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PHOTOGRAPHIC COMPOSITION CONTAINING ANTIPLUMMING AND ANTIBRONZING AGENTS

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6 Claims. (Cl. 95—7)

This invention relates to photography and more particularly to radiation-sensitive photographic elements including films, plates and papers. More particularly it relates to photographic silver halide emulsions and emulsion layers that contain (*a*) a chemical agent which improves the color and density of developed silver images and (*b*) a polymeric amino-nitrogen containing material. Still more particularly it relates to such elements that have at least one photographic silver halide emulsion layer which has dispersed therein a small amount of (1) a finely divided compound which prevents "plumming" and "bronzing" of the developed images and (2) a polymeric, amino-nitrogen containing material soluble in dilute aqueous acetic acid but insoluble in water and dilute alkalies. A preferred aspect of the invention relates to photographic elements having at least one silver halide emulsion layer that has dispersed therethrough particles of such a polymeric, amino-nitrogen containing material which particles contain a compound which prevents "plumming" or "bronzing" of developed silver images. The invention also relates to a method of making photographic silver halide emulsions and emulsion layers embodying such materials and compounds.

An object of this invention is to provide photographic elements with improved characteristics. Another object is to provide photographic elements with silver halide emulsion layers that are resistant to "plumming" or "bronzing" during the hot glazing of developed photographic silver images. A further object is to provide a more effective method of introducing and maintaining anti-plumming or anti-bronzing compounds in photographic silver halide emulsion layers. Still other objects will be apparent from the following description of the invention.

The above and other objects are attained and new and useful photographic silver halide emulsions and emulsion layers are obtained by incorporating with the emulsions (1) a chemical compound or agent which improves the color and density of the developed silver images, e. g., an anti-plumming or anti-bronzing agent and (2) a polymeric, amino-nitrogen containing material which is soluble in dilute aqueous acetic acid but insoluble in water and dilute alkalies. The latter material apparently has a protective action on the compound that improves the color or density of the silver images and prevents said compound from being washed out of the emulsion layer during a photographic developing operation. However, when the developed element is treated in an acid-stop bath or an acid-fixing bath the polymeric, amino-nitrogen containing material is dissolved thus releasing the compound so that it becomes effective during subsequent drying of the photographic element and prevents or reduces plumming or bronzing.

A practical method of making the improved photographic emulsions and emulsion layers comprises dissolving the anti-plumming or anti-bronzing agent in a water-immiscible organic solvent and adding the polymeric amino-nitrogen containing material or mixing a solution of the agent with a solution of the polymeric amino-nitrogen compound and then adding the resulting solution of the two materials to an aqueous solution or dispersion of a water-permeable colloid or an aqueous colloid silver-halide emulsion. The resulting colloidal dispersion contains finely divided particles of the polymeric amino-nitrogen containing material which particles contain the anti-plumming or anti-bronzing compounds. In some cases the anti-plumming or anti-bronzing agents which are of an extremely small size may be entirely surrounded by a coating of the polymeric amino-nitrogen containing material.

The preparation of the particles of the polymeric amino-nitrogen containing material which contains the anti-plumming or anti-bronzing agent is not limited to the solution methods just described but can be accomplished in other manners, for example, by grinding the anti-plumming or anti-bronzing agent in a solution of the polymeric amino-nitrogen containing material. High speed stirrers, homogenizers or colloid mills may be used advantageously to assist the dispersion of the agents in the amino-nitrogen containing material.

The particle size of the polymeric amino-nitrogen containing materials which contain the anti-plumming or anti-bronzing agent may vary over a fairly wide range, but, in general, should not be greater than approximately 30 microns. The minimum size is not critical and generally is controlled by the smallest molecular volume of the particular amino-nitrogen containing material in question.

In dispersing the particles in the water-permeable colloid solutions, it is generally advisable to employ a wetting or dispersing agent, e. g., cetyl trimethylammonium bromide, sodium dodecyl sulfate, sorbitan monolaurate, sorbitan trioleate containing at least 20 oxyethylene groups in at least three chains and other hexitan derivatives such as those described in Blake et al. U. S. Patent 2,400,532, the polyoxyethylene ether of dodecyl alcohol, etc.

The polymeric amino-nitrogen containing materials which are useful in accordance with the invention form hard resin-like films. They are insoluble in water and 5% aqueous ammonia, but are soluble in aqueous acetic acid of some concentration within the range 1 to 5%. Those soluble in 1% acetic acid are preferred. Useful polymeric amino-nitrogen containing materials may be divided in several groups as follows:

1. Those which may be termed cellulose derivatives. This includes deacetylated chitin and the alkylamino- and amino-alkylcelluloses.

2. Those which may be classified as synthetic resins in the formation of which ammonia in some instances and monomeric-amino-nitrogen containing bodies in other instances have been employed. This group is distinct from group 1 in that the highly polymeric molecules are built up wholly by syntheses. Among these materials are the resinous polymeric amino-alcohol esters of acrylic acid or of its homologs substituted in the alpha position by a hydrocarbon radical; the resinous reaction products of phenols, aldehydes and ammonia or primary or secondary amines, for example, the reaction product of meta-cresol, formaldehyde and dimethylamine; poly dimethylaminostyrene and the polymerization product of the olefinic compound made by simple pyrolysis of p-a-acetoxy-ethylbenzyldimethyl-ammonium acetate, etc.

3. Those which may be termed protein derivatives and contain sufficient amino-nitrogen groups to enable them to meet the solubility requirements of the definition given above.

Suitable specific compounds of the above types are described in U. S. P. 2,182,814 and the various patents which are referred to on pages 4 and 5 of that patent. One of the preferred polymeric amino-nitrogen containing materials is polymeric diethylaminoethyl methacrylate. It can be made from methyl methacrylate and diethylaminoethanol and subsequent polymerization in accordance with the following procedures:

PROCEDURE A.—PREPARATION OF MONOMER

The following compounds are admixed in the amounts by weight given in the following table in a reaction vessel provided with a packed distillation column in the outlet:

	Parts
Diethylaminoethanol	117
Methyl methacrylate	120
Benzene	112
Diphenyl-p-phenylene diamine	1.2

This mixture is dehydrated by distilling off a benzene-water azeotrope from 69° C. to 80° C. One fourth (0.016% sodium based on the weight of methyl methacrylate) of the total amount of sodium methylate catalyst dissolved in methanol is added cautiously to prevent sudden flooding of the packed column. The reaction usually starts upon the cautious addition of a second equal quantity of catalyst. The methanol-benzene azeotrope is distilled off at approximately 59° C. as rapidly as possible to minimize side reactions. Dehydrated benzene is added continuously to replace that which is removed in the azeotropic mixture. Additional 0.016% catalyst increments are introduced at a rate sufficient to maintain a steady removal of methanol, as indicated by a constant head temperature of 59° C. at a moderate reflux ratio. The fourth increment of the catalyst causes the final 25% of total reaction, but the rate of methanol formation is very slow. When the reaction is complete, the catalyst is neutralized with the theoretical amount of acetic acid, and the monomer distilled off at 89–91° C. under a pressure of 10 mm. of mercury. Purity of the product is indicated by determination of the neutralization equivalent and refractive index. Since the monomeric diethylaminoethyl methacrylate thus obtained polymerizes readily on standing, storage time should be held to a minimum, preferably under 8 hours. Dilution with xylene and low temperature setorage are effective short term measures for restraining polymerization.

PROCEDURE B.—PREPARATION OF POLYMER

A polymer-free solution composed of 50 parts by weight of monomeric diethylaminoethyl methacrylate in 40 parts by weight of xylene is heated to a polymerization temperature of 70–80° C. and 1.0%, based on the weight of the monomer, of azobisisobutyronitrile added as a polymerization catalyst or initiator. The molecular weight, and therefore the viscosity, of the polymer may be controlled by regulating the polymerization temperature. Because of more favorable solubility characteristics, toluene is used as the carrier for the initiator. For reaction times of 4 to 8 hours, 50% polymer solutions may be produced with viscosities of 2.0–3.7 poise containing less than 5% of the original monomer unpolymerized. Control of a peak temperature, which occurs from 5 to 15 minutes after adding the initiator, appears to be necessary, if it rises above 90° C., to minimize decomposition of the initiator. Progress of the polymerization may be followed conveniently by means of refractive index measurements. If the polymerization reaction rate becomes very slow due to rapid decomposition of the initiator at high (100–112° C.) peak temperatures, acceleration of the rate to secure increased viscosity is accomplished by adding more initiator and further heating at the polymerization temperature.

The invention will be further illustrated but is not intended to be limited by the following examples.

Example I

A solution was prepared, containing 0.1 g. of 1-phenyl-5-mercaptotetrazole as an anti-plumming agent dissolved in 12.5 ml. of ethyl alcohol containing methyl alcohol in the proportions, 100 parts 190 proof ethyl alcohol to 10 parts pure methyl alcohol. This was added to a solution which consisted of 5 g. of the diethylaminoethyl methacrylate polymer described in the above procedure B (48% polymer in toluene) dissolved in said alcohol mixture. The resultant solution was then dispersed in 150 ml. of distilled water containing 0.25 g. of dissolved cetyl trimethyl ammonium bromide, and the mixture was vigorously agitated in a blending mixer. The blending was continued for approximately three minutes after the initial mixing of the ingredients. The dispersion secured was diluted with distilled water to a total volume of 500 ml.

A chloro-bromide emulsion (AgCl=95.2 mole per cent, and AgBr=4.8 mole per cent) was prepared by a procedure which normally yields a standard contact printing speed emulsion. Immediately before coating this emulsion upon a baryta coated paper support, 50 ml. of the dispersion of 1-phenyl-5-mercaptotetrazole in the diethylaminoethyl methacrylate polymer was added to a quantity of the emulsion having a silver content equivalent to that contained in 12.5 ml. of 3N silver nitrate solution at 25° C. In all other respects the procedures for preparation and coating of contact type emulsion were followed. Control coatings were made at the same time with portions of the original emulsion, which included no 1-phenyl-5-mercaptotetrazole in one case, and 1-phenyl-5-mercaptotetrazole free from polymer in a second case. The coatings were dried, and samples cut and exposed to a standard negative in the standard testing setup for contact type emulsion to obtain matched prints. All prints were developed for 1 minute at 68° F. in a developer made by diluting 1 part of the following solution:

Water	ml	500
N-methyl-p-aminophenol sulfate	g	3.0
Sodium sulfite (anhydrous)	g	45.0
Hydroquinone	g	12.0
Sodium carbonate (anhydrous)	g	67.5
Potassium bromide	g	1.9

Add water to make 1.0 liter.

with 2 parts of water, rinsed in water and fixed in a fixing bath of the composition:

Water	ml	850
Sodium thiosulfate	g	240.0
Sodium sulfite (anhydrous)	g	15.0
Acetic acid (28%)	ml	48.0
Boric acid (crystals)	g	7.5
Potassium alum	g	15.0

Add water to make 1.0 liter.

for five minutes followed by washing for an hour in running water at room temperature. Processed prints from each coating were dried on a hot ferrotype plate, a cold ferrotype plate and on a cheese-cloth type screen to evaluate plumming. The results are tabulated as follows:

TABLE I

Emulsion	Grams 1-Phenyl-5-mercapto-tetrazole	Fog	Relative Exposure	Contrast Grade	Plummed?
Control	none	none	25	2	Yes.
With agent	1.360	none	30	2½	No.
With agent and polymer	0.400	none	25	2	Slight.

The last column of the table indicates whether or not plumming occurred on the hot ferrotype plate. The amount of 1-phenyl-5-mercaptotetrazole used in per emulsion unit which is defined as that quantity of emulsion having a silver content equivalent to that of 500 ml. of 3N $AgNO_3$ at 25° C.

Example II

To a solution containing 5 g. of the diethylaminoethyl methacrylate polymer described in procedure B above (48% polymer by weight in toluene) dissolved in 25 ml. of toluene was added slowly with agitation a solution prepared by dissolving 0.4 g. of 1-phenyl-5-mercaptotetrazole in 10 ml. of ethyl alcohol containing methyl alcohol in the proportion, 100 parts of 190 proof ethyl alcohol to 10 parts of pure methyl alcohol. The resulting solution was then dispersed in 150 ml. of water containing 0.8 g. of sodium dodecyl sulfate free from electrolytes as the dispersant. Again a blending mixer was employed to aid dispersion, agitation being continued for three minutes after mixing the solutions. After blending, the suspension was diluted to 500 ml. with distilled water. The dispersion thus obtained was tested in the same manner as described in Example I. A summary of the significant results is presented in Table II:

TABLE II

Emulsion	Grams 1-Phenyl-5-mercapto-tetrazole	Fog	Relative Exposure	Contrast Grade	Plummed on Hot Ferrotype?
Control	none	trace	27	2	Yes.
Containing Agent	1,360	none	34	2½	No.
Containing Agent and polymer	0.320	none	23	2	No.

Example III

To a solution containing 2.5 g. of the dimethylaminoethyl methacrylate polymer prepared according to procedure B (48% polymer by weight in toluene) described above dissolved in 15 ml. of toluene there was added slowly with agitation a solution made by dissolving 0.5 g. of 1-phenyl-5-mercaptotetrazole in 10 ml. of ethyl alcohol containing methyl alcohol in the proportions, 100 parts of 190 proof ethyl alcohol to 10 parts of pure methyl alcohol. The solution obtained was then dispersed in 150 ml. of water containing 2 g. of sorbitan trioleate polyoxyalkylene ether containing 2 to 20 —O—CH_2CH_2— groups of the type described in Blake et al. U. S. Patent 2,400,532, free from electrolytes as the dispersant. To aid suspension a blending mixer was used, agitation being carried on over a period of three minutes after mixing the solutions. Upon completion of blending, the suspension was diluted to 500 ml. with distilled water. The resultant dispersion was tested in the same manner as described in Example I. A tabulation of pertinent results is given in Table III. The last column of this table indicates whether or not plumming occurred on a hot ferrotype plate.

TABLE III

Emulsion	Grams 1-Phenyl-5-Mercaptotetrazole	Fog	Relative Exposure	Contrast Grade	Plummed?
Control	None	Trace	19	2	Yes.
Containing agent	2.00	None	23	2½	No.
Containing agent and polymer.	1.36	None	20	2	Some.

Example IV

To a solution containing 5 g. of the dimethylaminoethyl methacrylate polymer prepared according to procedure B (48% polymer by weight in toluene) described previously dissolved in 15 ml. of toluene there was added slowly with agitation a solution prepared by dissolving 0.5 g. of 1-phenyl-5-mercaptotetrazole in 10 ml. of ethyl alcohol containing methyl alcohol in the proportions, 100 parts of 190 proof ethyl alcohol to 10 parts of pure methyl alcohol. The solution obtained was then dispersed in 150 ml. of distilled water containing 2 g. of the sorbitan trioleate polyoxyalkylene ether described in Example III free from electrolytes as the dispersant. A blending mixer was used to aid dispersion, agitation being carried out for three minutes after mixing the solutions. Upon completion of blending, the suspension was diluted to 500 ml. with distilled water. The dispersion obtained was evaluated in the same manner described in Example I. The results are summarized in Table IV. The last column of this table indicates whether or not plumming occurred on a hot ferrotype plate.

TABLE IV

Emulsion	Grams 1-Phenyl-5-Mercaptotetrazole	Fog	Relative Exposure	Contrast Grade	Plummed?
Control	None	Trace	19	2	Yes.
Containing agent	2.00	None	23	2½	No.
Containing agent and polymer.	1.36	None	20	2	No.

Example V

A solution was prepared, containing 0.5 g. of 1-phenyl-5-mercaptotetrazole as an anti-plumming agent dissolved in 15 ml. of ethyl alcohol containing methyl alcohol in the proportions, 100 parts 190 proof ethyl alcohol to 10 parts pure methyl alcohol. This was added to a solution composed of 5 g. of diethylaminoethyl methacrylate polymer made according to procedure B (48% polymer by weight in toluene) dissolved in 25 ml. of toluene. The solution obtained was dispersed in 150 ml. of distilled water containing 2 g. of the sorbitan trioleate polyoxyalkylene ether described in Example III as the dispersing agent. Vigorous agitation in a blending mixer was employed for approximately three minutes to facilitate the formation of a uniform suspension. The resultant dispersion was diluted to 500 ml. with distilled water and tested as described in Example I. The results are presented in Table V. The last column of this table indicates whether or not plumming occurred on a hot ferrotype plate.

TABLE V

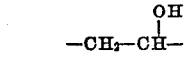
Emulsion	Grams 1-Phenyl-5-Mercaptotetrazole	Fog	Relative Exposure	Contrast Grade	Plummed?
Control	None	Trace	21	2	Yes.
Containing agent	2.00	None	30	2½	No.
Containing agent and polymer.	2.04	None	29	2¼	No.

In place of the specific anti-plumming agent described in the foregoing examples there may be substituted other such agents. Among the compounds which can be used for this purpose are the 5-mercaptotetrazoles having in the 1-position a group taken from the class consisting of a hydrogen atom and a hydrocarbon group which are described in Kendall et al., U. S. P. 2,403,927 including 1-methyl-, 1-ethyl-, 1-α-naphthyl-, 1-p-diethylaminophenyl-, 1-o-methoxyphenyl-, 1-p-chlorphenyl-, 1-benzyl, and 1-cyclohexyl-5-mercaptotetrazoles; the anti-plumming and anti-bronzing compounds disclosed in Knott et al. U. S. Patent 2,461,987 including S-ethylthiuronium bromide, S-n-butylthiuronium bromide, S-cetyl thiuronium iodide, S-amidoethylthiuronium chloride, S-2-thiazylamidomethylthiuronium chloride and S-2-pyridylamidomethylthiuronium chloride.

Similarly in place of the specific polymeric amino-nitrogen containing materials described in the foregoing examples there may be substituted any of such materials which are described above. Among the materials which are particularly useful are polydimethylaminomethylstyrene and polydialkylaminoethyl methacrylates which can be polymerized after the manner described in procedure B above using the same catalyst and similar temperature conditions. The dimethylaminoethyl methacrylate monomer can be made after the manner described in procedure A above by substituting dimethylaminoethanol in equivalent amount for the diethylaminoethanol.

Among the useful solvents or diluents which may be used as a medium for adding the anti-plumming or anti-bronzing agent and polymeric amino-nitrogen containing material to the colloid solution or dispersion are toluene, xylene, tri-o-cresyl phosphate, methyl phthalate, and ethyl alcohol and mixtures of two or more of such solvents.

While gelatin has been described in the foregoing examples as a suitable colloid for the silver halide emulsions other colloids can be substituted in like manner with similar results. Among such colloids are polyglycuronic acid, polyvinyl alcohol polyvinyl esters and ethers and acetals which contain sufficient intralinear



groups to make them hydrophilic or water-soluble in character, hydrolyzed ethylene/vinylacetate copolymers, agar agar, etc. Suitable colloids of these types are described in the following U. S. patents: Jennings et al. 2,397,864 and McQueen 2,397,866.

The examples illustrate that it is important to strike a proper concentration balance between the anti-plumming agent and the protecting polymer if adequate inertization is to be obtained. This also affords a means of regulating the ratio of inertized to non-inertized anti-plumming agent, which can be applied in some cases to fog control.

It will be apparent from the above examples that when a polymeric amino-nitrogen material is used one can obtain good anti-plumming effects with less than a third the amount of the anti-plumming agent normally required. When the anti-plumming agent is an efficient anti-fogging material, such as the 1-phenyl-5-mercaptotetrazole used in the foregoing examples, the use of the smaller amounts permitted by the presence of the polymeric amino-nitrogen material is not disadvantageous, since fogging can be controlled by the free agent present without affecting other photographic characteristics such as speed and contrast because of the small amounts re-

quired to minimize fog compared to the quantity needed to prevent plumming.

The invention is not limited to emulsions for photographic printing papers and similar papers, although that is the preferred aspect of the invention. The emulsions can be used in portrait and lithographic film and in seismographic recording materials, materials for recording spectographic line densities, etc.

An advantage of the invention is that it provides improved photographic elements. A further advantage is that it provides such elements which do not have adverse image densities or image color effects upon drying of the developed elements. A still further advantage is that the anti-plumming and/or anti-bronzing agents do not leach out during processing. They can be used in smaller amounts thus reducing or eliminating any unfavorable side effects, e. g., densitization. The above objects can be obtained in accordance with the invention in a simple manner and with relatively inexpensive materials. In many cases this technique makes it possible to divorce fog control from image color control. If the bronze image color is desired, fixing in plain sodium thiosulfate solution will minimize release of the anti-plumming agent and allow bronzing.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A photographic colloid-silver halide emulsion having dispersed therethrough particles of a polymeric amino-nitrogen containing organic material which is insoluble in water and 5% aqueous ammonia but soluble in 1% aqueous acetic acid and forms hard, resin-like films, said particles containing a sulfur-containing organic compound which has the property of preventing bronze- to plum-colored silver images upon the hot-drying of developed photographic silver images.

2. A photographic element comprising a paper sheet support bearing a photographic colloid-silver halide emulsion layer said emulsion having dispersed therethrough particles of a polymeric amino-nitrogen containing organic material which is insoluble in water and 5% aqueous ammonia but soluble in 1% aqueous acetic acid and forms hard, resin-like films, said particles containing a sulfur-containing organic compound which has the property of preventing bronze- to plum-colored silver images upon the hot-drying of developed photographic silver images.

3. A photographic gelatino silver halide emulsion having dispersed therethrough particles of a polymeric amino-nitrogen containing organic resin insoluble in water and 5% aqueous ammonia but soluble in 1% aqueous acetic acid and forms hard resinous films said particles containing a 5-mercapto-tetrazole having in the 1-position a group taken from the class consisting a a hydrogen atom and a hydrocarbon radical.

4. A photographic gelatino silver halide emulsion having dispersed therethrough particles of polymeric diethylaminoethyl methacrylate containing a 5-mercaptotetrazole having in the 1-position a group taken from the class consisting of a hydrogen atom and a hydrocarbon radical, said polymeric diethylaminoethyl methacrylate being insoluble in water and 5% aqueous ammonia and soluble in 1% aqueous acetic acid and forming hard, resin-like films.

5. An emulsion as set forth in claim 4 where said tetrazole is 1-phenyl-5-mercaptotetrazole.

6. A photographic gelatino silver halide emulsion having dispersed therethrough particles of polymeric dimethylaminoethyl methacrylate containing a 5-mercaptotetrazole having in the 1-position a group taken from the class consisting of a hydrogen atom and a hydrocarbon radical, said polymeric diethylaminoethyl methacrylate being insoluble in water and 5% aqueous ammonia and soluble in 1% aqueous acetic acid and forming hard, resin-like films.

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