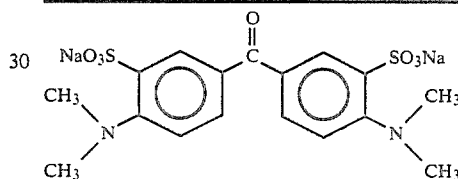
The coating liquid thus obtained was coated in to provide a coated silver weight of 1.3 g/m².

(5) Protective Layer 2 Formulation

Gelatin	1.0 g/m ²
α -Lipoic acid	10 mg/m ²
Sodium dodecylbenzenesulfonate	5 mg/m ²
Compound 6	40 mg/m ²
Compound 8	20 mg/m ²
Poly(styrenesulfonic acid), sodium salt	10 mg/m ²
1-Phenyl-5-mercaptotetrazole	5 mg/m ²
Compound 9	20 mg/m ²
Ethyl acrylate latex (average particle size 0.05 μ m)	200 mg/m ²
Compound 8	



-continued



(6) Protective Layer 3 Formulation

Gelatin	1.0 g/m ²
Finely powdered silicon dioxide particles (average particle size 3.5 μ m, pore diameter 25 Å, surface area 700 m ² /gram)	50 mg/m ²
Liquid paraffin (gelatin dispersion)	43 mg/m ²
Sodium dodecylbenzenesulfonate	20 mg/m ²
Potassium perfluorooctanesulfonate	10 mg/m ²
N-Perfluorooctanesulfonyl-N-propylglycine, potassium salt	3 mg/m ²
Poly(styrenesulfonic acid), sodium salt	2 mg/m ²
Sodium salt of the sulfate ester of poly-(degree of polymerization 5)-oxy-ethylene nonyl phenyl ether	20 mg/m ²
Colloidal silica (particle size 15 μ m)	20 mg/m ²

Method for the Preparation of an Emulsified Dispersion of a Hydrazine Derivative used in the silver halide emulsion layer 2

	Liquid I	
55	Compound 5	3.0 grams
	Compound 10	1.5 grams
	Poly(N-tert-butylacrylamide)	6.0 grams
	Ethyl acetate	30 ml
	Sodium dodecylbenzenesulfonate (72% methanol solution)	0.12 gram
60	Water	0.12 ml

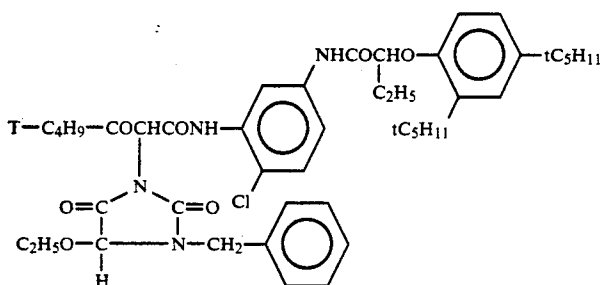
A uniform solution of Liquid I was prepared by heating to 65° C.

65	Liquid II	
	Gelatin	12 grams
	Compound 1	0.02 gram

-continued	
Liquid II	
Water	108 ml

A uniform solution of Liquid II was prepared by heating to 65° C.

Liquid I and liquid II were mixed together and stirred at high speed in a homogenizer (made by Nippon Seiki Seisakujo) to obtain a fine particle emulsified dispersion was obtained. The ethyl acetate was removed from this emulsion by heating under reduced pressure distillation, after which water was added to make a total of 250 grams. The residual ethyl acetate content was 0.2%.



The samples thus obtained were stored for 2 weeks at 25° C., 60% RH and were then evaluated in terms of the change in dimension during processing, dry adhesion properties and wet adhesion properties as described below.

Method of Evaluating the Change in Dimension During Processing

Two holes of diameter 8 mm were made with a spacing of 200 mm in the sample and, after storage at 25° C., 30% RH, the distance between the two holes was measured precisely using a pin gauge of 1/1000 mm accuracy. The length of the first measurement was taken to be X mm. Next, the sample was developed, fixed, washed with water for 20 seconds at 25° C. and dried for about 1 minutes in an automatic processor. The dimension was again measured 5 minutes after the completion of processing. The length of the second measurement was taken to be Y mm. The fractional change in dimension (%) on processing is reported herein as $[(Y-X)/200] \times 100$.

It is recognized in the industry that a fractional change in dimension within $\pm 0.01\%$ is acceptable in practice.

The development and fixing processing were each carried out for 20 seconds at 38° C. in an FG-660 automatic processor made by the Fuji Photographic Film Co. using GR-D1 developer and GR-F1 fixer made by the same company. The drying temperature was 45° C.

Method of Evaluating Adhesion

Seven longitudinal and transverse cuts were made with a razor in the surface of a sample which had been equilibrated for 3 days at 25° C. and 55% RH to form a

pattern of 36 squares. Sticky tape (Nitto Tape, made by Nitto Denki Kogyo Co.) was then adhered over the surface of the sample and pulled off rapidly in a direction of 180°. Using the above procedure, those samples wherein the unpeeled part was 95% or more of the total surface area were classified as being of grade A, those samples wherein the remaining part was 90% or more but less than 95% were classified as being of grade B, those samples wherein the remaining part was 60% or more but less than 90% were classified as being of grade C, and those samples wherein the remaining part was less than 60% were classified as being of grade D. An adhesive strength of practical value and satisfactory for durability is that classified as being grade A.

Compound 10

Method of Evaluating Adhesion When Wet

Scratches in the form of a cross were made using a pencil on the emulsion surface of the film in the processing bath during each of the stages of development, fixing and water washing. The crosses were then rubbed five times with the tip of a finger with about the same degree of applied pressure, and the strength of adhesion was assessed by the maximum width off peeling.

For samples where there was no peeling of the emulsion layer beyond the cut, the material was classified as being of grade A. For samples where the maximum width of peeling was within 2 mm, the material was classified as being of grade B. For samples where the maximum width of peeling was within 5 mm, the material was classified as being of grade C. All other samples were classified as being of grade D. A strength of adhesion sufficiently durable in practice for a photographic sensitive material is that classified as grade A among the four levels of assessment indicated above.

Moreover, the development processing was carried out under the conditions indicated below.

Development GR-D1 (made by Fuji Photographic Film Co.)	38° C., 20 seconds
Fix GR-F1 (made by Fuji Photographic Film Co.)	38° C., 20 seconds
Water Wash	25° C., 20 seconds

The results of these evaluations are shown in Table 1 below. It is clearly seen that the samples of the present invention provide remarkably superior dry adhesion properties.

TABLE 1

Sample Number	Vinylidene Chloride Latex	Thickness of First Under-Layer (μm) (%)	Change in Dimensions on Processing (%)	Adhesion When Dry	Adhesion When Wet
101 (Invention)	Prep. Compound 1	0.3	0.010	A	A

TABLE 1-continued

Sample Number	Vinylidene Chloride Latex	Thickness of First Under-Layer (μm) (%)	Change in Dimensions on Processing	Adhesion When Dry	Adhesion When Wet
102 (Invention)	As Above	0.4	0.009	A	A
103 (Invention)	As Above	0.5	0.009	A	A
104 (Invention)	As Above	0.7	0.007	A	A
105 (Invention)	As Above	0.9	0.006	A	A
106 (Invention)	Prep. Compound 2	0.9	0.007	A	A
107 (Invention)	Prep. Compound 3	0.9	0.006	A	A
108	Comparative Compound 101	0.9	0.007	D	A
109	Comparative Compound 102	0.9	0.006	C	A
110	Comparative Compound 103	0.9	0.006	D	A

EXAMPLE 2

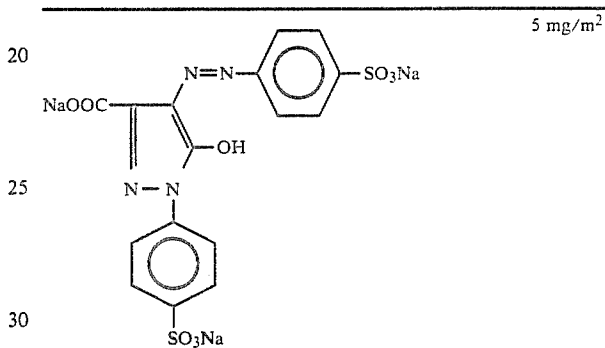
Undercoated supports 201-210 were prepared in the same way as in example 1 except that the type of vinylidene chloride latex used in the first under-layer was changed as shown in Table 2 below.

A silver halide emulsion layer and a protective layer 1 were coated in order from a first side of the support of the undercoated supports 201-210, and a backing layer and the protective layer 2 were coated in order the second side of the support to prepare samples 201-210.

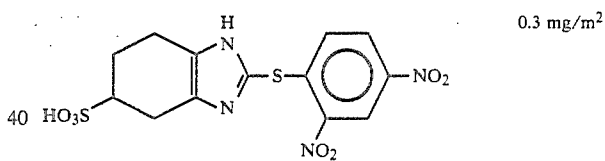
Liquid I:	Water 300 ml, gelatin 9 grams
Liquid II:	AgNO ₃ 100 grams, water 400 ml
Liquid III:	NaCl 37 grams, (NH ₄) ₂ RhCo ₆ 0.6 gram, water 400 ml

Liquids II and III were added at the same time and at a fixed rate to liquid I which was maintained at 40° C. After removing the soluble salts using a flocculation method well known in the industry, gelatin was added to the emulsion and 6-methyl-4-hydroxy-1,3,7-tetra-azaindene and 4-hydroxy-5,6-trimethylene-1,3,3a,7-tetra-azaindene were added as stabilizers. The resulting emulsion was a mono-disperse emulsion of average grain size 0.15 μm , and the gelatin content was 60 grams per kg of emulsion recovered.

The compounds indicated below were added to the emulsion thus obtained.



Poly(styrenesulfonic acid), sodium salt 10 mg/m²
 1,2-Bis(vinylsulfonylacetamido)ethane 100 mg/m²
 Ethyl acrylate latex (average particle size 0.1 μm) 500 mg/m²



The coating liquid obtained in this way was coated as to provide a coated silver weight of 3 g/m²

(2) Protective Layer 1 Formulation

5 mg/m²

Sodium dodecylbenzenesulfonate	25 mg/m ²
Sodium dihexyl- α -sulfosuccinate	10 mg/m ²
N-Perfluorooctanesulfonyl-N-propylglycine, potassium salt	2 mg/m ²
Poly(styrenesulfonic acid), sodium salt	3 mg/m ²
Ethyl acrylate latex (average particle size 0.1 μm)	200 mg/m ²
Colloidal silica	350 mg/m ²
Lipoic acid	8 mg/m ²

-continued

(3) Backing Layer Formulation

Gelatin	2 g/m ²
	30 mg/m ²
	180 mg/m ²
	50 mg/m ²

Sodium dihexyl- α -sulfosuccinate	20 mg/m ²
Sodium dodecylbenzenesulfonate	30 mg/m ²
Poly(styrenesulfonic acid), sodium salt	30 mg/m ²
1,3-Divinylsulfonyl-2-propanol	100 mg/m ²
Ethyl acrylate latex (average particle size 0.1 μ m)	200 mg/m ²

(4) Protective Layer 2 Formulation

Gelatin	1 g/m ²
Fine poly(methyl acrylate) particles as used in the emulsion protective layer	40 mg/m ²
Sodium dihexyl- α -sulfosuccinate acid	10 mg/m ²
Sodium dodecylbenzenesulfonate	30 mg/m ²
Poly(styrenesulfonic acid), sodium salt	25 mg/m ²
Sodium acetate	30 mg/m ²

The completed samples were stored for 2 weeks at 25° C., 60% RH and were evaluated in the same way as described in Example 1.

The results obtained are shown in Table 2.

EXAMPLE 3

Undercoated supports 301-310 were prepared in the same way as in Example 1 except that the type of vinyl-

TABLE 2

Sample Number	Vinylidene Chloride Latex	Thickness of First Under-Layer (μ m) (%)	Change in Dimensions on Processing	Adhesion When Dry	Adhesion When Wet
201 (Invention)	Prep. Compound 4	0.3	0.010	A	A
202 (Invention)	As Above	0.4	0.009	A	A
203 (Invention)	As Above	0.5	0.009	A	A
204 (Invention)	As Above	0.7	0.007	A	A
205 (Invention)	As Above	0.9	0.005	A	A
206 (Invention)	Prep. Compound 6	0.9	0.006	A	A
207 (Invention)	Prep. Compound 8	0.9	0.006	A	A
208	Comparative Compound 101	0.9	0.005	D	A
209	Comparative Compound 102	0.9	0.005	C	A
210	Comparative Compound 103	0.9	0.005	D	A

dene chloride latex used in the first under-layer was coated as indicated in Table 3.

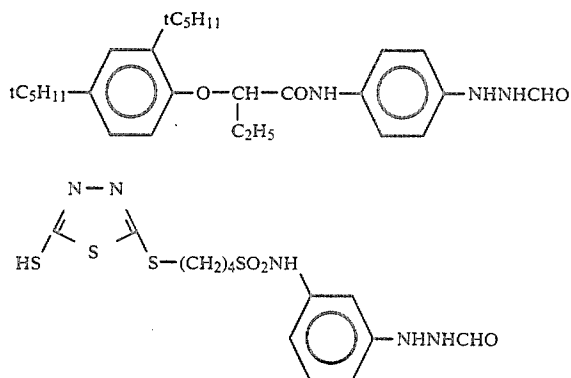
A silver halide emulsion layer, a protective layer 1 and a protective layer 2 were coated in order from the support on a first side of the undercoated supports 301-310. A backing layer and a protective layer 3 were also coated in order from the support onto the second side of the support to prepare samples 301-310.

(1) Silver Halide Emulsion Layer Formulation

An aqueous solution of silver nitrate and an aqueous

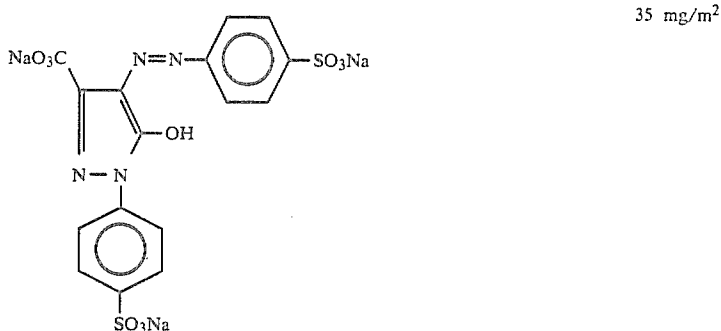
size 0.08 μm were obtained. After grain formation, the soluble salts were removed using a flocculation method well known in the industry, and then 4-hydroxy-6-methyl-1,3,3a,7-tetra-azaindene and 1-phenyl-5-mercaptotetrazole were added in an amount of 5×10^{-3} mol/mol-Ag and 5×10^{-4} mol/mol-Ag respectively, as stabilizers.

The compound represented by (Q-1) below was added to the emulsion in an amount of 1×10^{-3} mol/mol-Ag, and the compound represented by (Q-2) below was added in an amount of 1×10^{-4} mol/mol-Ag.



solution of sodium chloride containing 1.3×10^{-4} mol per mol-Ag of the ammonium salt of hexachlororhodium(III) acid were added at the same time over a period of 10 minutes to an aqueous gelatin solution maintained at 35° C. By controlling the potential to 200 mV, monodisperse cubic silver chloride grains of average particle

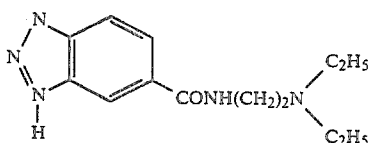
Moreover, poly(ethyl acrylate) was added in an amount of 50 wt % with respect to the gelatin as a solid fraction, and 35 mg/m² of the compound indicated below and 145 mg/m² of 2-bis(vinylsulfonylethyl)ethane as a hardening agent were added.



(2) Protective Layer 1 Formulation

Gelatin 1 g/m²
Thioctic acid 6 mg/m²

90 mg/m²

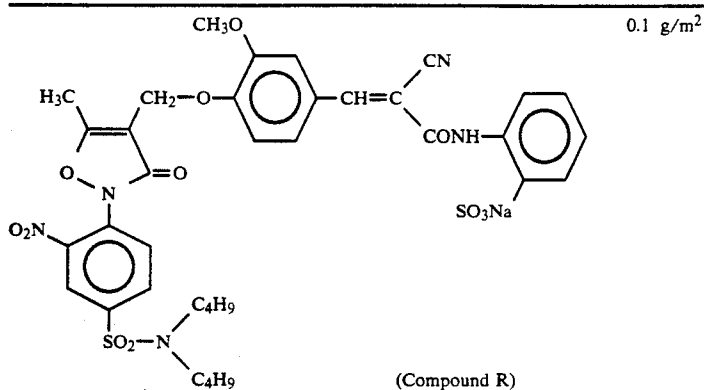


1,5-Dihydroxy-2-benzaldoxime 35 mg/m²
Sodium dodecylbenzenesulfonate 10 mg/m²
Poly(styrenesulfonic acid), sodium salt 20 mg/m²
Ethyl acrylate latex (average particle size 0.05 μm) 0.2 g/m²

(3) Protective Layer 2 Formulation

Gelatin 0.6 g/m²

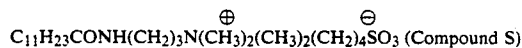
-continued

0.1 g/m²

Fine poly(methyl methacrylate particles (average particle size 2.5 μm)	20 mg/m ²
Fine silicon dioxide particles (average particle size 2.8 μm)	30 mg/m ²
N-Perfluorooctanesulfonyl-N-propyl- glycine, potassium salt	3 mg/m ²
Sodium dodecylbenzenesulfonate	20 mg/m ²
Hydroquinone	150 mg/m ²

Moreover, the compound R was added after forming a gelatin dispersion using the procedure indicated below.

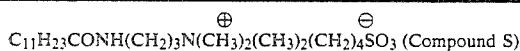
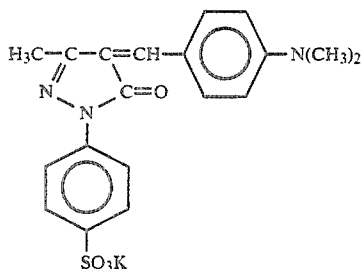
A solution obtained by dissolving 18.9 grams of compound R in 25 ml of N,N-dimethylsulfamide was mixed with agitation at 45° C. with 536 grams of a 6.5 wt % aqueous solution of gelatin to which 13 grams of compound S had been added to obtain the gelatin.



(4) Backing Layer Formulation

Gelatin	2.5 g/m ²
	0.26 g/m ²
	30 mg/m ²
	40 mg/m ²

-continued

90 mg/m²

Sodium dihexyl- α -sulfo succinate	30 mg/m ²
Sodium dodecylbenzenesulfonate	35 mg/m ²
1,3-Divinyldisulfonyl-2-propanol	130 mg/m ²
Ethyl acrylate latex (average particle size 0.05 μ m)	0.5 g/m ²
(5) Protective Layer 3 Formulation	
Gelatin	0.8 g/m ²
Fine poly(methyl methacrylate) particles (average particle size 3.4 μ m)	40 mg/m ²
Sodium dihexyl- α -sulfo succinate	9 mg/m ²
Sodium dodecylbenzenesulfonate	10 mg/m ²
Sodium acetate	40 mg/m ²

The samples 301-310 thus obtained were stored for 2 weeks at 25° C., 60% RH and then evaluated in the same way as described in Example 1. The results obtained are shown in Table 3.

size 0.2 μ m (Cl composition 95 mol %) was thus obtained.

The resulting emulsion was de-salted using a flocculation method, and then 1 mg/mol-Ag of thiourea dioxide

TABLE 3

Sample Number	Vinylidene Chloride Latex	Thickness of First Under-Layer (μ m) (%)	Change in Dimensions on Processing	Adhesion When Dry	Adhesion When Wet
301 (Invention)	Prep. Compound 15	0.3	0.009	A	A
302 (Invention)	As Above	0.4	0.008	A	A
303 (Invention)	As Above	0.5	0.007	A	A
304 (Invention)	As Above	0.7	0.007	A	A
305 (Invention)	As Above	0.9	0.006	A	A
306 (Invention)	Prep. Compound 16	0.9	0.005	A	A
307 (Invention)	Prep. Compound 20	0.9	0.006	A	A
308	Comparative Compound 101	0.9	0.006	D	A
309	Comparative Compound 102	0.9	0.005	C	A
310	Comparative Compound 103	0.9	0.005	D	A

EXAMPLE 4

Undercoated supports 401-410 were prepared in the same way as in Example 1 except that the type of vinylidene chloride latex used in the first under-layer was changed as indicated in Table 4 below.

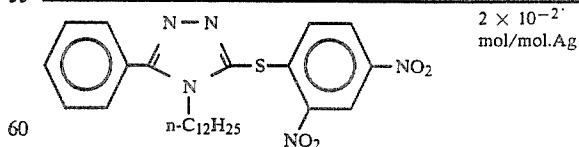
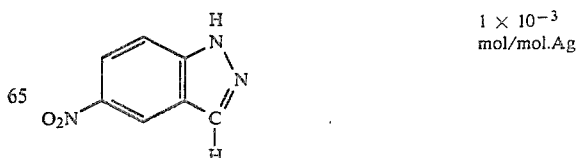
A silver halide emulsion layer and a protective layer 1 were coated in order from the support on a first side of the undercoated supports 401-410. A backing layer and a protective layer 2 were coated in order from the support onto the second side of the support to prepare samples 401-410.

(1) Silver Halide Emulsion Layer Formulation

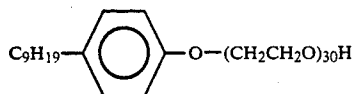
An aqueous solution of silver nitrate and a mixed aqueous solution of sodium chloride and potassium bromide were added at the same time over a period of 30 minutes and at a fixed rate in the presence of 2×10^5 mol/mol-Ag of rhodium chloride to an aqueous gelatin solution which was maintained at 50° C. A mono-disperse silver chlorobromide emulsion of average grain

and 0.6 mg/mol-Ag of chloroauric acid were added. The emulsion was ripened at 65° C. to attain maximum performance and the extent of fogging was controlled.

The compounds indicated below were also added to the emulsion.


 2×10^{-2}
mol/mol-Ag

 1×10^{-3}
mol/mol-Ag

-continued


 4×10^{-4}
mol/mol.Ag

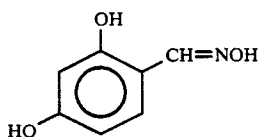
5

KBr	20 mg/m ²
Poly(styrenesulfonic acid), sodium salt	40 mg/m ²
2,6-Dichloro-6-hydroxy-1,3,5-triazine, sodium salt	30 mg/m ²

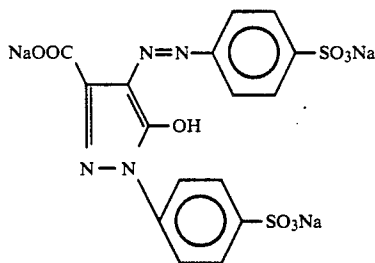
This coating liquid was coated to provide a coated silver weight of 3.5 g/m².

(2) Protective Layer 1 Formulation

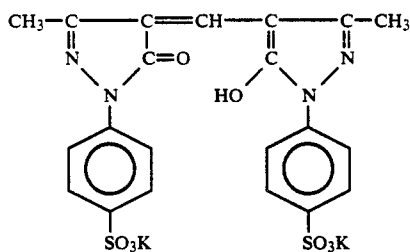
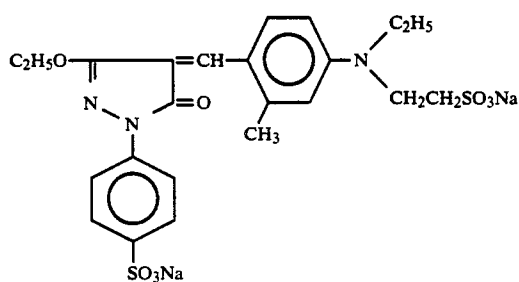
Gelatin	1.5 g/m ²
Fine SiO ₂ particles (average particle size 4 μm)	50 mg/m ²
Sodium dodecylbenzenesulfonate	50 mg/m ²

20 mg/m²

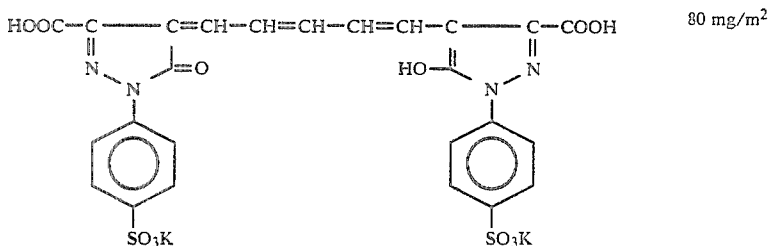
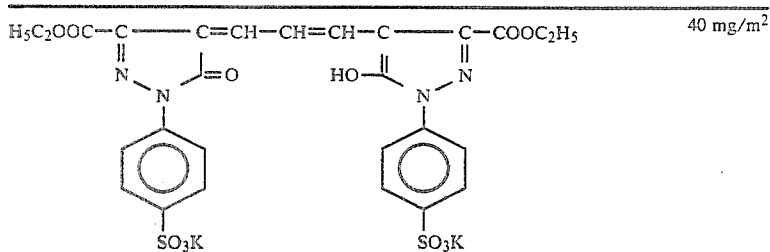
5-Nitroindazole	15 mg/m ²
1,3-Divinylsulfonyl-2-propanol	50 mg/m ²
N-Perfluorooctanesulfonyl-N-propylglycine, potassium salt	2 mg/m ²
Ethyl acrylate latex (average particle size 0.1 μm)	300 mg/m ²

100 mg/m²(3) Backing Layer Formulation

Gelatin	2.5 g/m ²
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30 mg/m²140 mg/m²

-continued



1,3-Divinylsufonyl-2-propanol	150 mg/m ²
Ethyl acrylate latex (average particle size 0.1 μm)	900 mg/m ²
Sodium dihexyl-α-sulfosuccinate	35 mg/m ²
Sodium dodecylbenzenesulfonate	35 mg/m ²
(4) Protective Layer 2 Formulation	
Gelatin	0.8 g/m ²
Fine poly(methyl methacrylate) particles (average particle size 3 μm)	20 mg/m ²
Sodium dihexyl-α-sulfosuccinate	10 mg/m ²
Sodium dodecylbenzenesulfonate	10 mg/m ²
Sodium acetate	40 mg/m ²

The finished samples were stored for 2 weeks at 25° C. and 60% RH, and were evaluated in the same way as described in Example 1. The results are shown in Table 4.

type of repeating unit represented the formulae (I), (III) and (IV):

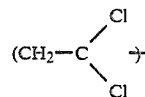
TABLE 4

Sample Number	Vinylidene Chloride Latex	Thickness of First Under-Layer (μm) (%)	Change in Dimensions on Processing	Adhesion When Dry	Adhesion When Wet
401 (Invention)	Prep. Compound 12	0.3	0.010	A	A
402 (Invention)	As Above	0.4	0.009	A	A
403 (Invention)	As Above	0.5	0.008	A	A
404 (Invention)	As Above	0.7	0.007	A	A
405 (Invention)	As Above	0.9	0.005	A	A
406 (Invention)	Prep. Compound 14	0.9	0.005	A	A
407 (Invention)	Prep. Compound 17	0.9	0.005	A	A
408	Comparative Compound 101	0.9	0.006	D	A
409	Comparative Compound 102	0.9	0.005	C	A
410	Comparative Compound 103	0.9	0.006	D	A

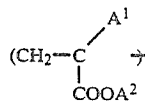
While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

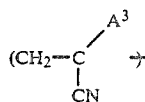
1. A silver halide photosensitive material comprising a polyester film support having thereon at least one hydrophilic colloid layer, at least one layer of which is a silver halide emulsion layer and at least one layer of which is a polymer latex containing hydrophilic colloid layer, said polyester film support having coated on each side thereof a vinylidene chloride copolymer having a weight average molecular weight not more than 45,000, said vinylidene chloride copolymer being a core/shell type latex, said core part containing at least one of each type of repeating unit represented by formulae (I) and (II) and the said shell part containing at least one of each

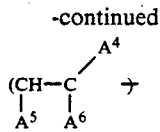


(II)



(III)





wherein A¹ represents a hydrogen atom, a methyl group or a halogen atom, A² represents a substituted or unsubstituted alkyl group or phenyl group, A³ represents a hydrogen atom or a methyl group, A⁴ represents a hydrogen atom, a methyl group or a —CH₂COOM group, A⁵ represents a hydrogen atom, a methyl group or a —COOM group, A⁶ represents a —COOM group or an alkoxy carbonyl group, phenyl group or N-alkylcarbamoyl group which is substituted with a —COOM group, and M represents a lithium, sodium, potassium or hydrogen atom.

2. A silver halide photosensitive material as in claim 1, wherein the vinylidene chloride copolymer has a weight average molecular weight of from 3,000 to 40,000.

3. A silver halide photosensitive material as in claim 1, wherein the proportion of repeating units represented by formula (I) contained in the whole of the vinylidene chloride copolymer core/shell latex particles is from 70 to 98.5 wt %.

4. A silver halide photosensitive material as in claim 1, wherein the proportion of repeating units represented by formula (II) contained in the whole of the vinylidene chloride copolymer core/shell latex particles is from 1.0 to 20 wt %.

(IV)

5. A silver halide photosensitive material as in claim 1, wherein the proportion of repeating units represented by formula (III) contained in the whole of the vinylidene chloride copolymer core/shell latex particles is from 0.1 to 5.0 wt %.

6. A silver halide photosensitive material as in claim 1, wherein the proportion of repeating units represented by formula (IV) contained in the whole of the vinylidene chloride copolymer core/shell latex particles is from 0.05 to 3.0 wt %.

7. A silver halide photosensitive material as in claim 1, wherein the shell part of the vinylidene chloride copolymer contains repeating units derived from monomer components having an active methylene group, a (poly)hydroxy phenyl group, a sulfonic acid group, an amino group, an active ester group, an active halogen atom, an active vinyl group or precursor thereof, an epoxy group or an ethyleneimino group.

8. A silver halide photosensitive material as in claim 1, wherein a coating liquid of the vinylidene chloride copolymer contains a hardening agent in an amount of from 0.001 to 30 grams per liter.

9. A silver halide photosensitive material as in claim 1, wherein the vinylidene chloride copolymer layer as coated on each side of the support has a thickness of from 0.3 μm to 5 μm.

10. A silver halide photosensitive material as in claim 1, wherein the polymer latex-containing hydrophilic colloid layer contains gelatin, and the polymer latex is contained in an amount of from 0.01 to 0.1 in terms of the dry weight ratio with the amount of gelatin contained in the same layer.

* * * * *

35

40

45

50

55

60

65