United States Patent [19]

Oftedahl

[11] **3,904,415**

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[54] **PHOSPHINE SENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS AND ELEMENTS**

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[21] Appl. No.: **492,956**

[52] **U.S. Cl.** **96/107;** 96/108; 96/109; 96/120

[51] **Int. Cl.²** **G03C 1/28**

[58] **Field of Search** 96/107, 108, 109, 120

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

1,295,463 11/1972 United Kingdom 96/107

195,872 7/1967 U.S.S.R. 96/107

OTHER PUBLICATIONS

Stauebe et al.: J. Am. Chem. Soc., Vol. 78, pages 976–977 (1956).

Primary Examiner—Won H. Louie, Jr.
Attorney, Agent, or Firm—C. O. Thomas

[57] **ABSTRACT**

A photographic silver halide emulsion is disclosed incorporating a sensitizing amount of a tris(dialkylamino)-phosphine or a tris(dialkylaminoalkylene)-phosphine. Gold and/or sulfur sensitizers can also be present as well as antifoggants, such as azaindenes.

21 Claims, No Drawings

PHOSPHINE SENSITIZED PHOTOGRAPHIC SILVER HALIDE EMULSIONS AND ELEMENTS

My invention relates to phosphine sensitized silver halide emulsions which can be further sensitized with chemical sensitizers and to photographic elements including such emulsions.

The use of phosphorus and its compounds as sensitizers for photographic silver halide emulsions and elements is known in the art. For example, British Patent 1,057,949, published Feb. 18, 1967, teaches the sensitization of silver bromide emulsions by developing in the presence of an amido-phosphoric acid polyethylene glycol ester. British Patent 1,295,463, published Nov. 8, 1972, teaches that silver halide emulsions can be sensitized through the use of gelatin which has been treated with phosphine or white phosphorus. Thurston U.S. Pat. No. 3,338,712, issued Aug. 29, 1967, teaches sensitizing emulsions containing labile sulfur compounds by the incorporation of organic phosphites. Carroll et al. U.S. Pat. No. 2,271,622, issued Feb. 3, 1942, teaches the sensitization of silver halide emulsions using cationic surface-active phosphonium salts. Lowe et al. U.S. Pat. No. 3,523,023, issued Aug. 4, 1970, teaches the sensitization of silver halide emulsions with hydroxyalkyl phosphonium salts. Willems et al U.S. Pat. No. 3,552,968, issued Jan. 5, 1971, teaches sensitization with phosphonitrile trimer and tetramer derivatives. Russian Patent 195,872, published July 11, 1967, discloses to be sensitizers for silver halide emulsions triphenyl phosphines, including those having alkyl, aryl, alkoxy or dialkylamino phenyl substituents.

While varied phosphorus containing compounds have been recognized to be sensitizers for photographic silver halide emulsions, it should not be assumed that phosphorus compounds are, in general, useful as silver halide sensitizers. Phosphorus compounds, in fact, cover the full gamut of performance characteristics, ranging from densensitizers to sensitizers. Even among those classes of phosphorus compounds known to be sensitizers unexplained variations in performance are observable. One difficulty with many phosphorus sensitizers has been their ineffectiveness and/or incompatibility with other chemical sensitizers. For example, some phosphorus sensitizers in combination with heavy metal sensitizers, such as gold sensitizers, produce no additional speed increase while others produce prohibitively large increases in fog.

I have discovered quite unexpectedly a class of phosphine compounds to be useful as sensitizers for silver halide emulsions. More surprisingly I have found these compounds to be capable of producing additional increases in photographic speed when employed in combination with conventional chemical sensitizers. Still further, silver halide emulsions containing these compounds as sensitizers either alone or in combination with other chemical sensitizers show surprisingly low fog levels. By contrast, I have observed distinctly inferior comparative performance for certain closely related and homologous phosphine compounds.

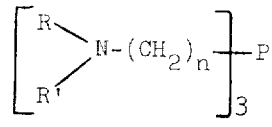
In one aspect then, my invention is directed to a photographic silver halide emulsion comprised of silver halide grains, a vehicle for dispersing said grains and a sensitizing amount of a tri(dialkylamino)phosphine or a tri(dialkylaminoalkylene)phosphine in which each of the alkyl groups contains at least two carbom atoms and each alkylene group contains from one to three

carbon atoms. In another aspect, my invention is directed to a photographic element incorporating such a photographic emulsion.

My invention may be better understood and appreciated by reference to the following detailed description:

The phosphine compounds which I employ in the practice of my invention are those having three dialkylamino groups attached directly to the phosphorus atom or through an intervening methylene linkage of up to three carbon atoms. The alkyl groups can be independently chosen, but in each instance include at least two carbon atoms.

Preferred phosphine compounds of this type are those represented by the following structural formula:

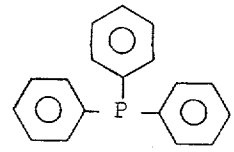


wherein, R and R' are alkyl groups having from 2 to 8 carbon atoms, preferably 2 to 5 carbon atoms, and *n* is an integer of from 0 to 3 inclusive.

Exemplary preferred phosphine compounds useful in the practice of this invention are set forth in Table I. The first two phosphine compounds listed in Table I, though closely structurally related to those that follow, form no part of my invention, but are included solely for purposes of comparison.

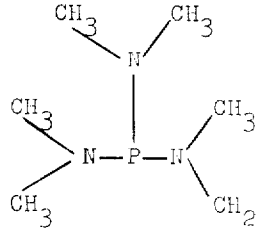
TABLE I

PS-1



triphenyl phosphine

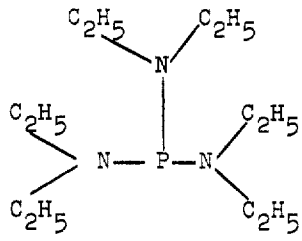
PS-2



tris(dimethylamino)phosphine

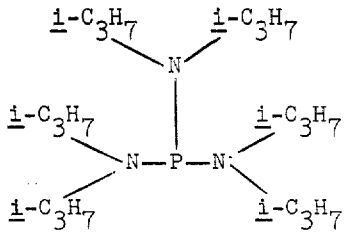
Table I – Continued

PS-3



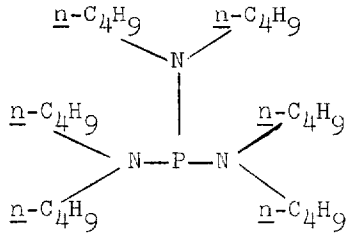
tris(diethylamino)phosphine

PS-4



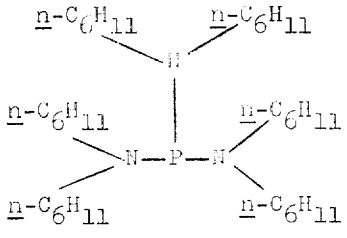
tris(di-i-propylamino)phosphine

PS-5



tris(di-n-butylamino)phosphine

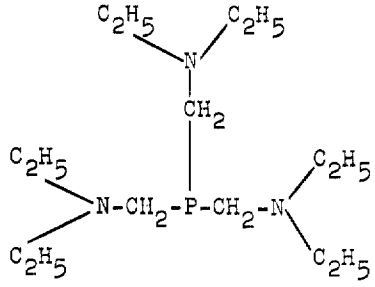
PS-6



tris(di-n-hexylamino)phosphine

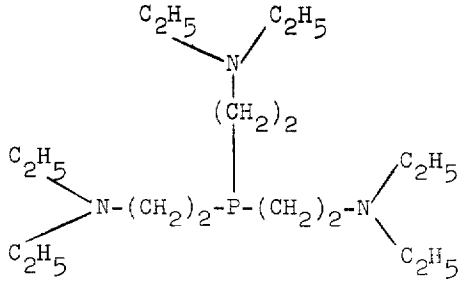
Table I – Continued

PS-7



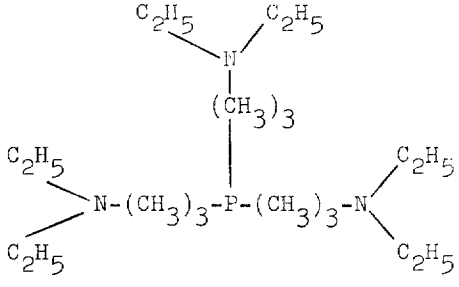
tris(diethylaminomethylene)phosphine

PS-8



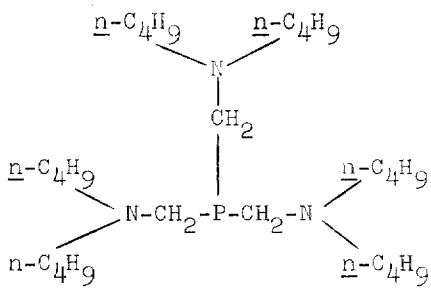
tris(diethylaminodimethylene)phosphine

PS-9



tris(diethylaminotrimethylene)phosphine

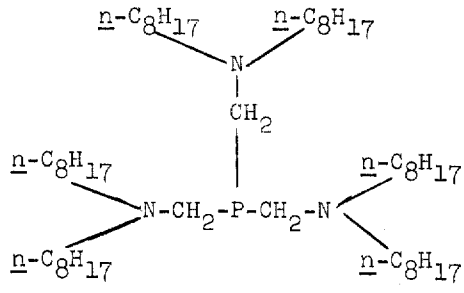
PS-10



tris(di-n-butylaminomethylene)phosphine

Table I—Continued

PS-11



tris(di-n-octylaminomethylene)phosphine

The preparation of compounds of this type is generally well known in the art. For example, an exemplarly technique suitable for preparing these compounds is disclosed by Carl Stauebe and Herman P. Lankelma in *J. Am. Chem. Soc.*, Volume 78, pages 976 through 977 (1956), in an article entitled "Hexaalkyl Phosphorus, Phosphoric and Phosphoricthioic Triamides."

The silver halide emulsions used in accordance with the sensitizers of my invention can comprise, for example, silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, silver chloroiodide, silver chlorobromoiodide and mixtures thereof. The emulsions can be coarse or fine grain emulsions prepared by any of the well-known techniques, e.g., single jet emulsions, such as those described in Trivelli and Smith, *The Photographic Journal*, Vol. LXXIX, May, 1939 (pp 330–338); double jet emulsions, such as those described in Glafkides, *Photographic Chemistry*, Vol. 1, Chapter 28, Fountain Press, London, 1958; ammoniacal, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. No. 2,222,264, issued Nov. 19, 1940; Illingsworth U.S. Pat. No. 3,320,069, issued May 16, 1967 and Jones U.S. Pat. No. 3,574,628, issued Apr. 13, 1971.

The silver halide emulsions utilized in this invention can be surface sensitized and/or internally sensitized. One convenient approach for forming internally sensitized emulsions is to sensitize the grain surfaces of an emulsion to be employed as a core emulsion followed by the further deposition of silver halide on the sensitized surfaces of the grains. Exemplary of internal image forming silver halide emulsions which can be used in the practice of this invention with phosphine sensitizers are those sensitized predominantly on the interior of the silver halide grains as described in Porter et al. U.S. Pat. No. 3,206,313, issued Sept. 14, 1965; Porter et al. U.S. Pat. No. 3,317,322, issued May 2, 1967; Spence et al. U.S. Pat. No. 3,690,891, issued Sept. 12, 1972; and Evans U.S. Pat. No. 3,761,276, issued Sept. 25, 1973.

The silver halide emulsions can be regular grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, Vol. 12, No. 5, Sept./Oct., 1964, pp 242–251 and German Patent 2,107,118. Negative type emulsions can be utilized, as well as direct-positive emulsions as described in Illingsworth U.S. Pat. No. 3,501,307, issued Mar. 17, 1970 and Berriman U.S. Pat. No. 3,367,778, issued Feb. 6, 1968; such emulsions being surface fogged in addition to being internally sensitized.

Inasmuch as the phosphine sensitizers of my invention produce further enhanced photographic speeds when employed in combination with known chemical sensitizers, silver halide emulsions employed in the practice of my invention are preferably chemically sensitized according to conventional practice in addition to including the phosphine sensitizers. My silver halide emulsions can be usefully sensitized with chemical sensitizers, such as with sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Procedures for chemically sensitizing silver halide emulsions are described in Sheppard et al. U.S. Pat. No. 1,623,499, issued Apr. 15, 1927; Waller et al. U.S. Pat. No. 2,399,083, issued Apr. 23, 1946; McVeigh U.S. Pat. No. 3,297,447, issued Jan. 10, 1967, and Dunn U.S. Pat. No. 3,297,446, issued Jan. 10, 1967.

My phosphine sensitizers can be added in a variety of ways to photographic emulsions and at various stages in the preparation thereof; however, I prefer to introduce the phosphine sensitizers of my invention immediately after chemical sensitization by conventional techniques has been completed and before other addenda have been incorporated into the emulsion. The sensitizers can be added with useful effects at the completion of Ostwald ripening and prior to one or more of the final digestion operations. The sensitizers are preferably added to the silver halide emulsion after the silver halide grains are substantially in their final size and shape. The phosphine sensitizers can be added in methanol, acetone or other innocuous organic solvents. To avoid thermally degrading the phosphine sensitizers it is generally preferred that the silver halide emulsion not be maintained above a temperature of about 50° to 60°C for an extended period in preparation steps subsequent to phosphine incorporation. Effective phosphine sensitization can be obtained by holding the emulsion at an elevated temperature of up to about 40°C or more for a period ranging from a few minutes to an hour or more—preferably 10 to 40 minutes.

Any sensitizing amount of the phosphine compounds of this invention can be usefully incorporated into the silver halide emulsion. Typically concentrations of from about 0.1 to 100 mg of phosphine sensitizer per mole of silver halide, preferably 0.5 to 50 mg of phosphine sensitizer per mole of silver halide, can be employed.

Since higher concentrations of the phosphine sensitizers can raise fog levels, the maximum concentrations of the phosphine sensitizers is a function of (a) the amount of background fog compatible with the particular photographic application and (b) whether or not an antifoggant is incorporated in the silver halide emulsion. While the phosphine sensitizers are generally compatible with known antifoggants and stabilizers, I have found the phosphine sensitizers employed in the practice of this invention to be particularly effective in combination with known azaindene antifoggants, most preferably tetrazaindene antifoggants. Exemplary antifoggants and stabilizers, each used alone or in combination include the following:

a. thiazolium salts described in Brooker et al. U.S. Pat. No. 2,131,038, issued Sept. 27, 1938 and Allen et al. U.S. Pat. No. 2,694,716, issued Nov. 16, 1954;

b. the azaindenes described in Piper U.S. Pat. No. 2,886,437, issued May 12, 1959 and Heimbach et al. U.S. Pat. No. 2,444,605, issued July 6, 1948;

c. the mercury salts as described in Allen et al. U.S. Pat. No. 2,728,633, issued Dec. 27, 1955;

d. the urazoles described in Anderson et al. U.S. Pat. No. 3,287,135, issued Nov. 22, 1966;

e. the sulfocatechols described in Kennard et al. U.S. Pat No. 3,326,652, issued Feb. 22, 1966;

f. the oximes described in Carroll et al. British Patent 623,448, issued May 18, 1949;

g. nitron;

h. nitroindazoles;

i. mercaptotetrazoles described in Kendall et al. U.S. Pat. No. 2,403,927, issued July 16, 1946; Kennard et al. U.S. Pat. No. 3,266,897, issued Aug. 16, 1966; and Luckey et al. U.S. Pat. 3,397,987, issued Aug. 20, 1968;

j. the polyvalent metal salts described in Jones U.S. Pat. No. 2,829,405, issued June 17, 1958;

k. the thiuronium salts described in Herz et al. U.S. Pat. No. 3,220,839, issued Nov. 30, 1965; **and**

l. the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. No. 2,566,263, issued Aug. 28, 1951; and Yutzy et al. U.S. Pat. No. 2,597,915, issued May 27, 1952.

In addition to the components above mentioned the silver halide emulsions include a vehicle for dispersing the silver halide grains. The vehicle is typically a hydrophilic colloid, such as gelatin, but can take any conventional form. In addition, the silver halide emulsion can contain any one or a variety of conventional photographic emulsion addenda, such as hardeners, spectral sensitizers, brighteners, coating aids, plasticizers and lubricants, absorbing and filter dyes, developing agents, development modifiers, etc. Typical conventional vehicles and addenda of this type useful in the practice of this invention are disclosed in *Product Licensing Index*, Vol. 92, December 1971, publication 9232, pages 107 through 110, here incorporated by reference.

The photographic emulsions according to my invention can be employed as coatings in single and multilayer photographic elements. Such elements typically include a conventional photographic support of the type disclosed specifically in paragraph X of *Product Licensing Index*, cited above. The photographic emulsion layers can be employed in combination with subbing, interlayers, Carey Lea silver layers, antihalation layers, etc., as is well understood in the art.

The photographic elements according to my invention can be applied to a variety of applications. The photographic elements can be used with X-rays or can be orthochromatic, panchromatic or infrared sensitive. The photographic elements can be employed to form black-and-white images or to form colored or multicolored images in one or a plurality of layers as taught specifically in paragraph XXII of *Product Licensing Index*, cited above. The photographic elements can be of a type which form images upon development in conventional silver halide developing solutions, which form images by dry physical development, which form images by image transfer, etc. The photographic elements can be employed as lithographic printing plates as taught in paragraph XXIV of *Product Licensing Index*, cited above. The photographic elements can be formed to produce positive or negative images and can be formed to be of the direct print type, as specifically disclosed in paragraph XXV of *Product Licensing Index*, cited above.

The following examples are intended to further illustrate my invention.

EXAMPLES 1 THROUGH 10

A silver bromide emulsion having a mean grain size of 0.4 micron in diameter was prepared using a conventional double jet technique. The emulsion was separated into equal portions and chemically sensitized to a maximum obtainable speed using none, one, or a combination of the sulfur sensitizer sodium thiosulfate and/or the gold sensitizer potassium chloraurate, as shown below in Table II. The emulsion samples were finished as shown in Table II, and the phosphine compound was then added as a coating addenda at the concentration shown in Table II. The phosphine sensitizer was added at 40°C and the emulsion sample was held at this temperature for 20 minutes. The emulsion samples were then coated on a film support at 20 mg silver per square decimeter, exposed, developed for 4 minutes in Kodak Developer D–19 (the composition of which is set forth at page 43 of Kodak Advanced Data Book J–1, titled Processing Chemicals and Formulas for Black-and-White Photography, 6th edition, published 1963), fixed, washed and dried.

In comparing Example 1 with Control 1 it is apparent that the phosphine sensitizer more than doubled the speed of the emulsion. In comparing Examples 2 and 3 with Controls 2 and 3 it is apparent that the phosphine sensitizer in combination with the sulfer sensitizer produced an emulsion more than 3 times faster than the emulsion containing the sulfur sensitizer alone. Comparing Examples 4, 5 and 6 with Controls 4, 5 and 6, adding the phosphine sensitizer to the sulfur and gold sensitized emulsion produced a greater than two-fold speed increase. Finishing the sulfur and gold sensitized emulsions improved speed, but was not essential to achieving further speed increases with the phosphine sensitizers. The phosphine sensitizer PS–3 increased fog by 0.01 or less in all instances, even when

TABLE II

	Sensitizers (mg/Ag mole)			Fin. Conditions		Fresh		
Example No.	Phosphine	Sulfur	Gold	Time (Minutes)	Temp. (°C)	Relative Speed	Gamma	Fog
Control-1	None	None	None	20	40	100	3.1	0.04
1	30 (PS-3)	None	None	20	40	224	3.4	0.04
Control-2	None	6.0	None	3	75	100	3.4	0.04
2	30 (PS-3)	6.0	None	3	75	363	3.4	0.04
Control-3	None	6.0	None	30	75	141	4.3	0.04
3	30 (PS-3)	6.0	None	30	75	575	4.5	0.04
Control-4	None	3.0	3.0	0	75	468	3.2	0.04
4	3 (PS-3)	3.0	3.0	0	75	1260	2.9	0.05
Control-5	None	3.0	3.0	30	75	1100	3.2	0.06
5	3 (PS-3)	3.0	3.0	30	75	2190	3.3	0.07
Control-6	None	None	3.0	8	75	490	2.1	0.13
6	3 (PS-3)	None	3.0	8	75	1100	1.6	0.14

TABLE II-continued

Example No.	Sensitizers (mg/Ag mole) Phosphine	Sulfur	Gold	Fin. Conditions Time (Minutes)	Temp. (°C)	Fresh Relative Speed	Gamma	Fog
Control-7,8	None	3.0	1.0	5	75	725	3.2	0.06
7	3 (PS-3)	3.0	1.0	5	75	1260	2.6	0.06
8	3 (PS-7)	3.0	1.0	5	75	1550	3.0	0.24
Control-9,10	None	3.0	1.0	30	75	1100	2.6	0.08
9	3 (PS-3)	3.0	1.0	30	75	1700	2.7	0.08
10	3 (PS-7)	3.0	1.0	30	75	1780	3.0	0.17

employed in combination with the gold sensitizer. While the phosphine sensitizer PS–7 in combination with the sulfur and gold sensitizer increased fog, this was by less than 0.20 and therefore clearly acceptable for many photographic applications.

EXAMPLES 11 THROUGH 26

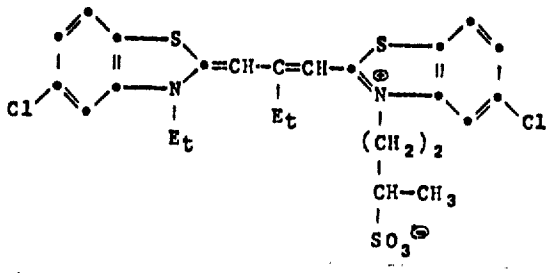
A silver bromoiodide emulsion containing 6 mole percent iodide was chemically sensitized to a maximum attainable speed using 12.0 mg of sodium thiosulfate and 4.4 mg of potassium chloraurate per silver mole. The emulsion was separated into equal portions, and the samples forming the examples were further sensitized with the phosphine compounds as set forth in Table III. The emulsion samples at the time of adding the phosphine compounds were stirred at 55°C, then lowered to 40°C. Spectral sensitizers were added to certain of the samples as indicated in Table III followed by holding for 10 minutes at 40°C. An antifoggant, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, was then added to certain of the emulsion samples, as indicated in Table III. The emulsion samples were coated as in Example 1. A portion of each film coating was exposed on an Eastman 1B sensitometer through a continuous step wedge and through either a Wratten 35 + 38A (Blue) filter or a Wratten 16 (Minus Blue) filter and processed as in Example 1. The results, summarized in Table III, show that both the blue and minus blue speeds of the spectrally sensitized silver halide emulsions are enhanced by the phosphine sensitizers of this invention used in combination with sulfur and gold sensitizers. Fog levels are not prohibitively high without the antifoggant being present, but are reduced to very low levels through the incorporation of the antifoggant.

TABLE III

Example No.	Phosphine Cmpd. mg/Ag mole	Spectral Sens. mg/Ag mole	Antifoggant g/Ag mole	Relative Blue Speed	Rel. Minus Blue Speed	Gamma (Blue/Minus Blue)	Fog
Control-11	None	None	None	100	*	1.6/*	0.10/0.08
Control-12	None	210(A) + 21(B)	None	110	100	2.0/2.1	0.07/0.07
Control-13	None	210(A) + 21(B)	2.95	110	107	2.0/2.7	0.08/0.08
11	(PS-3) 1.3	None	None	209	*	1.3/*	0.11/0.10
12	(PS-3) 1.3	None	2.95	182	*	1.5/*	0.06/0.06
13	(PS-3) 1.3	210(A) + 21(B)	None	135	95	1.6/1.7	0.10/0.10
14	(PS-3) 1.3	210(A) + 21(B)	2.95	155	148	1.7/1.8	0.09/0.09
15	(PS-3) 1.0	None	None	209	*	1.4/*	0.10/0.10
16	(PS-3) 1.0	None	2.95	174	*	1.5/*	0.06/0.06
17	(PS-3) 1.0	210(A) + 21(B)	None	135	115	1.7/1.8	0.09/0.09
18	(PS-3) 1.0	210(A) + 21(B)	2.95	148	132	1.7/1.7	0.09/0.09
Control-14	None	None	None	100	*	1.4/*	0.08/0.08
19	(PS-5) 15	None	2.95	257	*	1.3/*	0.21/0.22
20	(PS-5) 15	None	2.95	246	*	1.6/*	0.10/0.10
21	(PS-5) 30	None	None	269	*	1.4/*	0.41/0.40
22	(PS-5) 30	None	2.95	282	*	1.5/*	0.10/0.11
Control-15	None	386(C) + 33(D)	None	105	100	1.3/1.3	0.08/0.08
Control-16	None	386(C) + 33(D)	2.95	129	115	1.5/1.7	0.06/0.06
23	(PS-5) 15	386(C) + 33(D)	None	141	126	1.4/1.7	0.29/0.28
24	(PS-5) 15	386(C) + 33(D)	2.95	148	141	1.3/1.4	0.26/0.26
25	(PS-5) 30	386(C) + 33(D)	None	110	115	0.8/0.9	0.58/0.55
26	(PS-5) 30	386(C) + 33(D)	2.95	141	141	1.0/1.0	0.48/0.55

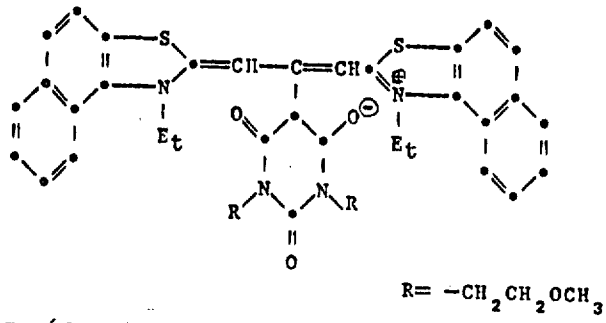
*Not Applicable

Dye A



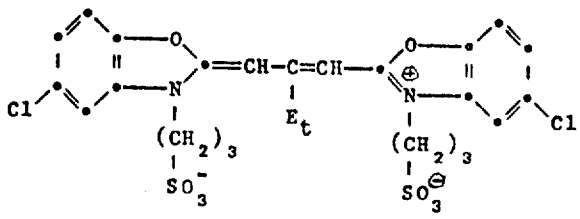
Anhydro-5,5'-dichloro-3,9'-diethyl-3'-(3-sulfobutyl) thiacarbocyanine hydroxide

Dye B



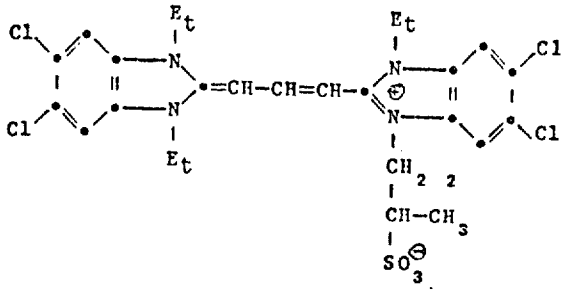
5-{[Bis(1-ethylnaphtho[1,2-d]thiazolin-2-ylidene)-methyl]methylene}-1,3-bis(2-methoxy-ethyl) barbituric acid

Dye C



Anhydro-5,5'-dichloro-9-ethyl-3,3'-bis-(3-sulfopropyl) oxacarbocyanine hydroxide, triethylamine salt

Dye D



Anhydro-5,5',6,6'-tetrachloro-1,1'-3-triethyl-3'(3-sulfobutyl) benzimidazolocarbocyanine hydroxide

EXAMPLES 27 AND 28

A silver bromoiodide emulsion containing 6 mole percent iodide was chemically sensitized to a maximum attainable speed using 12.0 mg of soidum thiosulfate and 4.4 mg of potassium chloroaurate per mole of silver. The emulsion was separated into equal portions, and phosphine compounds as set forth in Table IV were added to separate portions. The emulsion portions were at 55°C at the time the phosphine compound was added and were then reduced in temperature to 40°C and held for 20 minutes. The results are summarized below in Table IV.

Table IV

Example No.	Phosphine Compound	Concentration (mg/Ag mole)	Relative Blue Speed	Gamma	Fog
Control 17	None	None	100	1.5	0.08
Comparative Example	PS-1	13.2	100	1.5	0.07
Comparative Example	PS-2	3.0	105	1.5	0.06
Comparative Example	PS-2	30.0	94	1.6	0.05
27	PS-3	3.0	182	1.3	0.10
28	PS-3	6.0	246	1.5	0.13

In comparing Control 17 with the Comparative Examples employing triphenyl phosphine and tris(dimethylamino)phosphine, it is apparent that the properties of the emulsions are only marginally modified, if at all, by the incorporation of these phosphine compounds. On the other hand, when the phosphine sensitizer of this invention, tris(diethylamino)phosphine, is incorporated in the emulsion a very significant increase in the relative blue speed is apparent. This result could not be predicted from the comparative examples.

In addition to the phosphorus containing sensitizers disclosed herein, I have also discovered phosphorus imides of adamantane structure to be useful chemical sensitizers. These are disclosed in my commonly assigned, concurrently filed U.S. patent application Ser. No. 492,792, titled SILVER HALIDE EMULSIONS AND ELEMENTS INCLUDING SENSITIZERS OF ADAMANTANE STRUCTURE.

The invention has been described with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

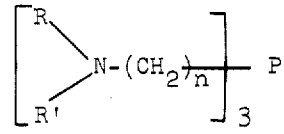
1. A photographic silver halide emulsion comprising photographic silver halide grains, a vehicle for dispersing said silver halide grains and a sensitizing amount of a tris(dialkylamino)phosphine or a tris(dialkylaminoalkylene)phosphine in which each of the alkyl groups contain at least two carbon atoms and the alkylene group contains from one to three carbon atoms.

2. A photographic silver halide emulsion according to claim **1**, in which said emulsion is additionally sensitized with a gold sensitizer, a sulfur sensitizer or a combination of gold and sulfur sensitizers.

3. A photographic silver halide emulsion according to claim **2** in which said emulsion additionally includes an antifoggant.

4. A photographic silver halide emulsion according to claim **2** in which said emulsion additionally includes at least one spectral sensitizer.

5. A photographic silver halide emulsion comprising a sensitizing amount of a compound of the formula



wherein

R and R' are alkyl groups having from 2 to 8 carbon atoms and n is an integer of from 0 to 3.

6. A photographic silver halide emulsion according to claim **5** in which n is 0 or 1.

7. A photographic silver halide emulsion according to claim **5** in which said emulsion is additionally sensitized with a gold sensitizer, a sulfur sensitizer or a combination of gold and sulfur sensitizers.

8. A photographic silver halide emulsion according to claim **7** in which said emulsion additionally includes an azaindene antifoggant.

9. A photographic silver halide emulsion according to claim **8** in which said emulsion additionally includes a spectral sensitizing dye.

10. A photographic silver halide emulsion according to claim **5** in which R and R' each contain from 2 to 5 carbon atoms.

11. A photographic silver halide emulsion according to claim **1** in which said phosphine sensitizer is present in an amount of from 0.1 to 100 mg per mole of silver halide.

12. A photographic silver halide emulsion comprising photographic silver halide grains,

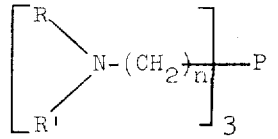
a vehicle for dispersing said silver halide grains and from 0.5 to 50 mg per mole of silver halide of tris(diethylamino)phosphine, tris(di-n-butylamino)phosphine, tris(diethylaminomethylene)phosphine or a combination of at least two of said phosphines.

13. In a photographic element comprised of a support and, as a coating on said support, a layer comprised of a photographic silver halide emulsion, the improvement in which said photographic silver halide emulsion is defined by claim **1**.

14. In a photographic element according to claim **13** the further improvement in which said silver halide emulsion is additionally sensitized with gold sensitizing means, sulfur sensitizing means or a combination of gold and sulfur sensitizing means.

15. In a photographic element according to claim **14** the further improvement in which said emulsion includes antifoggant means.

16. In a photographic element comprised of a support and, as a coating on said support, a layer comprised of a photographic silver halide emulsion, the improvement in which said emulsion is comprised of a sensitizing amount of a compound of the formula



wherein R and R′ are alkyl groups having from 2 to 5 carbon atoms and *n* is 0 or 1, and
said emulsion additionally includes a sensitizing amount of gold sensitizing means.

17. In a photographic element according to claim **16**, the further improvement in which said emulsion contains a sensitizing amount of at least one of tris(diethylamino)phosphine, tris(dibutylamino)phosphine or tris(diethylaminomethylene) phosphine.

18. In a photographic element according to claim **13**, the further improvement in which said phosphine sensitizer is present in an amount of from 0.1 to 100 mg per mole of silver halide.

19. In a photographic element comprised of a support and, as a coating on said support, a layer comprised of a photographic silver halide emulsion, the improvement in which said emulsion contains from 0.5 to 50 mg per mole of silver halide of tris(diethylamino)-phosphine.

20. In a photographic element comprised of a support and, as a coating on said support, a layer comprised of a photographic silver halide emulsion, the improvement in which said emulsion contains from 0.5 to 50 mg per mole of silver halide of tris(di-n-butylamino)phosphine.

21. In a photographic element comprised of a support and, as a coating on said support, a layer comprised of a photographic silver halide emulsion, the improvement in which said emulsion contains from 0.5 to 50 mg per mole of silver halide of tris(diethylaminomethylene)phosphine.

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