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PHOTOGRAPHIC EMULSIONS, ELEMENTS, AND PROCESSES

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This invention relates to photographic silver halide emulsions. More particularly it relates to improved emulsion layers for lithographic films. The invention also relates to photographic elements bearing such an emulsion layer.

Light-sensitive silver halide emulsion layers used by the graphic arts industry for the production of lithographic plates must meet very high requirement standards. The standards set for the physical, dimensional and photographic properties of such emulsion layers are particularly rigorous. Existing lithographic emulsion layers, however, only partially meet these requirements.

It is therefore an object of this invention to provide a lithographic film emulsion which when coated as a layer on a support exhibits improved dimensional stability, flexibility, impact resistance and anchorage, as well as improved photographic contrast, halftone dot quality and development and exposure latitude. Another object is to provide such an emulsion and layer comprising a novel combination of constituents. A further object is to provide such an emulsion which is readily adapted to existing emulsion manufacturing techniques. Still other objects will be apparent from the following description of the invention.

These and other objects are attained by providing a light-sensitive silver halide emulsion wherein the binding material comprises a mixture of gelatin and an aqueous dispersion of a polymeric vinyl compound, at least one amphoteric dispersing agent of the formula:

$$RNH_p[(CH_2)_nCOOM]_m$$

wherein R is an unsubstituted alkyl group of 12 to 18 carbon atoms, m and n are numbers of 1 and 2, m being preferably 2, p is a number of 2 minus m and M is a cation taken from the group consisting of sodium, potassium, ammonium and hydrogen, said emulsion containing per mole of silver halide, 40 to 80 grams of gelatin, 10 to 60 grams of a polymerized vinyl compound based on the weight of initial monomer in the polymerization reaction mixture and 0.2 to 2.5 grams of a polyoxyethylene compound of the formula:

$$RO(CH_2CH_2O)_nR_1$$

wherein R is hydrogen, alkyl of 1 to 18 carbon atoms, aryl of 6 to 12 carbon atoms, alkylaryl of 7 to 18 carbon atoms and arylalkyl of 7 to 18 carbon atoms, R_1 is hydrogen and alkyl of 1 to 3 carbon atoms and n is a number of 6 to 2500.

The preferred polymeric vinyl compound is an acrylic acid ester taken from the group consisting of a homopolymer of an acrylic acid ester, a homopolymer of an α-hydrocarbon substituted acrylic acid ester and a copolymer of said acrylic acid esters, said copolymer containing at least 90% by weight of units of said acrylic acid esters. This compound in the form of a hydrosol or colloidal dispersion is preferably dispersed with the aqueous silver halide gelatin emulsion by means of at least one amphoteric alkyliminodicarboxylate dispersing agent of the formula:

$$RN[(CH_2)_nCOOM]_2$$

wherein R is an unsubstituted alkyl group of 12 to 18 carbon atoms, n is a number of 1 and 2 and M is a cation taken from the group consisting of sodium, potassium, ammonium and hydrogen.

In a preferred embodiment of this invention an aqueous silver bromochloride lithographic emulsion containing a reduced amount of gelatin, as indicated below, is sensitized and digested in a manner familiar to those skilled in the art. After digestion, but prior to coating, there is added to the emulsion an aqueous acrylic acid ester polymeric dispersion containing an amphoteric amino acid dispersing agent of the type described above and a polyoxyethylene compound, also as described above. The emulsion is then coated to form an emulsion layer on a suitable support such as a cellulose ester or polyester photographic film base. It is preferred that, for each mole of silver halide, the emulsion contain from 40 to 80 grams of gelatin, from 10 to 60 grams of acrylic acid ester polymer, based on the initial weight of monomer in the polymerization reaction mixture, and from 0.2 to 2.5 grams of the polyoxyethylene compound. The coating is dried, exposed sensitometrically through a neutral density wedge, processed by developing, fixing, etc., and the image densities read on a conventional type of densitometer. The sensitometric behavior of the coating is essentially equivalent to that of conventional coatings such as those in which gelatin is the sole binder. The coating exhibits considerable improvement over conventional coatings, however, in its improved dimensional stability and halftone dot equality.

The aqueous polymeric dispersions used in this invention are prepared in a conventional manner, starting with a polymerizable liquid monomer. This monomer is emulsified with water by means of dispersing agents of the type described above, and subjected to a conventional emulsion polymerization using a free-radical initiator, e.g., hydrogen peroxide, an organic peroxide or an azobis-nitrile compound as disclosed in U.S. Patent 2,471,959, e.g., α,α'-azobis(isobutyronitrile). In Procedure A, to follow, a description is given of the preparation of a particularly preferred dispersion, i.e., polyethyl acrylate.

The invention will be further illustrated by but is not intended to be limited to the following procedures and examples wherein the dots were evaluated for quality, the coatings were evaluated for their humidity coefficient of expansion and for their dimensional stability as follows:

The dots were evaluated microscopically for characteristics desirable in halftone reproduction, e.g., sharpness of edge, scale ranging from small to large dots, the opacity of small dots, etc. They were rated subjectively on a numerical scale, in which

1.0 is excellent
2.0 is good
3.0 is acceptable
4.0 is poor, not acceptable

Decimals are used to estimate intermediate quality.

The coatings were also evaluated for their humidity coefficient of expansion (cm. change per cm. of film length per 1% change in relative humidity) and for their dimensional stability (processing size change in cm. change per cm. of film length) when put through a conventional processing cycle, including redrying.

In determining humidity coefficient of expansion, a 30-inch strip of a coating is scribed with a sapphire microgroove recording stylus so as to produce, near each end of the strip, fiducial marks which will be in close proximity to the fiducial marks of a calibrated nickel steel plate (e.g., Invar) when the strip and plate are brought into contact with one another. The strip is then conditioned for 24 hours at a constant temperature and humidity and then, while maintained at the same conditions, placed in flat contact with the nickel steel plate. Two Gaertner filar micrometer microscopes, having a

total magnification of 100× and micrometer least count of 2×10^{-5} inches, are mounted so that measurements may be obtained by means of a graduated glass scale of distances between the fiducial marks on the coating strips and the corresponding fiducial marks on the nickel steel plate. The steel plate, microscopes and coating strip are all housed in a conditioning cabinet equipped with arm ports and viewing windows. By vector addition of these distances and the known distance between the fiducial marks on the nickel steel plate, the distance is determined between the two fiducial marks on the strip at a known humidity. The process is repeated, with 24-hour preconditioning, to determine the distance between the strip's two fiducial marks at another known humidity. The change in length at the two humidity values divided by the average of the two lengths and divided by the difference in % relative humidity gives the humidity coefficient of expansion.

Dimensional stability in terms of processing size change is determined in a very similar manner. Distance between fiducial marks is determined on a coating strip which has been conditioned under constant temperature and humidity for 24 hours. The strip is then conventionally processed and dried, conditioned at the previous constant temperature and humidity for 24 hours, and measured to determine the change in distance between fiducial marks. The processing size change is calculated by dividing this change in distance by the average distance. "Effective contrast" in the tables is determined by drawing a straight line between the net optical densities of 0.1 to 2.4 on the net optical density vs. logarithm of the exposure plot and taking the tangent of the angle formed between the straight line and the log exposure axis.

PROCEDURE A

A 22-liter fluted, chemically resistant, glass reaction vessel was equipped with a thermometer, anchor stirrer, three-neck adapter containing a reflux condenser, a gas inlet tube and a stopper. The system was purged with nitrogen for 10 to 20 minutes and maintained under a positive nitrogen pressure throughout the polymerization. To the vessel were added 4 liters of distilled water, 2300 grams of a 20% by weight aqueous solution of disodium-N-tallow-β-iminodipropionate which was washed in with 600 ml. distilled water, 1000 grams of a 5% by weight aqueous solution of gelatin which was washed in with 600 ml. of distilled water, and 3300 grams ethyl acrylate from which polymerization inhibitor had been removed by extraction with alkali. The stirred reaction mixture was heated by a water bath to 80–85° C., was held for 10 minutes at that temperature and was cooled to 75° C. To the reaction mixture was added 130 ml. of an 18% by weight aqueous solution of hydrogen peroxide and the temperature maintained at 75° C. until the polymerization was initiated. Foaming was controlled by moderating with cold water. After the initial exothermic reaction had subsided, 3 liters of distilled water and 1700 grams of additional ethyl acrylate monomer were added. The temperature was adjusted to 75±3° C. and 70 ml. of an 18% by weight aqueous solution of hydrogen peroxide was added. After the second stage of the polymerization had subsided, the temperature was raised to 80–85° C. for 2 hours. The polymeric solution was then heated to 90° C., held at that temperature for 10 minutes and was steam distilled for 1 to 2 hours to remove residual monomer. The solution was cooled and filtered through felt to remove any residue. The composition by weight of the polymeric solution made by this procedure is as follows: 30% polyethyl acrylate; 2.77% disodium-N-tallow-β-iminodipropionate; 0.3% gelatin.

PROCEDURE B

The fluted reaction vessel described in Procedure A was flushed with nitrogen and maintained at a positive nitrogen pressure as described therein. To the vessel

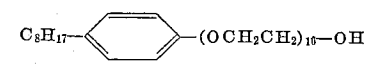
were added: 2400 ml. of distilled water, 4000 grams of a 20% by weight aqueous solution of disodium-N-tallow-β-iminodipropionate which was washed in with 500 ml. of distilled water, 1000 grams of a 5% by weight aqueous solution of gelatin washed in with 600 ml. of distilled water and 3300 grams of monomeric butyl acrylate from which polymerization inhibitor had been removed by extraction with alkali. The reaction mixture was heated by a water bath to 90–95° C., was held for 10 minutes at that temperature and was cooled to 85° C. To the mixture was added 130 ml. of an 18% by weight aqueous solution of hydrogen peroxide which caused the polymerization to initiate. The reaction was moderated when necessary with ice and/or cold water. After the initial exothermic reaction had subsided, 3 liters of distilled water and 1700 grams of additional butyl acrylate monomer were added. The vessel temperature was adjusted to 85±3° C. and 70 ml. of an 18% by weight aqueous solution of hydrogen peroxide was added. After the second stage of initiation had subsided, the vessel temperature was raised and held at 90–95° C. for 2 hours. The polymeric solution was steam distilled for 1 to 2 hours to remove any residual monomer. The resulting dispersion was cooled and filtered through felt to remove any residue. The composition by weight of the polymeric solution made by this procedure is as follows: 30% polybutyl acrylate; 4.8% disodium-N-tallow-β-iminodipropionate; 0.3% gelatin.

PROCEDURE C

Procedure B was repeated except that 4400 ml. of distilled water and 2000 grams of the 20% disodium-N-tallow-β-iminodipropionate solution were used in the initial charging of the vessel. The composition of a polymeric solution made by this procedure is as follows: 30% polybutyl acrylate; 2.4% disodium-N-tallow-β-iminodipropionate; 0.3% gelatin.

Example I

A lithographic emulsion having a silver halide composition of 30 mole percent AgBr and 70 mole percent AgCl and having 20 grams of gelatin present per mole of silver halide for the steps of precipitation and ripening was freed of unwanted, soluble, by-product salts by a coagulation and wash procedure as taught in Waller et al., U.S. Patent 2,489,341, wherein the silver halide and most of the gelatin were coagulated by an anionic wetting agent, sodium lauryl sulfate, using an acid coagulation environment. Following the washing step, the emulsion coagulate was redispersed in water together with 47 grams of additional bulking gelatin. This redispersed emulsion was treated with a conventional sensitizer and an optical sensitizer to confer sensitivity to green light, was digested at 55° C. to increase sensitivity, was cooled to a holding temperature of about 38° C. and treated with conventional post-sensitization additives and stabilizers such as additional halide, antifogger, etc., as is common in the art. Before coating, the emulsion was divided into three equal portions and there was added to these portions, per mole of silver halide, 0, 10 and 16.7 ml. of a 10% aqueous solution of a polyoxyethylene compound which has the formula



and 74 g. of an aqueous polyethyl acrylate dispersion prepared as described in Procedure A. The emulsions thus prepared were coated on polyethylene terephthalate photographic film base coated on both sides with a vinylidene chloride/methyl acrylate/itaconic acid copolymer, as described in Example IV of Alles, U.S. Patent 2,779,684, on which had been coated on both sides a thin anchoring substratum layer of gelatin (0.5 mg./dm.^{2}) over which, on the backing side, there had been coated an antihalation dye-containing layer of gelatin containing 25% by weight of polyethyl acrylate dispersed as disclosed in Procedure

A. The coating provided a silver halide coating weight equivalent to about 51 mg. of silver per square decimeter when dry. Samples of these coatings were given a 20-second, intensity-scale sensitometric step wedge exposure to a white light tungsten source. The exposure in each successive step increased by the factor of the fourth-root-of-two. The exposed samples were developed for 2¼ minutes in the following lithographic developer to determine their sensitometric characteristics:

Water	cc	500
Na_2SO_3, anhydrous	g	30.0
Paraformaldehyde	g	7.5
$NaHSO_3$	g	2.2
Boric acid	g	7.5
Hydroquinone	g	22.5
KBr	g	1.6

Water to make 1.0 liter.

Other samples of these coatings were exposed to a ruled glass halftone screen in an apparatus simulating the conditions used in the preparation of halftone copies, and similarly developed 2¼ and 2¾ minutes, respectively, to determine their ability to yield good halftone dots. After development, the coatings were treated in a conventional acid hardening and fixing bath containing 153 g. anhydrous $Na_2S_2O_3$ per liter, washed in tap water, and dried in a conventional manner. The sensitometric characteristics of these coatings are tabulated below, with a commercial lithographic film serving as a control.

TABLE I

Polyoxyethylene Derivative per Mole of Silver Halide	Fog	Sensitometric Properties			
		2¼ Minute Development		Halftone Dot Quality at Development Time	
		Relative Sensitivity	Effective Contrast	2¼ min.	2¾ min.
0 g	.01	100	8.0	2.0	3.5
1.0 g	.01	90	8.6	1.7	1.8
1.7 g	.01	70	9.1	1.5	1.5
Control	.01	100	6.5	2.2	2.8

It was observed that, while the polyoxyethylene compound has a tendency to decrease speed slightly, it increases contrast and improves halftone dot quality markedly. It is particularly effective in maintaining good dot quality over an extended range of development times, which enhances the working latitude of the film in use.

The dimensional characteristics of the improved gelatin silver halide emulsion layers of this invention containing reduced gelatin and the polyethyl acrylate dispersion were evaluated and compared with those of a normal gelatin control.

	Humidity Coefficient of Expansion	Processing Size Change
Experimental Films (Average values for first three films in Table I above)	1.5×10^{-5}	1.0×10^{-4}
Normal gelatin control	2.0×10^{-5}	2.0×10^{-4}

It has been found that reducing the gelatin content of the emulsion and replacing part of the gelatin with a preferred polymeric dispersion consistently improves dimensional stability relative to normal all-gelatin controls.

Example II

An aqueous gelatino-silver bromochloride lithographic emulsion prepared through the stages of sensitization described in Example I was divided into a number of portions just prior to coating. To each portion was added an aqueous dispersion of polybutyl acrylate prepared as described in Procedure B above in an amount equal to 177 g. of polymeric dispersion per mole of silver halide in the emulsion. In addition, to all of the emulsion portions except the control, there were added various polyoxyethylene compounds as 1% by weight aqueous solutions so as to give the concentrations, based on silver halide concentration, indicated in the table below. These emulsions were then coated on a dimensionally stable polyethylene terephthalate film base as described in Example I except that the antihalation dye-containing layer coated on the backing side was replaced by a gelatin antihalation layer containing no polyethyl acrylate dispersion. The emulsion coatings were then dried and tested for photographic speed, contrast, and dot quality as previously described, with the results being tabulated below.

TABLE II

Polyoxyethylene Derivative Added	G./mole of Silver Halide	Relative Speed	Effective Contrast	Halftone Dot Quality at Development Time	
				2¼ min.	2¾ min.
1—None		100	5.0	3.0	4.0
2—*a*	.033	100	6.8	2.0	3.0
3—*a*	.067	76	7.4	2.3	3.8
4—*b*	.4	98	6.5	2.0	3.8
5—*b*	.5	84	7.5	2.0	3.8
6—*c*	1.0	87	6.2	2.3	3.0
7—*c*	1.67	66	5.5	2.0	2.0
8—*d*	1.0	87	6.2	2.0	2.0
9—*d*	1.67	64	6.6	2.3	1.7
10—*e*	.266	71	5.9	2.0	2.3
11—*e*	.40	60	5.9	2.3	1.4
12—*f*	.133	81	6.5	3.0	3.8
13—*f*	.25	81	6.45	2.3	2.1

In the above table, the polyoxyethylene derivatives, coded *a, b, c, d, e* and *f*, have the general formula:

$$RO(CH_2CH_2O)_nR_1$$

where the values of *n*, R and R_1 are as follows:

Code	*n*	R	R_1
a	80	H	H
b	6-7	Octyl	H
c	9-10	Octylphenyl	CH_3
d	16	do	H
e	30	do	H
f	2,300	H	H

Example III

A lithographic emulsion was prepared as described in Example I through the stages up to and including the sensitization, cooled to about 38° C. and treated with convention post-sensitization additives and stabilizers as described in Example I. The emulsion was divided into ten portions. To two of the portions, serving as controls, no polymeric dispersion was added. To each of the remaining eight portions was added, per mole of silver halide, 80 g. of an aqueous dispersion containing 30 g. of polyethyl acrylate per 100 g. of the dispersion. Four different dispersions of the polymer were employed, as described below, all of which contained the same amount of dispersing agent as calculated on the basis of molar equivalents of carboxyl groups:

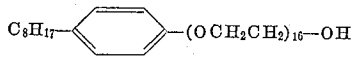
Dispersion a.—The dispersion described in Procedure A wherein the dispersing agent was disodium-N-tallow-β-iminodipropionate and where "tallow" is believed to represent a mixture of the high molecular weight hydrocarbon radicals corresponding to those present in the esters in tallow including oleyl, palmityl, stearyl and myristyl in order of decreasing concentration.

Dispersion b.—A dispersion prepared as in Procedure A except that the dispersing agent was the disodium salt of N-dodecyl-β-iminodipropionate.

Dispersion c.—A dispersion prepared as in Procedure A except that the dispersing agent was the sodium salt of N-alkyl-β-amino propionic acid wherein the alkyl groups contained from 8 to 18 carbon atoms and corresponded to such groups in the higher alcohols obtained from the hydrogenation of coconut oil.

Dispersion d.—A dispersion prepared as in Procedure A except that the dispersing agent was the sodium salt of N-dodecyl-β-amino propionic acid.

As is shown in the table below, there was added to 5 of these portions an aqueous solution containing 1% by weight of a polyoxyethylene compound of the formula



in such amount as to result in a concentration of 1.33 g. of the polyoxyethylene compound per mole of silver halide. The emulsions were coated on the film base support described in Example I, and the coatings were evaluated as described in Example I, giving results as shown in the following table.

TABLE III

Polymeric Dispersion	Polyoxyethylene Derivative per Mole Silver Halide, g.	Rel. Speed	Effective Contrast	Halftone Dot Quality at Development Time	
				2¼ m.	2¾ m.
1—None	0	100	8.3	2.1	2.8
2—None	1.33	69	9.7	1.5	1.6
3—Dispersion *a*	0	170	7.1	2.4	2.7
4—Dispersion *a*	1.33	69	7.4	1.6	1.6
5—Dispersion *b*	0	112	7.5	2.2	3.0
6—Dispersion *b*	1.33	74	8.7	1.7	1.7
7—Dispersion *c*	0	105	7.8	2.2	2.9
8—Dispersion *c*	1.33	72	8.8	1.6	1.6
9—Dispersion *d*	0	100	8.3	2.3	3.1
10—Dispersion *d*	1.33	85	8.3	1.7	1.7

It is apparent that, while all polymeric dispersions added above have a slight tendency to decrease halftone dot quality, the use of the polyoxyethylene compound with the polymeric dispersion provides a remarkable restoration of good dot quality. All of the films containing the dispersion had improved dimensional stability relative to the all-gelatin control.

Example IV

A polymeric solution was prepared as described in Procedure A except that the ethyl acrylate monomer was replaced by monomeric vinyl acetate. Example I was then repeated utilizing the aqueous polyvinyl acetate dispersion in place of the polyethyl acrylate of that example, similar results being obtained.

Example V

A polymeric solution was prepared as described in Procedure A except that vinylidene chloride was used as the monomer and the initial temperatures were maintained only slightly below the reflux temperature of the monomer. Example I was repeated utilizing the aqueous polyvinylidene chloride dispersion in place of the polyethyl acrylate of that example, similar results being obtained.

Example VI

Example V was repeated utilizing a copolymer of 70 parts of vinylidene chloride and 30 parts of ethyl acrylate in place of the homopolymer of Example V, similar results being obtained.

Example VII

A standard gelatin lithographic emulsion and a lithographic emulsion prepared as described in Example I were coated on respective sheets of polyethylene terephthalate photographic film base bearing a gelatin substratum described in Example I. The adhesive character of the gelatin substratum had been partially destroyed prior to the coating by hardening it with formaldehyde. Cross-hatched lines were scribed through the emulsion of each film with a stylus. Pressure-sensitive tape was then applied to the scribed area and rapidly pulled off. The standard emulsion was pulled off the film base in the areas adjoining the scribed lines whereas the emulsion

of this invention remained firmly anchored to the base.

Considerable latitude is possible in the choice of the polymeric vinyl dispersion used. A preferred class of polymers are the alkyl acrylates and methacrylates, e.g., polymers and copolymers of methyl, ethyl, butyl, ethylhexyl acrylate or methyl and butyl methacrylate. In addition, acrylic acid can be used in the preparation of the copolymers provided no more than 10 mole percent of such acid is used in the polymerization with the other constituents. Other useful classes of vinyl monomers used to prepare the water soluble polymeric and copolymeric dispersions are the vinyl esters such as the acetate, propionate, etc.; the vinyl and vinylidene halides such as vinylidene chloride; styrene and substituted styrenes; the dienes such as butadiene; acrylonitrile; alkenes such as ethylene or propylene and the like.

In general, best results are obtained with vinyl monomers which yield the lowest water sensitivity and lowest modulus of elasticity. Thus acrylates will generally be preferable to methacrylates and polyethylene to polyvinylidene chloride polymers and copolymers.

A critical characteristic of the dispersion is the particle size since the intended application requires freedom from light scattering. Particle size may be controlled by techniques of emulsion polymerization known in the art such as the use of adequate concentration of surfactants, the mode of stirring, the concentrations of reactants, temperature, rate of addition of monomers, etc. For most applications particle sizes below 100 mμ are desirable, but for less critical uses particle sizes up to 1μ are permissible.

While emulsion polymerization at ordinary pressures is a convenient technique for obtaining fine dispersions with the preferred acrylate esters, polymerizations under pressure or other techniques which yield fine polymeric dispersions may be more suitable with other monomers.

Amino acid dispersing agents suitable for use in this invention are disclosed in U.S. Patent 2,816,920. Two of these dispersing agents of very particular interest are disodium-N-tallow-β-iminodipropionate and the disodium salt of N-dodecyl-β-iminodipropionate. While the amphoteric alkyliminodicarboxylates are the preferred dispersing agents, alkylaminocarboxylates (i.e., the monocarboxylates) also give satisfactory results, e.g., the sodium salt of N-alkyl-β-aminopropionic acid wherein the alkyl group contains 8 to 18 carbon atoms, etc.

A number of polyoxyethylene derivatives, in addition to the polyoxyethylene compounds already described, are useful in this invention. These include the derivatives disclosed in Stanton, U.S. Patent 2,531,832, of the formula $R—(CH_2CH_2O)_n—R_1$ where R is hydrogen or an aliphatic carboxylic acyl radical of 1 to 18 carbon atoms and R_1 is hydrogen or an aliphatic carboxylic acid radical of 1 to 18 carbon atoms and *n* is 9 to 200 or more; the polyoxyalkylene ethers of ring-dehydration products of hexitols as disclosed in Blake et al., U.S. Patent 2,400,532; the polyoxyethylene ethers of ring dehydration products of hexitols as disclosed in Blake, U.S. Patent 2,533,990; and the oxyethylene compounds of the formula

$$R—(OCH_2CH_2)_n—OR_1$$

where R is taken from the group consisting of hydrogen, alkyl and alkyl-CO— groups of 1 to 18 carbon atoms, R_1 is taken from the group consisting of alkyl and alkyl-CO— groups of 1 to 18 carbon atoms and χ is 6 to 18. It is understood that the value for *n* in the polyoxyethylene compounds, i.e., 6 to 2500, is an average value because the compounds are mixtures of various weight polymers.

Although the preferred emulsions of this invention contain silver halide grains of bromochloride containing at least 50 mole percent chloride, some of the advantages, e.g., dimensional stability, etc., may be realized, where desirable, in aqueous gelatin emulsions containing other types of silver halide grains, e.g., bromide, iodobromide, iodochloride, etc., and mixtures thereof, such as are used

in cine negative, radiographic, microfilm, recording and astronomical films.

The aqueous gelatin emulsions useful in the invention may be prepared by various procedures, e.g., by standard precipitation, washing, sensitization and digestion operations or by precipitating with an anion soap the gelatin phase of a silver halide containing suspension and subsequently separating and washing the gelatin phase, redispersing the gelatin phase in an aqueous medium and digesting. A large number of anion soaps are useful in the emulsion preparation. The classification of these compounds is discussed in the book "Kolloidchemische Grundlagen der Textilveredlung" by Dr. E. Valko, 1937, at pages 519–522, to which reference is made for the meaning of the expression "anion soaps." Generally the class also includes soluble salts of long-chain alkyl carboxylic acids, e.g., soluble salts of fatty acids containing eight or more carbon atoms as, for example, lauric, oleic, ricinoleic, linoleic, stearic and palmitic. These compounds, however, are less satisfactory than long chain alkyl sulfates and sulfonates. Soluble salts of long-chain alkyl sulfonic acids, soluble salts of sulfated higher fatty alcohols in which the alkyl group contains at least 8 carbons and many other sulfonated and sulfated aliphatic and aromatic compounds which are water soluble and contain from 10 to 20 carbon atoms are suitable anion soaps.

The present invention is not limited to the use of a particular film base support as the emulsions may be coated on various films and plates composed of glass, metal, e.g., aluminum, various waterproof papers, cellulose derivatives, e.g., cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate-butyrate, and cellulose nitrate; superpolymers, e.g., nylon, polyvinyl chloride, poly (vinyl chloride co vinyl acetate), polystyrene, polymethylene terephthalates, polycarbonate, e.g., the polycarbonate of 2,2-bis-p-hydroxyphenyl propane, polyethylene terephthalate/isophthalate, etc. Other useful polyester films include those prepared from highly polymerized esters of terephthalic acid and at least one glycol of the formula $HOCH_2—W—CH_2OH$ where W is polymethylene or alkyl substituted polymethylene of 0 to 8 carbons, e.g., 2,2-dimethylpropylene-1,3 or a cycloalkylene radical of 5 to 6 carbon atoms, e.g., cyclopentyl-1,3, and cyclohexyl-1,4. Films comprising up to 20 mole percent of aliphatic dicarboxylic acids based on total moles of acids, e.g., succinic, glutaric, adipic, hexahydroterephthalic and sebacic acids, in addition to at least 15 mole percent terephthalic acid are also useful. The above-described polymers may contain a number, e.g., 1 to 12 or more, of ether groups in the polymer chain. Such ether groups may be added as part of ether containing glycol derivatives or formed by side reactions during polymerization.

Of course, various sublayers may be present to anchor the layer to the base as is common in photographic film and plate manufacture. A suitable example is the vinylidene chloride copolymer coated supports of Alles et al., U.S. Patent 2,627,088. Also, various other auxiliary layers may be employed such as antiabrasion layers and antihalation backing or undercoat layers. Suitable antihalation layers are disclosed in U.S. Patents 1,923,485; 2,085,736; 2,274,782; 2,282,890; etc. A preferred backing layer is prepared by mixing gelatin and an aqueous dispersion of a polymerized vinyl compound of the types disclosed above. For each 10 to 60 grams of polymer there is preferably 40 to 80 grams of gelatin in the backing layer. The ratio of polymer to gelatin can range from 10:80 to 60:40.

The emulsions may be modified by the addition of general emulsion sensitizers, e.g., alkyl thiourea, phenyl isothiocyanate, sodium thiosulfate, and alkyl isothiocyanate; metal compounds, e.g., of gold, platinum, palladium, iridium, rhodium, etc.; antifogging agents, e.g., 2-mercaptobenzothiazole, 1-phenyl-5-mercaptotetrazole, benzotriazole, triazindenes, tetrazindenes and 5-nitrobenzimidazole; sensitizing dyes; hardeners, e.g., formaldehyde and other aliphatic aldehydes, dimethylol urea, trimethylol melamine; chrome alum and other chromium compounds and other emulsion adjuvants.

The novel emulsions of this invention are useful in the manufacture of lithographic photographic films possessing improved physical properties and improved edge sharpness of halftone dots, and development and exposure latitude.

An advantage of the lithographic film bearing the improved photographic emulsion is that the dimensional stability of the emulsion and the coated film element is significantly improved. Another advantage is that the film element possesses improved flexibility, impact resistance and anchorage. Yet another advantage is that by use of the dispersing agents of this invention, polymer particles of sufficiently small size can be formed to provide a transparent film when mixed with gelatin, coated and dried.

The above advantages are achieved essentially without a sacrifice in sensitometric or other physical properties of the lithographic films. Still other advantages will be apparent to those skilled in the art.

What is claimed is:

1. A light-sensitive lithographic silver halide emulsion exhibiting improved halftone dot quality having a binding material which comprises a mixture of gelatin and a polymeric aqueous dispersion of a polymerized vinyl compound and at least one amphoteric dispersing agent of the formula:

$$RNH_p[(CH_2)_nCOOM]_m$$

wherein R is an unsubstituted alkyl group of 12 to 18 carbon atoms, m and n are numbers of 1 and 2, p is a number of 2 minus m, and M is a cation selected from the group consisting of sodium, potassium, ammonium and hydrogen, said emulsion containing a polyoxyethylene compound of the formula:

$$RO(CH_2CH_2O)_nR_1$$

wherein R is hydrogen, alkyl of 1 to 18 carbon atoms, aryl of 6 to 12 carbon atoms, alkylaryl of 7 to 18 carbon atoms and arylalkyl of 7 to 18 carbon atoms, R_1 is hydrogen and alkyl of 1 to 3 carbon atoms, and n is a number of 6 to 2500.

2. A light-sensitive silver halide emulsion having a binding material which comprises a mixture of gelatin and a dispersed acrylic acid ester polymeric compound selected from the group consisting of a homopolymer of an acrylic acid ester, a homopolymer of an α-hydrocarbon substituted acrylic acid ester and a copolymer of said acrylic acid esters, said copolymer containing at least 90% by weight of units of said acrylic acid esters, said polymeric compound dispersed with at least one amphoteric dispersing agent of the formula:

$$RNH_p[(CH_2)_nCOOM]_m$$

wherein R is an unsubstituted alkyl group of 12 to 18 carbon atoms, m and n are numbers of 1 and 2, p is a number of 2 minus m, and M is a cation selected from the group consisting of sodium, potassium, ammonium and hydrogen, said emulsion containing a polyoxyethylene compound of the formula:

$$RO(CH_2CH_2O)_nR_1$$

wherein R is hydrogen, alkyl of 1 to 18 carbon atoms, aryl of 6 to 12 carbon atoms, alkylaryl of 7 to 18 carbon atoms and arylalkyl of 7 to 18 carbon atoms, R_1 is hydrogen and alkyl of 1 to 3 carbon atoms and n is a number of 6 to 2500.

3. A silver halide emulsion as defined in claim 2 wherein the amount of gelatin in said emulsion per mole of silver halide ranges from 40 to 80 grams.

4. A silver halide emulsion as defined in claim 2 where-

in said dispersing agent contains at least one compound of the formula:

$$RN[(CH_2)_nCOOM]_2$$

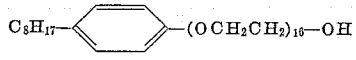
wherein R is an unsubstituted alkyl group of 12 to 18 carbon atoms, n is a number of 1 and 2 and M is a cation taken from the group consisting of sodium, potassium, ammonium and hydrogen.

5. A silver halide emulsion as defined in claim 4 wherein said dispersing agent is disodium-N-tallow-β-iminodipropionate.

6. A silver halide emulsion as defined in claim 4 wherein said dispersing agent is disodium-N-dodecyl-β-iminodipropionate.

7. A silver halide emulsion as defined in claim 2 wherein said polyoxyethylene compound present in said emulsion ranges from 0.2 to 2.5 grams per mole of silver halide.

8. A silver halide emulsion as defined in claim 2 wherein said polyoxyethylene compound has the formula:



9. A silver halide emulsion as defined in claim 2 wherein the dispersed acrylic acid ester polymeric compound is present in said emulsion in an amount of 10 to 60 grams based on the initial weight of monomer to form said polymer per mole of silver halide.

10. A silver halide emulsion as defined in claim 2 wherein said acrylic acid ester polymer is polyethyl acrylate.

11. A silver halide emulsion as defined in claim 2 wherein said acrylic acid ester polymer is polybutyl acrylate.

12. A silver halide emulsion as defined in claim 2 wherein said silver halide is silver bromochloride containing at least 50 mole percent chloride.

13. A photographic element comprising a support bearing at least one layer of the emulsion defined in claim 2.

14. An element as defined in claim 13 wherein said support is a macromolecular polyester material.

15. An element as defined in claim 13 wherein said support is coated with a layer of poly(vinylidene chloride co methyl acrylate co itaconic acid).

16. An element as defined in claim 13 wherein said support is a polyethylene terephthalate film base.

17. An element as defined in claim 13 having a backing layer composed of gelatin and a dispersed polymerized vinyl compound, said gelatin and dispersed polymer being present in said backing layer in a ratio of 1:8 to 3:2.

18. The process of making a light-sensitive lithographic silver halide emulsion exhibiting improved halftone dot quality involving precipitation, washing, sensitization and digestion operations, the steps which comprise admixing with said emulsion containing a reduced amount of gelatin, at some state after digestion and prior to coating said emulsion on a film base, an aqueous dispersion of (1) an acrylic acid ester compound selected from the group consisting of a homopolymer of an acrylic acid ester, a homopolymer of an α-hydrocarbon substituted acrylic acid ester and a copolymer of said acrylic acid esters, said copolymer containing at least 90% by weight of units of said acrylic acid esters, and (2) at least one amphoteric dispersing agent of the formula:

$$RNH_p[(CH_2)_nCOOM]_m$$

wherein R is an unsubstituted alkyl group of 12 to 18 carbon atoms, m and n are numbers of 1 and 2, p is a number of 2 minus m and M is a cation selected from the group consisting of sodium, potassium, ammonium and hydrogen, said emulsion containing a polyoxyethylene compound of the formula:

$$RO(CH_2CH_2O)_nR_1$$

wherein R is hydrogen, alkyl of 1 to 18 carbon atoms, aryl of 6 to 12 carbon atoms, alkylaryl of 7 to 18 carbon atoms and arylalkyl of 7 to 18 carbon atoms, R_1 is hydrogen and alkyl of 1 to 3 carbon atoms and n is a number of 6 to 2500.

19. The process of making a light-sensitive lithographic silver halide emulsion exhibiting improved halftone dot quality including precipitating with an anion soap the gelatin phase of a suspension of silver halide in an aqueous solution of gelatin, separating and washing said gelatin phase, redispersing said gelatin phase in an aqueous medium and digesting, the step which comprises admixing with said emulsion containing a reduced amount of gelatin, at some stage after digestion and prior to coating said emulsion on a film base, an aqueous dispersion of (1) an acrylic acid ester compound selected from the group consisting of a homopolymer of an acrylic acid ester, a homopolymer of an α-hydrocarbon substituted acrylic acid ester and a copolymer of said acrylic acid esters, said copolymer containing at least 90% by weight of units of said acrylic acid esters, and (2) at least one amphoteric dispersing agent of the formula:

$$RNH_p[(CH_2)_nCOOM]_m$$

wherein R is an unsubstituted alkyl group of 12 to 18 carbon atoms, m and n are numbers of 1 and 2, p is a number of 2 minus m and M is a cation selected from the group consisting of sodium, potassium, ammonium and hydrogen, said emulsion containing a polyoxyethylene compound of the formula:

$$RO(CH_2CH_2O)_nR_1$$

wherein R is hydrogen, alkyl of 1 to 18 carbon atoms, aryl of 6 to 12 carbon atoms, alkylaryl of 7 to 18 carbon atoms and arylalkyl of 7 to 18 carbon atoms, R_1 is hydrogen and alkyl of 1 to 3 carbon atoms and n is a number of 6 to 2500.

20. A process as defined in claim 19 wherein said dispersing agent is of the formula:

$$RN[(CH_2)_2COOM]_2$$

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