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3,481,739

INCREASED SPEED IN NONSILVER LIGHT SENSITIVE SYSTEMS BY INCORPORATING THEREIN ORGANIC N-OXIDES

Eugene Wainer, Shaker Heights, and John E. Shirey, Wickliffe, Ohio, assignors to Horizons Incorporated, a Division of Horizons Research Incorporated, a corporation of Ohio

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11 Claims

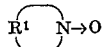
ABSTRACT OF THE DISCLOSURE

The addition of organic nitrogen compounds containing an N→O group to nonsilver photosensitive compositions is found to improve the photographic speed of such compositions applicable, for example, to the compositions of United States Patent 3,042,515.

This invention relates to photosensitive films and to the compositions thereof. More particularly, it relates to the improvement in photographic speed of known photosensitive compositions by the addition thereto of one or more organic nitrogen compounds represented by one of the following generic formulas



and



wherein the meaning of R and R¹ is as hereinafter defined.

The improvement in photographic speed which the use of such compounds produces is evidenced by the fact that a given exposure produces a higher density in the film containing the added compound than the identical exposure of an otherwise identical film composition from which the N→O compound has been omitted, or by the fact that the same density increase in the film composition may be achieved by shorter exposures of the film containing the N→O compound as compared with the same film composition from which the N→O compound has been omitted.

The known photosensitive compositions to which the present invention is particularly applicable to produce a remarkable increase in photographic speed include the photosensitive compositions in which an amine, styryl, cyanine or merocyanine dye base or other leuco di- or triphenylmethane compound is activated by an organic halogen compound or a sulfur containing compound as described in the following United States Patents, among others: Amines 3,042,515 and 3,147,117; Styryl and Cyanine Dye Bases 3,100,703, 3,102,810 and 3,095,303; Merocyanine Dye Bases 3,109,736; Leuco Di and Tri-Phenyl Compounds 3,121,632; Organic Halogen Compounds 3,042,515 and 3,147,117; Sulfur Containing Compounds 3,285,744; and Sulfur and Halogen Containing Compounds 3,113,024.

The disclosures of said patents are intended to be incorporated herein by reference and the following paragraphs enumerating typical compounds selected from the compounds to which the invention is applicable are to be considered illustrative and are not to be considered a complete listing of all of the compounds to which the invention is applicable.

(1) COLOR FORMING COMPOUNDS

(a) Amines

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The amines described in U.S. Patent 3,042,515 are those described by the formula



wherein R is an aryl nucleus such as benzene, naphthalene or anthracene which may be either unsubstituted or substituted with e.g., alkyl, halogen or aryl groups and X and Y are each selected from the group consisting of alkyl, aryl, aryalkyl, halogen and hydrogen and may be the same or different. Aniline, diphenylamine, o-toluidine, leuco crystal violet, leuco malachite green, and similar amines, or mixtures of two or more of such amines have been found to be suitable.

(b) Styryl and cyanine dye bases

Suitable styryl and cyanine dye bases include 2- and 4-(p-dimethylaminostyryl) quinoline, 2- or 4-[4-(p-dimethylaminophenyl)butadienyl] quinoline, 2-(3-ethyl-2(3H)benzothiazolyldene)propenyl benzothiazole.

(c) Merocyanine dye bases

Merocyanine dye bases which may be included in the compositions of this invention include those described in U.S. Patent 3,109,736 and others of a similar nature.

(d) Di- and tri-phenyl methane compounds

The di- and tri-phenyl methane compounds most suitable for this invention are the leuco bases of di- and tri-phenyl methane dyes such as leuco crystal violet, leuco malachite green, leuco opal blue, leuco methyl violet, leuco p-rosaniline, leuco Victoria blue and others of a similar nature.

In addition to the above named leuco compounds in which a central carbon atom is present to which two or three aryl groups are attached or which forms a portion of a heterocyclic ring in fused ring compounds such as xanthenes, thioxanthenes, acridines, dihydroanthracenes and the like, it is intended to include alkyl ethers and allyl ethers of such compounds within the context of the expression "leuco compound."

(2) ACTIVATORS

(a) Organic halogen compounds

The organic halogen compounds which may be included in the light sensitive compositions to which the present invention is applicable are those represented by the general formula A—C—X₃ wherein A represents halogen (Cl, Br or I), alkyl, substituted alkyl, including halogen substituted alkyl, aryl, substituted aryl, aroyl, and aralkyl and each X represents a halogen atom which may be either chlorine, bromine or iodine, it being understood that not all of the X atoms need be alike. Bromine is a preferred X and preferred compounds are halogen substituted alkanes, e.g., CBr₄, CHI₃, C₂BR₅, etc., and *aaa*-tribromoacetophenone.

(b) Sulfur containing compounds

The sulfur containing compounds which may be included in the light sensitive compositions to which the present invention is applicable are those represented by the formula R₁—SH or or R₁—S—S—R₁ wherein each R₁ represents an aryl or heterocyclic ring. Suitable compounds include 2-mercaptobenzothiazole, 5-methoxy-2-mercaptobenzothiazole, 1-phenyl-5-mercaptotetrazole, and pentachlorobenzenethio bis(dimethylthiocarbonyl)disulfide.

(c) Sulfur and halogen containing compounds

Activator compounds containing both halogen and sulfur and which are suitable for the present invention in-

clude the sulfonyl and sulfenyl halides described in United States Patent 3,113,024, e.g. 2,4-dinitrobenzene sulfonyl chloride, p-chlorobenzenesulfonyl chloride, o-nitrobenzenesulfonyl chloride and pentachlorobenzenesulfonyl chloride.

(3) BINDER

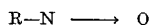
In addition, the compositions described in the above noted patents are usually formulated with a film-forming binder and are cast as a thin film from solution usually as a thin coating on a suitable substrate or the binder may be omitted and a porous substrate used as the support for the composition, paper being a preferred support when the binder is omitted from the composition. Among the binders which can be used are solutions of polystyrene, polyvinyl alcohol, copolymers of styrene and acrylonitrile, and others such as those described in United States Patents 3,100,703 and 3,147,117.

(4) ADDITIONAL CONSTITUENTS

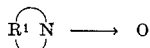
Many compounds which have been added to the above referred to photosensitive compositions are fully described in the above noted patents, including compounds to sensitize the compositions to certain wave lengths of light, stabilizers to permit storage of the compositions and additives which facilitate fixing of the compositions after exposure.

(5) THE N→O COMPOUNDS

The N→O compounds which may be used to increase the photographic speed of the known photosensitive compositions are those represented by one of the following formulas:

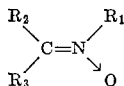


and



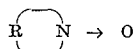
The R-N→O compounds include N→oxides of tertiary amines and nitrones and dinitrones. The N-oxides of the tertiary amines may be prepared as described in United States Patent 3,047,579 and include trialkylamine oxides, such as trimethyl-, triethyl-, methyl diethyl-, tripropyl-, tributyl-, etc.; triaryl such as triphenyl amine oxides, alkyl aryl amine oxides such as N,N-dimethyl aniline oxide, alkaryl amine oxides such as tribenzyl amine oxides, and halogen substituted amine oxides such as are described in the Witman patent noted above.

The nitrones and dinitrones are amines to which two valences of the amine nitrogen are attached to a carbon atom, i.e.



wherein R represents atoms of carbon, oxygen, nitrogen alkyl, alkenyl, aryl and substituted aryl. Examples of nitrones suitable for the present invention include α-N-diphenylnitron, α,α-diphenyl-N-methylnitron, N-ethylnitron, Δ'-tetrahydropyridine-N-oxide, 4,5,5-trimethyl-Δ'-pyrroline-N-oxide, N-methylcyclopentanone ketonitron, N-phenylfuronone ketonitron and dinitrones such as N, N'-diphenyl-p-quinonediimine-N, N'-dioxide.

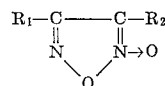
The heterocyclic N→oxides which may be used in the light sensitive compositions of the present invention are N-oxides and di-N-oxides represented by the formula



wherein R represents atoms of carbon, oxygen, nitrogen or sulfur necessary to complete a 5 or 6 membered ring or a fused ring such as the following: 2H-azirine N-oxide, N-ethylpyrrole-N-oxide, pyridine-N-oxides and substituted pyridine-N-oxides such as the picoline-N-oxides, lutidine-N-oxide, p-bromopyridine-N-oxide, azopyridine and azoxy pyridine-N-oxide, pyridylcarbinol-N-oxides, vi-

nylpyridine-N-oxide, N,N-dimethylaminostyrylpyridine-N-oxide, quinoline-N-oxide and substituted N-oxides such as quinaldine-N-oxide and lepidine N-oxide, phenazine-N-oxide, acridine-N-oxide as well as di-N-oxides such as phenazine 9,10-dioxide, the preparation of which is described in U.S. Patent 2,681,918.

One special class of compounds coming within the above formula are the furoxans which may be represented by the formula



wherein R₁ and R₂ can be alkyl or substituted alkyl, aryl or substituted aryl, amino, halogen, nitro, carboxyl, oxygen (as ether), either symmetrical or unsymmetrical and both R₁ and R₂ can be part of a ring system. Examples of furoxans suitable for the present invention include: diphenylfuroxan, dibenzoylfuroxan, amino(phenyl)furoxan, benzofuroxan, cyclohexenfuroxan, naphthofuroxan and derivatives thereof.

Proportions.—The proportions of the various N-oxides employed depending on the solubility of the particular N-oxide in the binder-solvent system used.

Base.—The formulations employed in this invention can be applied to any suitable film or paper substrate such as cellulose acetate, Mylar, baryta paper, etc.

Fixing.—Fixing of the exposed films employed in this invention can be accomplished by heat or solvent wash and has been described in the previous patents.

EXAMPLES 2-5

The following examples are illustrative of a few of the many ways in which the compounds referred to in this invention were used and are not intended as limitative thereof.

EXAMPLE 1

density of 0.55.

One and four-tenths (1.4) grams of carbon tetrabromide were dissolved in 4 cc. of a 10% solution of polystyrene (Styron 700, Dow) in benzene containing 100 mg. of leuco crystal violet and 15 mg. of 4-picoline-N-oxide. The mixture was coated on 300-D Mylar and allowed to dry. Exposer of the coating to a GE medium pressure mercury arc lamp (GE-H100A38-4) at a film-to-lamp distance of nine inches for 30 seconds through an Eastman No. 2 step wedge resulted in 15 visible steps with a density of 2.42 in the first step. Identical exposure of an otherwise identical coating made without the 4-picoline-N-oxide resulted in only 9 steps and a first step can be varied from as little as 0.1 part to as many as 2 parts by weight of the color forming compound em-

Example 1 was repeated using other N-oxides with the following results:

N-oxide	Weight (mg.)	No. of Steps	1 Step
2. 2,6-lutidine-N-oxide.....	15	18	1.95
3. 4-(p-N,N-dimethylamino styryl pyridine-N-oxide).....	10	13	2.28
4. Quinaldine-N-oxide hydrate.....	20	13	1.90
5. 1,3-dipyridylpropane-N,N'-dioxide.....	15	15	2.06

EXAMPLE 6

Similar results were obtained when 3,6-bis(dimethylamino) - 9 - (p-dimethylamino)phenylxanthene was used in place of the leuco crystal violet of Example 2.

EXAMPLE 7

Leuco malachite green was used in place of the leuco crystal violet of Example 1. Similar results were obtained.

EXAMPLES 8-10

Similar results were obtained when α-N-diphenylnitron, Δ-pyrroline-N-oxide, and diphenylfuroxan were each used with leuco malachite green as in Example 7,

EXAMPLE 11

Five hundred milligrams of carbon tetrabromide were dissolved in 4 cc. of a 10% solution of the copolymer of styrene and acrylonitrile (Tyrl 767, Dow) in methylene chloride containing 50 mg. of 2,7-bis(dimethylamino)-10 - p - dimethylaminophenyl-9,10-dihydro-9,9-dimethylanthracene, 100 mg. of triphenylstibine and 2 mg. of pyridine-N-oxide. The mixture was coated on 300-D Mylar and allowed to dry. Exposure of the coating of a visible light source in an Eastman Kodak sensitometer (Model 101) for one minute resulted in an image which indicated a speed increase of at least 10 times over a otherwise similar coating without pyridine-N-oxide.

EXAMPLES 12 and 13

Results similar to those obtained in Example 11 were obtained when cyclohexene furoxan and α -N-diphenyl nitron were each used in place of the pyridine-N-oxide of Example 11.

EXAMPLE 14

When leuco crystal violet was used in place of the 2,7-bis(dimethylamino) - 10 - p-dimethylaminophenyl-9,10-dihydro-9,9-dimethylanthracene of Example 11, similar results were obtained.

EXAMPLE 15

Example 1 was repeated using 25 mg. of 4-(p-dimethylaminostyryl)quinoline in place of the 100 mg. of leuco crystal violet. After the initial exposure, the coating was exposed to a 500-watt projector having a Corning No. 2030 glass filter in front of the lens. The resultant step wedge showed an increase in speed of 5 to 10 times over a coating without 4-picoline-N-oxide.

EXAMPLE 16

Example 15 was repeated using 2-(p-dimethylaminostyryl)quinoline in place of 4-(p-dimethylaminostyryl)quinoline, with a similar increase in speed.

EXAMPLE 17

Five hundred and seventy milligrams of carbon tetrabromide were dissolved in 5 cc. of a 10% solution of polyvinylchloride (PVC-450, Diamond Alkali) in cyclohexanone containing 100 mg. of 3 - ethyl-5-[(3-ethyl-2(3H) - benzothiazolylidene) - ethylidene]-2-(quinolylmethylene)-4-thiazolidone, 100 mg. of 2-mercaptobenzo-thiazole and 15 mg. of 4-picoline-N-oxide. The mixture was coated on 300-D Mylar and allowed to dry. Exposure to a 500-watt GE photoflood through an Eastman No. 2 step wedge resulted in image which indicated a two times to three times speed increase as compared with results obtained by exposing a coating without 4-picoline-N-oxide.

EXAMPLE 18

Example 17 was repeated replacing 4-picoline-N-oxide with cyclohexenefuroxan. A similar increase in speed was obtained.

EXAMPLE 19

In place of the merocarbocyanine of Example 17, a similar amount of carbocyanine 4 - [3 - (3-ethyl-2(3H)-benzothiazolylidene)propenyl]-quinoline was used. Similar increases in speed resulted.

EXAMPLE 20

One and four-tenths (1.4) grams of carbon tetrabromide were dissolved in 4 cc. of a 10% solution of polystyrene in benzene containing 50 mg. of leuco malachite green, 25 mg. of 4 - (p-dimethylaminostyryl)-quinoline, 10 mg. of the methoxy ether of malachite green and 2 mg. of 4-pyridylcarbinol-N-oxide. The mixture was coated on 300-D Mylar and allowed to dry. Exposure in an Eastman Kodak sensitometer (model 101) through a step wedge (Eastman No. 2) and post exposure to a Penetrat IR lamp for 6 minutes resulted in an image which

had 7 more steps than that obtained from a coating which contained no 4-pyridyl-carbinol-N-oxide.

EXAMPLE 21

Fifty milligrams of p - nitrobenzenesulfonyl chloride were dissolved in a mixture of 2.0 cc. of 10% solution of polystyrene in benzene plus 2.0 cc. of acetone containing 50 mg. of leuco opal blue and 30 mg. of 2-pyridylcarbinol-N-oxide. The mixture was coated on 300-D Mylar and allowed to dry. Exposure to a GE photoflood at 12 inches distance (lamp to film plane) through an Eastman No. 2 step wedge resulted in an image which had 10 more steps than that obtained with an otherwise identical coating with no 2-pyridylcarbinol-N-oxide.

EXAMPLE 22

When 2-mercaptobenzo-thiazole was used in place of the p-nitrobenzenesulfonyl chloride of Example 21 a similar speed increase was obtained.

EXAMPLE 23

When 300 mg. of iodoform were used in place of the p-nitrobenzenesulfonyl chloride of Example 21, similar results were obtained.

EXAMPLE 24

Five hundred milligrams of carbon tetrabromide were dissolved in 5 cc. of a 5% solution of the copolymer of styrene-acrylonitrile (Tyrl 767, Dow) in methylene chloride containing 10 mg. of leuco crystal violet, 10 mg. of Michler's ketone, 100 mg. of triphenylstibine and 2 mg. of 4-picoline-N-oxide. The mixture was coated on baryta photographic paper which has a polyvinyl alcohol coating on the surface, and dried. Exposure of the coating to a 35 mm. projector for 10 seconds gave a visible blue image. The entire coating was heated at 100° C. for two minutes for fixing. Without the N-oxide, the same coating exposed to the same dose of radiant energy required additional heating under a GE IR lamp at 6 inches for 2-3 seconds before any image was visible.

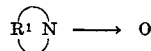
EXAMPLE 25

Example 24 was repeated using cyclohexenefuroxan in place of the 4-picoline-N-oxide. Similar results were obtained.

We claim:

1. A photosensitive composition comprising:

- (a) at least one color forming compound selected from the group consisting of leuco di- and tri-phenylmethane color forming compounds, and leuco dye bases;
- (b) at least one activator for accelerating the change in said leuco compound, produced as a result of exposure to a suitable dose of radiation, from the original compound to a product having a different color; and
- (c) at least one organic N $\rightarrow$ O compound in sufficient amount to further accelerate the change to said product directly as a result of said exposure of said dose of radiation, and wherein the N $\rightarrow$ O compound is selected from the group consisting of compounds represented by one of the general formulas R-N $\rightarrow$ O and

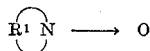


wherein R represents an organic moiety such that the resulting compound is an N-oxide selected from the group consisting of tertiary amines, nitrones and di-nitrones and R' represents atoms of carbon, oxygen, nitrogen or sulfur necessary to complete a 5 or 6 membered ring or a fused ring.

2. The composition of claim 1 wherein the N $\rightarrow$ O compound is one represented by the general formula R-N $\rightarrow$ O wherein R represents an organic moiety such that the resulting compound is an N-oxide selected from the group consisting of tertiary amines, nitrones, and di-nitrones.

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3. The composition of claim 1 wherein the N→O compound is one represented by the general formula



wherein R¹ represents atoms of carbon, oxygen, nitrogen or sulfur necessary to complete a 5 or 6 membered ring or a fused ring.

4. The composition of claim 1 wherein the activator is at least one compound represented by the general formula A—C—X₃ wherein A represents a monovalent radical selected from the group consisting of halogen, alkyl, substituted alkyl, including halogen substituted alkyl, aryl, substituted aryl, aroyl and aralkyl and each X represents a halogen atom selected from the group consisting of chlorine, bromine and iodine and all of the X's need not be the same.

5. The composition of claim 4 wherein the activator is a bromine substituted alkane.

6. The composition of claim 1 wherein the activator is a sulfur containing organic compound represented by a general formula selected from the group consisting of R₁—SH and R₁—S—S—R₁ wherein R₁ represents a ring selected from the group consisting of carbocyclic, heterocyclic and fused rings.

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7. The composition of claim 6 wherein the activator is a mercaptobenzothiazole.

8. The composition of claim 1 wherein there are between 0.1 and 2 parts by weight of N→O compound for each part by weight of color forming compound.

9. The composition of claim 1 which includes in addition, a film forming binder.

10. The process which comprises preparing the composition of claim 1 in a thin dry layer and thereafter photographically exposing said composition to a suitable dosage of radiation, whereby a color change occurs in the exposed portions of said layer, directly as a result of said exposure.

11. The composition of claim 2 wherein the N→O compound is 4 picoline-N-oxide.

References Cited

UNITED STATES PATENTS

2,426,894	9/1947	McQueen	96—90 X
3,342,603	9/1967	Sprague et al.	96—90
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NORMAN G. TORCHIN, Primary Examiner

R. E. FICHTER, Assistant Examiner

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,481,739

December 2, 1969

Eugene Wainer et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 11, "aryalkyl" should read -- arylalkyl --
line 57, " C_2BRr_5 " should read -- C_2HBr_5 --. Column 3, line 55,

"wherein R represents atoms of carbon, oxygen, nitrogen" should read -- where R_1 , R_2 and R_3 can be hydrogen, alkyl,

substituted --. Column 4, line 22, after "N-oxides" insert -- can be varied from as little as 0.1 part to as many as 2 parts by weight of the color forming compound em- --; line 32, cancel "EXAMPLES 2-5" and insert the same before line 53, same column 4 as a heading; line 39, cancel "density of 0.55" and insert the same after "step", second occurrence, in line 50, same column 4; same column 4, line 51, beginning with "can be" cancel all to and including "compound em-" in line 52, same column 4.

Signed and sealed this 27th day of October 1970.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents