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PHOTOGRAPHIC EMULSION

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17 Claims. (Cl. 95—7)

This invention relates to photographic emulsions and more particularly to photographic emulsions of the silver halide type.

It is known that the inherent sensitivity of photographic silver halide emulsions (whether spectrally sensitized or not) can be enhanced, and there has been a constant effort to produce higher speeds in photographic emulsions. For example, it is known that the speed of gelatino-silver-halide emulsions can be enhanced by an extended digestion or ripening of the emulsion. It is also known that the speed of silver halide emulsions (spectrally sensitized or not) can be enhanced by incorporating in the emulsions compounds containing a divalent atom of the sulfur group directly joined by a double bond to a single metalloid atom to which is attached at least another group of atoms. Examples of such compounds are allylisothiocyanate and allylthiourea.

We have now found that the speed of photographic silver halide emulsions can be increased by incorporating in the emulsions (spectrally sensitized or not), surface active substances, such as aqueous dispersing or wetting agents, for example, of the cationic sulfonium salt type. (Surface active substances are classified as anionic and cationic, or non-ionic, depending upon whether or not the substances ionize, and if so, depending upon whether the anion or the cation is surface active. Surface active materials are sometimes referred to as capillary active materials, lipophylic materials or materials which possess interface modifying properties.)

Our new method of sensitizing emulsions is an improvement over the known methods of enhancing sensitivity, since the speed increases attained by our new method are complementary to the speed increases that can be attained by the prior methods.

The surface active substances act on the emulsion in unknown manner to increase its effective sensitivity. As a result, the sensitivity is increased by about the same amount at any wavelength within the range of its spectral sensitivity, although in spectrally sensitized emulsions there is frequently observed an appreciable increase in relative sensitivity for longer wavelengths. Inasmuch as the silver ion and hydrogen ion concentration in our emulsions appear to undergo little or no change by virtue of the presence of the surface active substances, we shall refer to the action of the surface active substances as a kind of supersensitization, and we shall refer to mixtures of the surface active substances and spectral (optical) sensitizers as combinations, although we do not intend to imply that the surface active substance and the spectral sensitizer are chemically combined.

Our new supersensitized emulsions are an improvement over supersensitized emulsions known in the art. The increases in sensitivity which can be obtained with supersensitizing combinations of dyes can be enhanced by our new method. Furthermore, whereas with supersentizing combinations of sensitizing dyes (see U. S. Patents 2,075,046, 2,075,047 and 2,075,048, each dated March 30, 1937), the supersensitizing effect is confined more or less to a single spectral region, the sensitization attained in our new emulsions extends throughout the entire region in which the spectral sensitizer acts (and is fairly uniform in degree throughout the entire region), while at the same time the sensitivity in the violet and blue region (where the spectral sensitizer does not act) is also enhanced to about the same degree.

An object of our invention, therefore, is to provide new photographic emulsions. A further object is to provide emulsions sensitized with a supersensitizing combination of a sensitizing dye and a surface active material of the cationic sulfonium salt type. A further object is to provide a process for preparing such emulsions.

According to our invention, we incorporate in a photographic silver halide emulsion, a cationic surface active sulfonium salt substance. The surface active substance can be incorporated in any suitable form, e. g. in the form of a solution in a suitable solvent, such as water or methyl alcohol. The surface active material should be thoroughly incorporated in the emulsion. The surface active material can be added to the finished emulsion, or at any stage of the preparation of the emulsion.

In the case of spectrally sensitized emulsions, the surface active substance can be incorporated in the emulsion before, simultaneously with, or after the sensitizing dye, although in some cases, as hereinafter set forth, it is advantageous to incorporate the sensitizing dye before incorporating the surface active substance. The methods of incorporating sensitizing dyes in emulsions are, of course, well known to those skilled in the art. Ordinarily, it is advantageous to employ a solution of the sensitizing dye in a suitable solvent, e. g. methyl alcohol. Ethyl alcohol or acetone may be employed in cases where the solubility of the sensitizing dye in methyl alcohol is very low.

Sensitizing dyes are ordinarily incorporated in the washed, finished emulsions, and, in accordance with our invention, the surface active substances are also advantageously incorporated in the washed, finished emulsions. However, the surface active substance can be added to the emulsion during the preparation thereof, i. e. during the precipitation, the first digestion, or the second digestion (the ripening). After preparing the emulsions in the presence of the sur-

face active substance, the sensitizing dyes can be incorporated in the so-prepared emulsions.

As cationic sulfonium salt surface active substances, we have found that those which do not contain a hydrogen atom on the sulfonium sulfur atom (i. e. the so-called ternary sulfonium types) are advantageously employed. We have found that the sulfonium cation advantageously should contain at least one organic group containing a chain of at least eight members. Advantageously, such members are from the group consisting of carbon, oxygen, nitrogen and sulfur atoms. One or more aromatic rings, such as a benzene ring, for example, can take the place of one or more of the eight or more atoms. Thus, a benzene ring can take the place of one atom, while a naphthalene ring (two benzene rings fused together) can take the place of two atoms. The atoms attached to the eight or more atoms in the chain (where valence permits) can be hydrogen, oxygen, sulfur, carbon or halogen, for example. Any aromatic ring system in the chain can carry simple substituents. We have found that cationic sulfonium salt surface active substances having a sulfonium cation containing a lipophylic organic group which contains a chain composed of from nine to twelve members selected from the group consisting of carbon atoms, oxygen atoms, sulfur atoms and aromatic ring systems are advantageously employed.

The anion may be any acid radical, such as chloride, bromide, iodide, p-toluenesulfonate, perchlorate or alkylsulfate, for example. Of course, introduction of halide anions into photographic silver halide emulsions alters the halide concentration in the emulsion and compensating changes in the emulsion may be desirable, if such sulfonium salts are employed. For this reason, we ordinarily prefer to employ surface active substances containing anions other than halides. Perchlorates and p-toluenesulfonates are advantageously employed.

The following are representative of organic lipophylic groups containing a chain of at least eight members selected from the group consisting of carbon atoms, oxygen atoms, sulfur atoms and aromatic ring systems:

Nonyl, $CH_3-(CH_2)_8-$ (nine atom chain)
Decyl, $CH_3-(CH_2)_9-$ (ten atom chain)
Lauryl, $CH_3-(CH_2)_{11}-$ (twelve atom chain)
Cetyl, $CH_3-(CH_2)_{15}-$ (sixteen atom chain)
Heptoxymethyl, $CH_3-(CH_2)_6-O-CH_2-$ (nine atom chain)
Undecoxymethyl, $CH_3-(CH_2)_{10}-O-CH_2-$ (thirteen atom chain)
Heptylthiomethyl, $CH_3-(CH_2)_6-S-CH_2-$ (nine atom chain)
Carbnonoxymethyl,

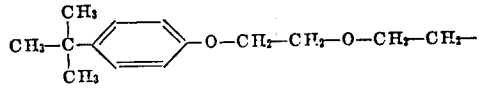
$$CH_3-(CH_2)_8-O-\overset{\overset{O}{\|}}{C}-CH_2-$$ (twelve atom chain)

Caproöxyethyl

$$CH_3-(CH_2)-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-$$

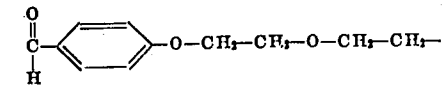
(nine atom chain)

Butoxyethoxyethyl, $CH_3-(CH_2)_3-O-(CH_2)_2-O-CH_2-CH_2-$ (ten atom chain)
Ter-butylphenoxyethoxyethyl



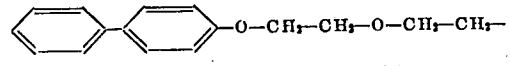
(eight atom+phenyl group chain)

Formylphenyloxyethoxyethyl



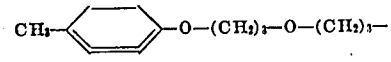
(seven atom+phenyl group chain)

Phenylphenoxyethoxyethyl



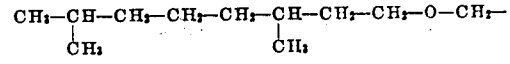
(six atom+two phenyl groups chain)

Methylphenoxypropoxypropyl



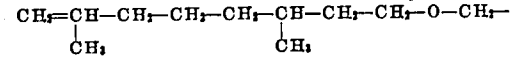
(nine atom+phenyl group chain)

3,7-dimethyloctanoxymethyl



(ten atom chain)

Citronelloxymethyl

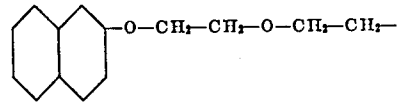


(ten atom chain)

(Alcohol radicals in commercial oil of sandalwood)—O—CH_2— (at least ten atom chain)

ω-Hydroxydecyl HO—CH_2—$(CH_2)_8$—CH_2— (eleven atom chain)

β-Naphthoxyethoxyethyl



(six atom two phenyl group chain)

We have found it advantageous to incorporate spectral sensitizers in the photographic emulsions prior to incorporation of the perchlorate surface active substances. With surface active substances containing anions other than perchlorate, the order of incorporation of the surface active substance with respect to the spectral sensitizer appears to be of small moment.

The quantity of surface active substance which is most advantageously employed varies with the nature of the surface active substance and with the nature of the emulsion. Ordinarily, the most advantageous concentration was found to be between about 20 mg. and about 200 mg. of the surface active substance per gram-mole of silver halide in the emulsion, although greater or smaller concentrations can be employed. We have found that excesses of the surface active substance are advantageously avoided, since excesses produce fog in the emulsions. For surface active substances containing a lipophylic group containing a chain of eight to ten members, we have found that as much as about 400 mg. of surface active substance per gram-mole of silver halide in the emulsion can ordinarily be employed without encountering excessive fog, while with surface active substances containing a lipophylic group containing a chain of eleven to 12 or more members, we have found that not more than about 200 mg. of surface active substance per gram-mole of silver halide should ordinarily be employed.

The optimum range of concentration for any particular surface active substance described herein is ordinarily fairly narrow and can best

be determined by employing a series of concentrations of the surface active substances, separately in several batches of the same emulsion and determining the sensitivity of the several batches before and after incorporation of the surface active substance, in the usual manner, which is, of course, well known to those skilled in the art. Briefly, the method of determining sensitivity of emulsions comprises coating the emulsion onto a glass plate to a suitable thickness and drying the coated emulsion and then testing the resulting photographic plate in a wedge spectrograph and a sensitometer, whereby spectral sensitivity and speed of the emulsion on the plate is determined.

When employing spectrally sensitized emulsions, the spectral sensitizers (sensitizing dyes) are advantageously employed in about their optimum concentration, which ordinarily lies between about 3 mg. and 20 mg. of spectral sensitizer per liter of emulsion containing about 0.25 grammole of silver halide, although concentrations above or below the optimum concentration can be employed. With fine-grain emulsions, which includes most of the ordinarily employed silver chloride emulsions, the ratio of concentration of sensitizing dye to the concentration of silver halide in the emulsion is advantageously larger than in the coarser grain emulsions where smaller amounts of sensitizing dyes usually give optimum sensitization. The optimum concentration, as above referred to, of a sensitizing dye (i. e. the concentration at which greatest sensitivity occurs) can be readily determined in a manner well known to those skilled in the art by measuring the sensitivity of a series of emulsions containing different concentrations of the sensitizing dye.

Our invention is directed particularly to the silver halide developing-out emulsions customarily employed in the art, including the gelatino-silver-chloride, the gelatino-silver-bromide and the gelatino-silver-bromiodide developing-out emulsions, for example. However, our invention can be employed with silver halide emulsions wherein the carrier is other than gelatin, for example, a resinous or cellulosic derivative substance which has substantially no deleterious effect on the light-sensitive materials in the emulsions.

As spectral sensitizers (sensitizing dyes) only those which are non-acidic can be employed in practicing our invention. Sensitizing dyes, such as Congo red, which disperse in water to give a colored anion, i. e. acidic sensitizing dyes, appear to interfere with the surface active agent, with the result that neither the acid dye nor the surface active substance exert a substantially beneficial effect on the emulsion. As non-acidic sensitizing dyes, we include all the known neutral and basic sensitizing dyes, i. e. those sensitizing dyes which do not give colored anions. Some of these non-acidic sensitizing dyes, such as the cyanine dyes, give colored cations. Exemplary of the non-acidic sensitizing dyes are the sensitizing cyanine dyes, (see, for example, United States Patents 1,846,300; 1,846,301; 1,846,302; 1,846,303 and 1,846,304, each dated February 23, 1932, United States Patent 1,861,836, dated June 7, 1932, United States Patent 1,939,201, dated December 12, 1933, United States Patent 1,942,854, dated January 9, 1934, United States Patent 1,957,869, dated May 8, 1934, United States Patent 1,962,124, dated June 12, 1934, United States Patent 1,969,446, dated August 7, 1934, United States Patent 1,973,462, dated September 11, 1934; United States Patent 1,990,507, dated February 12, 1935, United States Patent 2,094,580, dated October 5, 1937, United States Patent 2,112,140, dated March 22, 1938 and French Patent 757,813, published January 5, 1934), the sensitizing merocyanine dyes, (see United States Patent 2,078,233, dated April 27, 1937, United States Patent 2,089,729, dated August 10, 1937, United States Patent 2,153,169, dated April 4, 1939 and United States Patents 2,177,401, 2,177,402, and 2,177,403, dated October 24, 1939), the sensitizing hemi-cyanine dyes, (see United States Patent 2,166,736, dated July 18, 1939) and the sensitizing hemioxonol dyes, (see United States Patent 2,165,339, dated July 11, 1939 and French Patent 841,632, published May 24, 1939).

While the process of our invention is subject to variation, particularly as respects the nature and quantity of surface active substance employed, the nature and quantity of the spectral sensitizer employed, if any, the nature of the silver halide emulsion employed, and the manner of incorporating the surface active substance and the spectral sensitizer (if any) in the emulsions, the following example will serve to illustrate the manner of obtaining our new emulsions. This example is not intended to limit our invention.

Example 1

Into one liter of flowable, washed, finished gelatino-silver-bromide developing-out emulsion containing about 0.25 gram-moles of silver halide were incorporated slowly, with stirring, a methyl alcoholic solution of 2,2'-dimethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine chloride. Sufficient of the alcoholic solution was added to incorporate about 15 mg. of the carbocyanine chloride in the emulsion.

To the resulting emulsion were added slowly and with stirring, a 1% (by weight) aqueous solution of lauryldimethyl-sulfonium-p-toluenesulfonate. Sufficient of the aqueous solution was added to incorporate about 50 mg. of the p-toluenesulfonate in the emulsion.

Photographic elements can be made from emulsions prepared in the above manner by coating the emulsions to a suitable thickness on a suitable support and drying the coated emulsion in a manner well known to those skilled in the art. Suitable supports are, of course, glass, photographic paper support, and photographic film support. The photographic film support may, of course, be of cellulose acetate, cellulose nitrate or any other suitable cellulose derivative and be of any suitable resinous material, such as polyvinyl acetal resin, for example. Our new emulsions are advantageously coated on glass support.

Example 2

Nonyldimethylsulfonium p - toluenesulfonate was the specific salt employed as the addition agent in this example. This salt was incorporated into a sensitized emulsion by procedure comparable to that already described. The nonyldimethylsulfonium p-toluenesulfonate was added in an amount between 20–100 mg. per liter of emulsion. This compound appeared to exhibit very little tendency to cause fog and consequently high concentrations may be employed.

Example 3

In this example bis (laurylmethylsulfonium p-toluenesulfonate) diacetyl was the specific agent employed. Likewise, in this example the diacetyl compound was incorporated in the sensi-

tized emulsion by procedure comparable to that already described. Comparable proportions were employed and a sensitivity increase of in the neighborhood of 50% was obtained when the resultant emulsion was coated on glass or film base.

The following table contains a summary of some of the more practical results obtained according to the instant invention. In this table the "control" referred to is the emulsion without the sulfonium salt. In some instances, as in Table II, the control, as indicated, contains a sensitizing dye. The controls, of course, were processed and otherwise handled in exactly the same manner as the emulsions containing the sulfonium salts.

TABLE I.—*Undyed gelatino-silver-bromiodide emulsion*

Illustration No.	Composition	Speed	γ	Fog
59	Control	560	0.54	.05
60	n-Nonyl dimethyl sulfonium p-toluene sulfonate, 20 mg./liter.	645	0.55	.04

TABLE II.—*Sulfonium compounds in dye-sensitized gelatino-silver-bromiodide emulsion*

Illustration No.	Composition	White light exposure		Fog	No. 12 (minus blue) filter exp.	
		10/i speed	γ		10/i speed	γ
61	(Control) 2,2'-dimethyl-8-ethyl-thiacarbocyanine bromide, 15 mg./liter.	525	0.61	.07	132	0.62
71	n-Nonyl dimethyl sulfonium p-Toluene sulfonate, 30 mg./liter.	605	0.70	.08	190	0.62
72	n-Nonyl dimethyl sulfonium p-Toluene sulfonate 100 mg./liter.	690	0.78	.08	220	0.76
73	n-Octyl dimethyl sulfonium p-Toluene sulfonate 100 mg./liter.	645	0.78	.08	250	0.61
74	n-Decyl dimethyl sulfonium p-Toluene sulfonate 50 mg./liter.	830	0.75	.09	200	0.75
75	(Control) 1'-ethyl-2-methyl thia-2'-cyanine iodide 20 mg./liter.	490	0.69	.05	37	0.76
76	n-Nonyl-dimethyl sulfonium-p-toluene sulfonate 50 mg./liter.	550	0.80	.06	45	0.86
67	(Control) 2-diphenylamino-5(2-ethyl-1-benzothiazylidene ethylidene)-4-(5)-thiazolone, 15 mg./liter.	455	0.82	.06	126	0.83
77	n-Nonyl dimethyl sulfonium p-toluene sulfonate 50 mg./liter.	630	0.84	.09	235	0.75
78	(Control) 2 [4-(1-piperidyl)-1,3-butadienyl] β-naphthiazole ethiodide, 20 mg./liter.	575	0.76	.09	205	0.78
79	n-Nonyl dimethyl sulfonium p-toluene sulfonate, 50 mg./liter.	775	0.78	.10	225	0.78

It is readily apparent from the foregoing illustrations that our procedure of incorporating sulfonium compounds into photographic materials produces improved results. The introduction of sulfonium compounds which as already discussed may be introduced in a variety of ways, increases the speed of photographic emulsions not only to a noticeable extent, but this increase is substantial over a rather wide range. Furthermore, the increase is unaccompanied by undesirable changes in the emulsion such as tendencies to fog, even over wide ranges of concentration, it being kept in mind, however, that due regard is had for not exceeding the amounts herein described, depending upon whether long or short alkyl chain containing compounds are employed and other factors as already explained.

The sulfonium compound described herein may be obtained from various sources and by various methods provided the products are of sufficient purity and otherwise possess qualities rendering them capable of meeting photographic specifications.

The surface active sulfonium salts may be made by various published methods disclosed in patents and other disclosures (see for example United States Patent 2,090,890, dated August 24, 1937, and United States Patent 2,121,823, dated June 28, 1938). Hence, it is unnecessary to discuss the preparation of these compounds herein, since such surface active sulfonium salts per se form no part of the present invention.

It is apparent from the foregoing that our invention is susceptible of some modification; hence we do not wish to be restricted excepting insofar as may be necessitated by the prior art and the spirit of the appended claims.

What we claim as our invention and desire to be secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion sensitized with a cationic surface active sulfonium salt.

2. A photographic silver halide developing-out emulsion sensitized with a cationic surface active sulfonium salt.

3. A photographic gelatino-silver-halide emulsion sensitized with a cationic surface active ternary sulfonium salt.

4. A photographic gelatino-silver-halide developing-out emulsion sensitized with a cationic surface active ternary sulfonium salt.

5. A photographic gelatino-silver-halide developing-out emulsion sensitized with a supersensitizing combination of at least one non-acidic sensitizing dye together with a cationic surface active sulfonium salt.

6. A photographic silver halide emulsion sensitized with a cationic surface active ternary sulfonium salt.

7. A photographic silver halide developing-out emulsion sensitized with a cationic surface active ternary sulfonium salt.

8. A photographic silver halide developing-out emulsion sensitized with a supersensitizing combination of at least one non-acidic sensitizing dye together with a cationic surface active ternary sulfonium salt.

9. A photographic gelatino-silver-halide emulsion sensitized with a supersensitizing combination of at least one non-acidic sensitizing dye together with a cationic surface active ternary sulfonium salt.

10. A photographic gelatino-silver-halide developing-out emulsion sensitized with a supersensitizing combination of a non-acidic sensitizing dye together with a surface active ternary sulfonium salt, the cation of which contains at least one organic group containing a chain of at least eight members selected from the group consisting of carbon atoms, oxygen atoms, sulfur atoms, nitrogen atoms and benzene nuclei.

11. A photographic gelatino-silver-halide developing-out emulsion sensitized with a supersensitizing combination of a non-acidic sensitizing dye together with a surface active ternary sulfonium salt, the cation of which contains at

least one organic group containing a chain of from nine to twelve members selected from the group consisting of carbon atoms, oxygen atoms, sulfur atoms, nitrogen atoms and benzene nuclei.

12. A photographic gelatino-silver-halide developing-out emulsion sensitized with a non-acidic sensitizing dye and containing, in a concentration of from about 20 to about 400 milligrams per gram-mole of silver halide in the emulsion, a cationic surface active ternary sulfonium salt, the cation of which contains at least one organic group containing a chain of from 9 to 10 members selected from the group consisting of carbon atoms, sulfur atoms, oxygen atoms, nitrogen atoms and benzene nuclei.

13. A photographic gelatino-silver-halide developing-out emulsion sensitized with a non-acidic sensitizing dye and containing, in a concentration of from about 20 to about 200 milligrams per gram-mole of silver halide in the emulsion, a cationic surface active ternary sulfonium salt, the cation of which contains at least one organic group containing a chain of from 11 to 12 members selected from the group consisting of carbon atoms, nitrogen atoms, oxygen atoms, sulfur atoms and benzene nuclei.

14. A photographic gelatino-silver-halide developing-out emulsion, sensitized with a non-acidic sensitizing dye and containing, in a concentration of from about 20 to about 200 milligrams per gram-mole of silver halide in the emulsion, a cationic surface active ternary sulfonium salt, the cation of which contains at least one organic group containing a chain of from 9 to 10 members selected from the group consisting of carbon atoms, sulfur atoms, oxygen atoms, nitrogen atoms and benzene nuclei.

15. A photographic gelatino-silver-halide developing-out emulsion, sensitized with a non-acidic sensitizing dye and containing, in a concentration of from about 20 to about 200 milligrams per gram-mole of silver halide in the emulsion, a cationic surface active n-nonyl dimethyl sulfonium salt.

16. A photographic gelatino-silver-halide developing-out emulsion, sensitized with a non-acidic sensitizing dye and containing, in a concentration of from about 20 to about 200 milligrams per gram-mole of silver halide in the emulsion, a cationic surface active n-decyl dimethyl sulfonium salt.

17. A photographic gelatino-silver-halide developing-out emulsion, sensitized with a non-acidic sensitizing dye and containing, in a concentration of from about 20 to about 200 milligrams per gram-mole of silver halide in the emulsion, a cationic surface active n-octyl dimethyl sulfonium salt.

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