

UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC EMULSION

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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 obtain 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 allyl isothiocyanate 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, of the cationic phosphonium salt type. (Surface active substances are classified as anionic or 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, lipophyle 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 substances and the spectral sensitizer are chemically combined.

Our new supersensitized emulsions are an im-

provement over supersensitized emulsions known in the art. The increases in sensitivity which can be attained with supersensitizing combinations of dyes can be enhanced by our new method. Furthermore, whereas with supersensitizing combinations of sensitizing dyes (see United States Patents 2,075,047, 2,075,048 and 2,075,049, each dated March 30, 1937), the supersensitizing effect is confined more or less to a single spectral region, the supersensitization 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 about to 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 at least one sensitizing dye and a surface active substance of the cationic phosphonium 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 phosphonium 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 substance should be thoroughly incorporated in the emulsion. The surface active substance 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, or any other suitable solvent or other procedure may be used.

Sensitizing dyes are ordinarily incorporated in the washed, finished emulsions, and in accordance with our invention, the surface-active substances are advantageously also incorporated in the washed, finished emulsions. However, the surface-active substances can be added to the emulsion during the preparation thereof, i. e., during the precipitation of the silver halide, the

first digestion or the second digestion (ripening). After preparing the emulsions in the presence of the surface-active substance, the sensitizing dyes can be incorporated in the so-prepared emulsions.

As cationic phosphonium salt surface-active substances, we have found that those which do not contain a hydrogen atom on the phosphonium phosphorous atom (i. e. the so-called quaternary phosphonium types) are advantageously employed. We have found that in the case of the "mono" salts, the phosphonium cation should advantageously contain at least seven, eight or more 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 weight 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 phosphonium salt surface-active substances having a phosphonium 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.

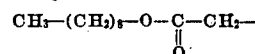
In the case of "poly" salts described in examples hereinafter and also in a copending application filed of even date in the names of the same inventors, other proportions and the like may be used. For example, in the case of agents having a bivalent organic radical having a chain of 1-6 members, amounts of 400 mg. may be employed. In the instance of chains of 7-14 members smaller amounts would be preferred, as will be discussed hereinafter with respect to the "mono" salts.

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 phosphonium salts are employed. Perchlorates and p-toluenesulfonates are advantageously employed because any such effects are negligible, and furthermore, the perchlorates possess certain other advantages.

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:

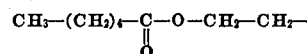
- Nonyl, $\text{CH}_3-(\text{CH}_2)_8$ —(nine atom chain).
 Decyl, $\text{CH}_3-(\text{CH}_2)_9$ —(ten atom chain).
 Lauryl, $\text{CH}_3-(\text{CH}_2)_{11}$ —(twelve atom chain).
 Cetyl, $\text{CH}_3-(\text{CH}_2)_{15}$ —(sixteen atom chain).
 Heptoxymethyl, $\text{CH}_3-(\text{CH}_2)_6-\text{O}-\text{CH}_2$ —(nine atom chain).
 Undecoxymethyl, $\text{CH}_3-(\text{CH}_2)_{10}-\text{O}-\text{CH}_2$ —(thirteen atom chain).
 Heptylthiomethyl, $\text{CH}_3-(\text{CH}_2)_6-\text{S}-\text{CH}_2$ —(nine atom chain).

Carbononoxymethyl



(twelve atom chain).

Caprooxyethyl



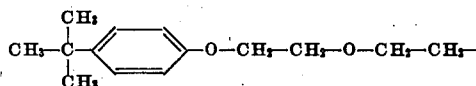
(nine atom chain).

Butoxyethoxyethyl



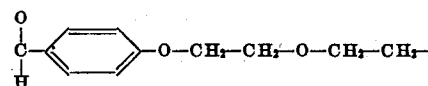
(ten atom chain).

Ter-butylphenoxyethoxyethyl



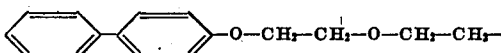
(eight atom+phenyl group chain).

Formylphenoxyethoxyethyl



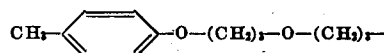
(seven atom+phenyl group chain).

Phenylphenoxyethoxyethyl



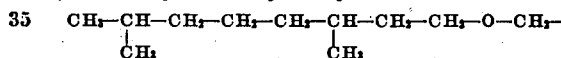
(six atom+two phenyl groups chain).

Methylphenoxypropoxypropyl



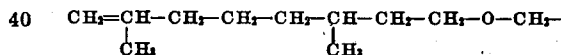
(nine atom+phenyl group chain).

3,7-dimethyloctanoxymethyl



(ten atom chain).

Citronelloxymethyl

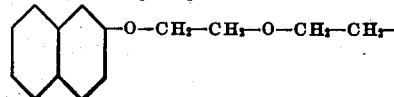


(ten atom chain).

(Alcohol radicals in commercial oil of sandalwood)—O—CH₂—(at least ten atom chain).

ω-Hydroxydecyl, HO—CH₂—(CH₂)₈—CH₂—(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 mem-

bers, 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 twelve 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 preferred amounts with respect to the "poly" salts (which may or may not be surface active) have already been described, and indicate to some extent the variation with the nature of the salt.

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 gram-mole 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 bene-

ficial 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 hemicyanine 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).

A further understanding of our invention will be had from a consideration of the following examples. It is to be understood that these examples are set forth primarily for the purposes of illustrating preferred embodiments and not for limiting our invention.

While phosphonium compounds from any source, as long as they are of satisfactory purity and otherwise meet photographic specifications, may be employed, we describe herein examples of the manufacture of certain of our compounds. The several examples immediately following, are illustrations of some of the procedures which may be followed in making various phosphonium derivatives useful in practicing our invention.

EXAMPLE 1. *n*-Dodecyltriethylphosphonium bromide

To 10 parts of crude triethylphosphine containing some ether (obtained by the action of phosphorus tribromide on ethylmagnesium bromide) was added 5 parts of *n*-dodecyl bromide. The mixture was heated under reflux at 125° C. for 2 hours. On cooling the mass solidified and 3½ parts of *n*-dodecyltriethylphosphonium bromide was collected by treating with anhydrous ether.

EXAMPLE 2.—*n*-Dodecyltriethylphosphonium perchlorate

Approximately 2 parts of *n*-dodecyltriethylphosphonium bromide (from Example 1) was treated in 5 parts of methyl alcohol with 2 parts of sodium perchlorate in 5 parts of warm water and chilled. By this treatment there is obtained 1-2 parts of *n*-dodecyltriethylphosphonium perchlorate, melting at 70° C.

EXAMPLE 3.—*n*-Decyltriethylphosphonium *p*-toluenesulfonate

A mixture of 4 parts of crude triethylphosphine

(obtained by the action of phosphorus tribromide on ethylmagnesium bromide) and 4 parts of n-decyl-p-toluenesulfonate was heated for 4 hours at 125–135° C. under reflux. While still warm the product was treated with 15 parts of acetone which effected solution. There was then added 30 parts of ether, and on chilling 4 parts of a white salt melting at 61–65° C. crystallized. It was essentially n-decyltriethylphosphonium p-toluenesulfonate.

EXAMPLE 4. — Tetramethylene-bis-triethylphosphonium bromide

To 6 parts of crude triethylphosphine (obtained by the action of phosphorus tribromide on ethylmagnesium bromide) was added 6 parts of decamethylene bromide and the mixture warmed slightly. A vigorous reaction set in and a white solid separated. After cooling, the reaction product was dissolved in 20 parts of methyl alcohol and allowed to stand until the bulk of the alcohol had evaporated. It was then treated with 20 parts of ether, and the white crystalline material resulting was collected on a filter. There was thus obtained 10 parts of tetramethylene-bis-triethylphosphonium bromide melting at 158° C.

EXAMPLE 5. — Ethylene-bis-oxymethyltriethylphosphonium chloride

To 15 parts of an ether solution of triethyl phosphine (containing an unknown amount of the latter) was added 5 parts of ethylene-bis-oxymethyl chloride and the mixture warmed to remove ether and then heated under reflux for 3 hours at 120° C. By treating the product with acetone and ether there was obtained a small amount of a white solid melting with decomposition at 160° C. It was essentially ethylene-bis-oxymethyl-triethylphosphonium chloride.

With particular reference to Example 2, further details respecting the production of perchlorate derivatives are set forth in Allen and Wilson application entitled "Surface-active materials," filed of even date.

As already pointed out, the phosphonium compound or mixture of compounds to be added to the photographic material may be added in various ways, various amounts, in the presence of dye sensitizers, or otherwise. However, for a

better understanding of our invention, we set forth an example describing the specific addition of one of our reagents to a certain photographic emulsion. Likewise, it is to be understood that this example is set forth merely for the purpose of illustration and is not to be considered a restriction on our invention.

EXAMPLE 6

A highly sensitive silver bromide gelatin was optically sensitized to give a panchromatic sensitization and divided into two portions. One of the portions was employed as a control. To the other portion was added approximately 10 mg. per liter of n-lauryltriethylphosphonium bromide, in accordance with our invention. Several plates were coated from each portion as described, dried together, exposed together, and processed together, in order that all conditions would be comparable and the beneficial effects of our novel addition of phosphonium compounds readily apparent.

Upon testing the process plates, the resulting sensitivities noted were as follows:

	Speed	γ	Fog
Control	1,480	1.23	0.10
Lauryltriethylphosphonium bromide, 10 mg./liter	1,860	1.24	0.10

Various other phosphonium compounds could be incorporated in a similar manner, as for example n-lauryltriethylphosphonium perchlorate, n-decyltriethylphosphonium p-toluenesulfonate or tetramethylene-bis-phosphonium perchlorate.

In all instances, our novel treatment of photographic materials with phosphonium compounds not only improved the speed of sensitized emulsions, but even unsensitized emulsions. The improvement as indicated in the specification, extended over the entire region, even into the violet and blue region, and enhanced the sensitivity about the same over the entire region. Furthermore, it will be noted that the improvement may amount to 25% or more.

Still further illustrations of our invention are set forth for convenience in the following table. It will be observed from the disclosure in the table that both sensitized and unsensitized photographic emulsions were treated.

Emulsion	Sensitizing dye	Surface active agent	White light			(White light minus blue) No. 12 filter	
			Speed	Gamma	Fog	Speed	Gamma
Highly sensitive gelatino-silver-bromide.	2-diphenylamino-5-(2-ethyl-benzothiazylidene ethylidene)-4-(5)-thiazolone, 15 mg./liter.	None	455	0.82	.06	126	0.83
Do.	do.	Tetramethylene bis triethyl phosphonium bromide 30 mg./liter.	590	0.88	.06	200	0.81
Do.	1,2-diethyl-3,4-benzothiazine iodide, 15 mg./liter.	None	280	0.82	.08	33	0.77
Do.	do.	Tetramethylene bis triethyl phosphonium bromide, 30 mg./liter.	725	0.69	.07	46	0.78
Do.	2,2'-dimethyl-8-ethyl thiacarbocyanine bromide, 15 mg./liter.	None	525	0.61	.07	132	0.62
Do.	do.	Tetramethylene bis triethyl phosphonium bromide 30 mg./liter.	615	0.76	.08	178	0.79
Do.	Unsensitized emulsion	None	590	0.61	.04		
Do.	do.	Tetramethylene bis triethyl phosphonium bromide 30 mg./liter.	830	0.66	.05		

Therefore, it will be seen that we have found that a substantial improvement may be made in photographic emulsions by incorporating a phosphonium compound or compounds therein in various ways. As indicated, in the instance where the photographic material contains a sensitizing dye, it is preferred to incorporate the dye sensitizer first and thereafter incorporate the phosphonium surface-active substance.

In the production of our various compounds, in place of the ether solvent, other suitable solvent may be employed. Or, other changes may be made in the process.

It is apparent from the foregoing that our invention is susceptible of some modification and hence is not 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 phosphonium salt.
2. A photographic silver halide developing-out emulsion sensitized with a cationic surface-active phosphonium salt.
3. A photographic gelatino-silver halide emulsion sensitized with a cationic surface-active phosphonium salt.
4. A photographic gelatino-silver-halide developing-out emulsion sensitized with a cationic surface-active phosphonium salt.
5. 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 phosphonium salt.
6. A photographic silver halide emulsion sensitized with a cationic surface-active quaternary phosphonium salt.
7. A photographic silver halide developing-out emulsion sensitized with a cationic surface-active quaternary phosphonium salt.
8. A photographic gelatino-silver-halide emulsion sensitized with a cationic surface-active quaternary phosphonium salt.
9. A photographic gelatino-silver-halide developing-out emulsion sensitized with a cationic surface-active quaternary phosphonium salt.
10. A photographic silver halide emulsion sensitized with a supersensitizing combination of at least one non-acidic sensitizing dye together with a cationic surface-active quaternary phosphonium salt.
11. 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 quaternary phosphonium salt.
12. A photographic gelatino-silver-halide emulsion sensitized with a supersensitizing combination of a non-acidic sensitizing dye together with a cationic surface active quaternary phosphonium 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.
13. A photographic gelatino - silver - halide emulsion sensitized with a supersensitizing combination of a non-acidic sensitizing dye together with a cationic surface active quaternary phosphonium salt, the cation of which contains at least one organic group containing a chain of from eight to twelve members selected from the group consisting of carbon atoms, sulfur atoms, oxygen atoms, nitrogen atoms and benzene nuclei.
14. A photographic gelatino - silver - halide emulsion sensitized with at least one 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 quaternary phosphonium salt, the cation of which contains at least one organic group containing a chain of from 8 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 emulsion sensitized with at least one 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 quaternary phosphonium 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, sulfur atoms, oxygen atoms, nitrogen atoms and benzene nuclei.

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