Silver halide photographic element and process for preparing a dispersion of discrete particles of water insoluble polymeric matting agent in aqueous compositions.

A process for providing a matt surface on a photographic element, which element comprises a support base, one or more light sensitive silver halide emulsion layers coated on said support base and at least one outer non-light sensitive protective layer, said process comprising:

1. providing a dispersion of a polymeric matting agent in water,
2. mixing the dispersion of step (1) in a hydrophilic colloid aqueous solution,
3. including the resulting hydrophilic colloid dispersion in said outer non-light sensitive protective layer, wherein said mixing step (2) is performed in presence of a stilbene polysulfonate compound.

A silver halide photographic element comprising a support base, one or more light-sensitive silver halide emulsion layers and at least one outer non-light-sensitive gelatin protective layer comprising discrete particles of a polymeric matting agent and a stilbene polysulfonate compound.
FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive element having incorporated in a hydrophilic colloid layer thereof discrete particles of a water-insoluble polymeric matting agent and to a process for preparing a dispersion of discrete particles of said polymeric matting agent in aqueous compositions.

BACKGROUND OF THE ART

In the field of photography, water-insoluble matting agents have been used in top or back hydrophilic colloid layers of silver halide light-sensitive materials to prevent adhesion when materials are stored in rolls, cartridges or cassettes in conditions of relatively high humidity and temperature, to prevent electrostatic charges by reducing the area of contact of the photographic material, to prevent the formation of Newton's rings during printing and enlargement, or to decrease the occurrence of scratches during storage or packing of the photographic material.

It is well known in the art that, in order to solve these problems, fine particles of inorganic substances such as silicon dioxide, magnesium oxide, calcium carbonate and the like, or organic substances such as polymethylmethacrylate, cellulose acetate propionate and the like are incorporated as matting agents into the outermost layers of a photographic material. These and other matting agents are described, for example, in US Pat. No. 3,411,907 and British Pat. No. 837,529. Said matting agents are insoluble in alkaline processing solutions and remain in the processed photographic material.

In same cases it is desired to remove the matting agents during or after development processing for the purposes of improving transparency and graininess of the final image. Therefore, matting agents insoluble in neutral or acidic solutions and soluble in alkaline medium have been described in the art. In particular, alkali-soluble matting agents consisting of methacrylic acid - methylmethacrylate copolymers have been described in US Pat. Nos. 2,391,181, 2,992,101, 3,767,448 and 4,142,894, and in British Pat. No. 878,520, and copolymers of styrene and a,β-ethylenically unsaturated carboxy containing monomers have been described in British Pat. No. 1,055,713. Such matting agents can be incorporated in the photographic layers in the form of discrete particles by dispersing a solution of the matting agent in a water-immiscible organic solvent in an aqueous gelatin solution, eliminating the organic solvent, and then introducing the obtained dispersion into the coating composition of the photographic layer. Organic solvents or combinations thereof have been studied with the copolymers of methacrylic acid and methylmethacrylate, the basic solvent being butanol and mixtures thereof with other solvents. Since butanol is a solvent with low volatility it must be removed by cooling the dispersion and washing with deionized water.

Alkali-soluble matting agents consisting of methacrylic acid - ethylmethacrylate copolymers containing from 20 to 50 % by weight of methacrylic acid have been described in US Pat. No. 4,447,525. These copolymers dissolve in high concentrations in highly volatile organic solvent such as ethylacetate, a solvent which can be easily removed by evaporation from the dispersion of the polymer in aqueous gelatin.

The matting agents are characterized by the number average particle sizes (APS) of their discrete particles and in the patents there are teachings on how to control the APS in the process of synthesis thereof.

Another characteristic of matting agents is their particle size distribution (PSD), in one aspect this is the measurement of the proportion of the larger size discrete particles present in the dispersion. The presence of huge particles having a dimension which exceeds 10 μm in diameter may cause undesirable side effects such as disturbance of coating uniformity of the photographic material and disturbance of distinct layer relationships of a plurality of superposed layers of the photographic material. EP Appl. No. 370,405 discloses matting agents having a PSD not exceeding 10 μm which do not give rise to the above undesirable side effects. In spite of this, when the polymeric matting agent dispersion is mixed with aqueous gelatin, agglomeration of the beads can take place. The formation of aggregates in coating solutions may effectively form larger size particle groupings which cause undesirable side-effects such as a disturbance of coating uniformity, a formation of a haze in the processed light sensitive elements, an impairment of the trasparency of the image formed, and a deterioration of the graininess of the image.

US Patent No. 4,142,894 discloses a copolymer of methyl methacrylate and methacrylic acid with a molar ratio of 6:4 to 9:1 which does not form aggregates in coating solution even when the copolymer particles are used in a large quantity. GB Patent No. 1,496,534 discloses a silver halide photographic material having a surface layer containing at least one organic fluoro-compound and at least one carboxy compound containing a hydrophobic group, said material suffering less aggregation of matting agent in coating solution. These solutions are, from one way, referred to a selected and preferred matting agent, and
SUMMARY OF THE INVENTION

The present invention relates to a process for providing a matt surface on a photographic element, which element comprises a support base, one or more light sensitive silver halide emulsion layers coated on said support base and at least one outer non-light sensitive protective layer, said process comprising:

1. providing a dispersion of a polymeric matting agent in water,
2. mixing the dispersion of step (1) in a hydrophilic colloid aqueous solution,
3. including the resulting hydrophilic colloid dispersion in said outer non-light sensitive protective layer, wherein said mixing step (2) is performed in presence of a stilbene polysulfonate compound.

In another aspect the present invention relates to a silver halide photographic element comprising a support base, one or more light-sensitive silver halide emulsion layers and at least one outer non-light sensitive protective layer comprising discrete particle of a polymeric matting agent and a stilbene polysulfonate compound.

DETAILED DESCRIPTION OF THE INVENTION

 Accordingly, the present invention relates to a process for providing a matt surface on a photographic element, which element comprises a support base, one or more light sensitive silver halide emulsion layers coated on said support base and at least one outer non-light sensitive protective layer coated on said layers or the back side of said support base, said process comprising:

1. providing a dispersion of a polymeric matting agent in water,
2. mixing the dispersion of step (1) in a hydrophilic colloid aqueous solution,
3. including the resulting hydrophilic colloid dispersion in said outer non-light sensitive protective layer, wherein said mixing step (2) is performed in presence of a stilbene polysulfonate compound.

Examples of ethylenic unsaturated monomers having carboxyl groups thereon from which can derive the repeating units (a) of the polymeric matting agent include acrylic acid, methacrylic acid, maleic acid (including monosubstituted maleates such as monomethyl maleate, monoethyl maleate and monophenyl maleate), itaconic acid (including monosubstituted itaconate such as monomethyl itaconate, monoethyl itaconate and monobutyl itaconate), fumaric acid (including monosubstituted fumarate such as monomethyl fumarate and monoethyl fumarate), crotonic acid, citraconic acid, N-(meth)acryloylamino acids such as N-acrylylglycine, N-methacryloylglycine, N-acryloylalanine, N-methacryloylalanine and N-acryloylproline, vinylbenzoic acid, maleic acid monoamide, N-alkylmaleic acid monoamides such as N-ethylmaleic acid monoamide and N-butylmaleic acid monoamide, itaconic acid monoamide, N-alkylitaconic acid monoamide such as N-ethylitaconic acid monoamide and N-butylitaconic acid monoamide.

Examples of ethylenic unsaturated monomers from which can derive the repeating units (b) of the polymeric matting agent include acrylic acid esters such as methyl acrylate, ethyl acrylate, n-buty1 acrylate and phenyl acrylate, methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, isopropyl methacrylate and p-chlorophenyl methacrylate, styrenes such as styrene, methylstyrene, α-methylstyrene, chloromethylstyrene and bromostyrene, vinyl esters such as vinyl benzoate, vinylphenyl acetate and vinyl naphthoate, vinyl ethers such as allyl butyl ether, methoxymethyl vinyl ether and phenyl vinyl ether, olefins such as ethylene, propylene, 1-butene and 1-pentene, unsaturated nitriles such as acrylonitrile and methacrylonitrile, vinyl ketones such as vinyl methyl ketone and methoxymethyl vinyl ketone, and vinyl chloride.

Of such monomers, methacrylic acid is particularly preferable as the ethylenic unsaturated monomers having carboxyl groups thereon from which derive the repeating units (a) above and methacrylic acid esters such as methyl methacrylate and ethyl methacrylate are particularly preferable as ethylenic unsaturated monomers from which derive the repeating units (b) above.

Accordingly, the preferred polymeric matting agent for use in the process of the present invention may be represented by the following formula:
wherein \( m + n \) is equal to 100 (approximately 100 as end-capping groups may be present) and each of \( m \) and \( n \) represents respectively the percentage by weight of said repeating units (a) and (b) of said polymeric matting agent and \( R \) represents methyl or ethyl.

In a particular embodiment, the polymeric matting agent useful in the process of the present invention can be represented by the following formula:

\[
\text{CH}_3 \\
\left(-\left(\text{CH}_2-\text{C}^\cdot\right)_m-\left(\text{CH}_2-\text{C}^\cdot\right)_n\right) \text{COOH} \\
\text{CH}_3 \\
\left(-\left(\text{CH}_2-\text{C}^\cdot\right)_p\right) \text{COOR}
\]

wherein \( p \) is an integer of from 1,000 to 10,000, preferably from 3,000 to 7,000 and \( R \) represents methyl or ethyl.

Said polymers can be prepared from the polymerization through ethylenically unsaturated groups of the monomers described above, using any conventional polymerization mechanism, preferably free radical polymerization. In general, the free radical polymerization is carried out by heating a reaction mass at a proper temperature (which usually does not exceed 100 °C and preferably is between 50 °C and 100 °C) in a proper solvent (usually ethanol or methanol). The reaction mass contains the monomer (or a mixture of the two monomers) in a proper concentration with respect to the solvent (usually at a concentration that does not exceed 40% by weight of the monomer [or a mixture of the two monomers] with respect to the solvent, preferably between 15% to 30%) in the presence of a polymerization catalyst (for example of the free radical type, such as benzoyl peroxide or cumene hydroperoxide, or of the azoic type, such as \( \alpha,\alpha' \)-azobisisobutyronitrile). The obtained polymer can be then separated from the reaction mixture for example by precipitation into a non-solvent, such as water, and drying.

The present invention is not limited to the specific examples of polymeric matting agents described above, said examples representing a particular embodiment only. Any polymeric matting agents known in the photographic art can be used in combination with said polysulfonate stilbene compounds to reduce particle aggregation in coating solutions. Other examples of said polymeric matting agents can be found in Research Disclosure, December 1989, Item 308119, Section XVI.

According to the process of the present invention, before the mixing step with an aqueous hydrophilic colloid solution, a dispersion in water of the polymer described above is provided. Any method known in the art can be used to provide the dispersion. For example, the polymeric matting agent may be dissolved in a water insoluble organic solvent and then the obtained solution dispersed in water. According to another method, the polymeric matting agent dispersion can be obtained directly from the polymerization under agitation of the monomer in water and/or an organic solvent, which is a solvent for the monomer(s) but not for the polymer. Generally, the organic solvent is eliminated from the dispersion by washing the dispersion with pure water or by heating, as known in the art. These and other methods are widely disclosed in the art, for example, in US Patent No. 2,391,181, 2,701,245, 3,767,448, 4,447,525, GB Patent No. 878,520, 1,055,713, 2,078,992, Research Disclosure, December 1989, Item 308119 and April 1982, Item 21617.

Useful organic solvents to prepare the above described dispersion include halogenated hydrocarbons such as chloroform, dichloromethane, carbon tetrachloride, 1,1-dichloromethane, 1,2-dichloroethane and 1,1,1-trichloroethane, aliphatic esters such as ethyl acetate, butyl acetate and isopropyl acetate, aromatic hydrocarbons such as benzene, toluene and xylene, aliphatic hydrocarbons such as pentane and \( n \)-hexane, aliphatic ketones such as methyl ethyl ketone and methyl isobutyl ketone, higher aliphatic alcohols such as \( n \)-butanol and isobutanol, and the like. Said organic solvents have a boiling point which is preferably less than 150 °C, and more preferably less than 100 °C. The solvents also may have a solubility in water at 20 °C which is preferably less than 20 grams per liter, and more preferably less than 10 grams per liter.

The dispersion is then mixed with an aqueous hydrophilic colloid solution. The hydrophilic colloid is preferably gelatin, but also gelatin derivatives and any of the many other polymeric compounds known in the photographic art, such as albumin, polyvinyl alcohol, alginates, cellulose hydrodized esters, hydrophilic
polyvinyl polymers, dextrans, polyacrylamides, acrylamide and alkylacrylate hydrophilic copolymers, can also be used, alone or in combination with gelatin.

According the present invention said mixing step is performed in the presence of a stilbene polysulfonate compound (i.e., a compound having a nucleus consisting of two polysulfonate benzene rings joined by an ethylene group, said benzene rings being optionally substituted with organic substituents).

Said stilbene polysulfonate compound is represented by the following formula (I):

\[
\begin{align*}
\text{(Y)}_n & \quad \text{SO}_3\text{H} \\
\text{CH}=\text{CH} & \quad \text{(X)}_n \\
\text{(Y)}_n & \quad \text{(X)}_n
\end{align*}
\]

wherein X is SO\(_3\)H or SO\(_3\)M, in which M is an alkaline or alkaline earth metal, Y is represented by the following formula:

\[
\begin{align*}
\text{R}_1 & \quad \text{A} \\
\text{C} & \quad \text{Z} \\
\text{R}_2 & \quad \text{NH} \\
\text{(X)}_n & \quad \text{CH}=\text{CH} \\
\text{(X)}_n & \quad \text{(II)}
\end{align*}
\]

in which A is a bivalent atom or group of atoms, Z is a group of atoms capable of completing a 5- or 6-membered heterocyclic ring, said ring containing from 1 to 3 nitrogen atoms and 2 to 5 carbon atoms, \(\text{R}_1\) and \(\text{R}_2\) independently may be a hydrogen atom, a hydroxyl group, an aryloxy group, (e.g., phenoxyl, o-toloxyl, p-sulfoenoxyl, etc.), an alkoxyl group, (e.g., methoxyl, ethoxyl, propoxyl, butoxyl, isopropoxyl, isobutoxyl, isopentoxy, etc.), a polyoxyalkylene, a halogen atom, (e.g., chlorine, bromine, etc.) a heterocyclic radical, (e.g., morpholynyl, piperidyl, etc.), an alkylthio group, (e.g., methylthio, ethylthio, etc.), an arylthio group, (e.g., phenylthio, tolythio, etc.), a heterocyclylthio group, (e.g., benzothiazylthio, etc.) an amino group, an alkylamino group, (e.g., methylamino, ethylamino, propylamino, dimethylamino, diethylamino, dodecylamino, cyclohexylamino, \(\text{C}-\text{H}\))-hydroxyethylamino, di-\(\text{C}-\text{H}\))-hydroxyethylamino, \(\text{C}-\text{H}\))-sulfoethylamino, etc.), or an arylamino group, (e.g., anilino, o-\(\text{C}-\text{H}\))- and p-sulfoanilino, o-\(\text{C}-\text{H}\))- and p-chloroanilino, o-\(\text{C}-\text{H}\))- and p-anisylanilino, o-\(\text{C}-\text{H}\))- and p-toludino, o-\(\text{C}-\text{H}\))- and p-carboxyanilino, o-\(\text{C}-\text{H}\))- and p-aminoanilino, o-\(\text{C}-\text{H}\))- and p-hydroxylanilino, p-acetamidoanilino, sulfonaphthylamino, etc.), and wherein n is 1 to 4, and m is 0 to 1.

Said stilbene polysulfonate compound is preferably represented by the following formula (II):

\[
\begin{align*}
\text{R}_1 & \quad \text{N} \\
\text{R}_2 & \quad \text{N} \\
\text{X} & \quad \text{CH}=\text{CH} \\
\text{X} & \quad \text{(X)}_n \\
\text{R}_1 & \quad \text{N} \\
\text{R}_2 & \quad \text{N} \\
\text{(X)}_n & \quad \text{(II)}
\end{align*}
\]

wherein X, \(\text{R}_1\), \(\text{R}_2\), and n are the same described in formula (I) above.

Examples of such stilbene polysulfonate compounds useful in the process of the present invention are listed below, but these are not the sole examples that can be used in the present invention. Other useful stilbene polysulfonate compounds are disclosed, for example, in US Pat. Nos. 2,875,058, 2,933,390, 2,945,762, 2,961,318 and in Research Disclosure, Item 17804, February 1979 and Item 308119, December 1989, Section V. As disclosed in these references, said stilbene compounds have been previously employed in the textile field, paper field and photographic field as whitening agents, brighteners and/or
supersensitizers in combination with carbocyanine derivatives. EP Appl. No. 251,282 discloses the use of a stilbene polysulfonate compound as deaggregant of carbocyanine dyes to obtain the proper absorption wavelength (other deaggregants are suggested and reference about dye aggregation, a different problem as compared with polymeric matting agent aggregation, is shown in Herz, Photographic Science and Engineering, 18, pp. 323-335, May/June 1974). These references do not disclose said stilbene polysulfonate compounds as deaggregants for polymeric matting agents in photographic layers. Such stilbene polysulfonate compounds are sold under various trade names such as Leucophor B, Calcofluor White MR, Tinopal (SP, SFP, STP, MSP, WR, BV277, 2B, GS, NG), Blancofor SC, Hiltamine (BSP, N, 6T6), and the like.
The stilbene polysulfonate compounds above can be present in an amount of from 0.05 to 5% by weight, preferably from 0.1 to 1%, of the total weight of the resulting hydrophilic colloid dispersion. In a preferred embodiment of the process of the present invention said stilbene polysulfonate compound is dissolved in the hydrophilic colloid solution and then to that resulting solution is added the polymeric matting agent aqueous dispersion.

The polymeric matting agents above become dispersed in the aqueous solution of the hydrophilic colloid in the form of finely divided particles with fewer than 1% of any particle aggregates having more than three particles. Preferably, there are substantially no aggregates of more than three particles. Said dispersions are then introduced into the coating composition of the outer light-insensitive layer of a silver halide light sensitive element. Said outer layer may be a surface protective layer coated on the silver halide emulsion layers, or a backing protective layer coated on the support base on the side opposite to that containing the light-sensitive layers, or may be both of them. It is more preferred to incorporate said dispersion into the surface protective layer.

Accordingly, in another aspect the present invention relates to a silver halide photographic element
comprising a support base, one or more light-sensitive silver halide emulsion layers and at least one outer non-light-sensitive protective layer coated on said layers or the back side of said support base, said at least one outer protective layer comprising discrete particles of a polymeric matting agent and a stilbene polysulfonate compound represented by the formula (I) above.

In a preferred embodiment said stilbene polysulfonate compound is represented by the formula (II) above.

Examples of stilbene compounds useful in the photographic element of the present invention are the same listed above.

The dispersion of polymeric matting agent in hydrophilic colloid solution containing the stilbene polysulfonate compounds is present in an outer layer of the photographic element of the present invention.

In the photographic elements of the present invention, the matting agents are incorporated in a quantity of about 50 to about 600 mg., and more preferably from about 150 to about 400 mg. per square meter of the surface layer. The binding agent of such layer preferably is gelatin, but treated gelatins like the so-called acid or basic gelatins, the gelatins treated with enzymes, gelatin derivatives and modified gelatins, albumin, polyvinyl alcohol, alginites, cellulose hydrolyzed esters, hydrophilic polyvinyl polymers, dextrans, polyacrylamides, acrylamide and alkylacrylate hydrophilic copolymers, can also be used, alone or in combination with gelatin.

Several additives, such as those known in the art, including, but not limited to, hardeners, plasticizers, surfactants, antistatic agents, polymeric latexes, anticalcium and antispot agents can be incorporated into said surface layer.

The light-sensitive silver halide photographic elements of this invention may be any photographic color element such as color negative films, color reversal films, color papers, etc., as well as any black-and-white photographic element such as X-ray light-sensitive elements, black-and-white photographic printing papers, black-and-white negative films, etc.

In a particular embodiment the photographic element of the present invention may be a color photographic element which comprises a plurality of hydrophilic (i.e., permeable to the water photographic processing solutions) emulsion layers containing silver halides dispersed in gelatin, associated with auxiliary hydrophilic gelatin layers, interlayers, antihalo layers, backing layers, said plurality of layers being coated onto a hydrophobic support base. Such silver halide emulsions are sensitive or sensitized to the blue and associated with non-diffusing yellow-forming couplers (upon color development with p-phenylene diamine after exposure), or are sensitized to the green and associated with non-diffusing magenta (blue red) forming couplers, or sensitized to the red and associated with non-diffusing cyan (blue-green) forming couplers.

The photographic element can contain silver halide emulsions, chemical sensitizers, spectral sensitizers and desensitizers, optical brighteners, antifoggants and stabilizers, couplers, acutance dyes, hydrophilic colloids and gelatin substituents, coating aids, hardeners, plasticizers and antistatic agents, as known to the man skilled in the art and can be prepared by following known coating techniques applied to known support bases, as described in Research Disclosure, December 1978, 17643 and December 1989, 308119, which is incorporated herein as reference.

The photographic elements of this invention, after exposure, are processed to form a visible image upon association of the silver halide with an alkaline water medium in the presence of a developing agent contained in the medium or in the elements themselves, as known in the art. In the case of color photographic elements, the processing comprises at least a color developing bath and, optionally, a pre-hardening bath, a neutralizing bath, a first (black and white) developing bath, etc. These and other baths which complete the photographic processing (e.g., bleaching, fixing, bleach-fixing, intensifying, stabilizing and washing baths) are well-known in the art and are described for instance in Research Disclosure 1978, 17643 and December 1989, 308119, incorporated as described above as reference.

In another aspect, the photographic element of the present invention may be an X-ray photographic element which comprises a polymeric base of the type commonly used in radiography, for instance a polyester base, and in particular a polyethylene terephthalate base.

On at least one surface, preferably on both surfaces of the base there is coated a silver halide emulsion layer in a hydrophilic colloid. The emulsions coated on the two surfaces may also be different and comprise emulsions commonly used in photographic elements, such as silver chloride, silver iodide, silver chlorobromide, silver chloro-bromo-iodide, silver bromide and silver bromo-iodide emulsions, the silver bromo-iodide emulsions being particularly useful for the X-ray elements. The silver halide crystals may have different shapes, for instance cubic, octahedral, spherical, tabular shapes, and may have epitaxial growth. They generally have mean sizes ranging from 0.2 to 3 μm, more preferably from 0.4 to 1.5 μm. The emulsions are coated on the base at a total silver coverage comprised in the range from about 2 to 7 or 3 to 6 grams per square meter. The silver halide binding material used is a water-permeable hydrophilic colloid,
which is preferably gelatin, but other hydrophilic colloids, such as gelatin derivatives, albumin, polyvinyl alcohol, alginites, cellulose hydrolyzed esters, hydrophilic polyvinyl polymers, dextran, polyacrylamides, acrylamide hydrophilic copolymers and alkylacrylates can also be used alone or in combination with gelatin.

In addition to the features specifically described above, the photographic elements of this invention, in the light-sensitive silver halide emulsion layers or in other layers, can include additional addenda of a conventional nature, such as stabilizers, antifoggants, brighteners, absorbing materials, hardeners, coating aids, plasticizers, lubricants, matting agents, antikinking agents, antistatic agents, and the like, as described in Research Disclosure, Item 17643, December 1978 and in Research Disclosure, Item 18431, August 1979.

Preferred radiographic elements are of the type described in BE Patent 757,815 and in US Patent 3,705,858, i.e. elements wherein at least one light-sensitive silver halide emulsion layer is coated on both surfaces of a transparent support, the total silver coverage per surface unit for both layers being lower than about 6 g/m², preferably lower than 5 g/m². Such supports are preferably polyester film supports, such as polyethylene terephthalate films. Generally said supports for use in medical radiography are blue tinted. Preferred blue tinting dyes are anthraquinone dyes, such as those described in US Patents 3,488,195; 3,848,139; 3,918,976; 3,933,502; 3,948,664 and in UK Patents 1,250,983 and 1,372,668.

The exposed radiographic elements can be processed by any of the conventional processing techniques. Such processing techniques are illustrated for example in Research Disclosure, Item 17643, cited above. Roller transport processing is particularly preferred, as illustrated in US Patents 3,025,779; 3,515,556; 3,545,971 and 3,647,459 and in UK Patent 1,269,268. Hardening development can be undertaken, as illustrated in US Patent 3,232,761.

As regards the processes for the silver halide emulsion preparation and the use of particular ingredients in the emulsion and in the light-sensitive element, reference is made to Research Disclosure 18,431 published in August 1979, wherein the following chapters are dealt with in deeper details:

IA. Preparation, purification and concentration methods for silver halide emulsions.
IB. Emulsion types.
IC. Crystal chemical sensitization and doping.
II. Stabilizers, antifogging and antifolding agents.
II(A). Stabilizers and/or antifoggants.
II(B). Stabilization or emulsions chemically sensitized with gold compounds.
II(C). Stabilization of emulsions containing polyalkylene oxides or plasticizers.
II(D). Fog caused by metal contaminants.
II(E). Stabilization of materials comprising agents to increase the covering power.
II(F). Antifoggants for dichroic fog.
II(G). Antifoggants for hardeners and developers comprising hardeners.
II(H). Additions to minimize desensitization due to folding.
II(I). Antifoggants for emulsions coated on polyester bases.
II(J). Methods to stabilize emulsions at safety lights.
II(K). Methods to stabilize x-ray materials used for high temperature. Rapid Access, roller processor transport processing.
III. Compounds and antistatic layers.
IV. Protective layers.
V. Direct positive materials.
VI. Materials for processing at room light.
VII. X-ray color materials.
VIII. Phosphors and intensifying screens.
IX. Spectral sensitization.
X. UV-sensitive materials
XI. Bases

The present invention is now illustrated by reference to the following examples.

EXAMPLE 1

A set of seven dispersions using some surface active coating aids and/or dispersing agents was prepared as follows.

An aqueous solution of surfactant or dispersing agents of table 1 was added to 24 ml of a 10% aqueous solution of gelatin at 45 °C with stirring.

After a pause of three minutes, always at 45 °C and under low stirring, to the resultant solution was added 80 ml of a 10% aqueous solution of polymethylmethacrilate (PMMA) having particles with an average
diameter of 4 μm. Finally, water was added to the whole dispersion to make 100 g and stirred for additional three minutes.

## TABLE 1

<table>
<thead>
<tr>
<th>DISPERSION</th>
<th>DISPERSING AGENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>TRITON™ X-100 10% w/w</td>
</tr>
<tr>
<td>B</td>
<td>L-9342 5% &quot; 10 ml</td>
</tr>
<tr>
<td>C</td>
<td>TEGITOL™ 4 10% &quot; 4.5 ml</td>
</tr>
<tr>
<td>D</td>
<td>TEGOBETAINET™ 5% &quot; 10 ml</td>
</tr>
<tr>
<td>E</td>
<td>TAMOL™ 850 10% &quot; 2.5 ml</td>
</tr>
<tr>
<td>F</td>
<td>TAMOL™ 850 10% &quot; 2.5 ml</td>
</tr>
<tr>
<td>G</td>
<td>+ COMPOUND A 10% &quot; 3.5 ml</td>
</tr>
<tr>
<td></td>
<td>+ COMPOUND A 10% &quot; 4 ml</td>
</tr>
</tbody>
</table>

Compound A is a polysulfonated triazinyl stilbene compound, within the general formulas I and II above, and sold by Ciba-Geigy AG under Tinopal™ SFP tradename. Triton™ is a tradename of polyethoxylated alkyl phenols sold by Rohm and Haas Co., Tamol™ is a tradename of soluble salts of polymeric carboxylic acids, Tergitol™ is a tradename of sodium salts of alkanol sulfates sold by Union Carbide Co. Chemical Division, Tegobetaine™ is a tradename of betaine derivatives sold by Th. Goldschmidt AG, and L-9342 is a fluorinated salt corresponding to the formula:

\[
\text{CH}_3 \text{CH-NH}_2 \cdot \text{C}_{8} \text{F}_{17} \text{SO}_3 \text{H}
\]

\[
\text{CH}_2 \cdot (\text{OCH}_2 \text{CH}_2)^a (\text{OCH}_2 \text{CH}_2)^b (\text{OCH}_2 \text{CH})^c \text{NH}_2 \cdot \text{C}_{8} \text{F}_{17} \text{SO}_3 \text{H}
\]

wherein \(b = 8.5\) and \(a + c = 2.5\), sold by Dow Corning Co.

All dispersions were tested in the top coat of a XD/A 3M X-Ray Film. Sample of films have been processed into a 3M XAF/2 fixing bath and PMMA particles are then observed under a microscope. Results are summarized in the following table 2.

## TABLE 2

<table>
<thead>
<tr>
<th>DISPERSION</th>
<th>AGGREGATES (WITH 3 OR MORE BEADS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20%</td>
</tr>
<tr>
<td>B</td>
<td>15%</td>
</tr>
<tr>
<td>C</td>
<td>25%</td>
</tr>
<tr>
<td>D</td>
<td>20%</td>
</tr>
<tr>
<td>E</td>
<td>20%</td>
</tr>
<tr>
<td>F</td>
<td>5-10%</td>
</tr>
<tr>
<td>G</td>
<td>0%</td>
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</tbody>
</table>
EXAMPLE 2

A set of twenty dispersions using some surface active coating aids and/or dispersing agents was prepared, following the same procedure of example 1. All dispersions were tested as in example 1. In table 3 the adjuvants added for each dispersion, and the results obtained according the procedure of example 1, are summarized. The term "AGGREGATES" of Table 3 means clusters of more than three particles.

<table>
<thead>
<tr>
<th>DISPERSION</th>
<th>DISPERSING AGENT</th>
<th>AGGREGATES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>COMPOUND A</td>
<td>10% w/w 2.5 ml NO</td>
</tr>
<tr>
<td>2</td>
<td>COMPOUND A</td>
<td>10% &quot; 4 ml NO</td>
</tr>
<tr>
<td>3</td>
<td>COMPOUND A</td>
<td>10% &quot; 8 ml NO</td>
</tr>
<tr>
<td>4</td>
<td>COMPOUND B</td>
<td>10% &quot; 2.5 ml NO</td>
</tr>
<tr>
<td>5</td>
<td>COMPOUND C</td>
<td>10% &quot; 2.5 ml NO</td>
</tr>
<tr>
<td>6</td>
<td>COMPOUND D</td>
<td>10% &quot; 2.5 ml NO</td>
</tr>
<tr>
<td>7</td>
<td>TAMOL™850</td>
<td>10% &quot; 8 ml YES</td>
</tr>
<tr>
<td>8</td>
<td>TAMOL™850</td>
<td>10% &quot; 4 ml YES</td>
</tr>
<tr>
<td>9</td>
<td>TAMOL™850</td>
<td>10% &quot; 2.5 ml YES</td>
</tr>
<tr>
<td>10</td>
<td>COMPOUND B</td>
<td>10% &quot; 4 ml NO</td>
</tr>
<tr>
<td></td>
<td>+ TAMOL™850</td>
<td>10% &quot; 4 ml</td>
</tr>
<tr>
<td>11</td>
<td>COMPOUND C</td>
<td>10% &quot; 4 ml NO</td>
</tr>
<tr>
<td></td>
<td>+ TAMOL™850</td>
<td>10% &quot; 4 ml</td>
</tr>
<tr>
<td>12</td>
<td>TRITON™X-100</td>
<td>10% &quot; 5 ml YES</td>
</tr>
<tr>
<td>13</td>
<td>TRITON™X-305</td>
<td>10% &quot; 5 ml YES</td>
</tr>
<tr>
<td>14</td>
<td>TRITON™X-405</td>
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</tr>
<tr>
<td>15</td>
<td>TRITON™X-200</td>
<td>5% &quot; 10 ml YES</td>
</tr>
<tr>
<td>16</td>
<td>BRIJ™35</td>
<td>5% &quot; 10 ml YES</td>
</tr>
<tr>
<td>17</td>
<td>BRIJ™56</td>
<td>5% &quot; 10 ml YES</td>
</tr>
<tr>
<td>18</td>
<td>NIAPROOF™</td>
<td>10% &quot; 5 ml YES</td>
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<tr>
<td>19</td>
<td>MAPROFIX™</td>
<td>10% &quot; 5 ml YES</td>
</tr>
<tr>
<td>20</td>
<td>HOSTAPUR™SAS</td>
<td>10% &quot; 5 ml YES</td>
</tr>
</tbody>
</table>

Compounds A,B,C,D, are polysulfonated triazinyl stilbene compounds, included within the general formulas I and II above, respectively sold by Ciba-Geigy AG under Tinopal™SFP, 2B, STP, CH3517 tradenames. Brij™ is a tradename of polyoxyethylene alkyl ether nonionic surfactants sold by Atlas Chemical Ind., Maprofix™ is a tradename of sodium salts of alkyl sulfates sold by Onix Chemical Company, Niaproof™ is a tradename of sodium salts of alkanol sulfates sold by Niacet Co., and Hostapur™ is a tradename of alkyl sulfonates sold by Hoechst AG.

Claims

1. A process for providing a matt surface on a photographic element, which element comprises a support base, one or more light sensitive silver halide emulsion layers coated on said support base and at least one outer non-light sensitive protective layer, said process comprising:
(1) providing a dispersion of a polymeric matting agent in water,
(2) mixing the dispersion of step (1) in a hydrophilic colloid aqueous solution, and
(3) including the resulting hydrophilic colloid dispersion in said outer non-light sensitive protective layer,
said process being characterized by said mixing step (2) being performed in the presence of a stilbene polysulfonate compound.

2. The process according to claim 1 characterized in that said stilbene polysulfonate compound is represented by the following formula:

\[
\begin{align*}
(X)_{n} & \quad \text{(wherein } X \text{ is } -\text{SO}_{3}\text{H or } -\text{SO}_{3}\text{M, in which } M \text{ is an alkaline or alkaline earth metal, } Y \text{ is represented by the following formula:}} \\
\end{align*}
\]

\[
\begin{align*}
\text{(X)_{n}} & \quad \text{(wherein } A \text{ is a bivalent atom or group of atoms, } Z \text{ is a group of atoms capable of completing a 5 or 6 membered heterocyclic ring containing from 1 to 3 nitrogen atoms and 2 to 5 carbon atoms, } R_{1} \text{ and } R_{2} \text{ may be the same or different groups and each represents a hydrogen atom, a hydroxyl group, an aryloxy group, a polyoxyalkylene, a halogen atom, a heterocyclic radical, an alkylthio group, an arylthio group, a heterocyclylthio group, an amino group, an alkylamino group, or an arylamino group, and wherein } n \text{ is 1 to 4, and } m \text{ is 0 to 1.}} \\
\end{align*}
\]

3. The process according to claim 1 characterized in that said stilbene polysulfonate compound is represented by the following formula:

\[
\begin{align*}
\text{(X)_{n}} & \quad \text{wherein } X \text{ is } -\text{SO}_{3}\text{H or } -\text{SO}_{3}\text{M, in which } M \text{ is an alkaline or alkaline earth metal, } R_{1} \text{ and } R_{2} \text{ may be the same or different groups and each represents a hydrogen atom, a hydroxyl group, an aryloxy group, a polyoxyalkylene, a halogen atom, a heterocyclic radical, an alkylthio group, an arylthio group, a heterocyclylthio group, an amino group, an alkylamino group, an arylamino group, and wherein } n \text{ is 1 to 4.}} \\
\end{align*}
\]

4. The process according to claim 1 characterized in that said stilbene polysulfonate compound is added
in an amount of from 0.05 to 5% by weight of the resulting hydrophilic colloid dispersion.

5. The process according to claim 1 characterized in that said stilbene polysulfonate compound is added in an amount of from 0.1 to 1% by weight of the resulting hydrophilic colloid dispersion.

6. The process according to claim 1 characterized in that said stilbene polysulfonate compound is dissolved in said hydrophilic colloid aqueous solution.

7. The process according to claim 1 characterized in that said stilbene polysulfonate compound is added in an amount of from 0.05 to 5% by weight of the resulting hydrophilic colloid dispersion.

8. The process according to claim 7 characterized in that said polymeric matting agent comprises a backbone of the following formula:

\[
\begin{align*}
\text{CH}_3 & \quad \text{COOH} \\
\hline
\text{CH}_3 & \quad \text{COOR} \\
\end{align*}
\]

wherein \( m + n \) is equal to 100 and each of \( m \) and \( n \) represents respectively the percentage by weight of said repeating units (a) and (b) of said polymer and \( R \) represents methyl or ethyl.

9. The process according to claim 7 characterized in that said polymeric matting agent comprises a backbone of the following formula:

\[
\begin{align*}
\text{CH}_3 & \quad \text{COOR} \\
\hline
\end{align*}
\]

wherein \( p \) is an integer from 1,000 to 10,000, and \( R \) represents methyl or ethyl.

10. The process according to claim 1 characterized in that said hydrophilic colloid comprises gelatin, gelatin derivatives, or organic synthetic polymeric materials.

11. A silver halide photographic element comprising a support base, one or more light-sensitive silver halide emulsion layers and at least one outer non-light-sensitive protective layer comprising both discrete particles of a polymeric matting agent and a stilbene polysulfonate compound.

12. The silver halide photographic element according to claim 11 characterized in that said stilbene polysulfonate compound is represented by the following formula:

\[
\begin{align*}
\text{Y}_m & \quad \text{X}_n \\
\hline
\text{X}_n & \quad \text{Y}_m \\
\end{align*}
\]

wherein \( X \) is \(-\text{SO}_3\text{H}\) or \(-\text{SO}_3\text{M}\), in which \( M \) is an alkaline or alkaline earth metal, \( Y \) is represented by the following formula:
in which $A$ is a bivalent atom or linking group, $Z$ is a group of atoms capable of completing a 5- or 6-membered heterocyclic ring containing from 1 to 3 nitrogen atoms and 2 to 5 carbon atoms, $R_1$ and $R_2$ may be the same or different groups and each represents a hydrogen atom, a hydroxyl group, an aryloxy group, an alkoxyl group, a polyoxyalkylene, a halogen atom, a heterocycle radical, an alkylthio group, an arythio group, a heterocyclithio group, an amino group, an alkylamino group, or an arylamino group,

and wherein $n$ is 1 to 4, and $m$ is 0 to 1.

13. The photographic element according to claim 11 characterized in that said stilbene polysulfonate compound is represented by the following formula:

$$\begin{align*}
\text{R}_1 & \quad \text{R}_2 \\
\text{N} & \quad \text{NH} \\
\text{N} & \quad \text{N} \\
\text{X} & \quad \text{X} \\
\text{X} & \quad \text{X} \\
\text{CH} & \quad \text{CH} \\
\text{N} & \quad \text{N} \\
\text{R}_1 & \quad \text{R}_2
\end{align*}$$

wherein $X$ is $-\text{SO}_3\text{H}$ or $-\text{SO}_3\text{M}$, in which $M$ is an alkaline or alkaline earth metal, $R_1$ and $R_2$ may be the same or different groups and each represents a hydrogen atom, a hydroxyl group, an aryloxy group, an alkoxyl group, a polyoxyalkylene, a halogen atom, a heterocycle radical, an alkylthio group, an arythio group, a heterocyclithio group, an amino group, an alkylamino group, or an arylamino group,

and wherein $n$ is 1 to 4.

14. The silver halide photographic element according to claim 11 characterized in that said protective layer is coated on said silver halide emulsion layers.
### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
<th>Relevant to claim</th>
<th>CLASSIFICATION OF THE APPLICATION (Int. Cl.5)</th>
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<tbody>
<tr>
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<td>(&amp; US-A-4 142 894)</td>
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The present search report has been drawn up for all claims.

**TECHNICAL FIELDS SEARCHED (Int. Cl.5)**

G 03 C