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Kogure et al.

[11] **3,893,861**
[45] **July 8, 1975**

[54] SILVER HALIDE PHOTOSENSITIVE MATERIAL

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[52] **U.S. Cl.** **96/67;** 96/85; 96/114
[51] **Int. Cl.²** **G03C 1/72**
[58] **Field of Search** .... 96/67, 84 R, 50 PL, 84 A, 96/53, 73, 78, 114, 85

[56] **References Cited**

UNITED STATES PATENTS

2,882,156	4/1959	Minsk	96/84 A

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Assistant Examiner—Alfonso T. Suro Pico
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[57] ABSTRACT

An improved silver halide photosensitive material is disclosed from which a sticking phenomenon has been removed. The photosensitive material comprises at least one of the outermost layers containing, as the major component, a polymer which has monomer units having a guanidinoimino or guanidinoamino group in the side chain.

7 Claims, No Drawings

SILVER HALIDE PHOTOSENSITIVE MATERIAL

This invention relates to a silver halide photosensitive material, More particularly, the invention relates to a silver halide photosensitive material having a specific kind of an outermost layer.

In general, silver halide photosensitive materials are kept in the wound or lapped state in storage or use. In such case, the front surface of one photosensitive material has a contact with the back surface of another photosensitive material, or the surface of photosensitive material has a contact with other material such as an interposition paper or a sensitizing paper for Roentgen photography, and there is frequently observed a phenomenon that a part or all of a structural layer of the photosensitive material such as a front surface layer or back surface layer of the photosensitive material is peeled by adhesion or sticking. This phenomenon is called sticking. This sticking phenomenon tends to occur frequently under high temperature and high humidity conditions, and it results in serious damages to photosensitive materials.

Many improvements have heretofore been made to prevent occurrence of this sticking phenomenon. For instance, as typical known method there can be mentioned a method comprising making a considerable amount of a matting agent present in the surface area of the photosensitive material to threby reduce the contact surface area and a method comprising coating a waxy substance or this substance optionally together with a high molecular substance on the surface of the photosensitive material to thereby increase the surface slipping ability.

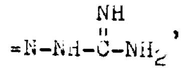
However, these methods involve defects. For instance, in the case of a matting agent, no particular effect is obtained when it is used in a small amount, and when it is used in a large amount, the transparency of the photosensitive material is lost and the photographic characteristics are adversely affected. For example, such undesired phenomena as increase of fog and desensitization are brought about. Moreover, since the surface smoothness of the photosensitive material is excessively heightened, such troubles as slippage of a photosensitive material from feed rollers are readily caused at the steps of preparation of photosensitive materials.

In such conventional methods, it is impossibke to prevent occurence of sticking completely and stably, especially under high temperature and high humidity conditions.

It is a primary object of this invention to provide a silver halide photosensitive material in which the above defects in the conventional techniques can be fully overcome and occurrence of sticking can be completely prevented. In accordance with this invention there is provided a silver halide photosensitive material having an outermost layer comprising a polymer containing units of a monomer having a guanidylimino or guanidinoamino group in the side chain or an outermost layer comprising said polymer as a main constituent. This invention is based on the finding that this photosensitive material has a very high sticking-preventive effect.

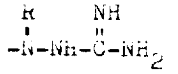
As a result of our reserch works, it has been found that when the above polymer is incorporated in a layer other than the outermost layers of the material, e.g., a photosensitive layer or an intermediate layer, no sticking-preventive effect can be obtained, and that if the above polymer is used as the constituent of the outermost layer, a prominent sticking-preventive effect can be obtained. This is quite a surprising finding.

When polymers containing in the side chain a guanidinoamino group,



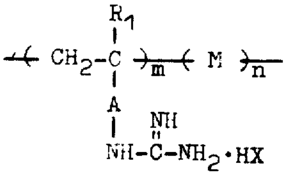
$$=N-NH-\overset{NH}{\overset{\|}{C}}-NH_2,$$

or guanidylamino group,



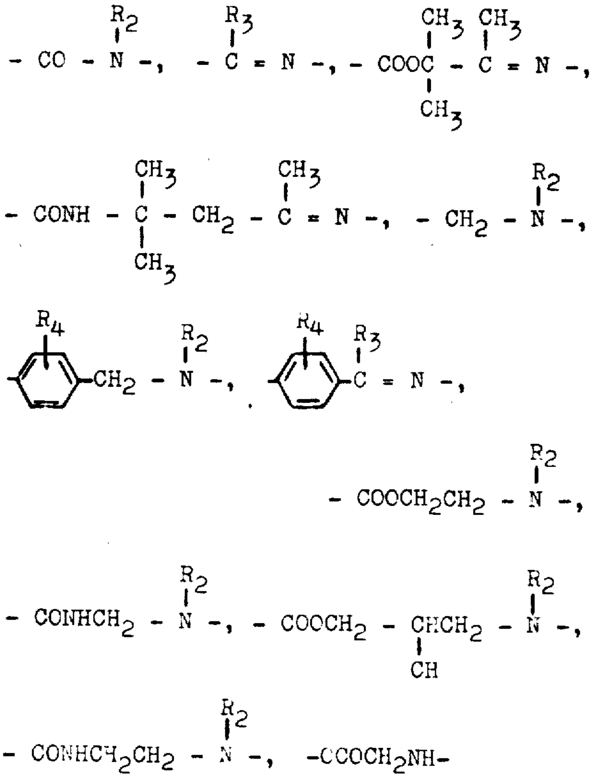
$$-\overset{R}{\overset{|}{N}}-NH-\overset{NH}{\overset{\|}{C}}-NH_2$$

(in which R is a hydrogen atom or a substituent such as a lower alkyl group), are empolyed, a good sticking-preventive effect can be obtained in the case of each polymer. It has been found that among the foregoing polymers, those expressed by the following general formula give an especially good sticking-preventive effect:



$$-\!\left(CH_2-\underset{\underset{NH-\overset{NH}{\overset{\|}{C}}-NH_2\cdot HX}{\overset{|}{A}}}{\overset{R_1}{\overset{|}{C}}}\right)_m\!-\!\left(M\right)_n-$$

wherein R_1 is a hydrogen atom or a lower alkyl group, A is a divalent group selected from the groups consisting of



$$-CO-\overset{R_2}{\overset{|}{N}}-,\quad -\overset{R_3}{\overset{|}{C}}=N-,\quad -COO\underset{CH_3}{\overset{CH_3}{C}}-\overset{CH_3}{\overset{|}{C}}=N-,$$

$$-CONH-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{\overset{|}{C}}=N-,\quad -CH_2-\overset{R_2}{\overset{|}{N}}-,$$

$$-COOCH_2CH_2-\overset{R_2}{\overset{|}{N}}-,$$

$$-CONHCH_2-\overset{R_2}{\overset{|}{N}}-,\quad -COOCH_2-\underset{CH}{CH}CH_2-\overset{R_2}{\overset{|}{N}}-,$$

$$-CONHCH_2CH_2-\overset{R_2}{\overset{|}{N}}-,\quad -CCOCH_2NH-$$

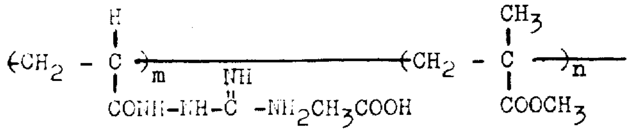
R_2 is a hydrogen atom or a lower alkyl group, R_3 is a hydrogen atom, or a lower alkyl group, a phenyl group or a substituted phenyl group, R_4 is a hydrogen or halogen atom or a lower alkyl group, X is an anion, M indicates a copolymerizable monomer, and *m* and *n* indicate the mole percentages of the copolymerizable monomer components, respectively, the sum of *m* and *n* being 100 %, *m* being within a range of from about 20 to 100 % and *n* being within a range of about 80 to 0 %.

As the monomer M in the above general formula repesenting the polymer of this invention, there are prefrably used acrylates such as methyl methacylate, ethyl acrylate, ethyl acrylate, diacetone acrylate, dicetone methacrylate, 2-chloroethylacrylate, 2-hloroethyl methacrylate, chloromethyl acrylate, chloomethyl methacrylate, glycidyl acrylate and glycidyl ethacrylate; acrylamides such as acrylamide, N-henylacrylamide, N-alkylacrylamides, diacetone-crylamide, diacetone-methacrylamide, N,N-thyleneimino-acrylamide, N-methoxymethyl-crylamide, N-ethoxymethacrylamide, N-butoxymethl-acrylamide and N-hydroxymethyl-acrylamide; styene type monomers such as styrene, p-hloromethylstyrene, p-formylstyrene, p-acetylstyrene nd p-benzoylstyrene; vinyl acetate type monomers uch as vinyl acetate and vinyl chloroacetate; vinyl ethers such as methylvinylether; unsaturated acids such as acrylic acid, itaconic acid and maleic anhydride; vinyl ketones such as acrolein, vinylmethylketone, vinylethylketone and vinylphenylketone; vinyl alcohol type monomers such as vinyl alcohol; unsaturated chlorides such as vinyl chloride vinylidene chloride and allyl chloride; and nitriles such as acrylonitrile and methacrylonitrile.

These polymers containing units of a monomer having a guanidylimino or guanidinoamino group in the side chain and methods for the synthesis of these polymers are disclosed in Journal of Organic Chemistry, 23, **1117** (1958), Journal of Polymer Science, 32, 83 (1958) and French Pat. No. 2,079,149, U.S. Pat. No. 2,882,156 and German Pat. No. 2,113,381.

As typical instances of this polymer containing units of a monomer having a guanidinoamino or guanidylamino group in the side chain, the following polymers can be mentioned (in each structural formula, *m* and *n* indicate the mole precentages of the copolymerizable monomer components, respectively);

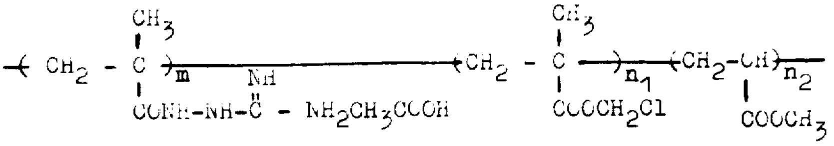
(1)



$$\left(CH_2-\underset{CONH-NH-\overset{NH}{\overset{\|}{C}}-NH_2CH_3COOH}{\overset{H}{C}}\right)_m\left(CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}\right)_n$$

in which *m* is about 40 and *n* is about 60.

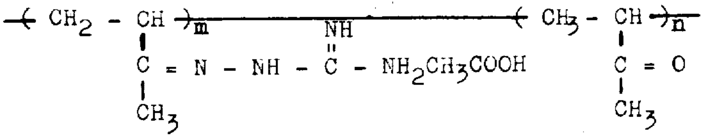
(2)



$$\left(CH_2-\underset{CONH-NH-\overset{NH}{\overset{\|}{C}}-NH_2CH_3COOH}{\overset{CH_3}{C}}\right)_m\left(CH_2-\underset{COOCH_2Cl}{\overset{CH_3}{C}}\right)_{n_1}\left(CH_2-\underset{COOCH_3}{CH}\right)_{n_2}$$

in which the sum of n_1 and n_2 corresponds to *n*, n_1 is about 30, n_2 is about 35, and *m* is about 35.

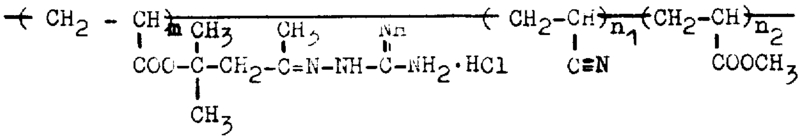
(3)



$$\left(CH_2-\underset{\underset{CH_3}{C}=N-NH-\overset{NH}{\overset{\|}{C}}-NH_2CH_3COOH}{CH}\right)_m\left(CH_3-\underset{\underset{CH_3}{C}=O}{CH}\right)_n$$

in which *m* is about 35 and *n* is about 65.

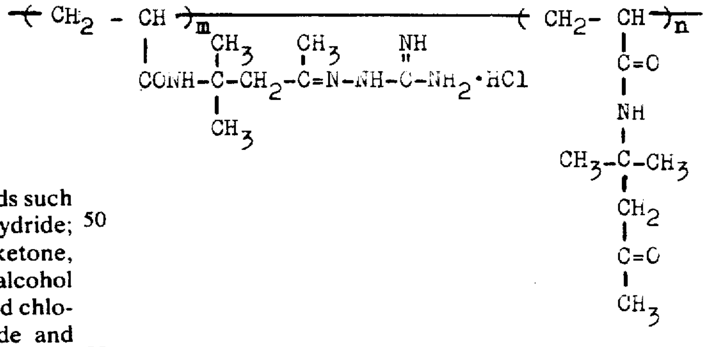
(4)



$$\left(CH_2-\underset{COO-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=N-NH-\overset{NH}{\overset{\|}{C}}-NH_2\cdot HCl}{CH}\right)_m\left(CH_2-\underset{C\equiv N}{CH}\right)_{n_1}\left(CH_2-\underset{COOCH_3}{CH}\right)_{n_2}$$

in which the sum of n_1 and n_2 corresponds to *n*, *m* is about 60, n_1 is about 20, and n_2 is about 20.

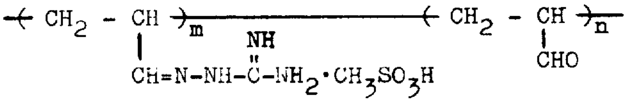
(5)



$$\left(CH_2-\underset{CONH-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=N-NH-\overset{NH}{\overset{\|}{C}}-NH_2\cdot HCl}{CH}\right)_m\left(CH_2-\underset{\begin{array}{c}|\\C=O\\|\\NH\\|\\CH_3-C-CH_3\\|\\CH_2\\|\\C=O\\|\\CH_3\end{array}}{CH}\right)_n$$

in which *m* is about 50 and *n* is about 50.

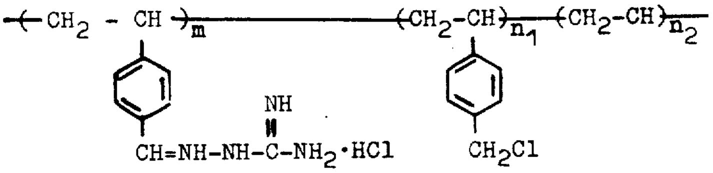
(6)



$$\left(CH_2-\underset{CH=N-NH-\overset{NH}{\overset{\|}{C}}-NH_2\cdot CH_3SO_3H}{CH}\right)_m\left(CH_2-\underset{CHO}{CH}\right)_n$$

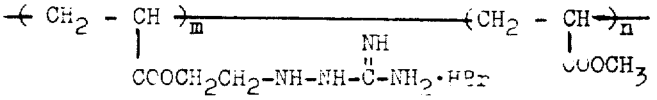
in which *m* is about 70 and *n* is about 30.

(7)



in which the sum of n_1 and n_2 corresponds to *n*, *m* is about 60, n_1 is about 5, and n_2 is about 35.

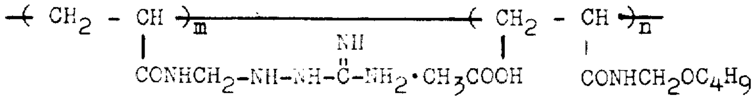
(8)



$$-\!\!\left(CH_2-\underset{COOCH_2CH_2-NH-NH-\overset{NH}{\overset{\|}{C}}-NH_2\cdot HBr}{CH}\right)_m\!\!-\!\!\left(CH_2-\underset{COOCH_3}{CH}\right)_n\!\!-$$

in which m is about 50 and n is about 50.

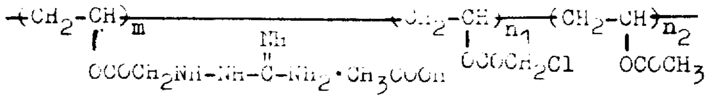
(9)



$$-\!\!\left(CH_2-\underset{CONHCH_2-NH-NH-\overset{NH}{\overset{\|}{C}}-NH_2\cdot CH_3COOH}{CH}\right)_m\!\!-\!\!\left(CH_2-\underset{CONHCH_2OC_4H_9}{CH}\right)_n\!\!-$$

in which m is about 80 and n is about 20.

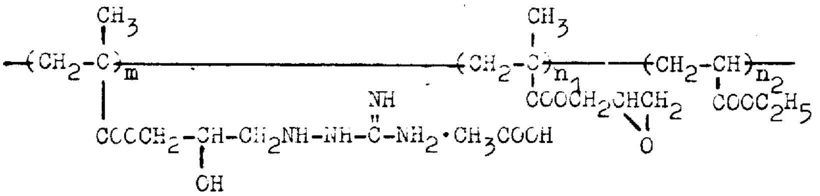
(10)



$$-\!\!\left(CH_2-\underset{COOCH_2NH-NH-\overset{NH}{\overset{\|}{C}}-NH_2\cdot CH_3COOH}{CH}\right)_m\!\!-\!\!\left(CH_2-\underset{COOCH_2Cl}{CH}\right)_{n_1}\!\!-\!\!\left(CH_2-\underset{OCOCH_3}{CH}\right)_{n_2}\!\!-$$

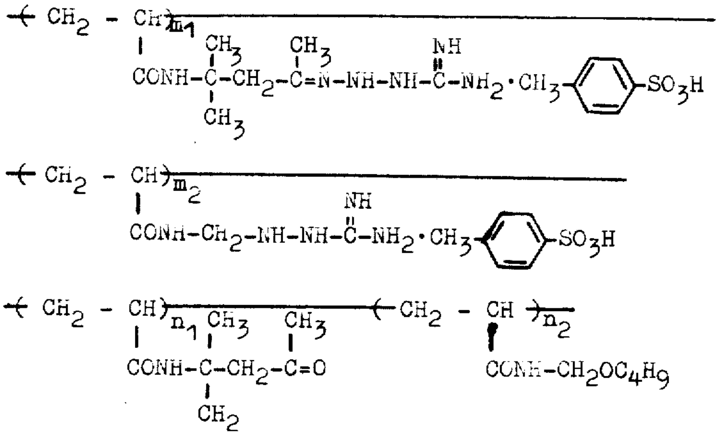
in which the sum of n_1 and n_2 corresponds to n, m is about 35, n_1 is about 60, and n_2 is about 5.

(11)



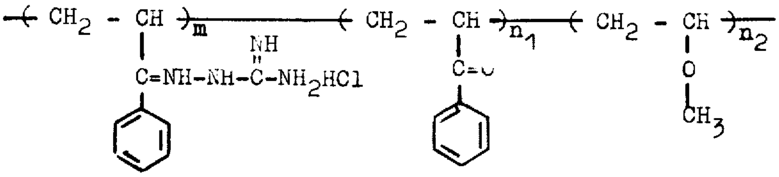
in which the sum of n_1 and n_2 corresponds to n, m is about 40, n_1 is about 40, and n_2 is about 20.

(12)



in which the sum of m_1 and m_2 corresponds to m, the sum of n_1 and n_2 corresponds to n, m_1 is about 30, m_2 is about 15, n_1 is about 30 and n_2 is about 25.

(13)



in which the sum of n_1 and n_2 corresponds to n, m is about 35, n_1 is about 20 and n_2 is about 45.

Such polymer is applied to an outermost layer of the silver halide photosensitive material. Namely, the polymer is used as the front surface layer or back surface layer of the silver halide photosensitive material or as both the front surface layer and the back surface layer. In case the polymer is applied to the so called front surface layer positioned on the photosensitive layer side of the silver halide photosensitive material (when photosensitive layers are provided on both the surfaces of a support, the polymer may be applied to either or both of front surface layers) in view of the preparation facility and the photographic characteristics, it is generally preferred that a layer of the polymer is formed by applying the polymer in the from of an aqueous solution and then drying it. In this case, if the polymer used is one expressed by the above general formula, it is preferred that the value of m is at least 30 %. In case the polymer is applied to the surface opposite to the side of the photosensitive layer of the photosensitive material, namely the so called back surface layer, the application method differs depending on the kind of a layer formed on the back surface side of the support, but the polymer is generally applied in the form of an aqueous solution or an organic solvent solution, preferably in the form of an organic solvent solution. As typical instances of the organic solvent to be used, there can be mentioned methanol, ethanol, propanol, acetone, etc. It is possible, if required, to employ mixed solvents formed by incorporating into such organic solvent another organic solvent of a relatively high boiling point, such as ethylene glycol, ethylene glycol monomethyl ier, dioxane, etc. The organic solvent to be used in s case should be so selected that it does no harm to ier layers formed on the back surface side, such as antistatic layer, a curl balance-processed layer, a atch preventive layer, an anti-halation layer, etc. d it does not degrade the properties of these layers.

When the outer most layer composed of the above-ntioned polymer or comprising it as a main constitut is formed on a silver halide photosensitive material, e sticking-preventive effect attained is especially ominent in the case of a photosensitive material of e type which has an anti-halation layer.

This anti-halation layer is colored so as to prevent so lled halation, and it generally contains as a coloring mponent carbon black or an alkali-soluble dye and a binder constituent a water-soluble or alkali-soluble sin. Because of characteristics required of this layer at the layer should be decolored or removed at the velopment step this layer should be selected so that has a good compatibility with a layer formed on the le of the photosensitive layer. Therefore, when conntional photosensitive materials including such antilation layer are kept in the wound or lapped state, e front surface of the photoconductive material has contact with the back surface (the surface of the antilation layer), partial or entire adhesion (sticking) ocurs, and when the sticked surfaces are separated at the ne of application, it is frequently observed that the nti-halation layer is peeled partially or entirely and is ansferred to the front surface of the photosensitive aterial. This results in uneven light exposure and uneven development, and the photographic characteristics of the photosensitive materials are greatly deaded.

Even in the case of a silver halide photosensitive marial having an anti-halation layer which has prominent tendency to occur a sticking, if the above mentioned polymer according to this invention is applied to silver halide photosensitive material as an outermost yer, sticking is not caused to occur even under high mperature and high humidity conditions and no bad fluences are given to the photographic characteristics.

Accordingly, especially prominent effects can be attained when this invention is applied to a silver halide hotosensitive material of the type including an antilation layer. As pointed above, this anti-halation yer generally contains as main ingredients a dye or igment and a water-soluble or alkali-soluble high-molecular substance. As the water-soluble or alkaliluble substance, there can be mentioned, for instance, condensates of formaldehyde with aromatic rboxylic acids disclosed in U.S. Pat. No. 2,089,764, erman Pat. No. 584,622 and British Pat. Specification o. 1,142,688, such as phenoxyacetic acid-formaldehyde resins and salicylic acid-formaldehyde esins; polyvinyl alcohol-acid anhydride reaction products disclosed in U.S. Pat. No. 2,131,747, U.S. Pat. No. ,271,234, U.S. Pat. No. 2,319,080 and U.S. Pat. No. ,511,660, such as polyvinyl phthalate resins and polynyl acetophthalate resins; reaction products between cyl derivatives of cellulose or pyranose ring-containing natural substances such as gum arabic or emi-synthesized products thereof and anhydrous carboxylic acids, disclosed in U.S. Pat. No. 2,275,817, I.S. Pat. No. 2,289,799, U.S. Pat. No. 2,333,809, U.S. at. No. 2,271,234, U.S. Pat. No. 2,346,078, U.S. Pat. lo. 2,824,097, U.S. Pat. No. 2,376,175, U.S. Pat. No. ,201,249, U.S. Pat. No. 3,022,287, U.S. Pat. No. 3,511,660, Japanese Pat. Publication No. 3408/68, Japanese Pat. Publication No. 8835/70 and German Pat. No. 2,116,780, such as cellulose acetate phthalate, cellulose butyrate phthalate, cellulose acetate succinate, cellulose acetate maleate, ethyl cellulose acetate pyromellitate, ethyl cellulose phthalate, cellulose acetate hexahydrophthalate, cellulose acetate tetrahydrophthalate, methyl-hydroxypropyl cellulose hexahydrophthalate and phthalic acid ester of gum arabic; vinyl carboxylate-containing copolymers disclosed in U.S. Pat. No. 2,077,769, U.S. Pat. No. 2,161,788, U.S. Pat. No. 2,282,890, U.S. Pat. No. 2,755,186, U.S. Pat. No. 2,913,351, U.S. Pat. No. 2,984,568, U.S. Pat. No. 3,162,028, U.S. Pat. No. 3,201,249, Japanese Pat. Publication No. 1403/70, Japanese Pat. Publication No. 8835/70, Japanese Pat. Publication No. 7864/60, German Pat. No. 1,422,810 and German Pat. No. 1,299,220, and Japanese Pat. Application Laid-Open Specifications Nos. 1631/71, 2783/71 and 593/72, such as copolymers of at least one vinyl monomer selected from vinyl chloride, vinyl butyl ether, vinyl ethyl ether, styrene, acrylonitrile, nitrostyrene, vinyl acetate and ethylene and maleic anhydride, copolymers of said vinyl monomer and a semiester of fumaric acid or maleic acid with an alkyl alcohol; a lactone resin of said vinyl monomer and a glycolic acid, copolymers of at least one vinyl monomer selected from vinyl acetate, alkyl acrylates, alkyl methacrylates and styrene with a copolymerizable unsaturated acid such as acrylic acid, methacrylic acid and crotonic acid, and copolymers of vinyl acetate with an aryloxyacetic acid; polyvinyl substituted acetals having a carboxylic acid or sulfonic acid in the side chain, such as those disclosed in U.S. Pat. No. 2,462,527; and polycarbonates having a carboxylic acid in the side chain, such as those disclosed in U.S. Pat. No. 3,022,171 and U.S. Pat. No. 3,043,800. In these copolymers, the carboxylic acid may be in the form of an alkali metal salt or ammonium salt.

As the light-shielding substance of the antihalation layer, there can be used, for instance, pigments such as carbon black, Prussian Blue, titanium white, zinc oxide and organic lake pigments, and various dyes disclosed in U.S. Pat. No. 2,150,695, U.S. Pat. No. 2,278,457, U.S. Pat. No. 2,282,890, U.S. Pat. No. 2,462,527, U.S. Pat. No. 2,984,568, U.S. Pat. No. 3,018,177, U.S. Pat. No. 3,364,029, British Pat. Specification No. 790,023, Japanese Pat. Publication No. 1716/64, Japanese Pat. Publication No. 8835/70, French Pat. No. 1,479,826, German Pat. No. 1,035,472, German Pat. No. 1,038,395 and German Pat. NO. 1,347,836, and Japanese Pat. Application Laid-Open Specification No. 593/72, such as triphenylmethane dyes, stryl dyes, azomethine dyes and pyrazolone dyes.

The anti-halation layer comprising as the main constituents such water-soluble or alkali-soluble high-molecular substance as mentioned above and such dye or pigment as mentioned above is prepared, for instance, by a customary method comprising coating a coating liquid, which is prepared in the manner described below, directly or indirectly on the entire surface of a support on which a suitable undercoating has been formed in advance according to need, and drying the coated surface. In case carbon black is used as the light-shielding substance, the coating liquid is prepared, for instance, by a method such as disclosed in U.S. Pat. No. 2,327,828, namely a method comprising mixing an alkali-soluble high-molecular substance and carbon black with a solvent for said highmolecular substance, dispersing the solids sufficiently in the liquid and diluting a viscous dispersion of carbon black with a suitable solvent. In case a dye is used as the light-shielding substance, a highmolecular substance is dissolved and diluted and a suitable amount of the dye is added to the resulting dilution to form a coating liquid. As the solvent for the water-soluble or alkali-soluble highmolecular substance to be used for preparation of such coating liquid, there can be mentioned, for instance, alcohols such as methanol, ethanol, propanol, butanol, amyl alcohol, diacetone alcohol, ethylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monoacetate, ethylene glycol monopropionate, ethylene glycol monobutyrate, diethylene glycol, diethylene glycol monomethyl ether and diethylene glycol monoethyl ether; ethers such as dioxane ethylene glycol dimethyl ether, ethylene glycol diethyl ether and anisole; ketones such as acetone, ethylmethylketone, isobutylmethylketone and cyclohexanone; esters such as methyl acetate, ethyl acetate, butyl acetate and methyl propionate; halogenated hydrocarbons such as methylene dichloride, ethylene dichloride, chlorobromomethane, chloroform and trimethylene dichloride; water, aqueous ammonia and alkaline aqueous solutions.

In order to improve the dispersibility of a pigment or the like, it is preferred that a certain additive such as a surface active agent is added to an anti-halation layer-forming coating liquid. As such surface active agent, there can be mentioned those disclosed in U.S. Pat. No. 2,271,234, U.S. Pat. No. 2,333,809, U.S. Pat. No. 2,278,457, U.S. Pat. No. 2,801,191, U.S. Pat. No. 2,976,160, British Pat. No. 536,680, Japanese Pat. Publication No. 13499/68, Japanese Pat. Publication No. 14503/67 and Japanese Pat. Publication No. 33466/70. For instance, there can be used higher fatty acid esters of glycerin, higher fatty acid esters of sorbitol, higher fatty acid esters of polyoxyethylene sorbitol, fatty acid esters of polyoxyethylene, aliphatic alcohol ethers of polyoxyethylene, alkyl phenyl ethers of polyoxyethylene, alkyl sulfuric acid ester salts, polyoxyethylene alkyl alkyl ether sulfuric acid ester salts, alkyl sulfosuccinic acid salts, N-acylsarcosine salts, alkyl (polyoxyethylene) phosphoric acid esters, fatty acid esters, etc.

This invention has been detailed as regards a silver halide photosensitive material of the type including an anti-halation layer, but in this invention the silver halide photosensitive material to be used is not limited to this type and this invention can be applied to any other silver halide photosensitive material. For instance, in the case of a silver halide photosensitive material having silver halide photosensitive layers on both the surfaces of a support or a silver halide photosensitive material being free of an anti-halation layer but having a silver halide photosensitive layer on the one surface of a support, sticking occurs when the photosensitive material is kept in the lapperd state especially under high temperature and high humidity conditions. If this invention is applied to such silver halide photosensitive materials, occurrence of sticking can be completely prevented with no bad influences to photographic characteristics.

In frequently happens that a photosensitive material for Roentgen photography is packed in a cassette in a dark room in which either the temperature or the humidity is not controlled and allowed to stand in this state for a long time. When such photographic material is employed, sticking occurs and results in degradation of photographic characteristics. For instance, occurrence of fog and desensitization are observed.

However, when a polymer containing units of a monomer having a guanidylimino or guanidylamino group in the side chain is applied at least to an outermost layer of such silver halide photosensitive material according to this invention, occurence of blocking can be effectively prevented regardless of the kind of the photosensitive material. Accordingly, this invention can overcome the defects involved in the conventional sticking-preventing methods.

In this invention it is preferred that the polymer containing units of a monomer having a guanidylimino or guanidylamino group in the side chain is applied in an amount of about 0.001 to about 1 g per m^2 of the photosensitive material. A layer of such polymer is formed as an outermost layer of a photosensitive material by employing a solution of the polymer in aqueous liquid or an organic solvent such as mentioned above by means of coating or the like at a suitable stage of the photosensitive material manufacturing process.

The sticking-preventive effect of the polymer is not greatly influenced by the average molecular weight thereof, but it is preferred that the polymer has an average molecular weight of about 5,000 to about 100,000. An aqueous solution or organic solvent solution of the polymer may include various additives in addition to the polymer. For instance, amphoteric, non-ionic or cationic polymers miscible with said polymer, such as gelatin, non-ionic, cationic or amphoteric surface active agents, amphoteric, non-ionic or cationic antistatic agents, matting agents such as starch, colloidal silica, powdery silica and polymer beads, and lubricants can be optionally used according to need.

A silver halide photosensitive material to be used in this invention is formed by applying at least one layer of a silver halide photosensitive emulsion to one or both surfaces of a suitable support such as paper, resin laminated paper, glass, acetyl cellulose film, polyester film, polyamide film, polystyrene film and the like. Emulsions prepared by dispersing a suitable silver halide such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodobromide, silver chloroiodobromide and the like into a hydrophilic protective colloid are generally used as the silver halide emulsion. As the hydrophilic protective colloid there can be used various substances such, for example, as gelatin, colloidal albumin, casein, cellulose derivatives, polyvinyl alcohol and polyacrylamides disclosed in U.S. Pat. No. 2,541,741. This emulsion can be chemically sensitized with use of a chemical sensitizer such, for example, as activated gelatin; sulfur compounds; noble metals (such as gold, rhodium, palladium iridium and platinum), typical instances of which are ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladite, and most preferably gold salts such as potassium chloroaurate, potassium auric thiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole metochloride; and reducingg agents. Furthermore, this emulsion can be optically sensitized with optical sensitizer such as cyanine dyes, merocyanine dyes and the like, and it can be stabilized with such stabilizers as triazoles, azaindenes, quaternary benzothiazolium compounds and cadmium compounds. This emulsion may further comprise a sensitizer of the quaternary ammonium salt type or polyethylene glycol type, and in some case, it may comprise a plasticizer such as glycerin, hydroxyalkanes, ethylene bis-glycol esters, bis-succinates and acid amides. of the acrylic acid series.

Still further, this emulsion may comprise various photographic additives such as film-hardening agents, e.g., formaldehyde, chromalum, glyoxal and mucobromic acid; surfactants, e.g., saponin, lauryl and oleyl ethers of polyethylene glycol and sulfated polyethylene glycol ethers; anti-foggants; color coupler such as pyrazolone type magenta couplers, phenol type cyane couplers, yellow couplers and so called masking couplers (these couplers may be of either the protected type or Fisher dispersion type); and dispersing agents for color coupler, e.g., protecting solvents. This silver halide emulsion is formed on a substrate, if necessary, through an undercoat layer. Formation of a silver halide emulsion layer is generally accomplished by coating.

A protective layer is generally formed on this silver halide emulsion layer, and when two or more silver halide emulsion layers are formed, an intermediate layer or filter layer can be formed between the silver halide emulsion layers. Further, this silver halide emulsion layer may be composed of a layer of a high sensitivity and a layer of a low sensitivity.

Any of silver halide photosensitive materials for the high resolution photography, the X-ray photography, the electron ray photography, the cinematography (monochromatic or color cinematography), the microcopy and for the ordinary photography (monochromatic or color photography) can be used in this invention. When the above-mentioned polymer is applied as a front surface layer or back surface layer to one or both surfaces of such silver halide photosensitive material according to this invention, occurrence of sticking is prevented, and when such photosensitive material is allowed to stand under high temperature and high humidity conditions, there is no fear of occurrence of sticking. Thus, according to this invention, the defects involved in silvler halide photosensitive materials formed by conventional sticking-preventing methods can be overcome.

This invention will now be illustrated more detailedly by reference to Examples, but it must be noted that embodiments of this invention are not limited to those illustrated in these Examples.

EXAMPLE 1

An anti-halation layer comprising a carbon black dispersed lauryl alcohol-modified maleic anhydride vinyl acetate copolymer was formed on one surface of an undercoated polyethylene terephthalate film. A water-acetone-butanol solution (3:6:1) containing 0.3% of the exemplified compound (1) (average molecular weight = about 15,000; m = about 40; n = about 60) and a small amount of a matting agent of the silica type was coated on the anti-halation layer in an amount of 13 cc per m^2 of the film, and the coated solution was dried. Then, an ordinary monochromatic silver halide emulsion layer was formed on the other surface of the film. The resulting photosensitive material was cut into a width of 16 mm and 30 m of the photosensitive material was wound on one reel. When the wound photosensitive material was allowed to stand at a temperature of 50°C. and a relative humidity of 80% for 5 hours, transfer of the antihalation layer to the photosensitive layer by the sticking phenomenon was not observed at all. After the development treatment it was confirmed that the photographic characteristics were not adversely affected by provision of the above polymer layer.

For comparison, a photosensitive material was prepared in the same manner as above except that an outermost layer of the compound (1) was not formed, and it was tested in the same manner as above. It was found that sticking occurred at several parts.

EXAMPLE 2

An anti-halation layer comprising a carbon black dispersed hydroxypropyl cellulose phthalate and methyl cellulose phthalate was formed on one surface of an acetyl cellulose film, and a methanol aqueous solution (1:1) containing 0.5% of the exemplified compound (5) (average molecular weight = about 20,000; m = about 50; n = about 50) and a small amount of polyethylene glycol lauryl ether was coated on the anti-halation layer in an amount of 20 cc per m^2 of the film and dried. An ordinary color silver halide photosensitive emulsion was coated on the other undercoated surface of the film and a protective gelatin layer was formed on the photosensitive layer according to a customary method to obtain a photosensitive material.

The formed photosensitive material was wound in such a manner that the front surface was contacted with the back surface and it was allowed to stand in this state at a temperature of 50°C. and a relative humidity of 80% for 5 hours. No sticking was observed between th anti-halation layer and the photosensitive layer. Further, even when the above photosensitive material was allowed to stand still at a temperature of 30°C. and a relative humidity of 60% for 6 months, no trouble was brought about.

When the development was conducted and the photographic characteristics were examined, it was found that no change was brought about in the photographic characteristics.

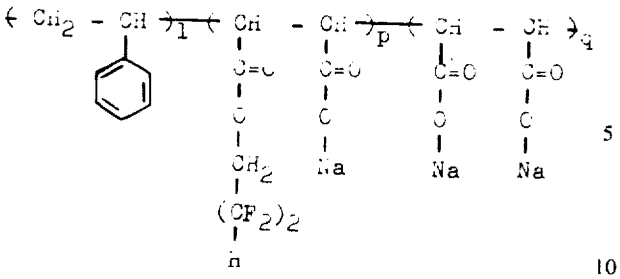
EXAMPLE 3

A silver halide emulsion for the Roentgen photography was coated on both undercoated surfaces of a polyethylene terephthalate film and dried. A protective gelatin layer was formed on either of the photosensitive layers. Then, a water-methanol solution (1:1) containing 0.5 weight % of the exemplified compound (9) (average molecular weight = about 8,000; m = about 80; n = about 20) and 0.2 weight % of a 4-nonylphenol-formalin resin (degree of polymerization of about 50) added with 30 moles of ethylene oxide was coated on both the surfaces of the above photosensitive material in an amount of 15 cc per m^2 of the film, and dried to obtain a photosensitive material for the Roentgen photography according to this invention. The obtained photosensitive material was inserted between two sheets of a sensitizing paper having a cellulose ester-treated surface and allowed to stand still at a temperature of 50°C. and a relative humidity of 80% for 1 day. Then, it was put into a cassette and packed therein by application of a pressure. Then, the packed photosensitive material was allowed to stand still for 1 day, and it was taken from the cassette and covered with a lead plate. Then, it was exposed to X-rays and developed.

It was found that no trouble was caused by the sticking phenomenon and the photographic characteristics were not at all degraded.

EXAMPLE 4

0.1 g of a water-soluble highmolecular compound (the relative viscosity of 1% aqueous solution to water being 7.35 as measured at 25°) having the following structure



in which *l* is about 50, *p* is about 8 and *q* is about 42, was dissolved in 5 cc of water, and the resulting solution was incorporated into 95 cc of a methanol solution containing 1.5 g of resorcin to form an undercoating solution. Then the undercoating solution was coated on one surface of a biaxially stretched polyethylene terephthalate film having a thickness of 100 μ at a rate of 15 m/min in a thickness of 15 μ by means of a roll coater. Then, the drying was conducted at 95°C. for 1 minute and 30 seconds.

3 g of cellulose acetate phthalate, 1.2 g of carbon black, 34 cc of dioxane and 62 cc of acetone were kneaded and diluted (according to, for instance, a kneading method disclosed in U.S. Pat. No. 2,327,827), and the resulting solution was coated on the above coated surface of the film in a thickness of about 32 μ and dried. Then, on the coated surface was further coated a water-acetone-methanol solution (4:3:3) containing 0.5% of the exemplified compound (3) (average molecular weight = about 13,000; *m* = about 35; *n* = about 65), followed by drying. The above solution was coated in an amount of 15 cc per m² of the film.

An undercoating solution prepared in the same manner as above except that 0.02 g of bis-hexylene ethyleneimino ureide was further added was coated on the other surface of the film in the same manner as above. A silver halide emulsion for the electronic recording was formed on the formed undercoating to form a photosensitive material.

The photosensitive material was cut into a width of 8.75 mm and 50 m of the photosensitive material was wound on one reel. The wound photosensitive material was allowed to stand still at a temperature of 40°C. and a relative humidity of 85% for 1 day. No sticking was observed and the photographic characterristics were not degraded at all.

EXAMPLE 5

A photosensitive material for formation of cut film comprising a cellulose triacetate film having a thickness of 200 μ, a layer of a silver halide emulsion for the monochromatic photography formed on one surface of the film and a gelatin layer formed on the other surface was prepared, and 2% aqueous solution containing 0.1 g of the exemplified compound (13) (average molecular weight = about 6,000; *m* = about 35; n_1 = about 20; n_2 = about 45) and 0.1 g of gelatin was coated on the gelatin layer of the above photosensitive material and dried. Then, cut films of a size of 100 mm = 125 mm were cut from the above photosensitive materials, and about 10 of such cut films were lapped in such a manner that the front surface of one cut film was contacted with the back surface of another cut film. A glass plate was placed on the lapped cut films and a load of 5 Kg was imposed on the glass sheet. In this state, the cut films were allowed to stand still at a temperature of 50°C. and a relative humidity of 80 % for 5 hours.

No sticking was observed and no bad influences were given to the photographic characteristics by the use of the polymer of this invention.

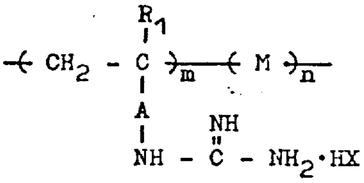
What is claimed is:

1. A silver halide photosensitive material which comprises at least one of the outermost layers containing, as the major component, a polymer which has monomer units having a guanidinoimino or gaunidinoamino group in the side chain.

2. A silver halide photosensitive material according to claim **1**, wherein said polymer has an average molecular weight of 5,000 to 100,000.

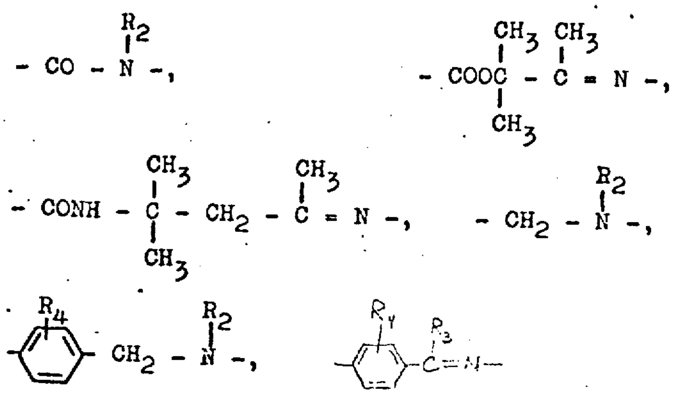
3. A silver halide photosensitive material according to claim **1**, wherein the amount of said polymer is 0.001 to 1g per m² of the photosensitive material.

4. A silver halide photosensitive material which comprises at least one of the outermost layers containing, as the major component, a polymer represented by the following formula:



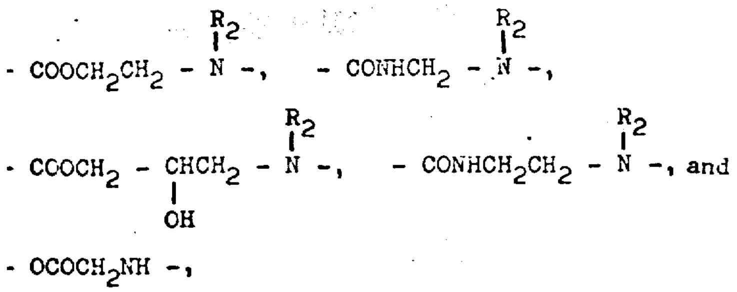
$$-\!\!\left(\mathrm{CH_2} - \underset{\substack{|\\ \mathrm{A}\\ |\\ \mathrm{NH} - \overset{\overset{\mathrm{NH}}{\|}}{\mathrm{C}} - \mathrm{NH_2 \cdot HX}}}{\overset{\overset{\mathrm{R_1}}{|}}{\mathrm{C}}}\right)_{\!m}\!\!-\!\!\left(\mathrm{M}\right)_{\!n}\!\!-$$

wherein R_1 is hydrogen or lower alkyl, A is a divalent group selected from



$$-\mathrm{CO} - \overset{\overset{\mathrm{R_2}}{|}}{\mathrm{N}} -,\qquad -\mathrm{COO}\underset{\underset{\mathrm{CH_3}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}} - \overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}} = \mathrm{N} -,$$

$$-\mathrm{CONH} - \underset{\underset{\mathrm{CH_3}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}} - \mathrm{CH_2} - \overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}} = \mathrm{N} -,\qquad -\mathrm{CH_2} - \overset{\overset{\mathrm{R_2}}{|}}{\mathrm{N}} -,$$



$-COOCH_2CH_2-\overset{R_2}{\overset{|}{N}}-$, $-CONHCH_2-\overset{R_2}{\overset{|}{N}}-$,

$-COOCH_2-\underset{\underset{OH}{|}}{CH}CH_2-\overset{R_2}{\overset{|}{N}}-$, $-CONHCH_2CH_2-\overset{R_2}{\overset{|}{N}}-$, and

$-OCOCH_2NH-$,

wherein R_2 is hydrogen or lower alkyl R_3 is hydrogen, lower alkyl phenyl or substituted phenyl, R_4 is hydrogen, halogen, or lwoer alkyl, X is an anion, M is a copolymerizable monomer, and *m* and *n* indicate the mole percentages of the copolymerizable monomer components respectively, the sum of *m* and *n* being 100%, *m* being within a range of from about 20 to 100% and *n* being within a range of about 80 to 0%.

5. A silver halide photosensitive material according to claim **4**, wherein M in the general formula is selected from the group consisting of acrylates, acrylamides, styrene type monomers, vinyl acetate type monomers, vinyl ethers, unsaturated acids, vinyl alcohol type monemers, unsaturated chlorides, and nitriles.

6. A silver halide photosensitive material according to claim **5**, wherein said group consists of methyl methacrylate, methyl acrylate, ethyl acrylate, diacetone acrylate, diacatone methacrylate, 2-chloroethylacrylate, 2-chloroethyl methacrylate, chloromethyl acrylate, chloromethyl methacrylate, glycidyl acrylate, glycidyl methacrylate, acrylamide, N-phenyl-acrylamide, N-alkylacrylamide, diacetone acrylamide, diacetone methacrylamide, N,N-ethyl-eneimino-acylamide, N-methoxymethyl-acrylamide, N-ethoxy methylacrylamide, N-butoxymethyl-acrylamide, N-hydroxy methyl acrylamide, styrene, P-chloromethylstyrene, P-formylstyrene, P-acetylstyrene, P-benzoylstyrene, vinyl acetate, vinyl chloroacetate, methylvinylether, acrylic acid, itaconic acid, maleic anhydride, acrolein, vinylmethylketone, vinylethylketone, vinylphenylketone, vinylalcohol, vinyl chloride, vinylidene chloride, allyl chloride, acrylonitrile, and methacrylonitrile.

7. A silver halide photosensitive material according to claim **4**, wherein the value of *m* in the general formula is at least 30%.

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