

[54] **SILVER HALIDE EMULSION
SUPERSENSITIZED WITH A
MEROCYANINE DYE AND A TERTIARY
PHOSPHINE SULFIDE**

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96/122

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G03c 1/34

[58] **Field of Search** 96/109, 122, 100, 107,
96/95

[56] **References Cited**

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Primary Examiner—Won H. Louie, Jr.

Attorney, Agent, or Firm—Connolly and Hutz

[57] **ABSTRACT**

Photographic silver halide emulsions are spectrally sensitized with neutral methine dyes (merocyanines, including openchain merocyanines and hemioxonoles) and the sensitization is increased and stabilized by the action of phosphine sulfides of the formula



wherein R₁, R₂ and R₃ are alkyl, cycloalkyl, aralkyl aryl or heterocyclic groups attached to the phosphorus atom either directly or by connecting members as defined hereinafter.

3 Claims, No Drawings

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SILVER HALIDE EMULSION SUPERSENSITIZED WITH A MEROCYANINE DYE AND A TERTIARY PHOSPHINE SULFIDE

This invention relates to a light-sensitive photo-
graphic material containing at least one silver halide
emulsion layer which is spectrally sensitized with a
merocyanine and the sensitivity of which layer can be
substantially increased by the addition of phosphine
sulfides.

It is known that the sensitizing action which sensitizing dyes exert on photographic silver halide emulsions can be considerably increased by certain additives which need not themselves be sensitizing dyes. This effect is known as supersensitization. The sensitization achieved in this way is, however, in many cases found to be extremely susceptible to the deleterious action of other necessary additives such as wetting agents, emulsifiers, stabilizers, color couplers or other non-sensitizing dyes. This susceptibility to the action of other additives is a particularly serious problem in color photographic materials which contain color couplers or dyes which can be bleached, and it results in insufficient sensitization and in considerable loss of sensitivity in storage under extreme conditions such as high temperature and high atmospheric moisture. Another disadvantage of conventional supersensitization is that the sensitivity to light is in many cases increased only under conditions of low exposure, with the result that the gradation curve as a whole is flattened.

It is an object of the invention to achieve a permanent increase in the spectral sensitivity of photographic silver halide emulsions, especially of those which contain color couplers, and, at the same time, to obtain sufficient gradation without any increase in the tendency to fogging even under extreme storage conditions.

It has now been found that the sensitization of silver halide emulsions which is achieved by means of merocyanines can be considerably increased by the addition of phosphine sulfides. Under phosphine sulfides in the context of this application, there are to be understood generally phosphorus compounds having a sulfur atom double bonded to a phosphorus atom that further carries three radicals other than hydrogen. The sensitization achieved by the combination of merocyanines and phosphine sulfides is found to be stable even in the presence of color couplers and under extreme conditions of storage.

This invention thus relates to a light-sensitive photographic material containing at least one silver halide emulsion layer which is spectrally sensitized with a merocyanine. The material is characterized in that the emulsion layer in addition to the merocyanine contains phosphine sulfide of the following formula



in which

R_1 and R_2 which may be the same or different, represent the following groups attached to the phosphorus atom either directly or via a connecting member X_1, X_2 as defined hereinafter

1. a saturated or unsaturated aliphatic hydrocarbon group, e.g. an alkyl group containing up to 20 car-

bon atoms, preferably 1 to 6 carbon atoms, which may be further substituted, e.g. by an amino group, a hydroxyl group, an alkoxy, alkylthio or alkylseleno group a carboxyl group, a carbonamide group, a cyano group, a heterocyclic group such as furane or tetrahydrofurane or a halogen atom such as fluorine or chlorine; or

2. a cycloalkyl group, e.g. cyclohexyl or adamantyl;
 3. an aralkyl group, e.g. benzyl or phenylethyl,
 4. an aryl group such as phenyl or naphthyl, including substituted and condensed aryl groups such as tolyl, xylyl, dodecylphenyl, anisyl, chlorophenyl, dialkylaminophenyl, trifluoromethylphenyl, methylthiophenyl, methylene dioxypheyl, acetylphenyl, carbalkoxyphenyl, methylsulfonylmethyl, sulfonylphenyl, biphenyl, tetrahydronaphthyl, benzylphenyl, benzothiazol-2-yl-phenyl, pyrenyl, chrysenyl or phenylthiophenyl, or
 5. a heterocyclic group, preferably one comprising a 5-, 6- or 7-membered heterocyclic ring which heterocyclic group may also contain condensed benzene rings and may carry further substituents, e.g. a pyrrolidine, piperidine, morpholine, piperazine, hexamethyleneimine, pyridine, thiazole, selenazole, oxazole, imidazole, indole, dihydroindole, pyrimidine, purine, pyrazole, pyrazolone, quinoline, thiadiazole, oxadiazole, triazole, tetrazole, diazine, thiazine, thiadiazine or 1,1-dioxothiolan group;
- R₁** and **R₂** may further together with the phosphorus atom form a phosphorus-containing heterocyclic ring, for example a phospholine ring



X₁ and X₂ which may be the same or different, represent a connecting member that contains hetero atoms, such as for example —O—, —S—, —Se—, —NR— (R stands for hydrogen or one of the groups defined under R₁ and R₂), —NH—N=, —NH—NH—SO₂—, —NH—SO₂—, —NH—CO—, —NH—CS—, —NH—CS—NH— or —NH—NH—CS—NH—.

R_3 represents a group as defined under R_1 and R_2 that is attached to the phosphorus atom either directly or via a connecting member as defined under X_1 and X_2 , R_3 further may represent a hydroxyl ($-\text{OH}$) or a thiol ($-\text{SH}$) group, the latter being presented possibly in anionic form ($-\text{S}-$), for example as a $-\text{SNH}_4$ group. R_3 however does not represent a radical bonded to the phosphorus atom via a connecting $-\text{O}-$ atom, when X_1 and X_2 both represent such connecting $-\text{O}-$ atoms.

55 Any group represented by R_3 if substituted may carry either directly or via one of the connecting members defined above for X_1 and X_2 and additional

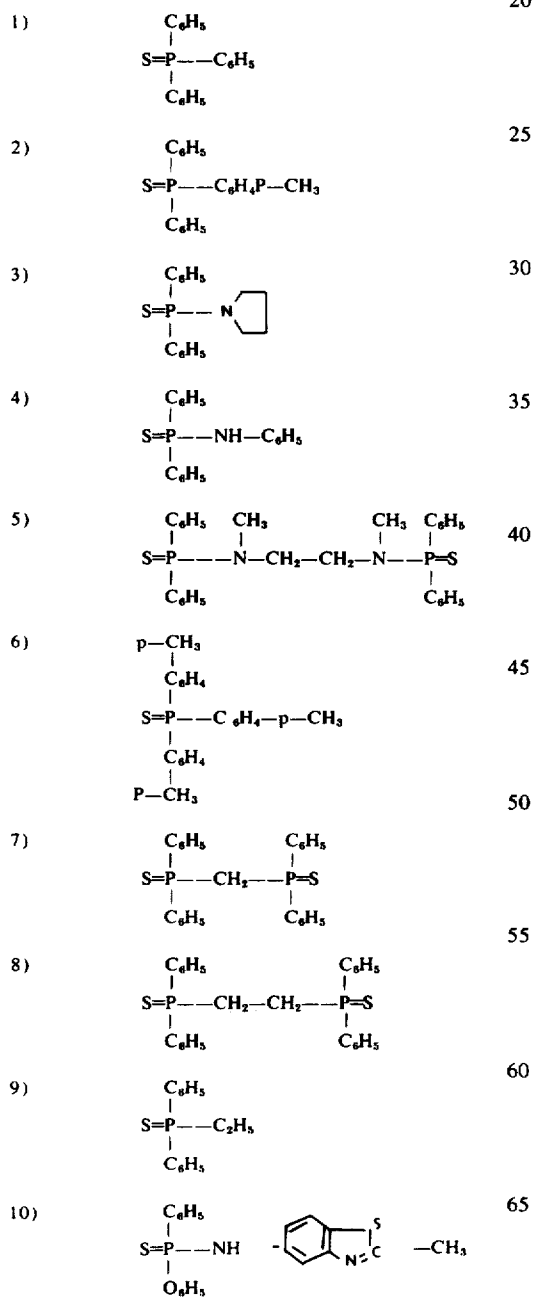


group wherein R₁ and R₂ have the same meaning as
65 mentioned above. Any heterocyclic group represented
by one of R₁, R₂ and R₃ may be bonded to the phosphorus
atom or to the connecting member either through
one of its hetero atoms or through one of its carbon

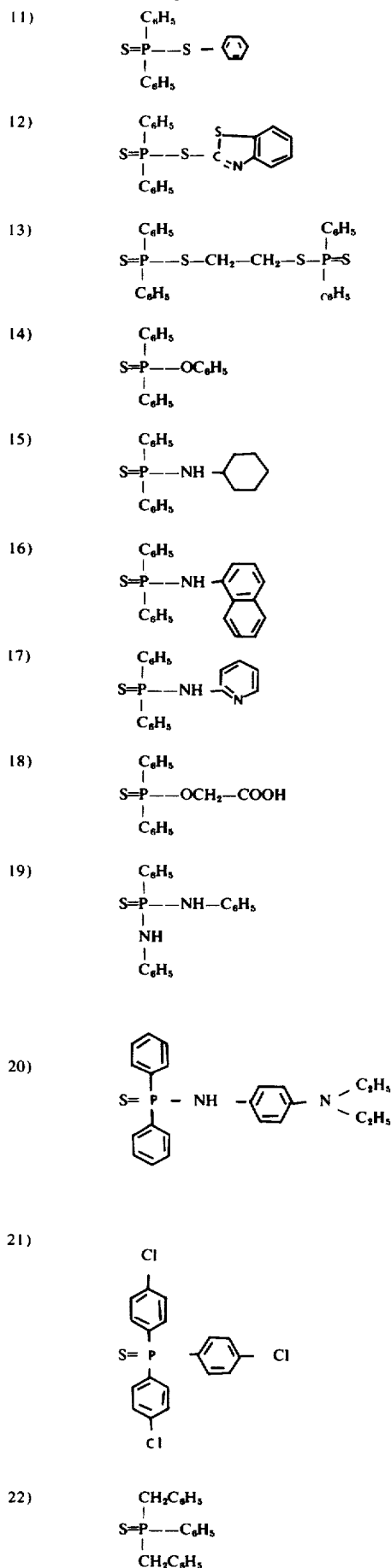
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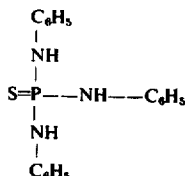
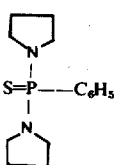
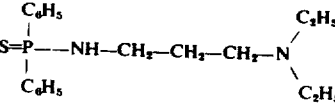
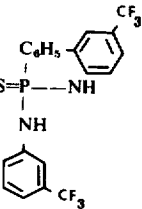
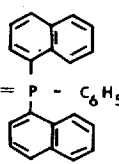
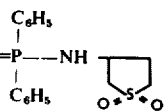
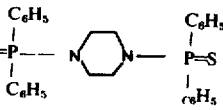
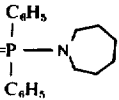
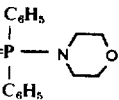
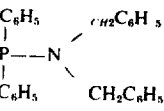
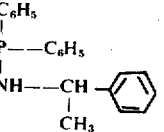
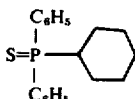
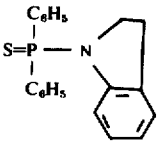
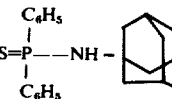
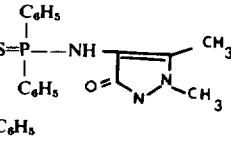
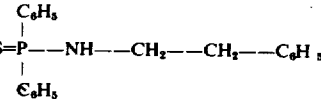
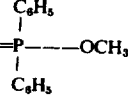
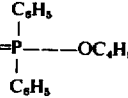
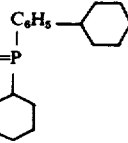
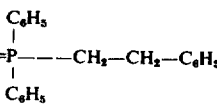
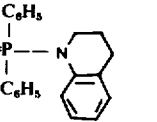
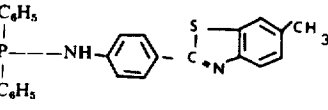
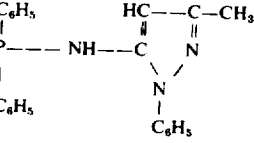
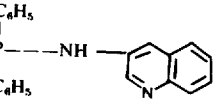
atoms. If there is no connecting member, then the heterocyclic group is preferably bonded to the phosphorus atom through one of its hetero atoms (generally a nitrogen atom). For example, a pyrrolidyl group is bonded directly to the phosphorus atom preferably through its nitrogen atom thus constituting a P—N bond. On the other hand if there is any connecting member then the heterocyclic group is bonded to the connecting member preferably through one of its carbon atoms. Such a carbon atom may be part of the heterocyclic ring or of a benzene ring condensed thereto. For example, a benzothiazole group may be bonded to the connecting member through any of its carbon atoms.

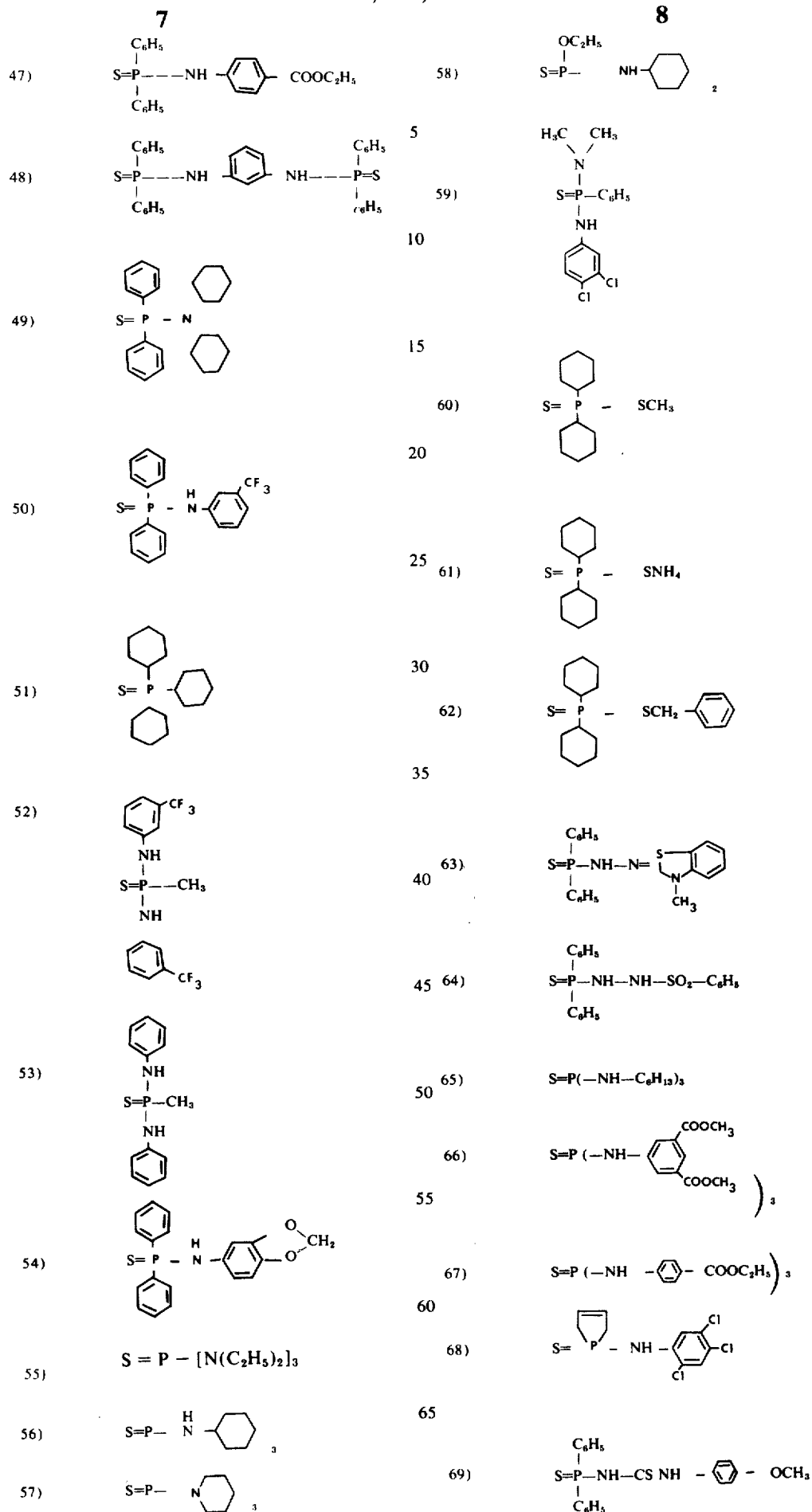
The following are examples of compounds which are particularly suitable for intensifying the sensitization effect of silver halide emulsion layers achieved with merocyanines:

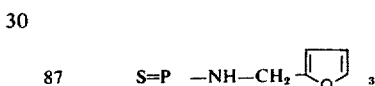
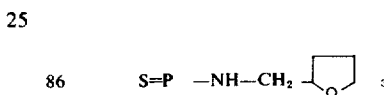
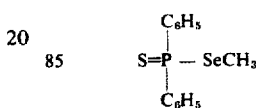
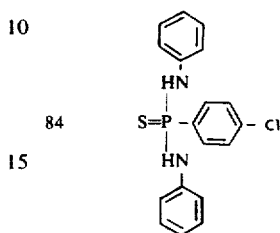
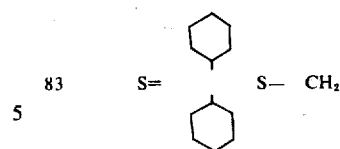
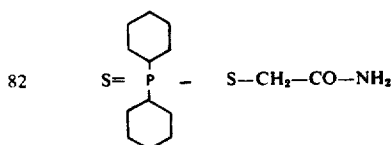
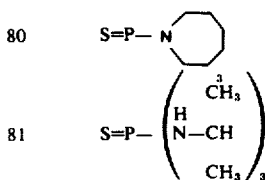
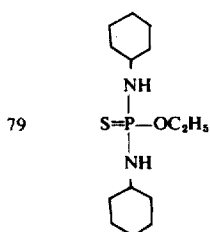
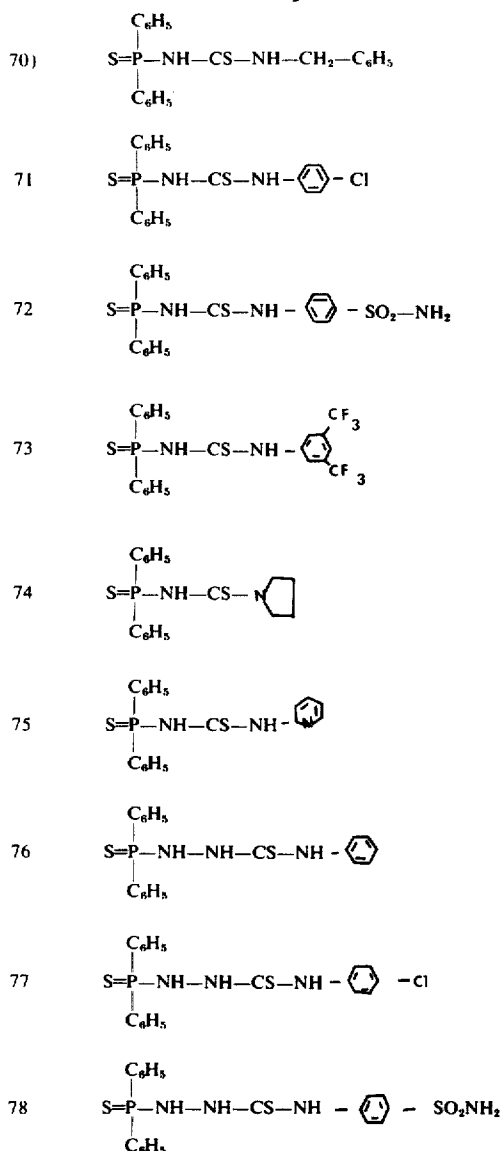


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- 5
- 23)  5
- 24)  10
- 25)  15
- 26)  20
- 27)  25
- 28)  30
- 29)  35
- 30)  40
- 31)  45
- 32)  50
- 33)  55
- 6
- 34)  5
- 35)  10
- 36)  15
- 37)  20
- 38)  25
- 39)  30
- 40)  35
- 41)  40
- 42)  45
- 43)  50
- 44)  55
- 45)  60
- 46)  65





The compounds of the above general formula are, from a formal point of view, not all genuine phosphine sulfides but in some cases derivatives (O-esters, S-esters or amides) of the various sulfur analogues of phosphinic acid, phosphonic acid or phosphoric acid, depending on the number of carbon atoms which are indirectly attached to the central phosphorus atom, i.e. by way of a hetero atom.

These compounds are well known. For methods of their preparation, reference may be had, for example, to the following literature:

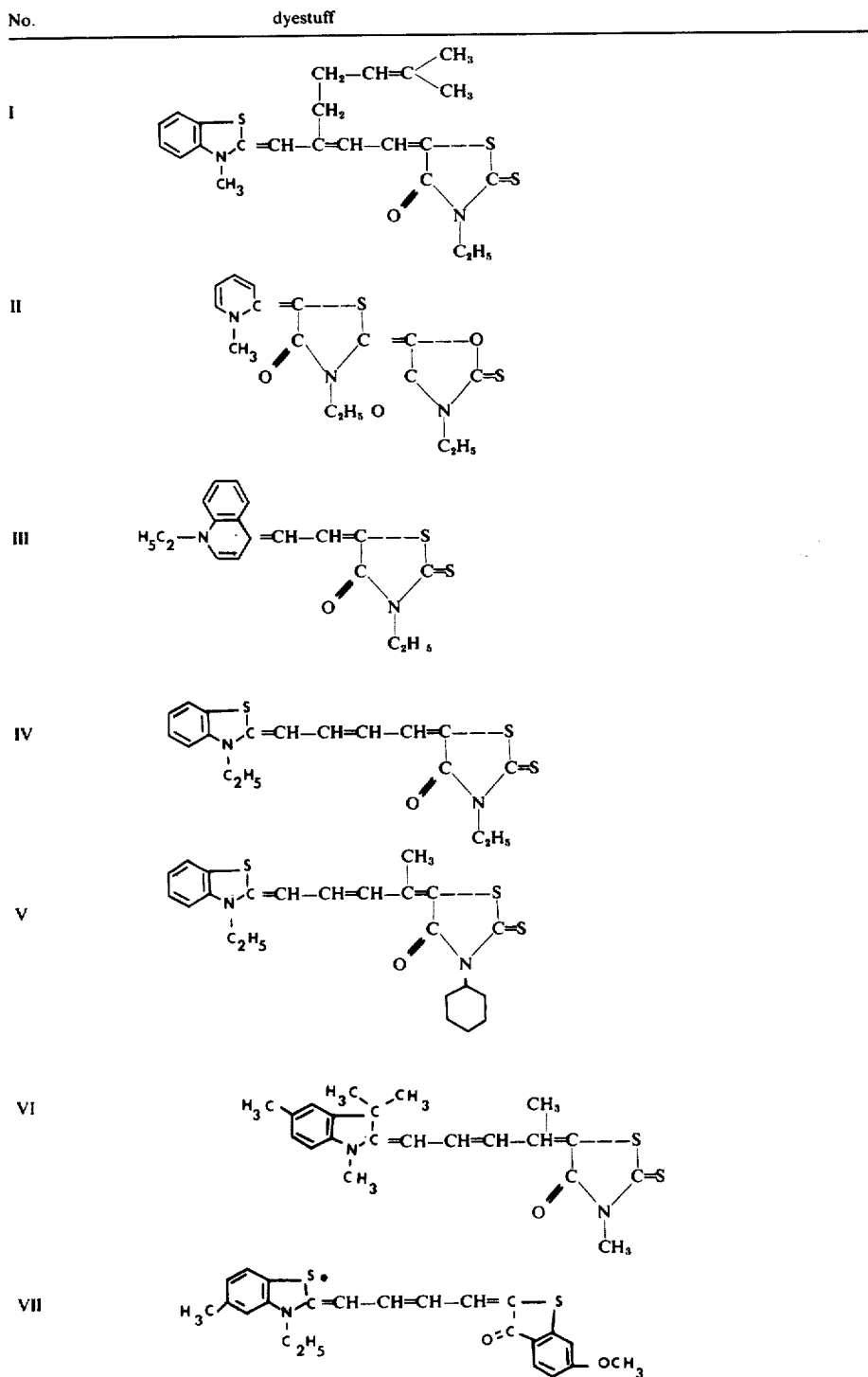
- a. Houben-Weyl, Methoden der Organischen Chemie Vol. XII/1, Fourth Edition, (1963) pages 168 - 174, pages 278-287 pages 564-598; and Vol. XII/2, Fourth Edition, (1964) pages 623 - 795;
- b. G. M. Kosolapoff, Organophosphorus Compounds, New York, John Wiley and Sons, Inc., 1950, page 98;
- c. Z. Chem. 12, 137-138 (1972).
- d. Article of Chr. Fest and K. J. Schmidt in "Chemie der Pflanzenschutz- und Schadlingsbekämpfungsmittel", Springer Verlag 1970, Vol. I, pages 248 - 253.

Merocyanines in the context of this application are understood to be neutral cyanine dyes in general as opposed to cationic or anionic cyanine dyes. Merocyanines in this application therefore include not only the merocyanines proper, in which a basic and an acid heterocyclic group are linked together, optionally through an even number of methine groups, but also those merocyanines in which the acid heterocyclic group (cyclic ketomethylene compound) has been replaced by an open chain ketomethylene compound such as malodinitrile, sulfonylacetonitrile or α -cyanoacetic acid (the so-called open neutrocyanines) as well as those which contain a simple amino group instead of

the basic heterocyclic group (the so-called hemioxonoles). In the latter case, the aminonitrogen is linked to the ketomethylene group through an odd number of methine groups; but it should be remembered here that in the case of the usual merocyanines, a methine group forms part of the basic heterocyclic group and as such does not appear as part of the methine chain. As regards merocyanines in their broadest aspect which can be used according to the present invention reference is

made to Houben-Weyl, "Methoden der Organischen Chemie", Georg Thieme Verlag Stuttgart, Vol V/1 d, 1972, pages 284-295 and to Hamer, "Cyanine Dyes and Related Compounds", Interscience Publishers 1964, pages 485 - 488 and 511 - 611.

The following are given as examples of merocyanine dyes whose sensitizing effect on silver halide emulsion layers can be enhanced by phosphine sulfides in accordance with the invention:



The combinations according to the invention of merocyanines and phosphine sulfides may be used in any silver halide emulsions. Suitable silver halides for the emulsions are silver chloride, silver bromide or mixtures thereof, which may have a small silver iodide content of up to 10 mols percent.

The silver halides may be dispersed in the usual hydrophilic binders, for example in carboxymethylcellulose, polyvinyl alcohol, polyvinyl pyrrolidone, alginate acid and its salts, esters or amides or, preferably, in gelatine. The silver halide emulsions may be the usual negative emulsions or such emulsions useful for forming positive images, for example such emulsions that form latent images predominantly inside the silver halide grains.

The phosphine sulfides used according to this invention may be added to the silver halide emulsion at any stage during preparation of the emulsion, for example at the silver halide precipitation stage or latter, e.g. before, during or after chemical ripening. They may be added together with the merocyanines or at an earlier or later stage. The method by which they are added is generally not critical and depends on the solubility properties of the phosphine sulfide used. The usual solvents may also be used for the addition of sensitizing dyes, for example alcohols such as methanol or ethanol, acetone, dimethylformamide, pyrrolidone hydroxypropionitrile, pyridine or phenols, for example cresol, but the compounds may also be added to the emulsion in the form of aqueous dispersions, e.g. dispersions in a dilute gelatine solution. They may also be applied to the emulsion by bathing or immersion or from an adjacent layer. The solvents must, of course, be compatible with gelatine and must not have any deleterious effect on the photographic properties of the emulsion. The quantity of phosphine sulfide added depends on the merocyanine used and on the intensity of the effect desired. Quantities of between 1.5 and 50×10^{-4} mol per mol of silver halide are generally suitable, the quantities preferably used being 5 to 15×10^{-4} mol per mol of silver halide. The quantity of phosphine sulfide used is of much the same order of magnitude as that of the merocyanine, being preferably 1 to 20 times the molar quantity of merocyanine used. The most suitable concentration of phosphine sulfide and merocyanine for any given emulsion can easily be determined by conventional tests employed in the photographic art.

Since the sensitization obtained with the combination according to the invention is substantially unaffected by the presence of color couplers, it is particularly advantageous to use such a combination in color photographic materials which contain color couplers. This applies to all classes of color couplers, e.g. cyan couplers based on phenol or naphthol, magenta couplers based on pyrazolone or indazolone and yellow couplers based on open chain ketomethylene compounds. It is immaterial whether the couplers are hydrophobic couplers that preferably are incorporated in the binder from an organic water immiscible solvent or whether they contain one or more watersolubilizing groups, and accordingly may be brought in from aqueous solution. The combination of merocyanines and phosphine sulfides may advantageously also be used in color photographic materials that contain dye-giving compounds for imagewise producing diffusing dyes which can be transferred by diffusion into image receiving layers.

The emulsions may also be chemically sensitized, e.g.

by adding other sulfur compounds such as allylthiocyanate, allylthiourea or sodium thiosulfate at the chemical ripening state. Certain reducing agents may also be used as chemical sensitizers, e.g. the tin compounds described in Belgian Patent Specifications No. 493,464 and 568,687, polyamines such as diethylene triamine or aminomethylsulfonic acid derivatives, e.g. according to British Patent Specification No. 789,823.

Noble metals such as gold, platinum, palladium, iridium, ruthenium and their compounds are also suitable chemical sensitizers. This method of chemical sensitization has been described in the article by R. Kossowsky, Z. Wiss. Phot. 46, 65 - 72 (1951).

The emulsions may also be sensitized with polyalkylene oxide derivatives, e.g. polyethylene oxide with a molecular weight of between 1000 and 20,000, or with condensation products of alkylene oxides and aliphatic alcohols, glycols, cyclic dehydration products and hexitols, alkyl substituted phenols, aliphatic carboxylic acids, aliphatic amines, aliphatic diamines and amides. The condensation products should have a molecular weight of at least 700 and preferably more than 1000. Combinations of these sensitizers may of course also be used in order to achieve special effects, as described in Belgian Patent Specification No. 537,278 and in British Patent Specification No. 727,982.

The emulsions may also in addition contain other spectral sensitizers, e.g. the usual monomethine or polymethine dyes such as basic or acid cyanines, hemicyanines, streptocyanines, oxonoles, styryl dyes, and other that also may have three or more heterocyclic nuclei, such as rhodacyanines and neocyanines. Sensitizers of this type have been described in the work by F. M. Hamer "The Cyanine Dyes and Related Compounds" Interscience Publishers, 1964.

The emulsions according to the invention may contain the usual stabilizers, e.g. homopolar or ionized compounds of mercury which contain aromatic or heterocyclic rings, such as mercurymercaptotriazoles, simple mercury salts and sulphonium mercury double salts. Azaindenes are also suitable stabilizers, especially tetra- or penta-azaindenes and particularly those which are substituted with hydroxyl or amino groups. Such compounds have been described in the article by Birr, Z. Wiss. Phot. 47, 2 - 58 (1952). Quaternary benzothiazole derivatives, benzotriazole and the like are also suitable stabilizers, among others. Certain heterocyclic mercapto compounds containing substituents which confer a negative charge have been disclosed in German Auslegeschrift No. 1,447,577. These act both as stabilizers and as supersensitizing additives and produce particularly advantageous results when used with the combination according to the invention.

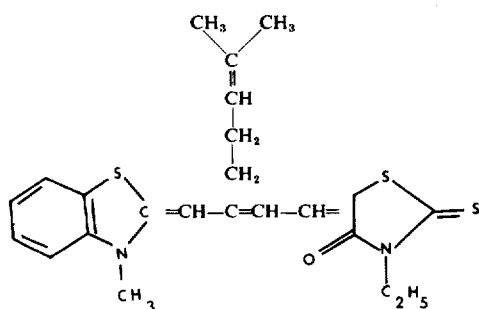
The emulsions may also contain white toners such as the known diaminostilbene derivatives as well as so-called masking or sharpening dyes from the series of anthraquinone, triphenylmethane or azo dyes. The emulsions may be hardened in the usual manner, for example with formaldehyde or halogenated aldehydes which contain a carboxyl group, such as mucobromic acid, diketones, methane sulphonic acid esters, dialdehydes, dimethylolurea, and dimethylolbenzimidazolone.

The invention will now be explained with the aid of the following Examples.

EXAMPLE 1

A silver halide emulsion which contains per kg 19 g

of silver, of which 35 mols percent are silver bromide and 65 mols percent silver chloride, is used. 3 mg of a merocyanine of the following formula dissolved in acetone (1 : 2000) is added to 1 kg of this emulsion as spectral sensitizer:



Preparation of this dye is carried out by a method analogous to that used for preparation of the corresponding dye which is unsubstituted in the methine chain, described in Houben-Weyl, "Methoden der organischen Chemie", Volume V/1d, page 290.

A sensitization maximum in deep red at 702 nm is obtained with this dye.

The emulsion is divided into two parts, each of which is cast on a baryta paper substrate. 60 mg of triphenylphosphine sulfide (Compound 1) dissolved in acetone (1:500) are added to one of these parts.

The material is exposed behind a step wedge ($\sqrt[3]{2}$) and an Agfa-Gevaert L 622 red filter (permeable to light above 622 nm) and developed for 2 minutes at 20°C in a developer of the following composition:

p-Methylaminophenol	1 g
Hydroquinone	3 g
Anhydrous sodium sulphide	13 g
Anhydrous sodium carbonate	26 g
Potassium bromide	1 g
Made up with water to	1000 ml.

The material is then fixed and washed in the usual manner. The sensitivities obtained are shown in the following Table, expressed as number of visible steps $\sqrt[3]{2}$.

Table 1

	Fresh	Heat	Tropical conditions
Without additive	19	20	22
+ 60 mg of triphenylphosphine sulfide (Compound 1) (1 : 500 dissolved in acetone)	24	27	25

In the above Table, "fresh" means that the material is processed a few hours after it has been cast. "heat" means that exposure and development are carried out after the samples have been stored for 3 days at 60°C and 40% relative humidity and "tropical conditions" means that the samples are stored for 3 days at 30°C and 80% relative humidity before exposure and development.

All the samples are practically free from fogging.

EXAMPLE 2

10 g of the sodium salt of 1-hydroxy-4-sulfo-N-octadecyl-2-naphthamide are added in the form of a 5% aqueous solution to a silver halide emulsion which has been prepared as described in Example 1 and sensitized with 10 mg of Dye I. The results shown in the following Table are obtained after exposure behind a $\sqrt[3]{2}$ step wedge and the aforesaid L 622 Red filter:

Table 2

		Fresh	Heat	Tropical conditions
Without additive		23	24	23
Compound 2	mg			
	30	27	28	24
	60	27	30	25
	90	28	31	27
(1:500 in acetone)	120	28	31	28

The samples were developed for 5 minutes at 20°C in a developer of the following composition to produce a blue dye image:

Hydroxylamine sulfate	3 g
N-butyl-N- ω -sulfobutyl-p-phenylenediamine	6 g
Potassium carbonate	87 g
Potassium bromide	1 g
Sodium sulfite	5 g
Sodium hexametaphosphate	2 g
made up with water to 1000 ml.	

The samples were then washed for 2½ minutes and fixed in a short stop fixing bath for 5 minutes. They were then bleach fixed for 5 minutes and finally washed for 10 minutes.

EXAMPLE 3

The sensitivity values obtained when other phosphine sulfides are added to the emulsion described in Example 2 (10 mg of Dye I; 10 g of the aforesaid cyan-forming coupler) are shown in Table 3.

Table 3

	Fresh	Heat	Tropical conditions
Without additive	23	23	23
60 mg of Compound 1	27	29	25
60 mg of Compound 3	26	28	25
60 mg of Compound 4	26	28	25
60 mg of Compound 5	26	27	27
150 mg of Compound 6	28	30	27
45 mg of Compound 7	26	27	27
45 mg of Compound 8	27	27	27
30 mg of Compound 9	26	28	22

EXAMPLE 4

When the following color couplers (in each case 10 g) are added to 10 mg of Dye I and 30 mg of triphenylphosphine sulfide (Compound 1) per kg of the silver halide emulsion described in Example 1, the sensitivity values shown in Table 4 below are obtained after color development carried out as described in Example 2.

A. 1-(4'-phenoxy-3'-sulfophenyl)-3-heptadecylpyrazolone-5 as a 2.5% solution;

EXAMPLE 7

- B. 3,5-dicarboxy- α -(4'-stearoylamino benzoyl)acetanilide as a 3.3% solution;
- C. 1-(3'-Carboxyphenyl)-3-(p-stearoylamino phenyl)-pyrazolone-5 as a 2.5% solution;
- D. 1-hydroxy-[2'-(N-methyl-N-octadecylamino)-5'-sulfo]-2-naphthanilide as a 6% solution;
- E. 2-Heptadecyl-7-sulfo-pyrazolo-[1,5-a]-benzimidazole as a 2.5% solution.

Table 4

Color coupler		Fresh	Heat
A.	without additive	24	25
	Compound I	26	28
B.	without additive	21	21
	Compound I	22	24
C.	without additive	24	25
	Compound I	26	27
D.	without additive	23	27
	Compound I	25	30
E.	without additive	23	24
	Compound I	24	25

EXAMPLE 5

The sensitivities to red obtained with increasing quantities of triphenylphosphine sulfide (Compound I) added to a silver chlorobromide emulsion described in Example 1 which contains 10 mg of Dye III and 10g of the cyan-forming coupler mentioned in Example 2 per kg of emulsion are shown in the Table below. Sensitization maxima are observed at 615 and 663 nm.

Table 5

	Fresh	Heat	Tropical conditions
Without additive	28	27	27
+ 10 mg of Compound I	28	27	27
30 mg of Compound I	29	28	28
60 mg of Compound I	30	29	29

Example 6

In the sensitizing dye mentioned in Example 2 is replaced by 10 mg of the other sensitizing dyes, the values shown in Table 6 are obtained.

	Sensitization maximum (nm)	Fresh	Heat	Tropical conditions
Dye IV	692			
Without additive		23	24	24
45 mg of Compound I		26	27	25
Dye V	712			
without additive		26	25	25
60 mg of Compound I		29	29	28
Dye VI	700			
Without additive		24	25	24
45 mg of Compound I		27	28	27
Dye VII	655			
Without additive		18	18	14
45 mg of Compound I		24	25	17
Dye VII	740			
Without additive		22	24	21
45 mg of Compound I		26	25	26
Dye IX	690			
Without additive		25	24	23
60 mg of Compound I		28	28	27
Dye X	672			
Without additive		24	26	27
60 mg of Compound I		28	30	29
Dye XI	700			
Without additive		23	24	24
60 mg of Compound I		27	28	25

10 mg of the following neutrocyanines dissolved in acetone to a dilution of 1 : 2000 are added to 1 kg of a silver chloride emulsion prepared according to T. TH. Baker, Photographic Emulsion Technique (American Photographic Publishing Co. Boston/Mass.), 1948, page 217. Table 7 below shows the sensitivity values obtained with and without the addition of 60 mg of triphenylphosphine sulfide (Compound I) after exposure behind a step wedge ($3\sqrt{2}$) and a pale yellow filter which absorbs below 435 nm ("GG 435" of Agfa-Gevaert AG) and therefore excludes the intrinsic sensitivity of the emulsion.

Table 7

Dye	Without phosphine sulfide	With compound I	Sensitization maximum (nm)
XIV	4	17	465
XV	22	26	575
XVI	21	24	570
XVII	5	13	498

EXAMPLE 8 -naphthamide.

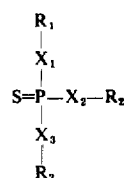
To 1 kg of a silver chlorobromide emulsion as described in Example 1 are added 10 mg of Dye I and 10 of the sodium salt of 1-hydroxy-4-sulfo-N-octadecyl-2-naphthamide. To different sample of this emulsion are further added a phosphine sulfide as indicated in the following table 8 in an amount of 60 mg per kg of emulsion. The samples are then cast on a photographic paper base. The dried layer is then exposed to light behind a red filter that is transparent above 622 nm and a $3/2$ step wedge, and is subsequently color developed, bleach fixed and rinsed. Table 8 shows the sensitivity of the different materials indicated by number of visible steps.

Table 8

	no additional compound (= standard)	visible steps $3\sqrt{2}$ after exposure behind red filter
		21
60 mg of compound	42	26
	43	26
	44	25
	45	24
	46	25
	47	26
	48	25
	53	25
	54	26
	55	25
	57	26
	58	26

What is claimed is:

1. A light sensitive photographic material comprising at least one silver halide emulsion layer containing a merocyanine spectral sensitizing agent and a sensitizing and stabilizing tertiary phosphine sulfide having the general formula:



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wherein

R_1 and R_2 may be the same or different and represent a saturated aliphatic hydrocarbon group; a cycloalkyl group; an aralkyl group an aryl group; a heterocyclic group comprising a 5-, 6- or 7-membered heterocyclic ring;

and R_1 and R_2 together with the phosphorus atom may form a phospholine ring;

R_3 represents a saturated or unsaturated aliphatic hydrocarbon group; a cycloalkyl group; an aralkyl group; an aryl group; a heterocyclic group comprising a 5-, 6- or 7-membered heterocyclic ring; a hydroxyl group or a thiol group;

X_1 and X_2 and X_3 represent a chemical bond or linking member containing hetero-atoms and being selected from the group consisting of $-O-$, $-S-$, $-Se-$, $-NR_4-$ (wherein R_4 stands for hydrogen,

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alkyl, aralkyl or cycloalkyl), $-NH-N=$, $-N-H-NH-SO_2-$, $-NH-SO_2-$, $-NH-CO-$, $-NH-CS-$, $-NH-CS-$, $-NH-CS-NH-$ and $-NH-NH-CS-NH-$;

X_1 , X_2 and X_3 may be the same or different but do not simultaneously all three represent $-O-$, said phosphine sulfides being present in an effective amount to increase and stabilize the spectral sensitization.

2. Material according to claim 1, characterised in that the tertiary phosphine sulfide is contained in the silver halide emulsion layer in quantities of 1.5 to 50×10^{-4} mol per mol of silver halide.

3. Material according to claim 1, characterised in that the silver halide emulsion layer in addition contains a color coupler.

* * * * *

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