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PHENOLIC STABILIZER IN NON-SILVER PHOTOSENSITIVE COMPOSITION

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U.S. Cl. 96—90 8 Claims

ABSTRACT OF THE DISCLOSURE

The addition of a phenolic compound to non-silver photosensitive compositions which include an organic N→O compound, the phenolic compound appears to act as an infrared stabilizer and prevents the unexposed areas of the film from developing color or fog.

This invention relates to photosensitive films and to the compositions thereof. More particularly, it relates to materials having a longer shelf life than those heretofore known.

In a patent application filed Apr. 22, 1966, Ser. No. 544,395, entitled "Photography," photosensitive compositions are described in which N→O compounds have been utilized to improve the photographic speed of the compositions. The compositions of that invention comprise at least one of each of the following groups of constituents:

(I)

(a) A leuco compound as hereinafter described
(b) Styryl dye bases
(c) Cyanine dye bases
(d) Merocyanine dye bases

(II)

(a) Organic halogen compound
(b) Sulfonyl and sulfenyl halides
(c) Mercapto compound

(III)

(a) N-oxides of tertiary amines
(b) N-oxides and di-N-oxides of heterocyclic amines
(c) Nitrones and dinitrones
(d) Furoxans

(IV)

A suitable binder and

(V) (optional)

A triaryl compound of Sb, As, B or P.

The present invention resides in the addition thereto of

(VI)

A phenolic compound hereinafter described which appears to act as an infrared stabilizer and prevents the unexposed areas of the film from developing color or fog. This compound serves as an aid in giving the material better shelf life for improved keeping qualities.

I. COLOR FORMING COMPOUNDS

The color forming compounds useful in the present invention are those set forth in the above-noted copending application Ser. No. 544,395 and include the amines described in United States Patent 3,042,515 and include Leuco Crystal Violet, Leuco Opal Blue, Leuco Malachite Green, Leuco Xanthenes, Leuco Anthracenes, Leuco Cyanides and numerous other leuco compounds of similar structure usually having a central carbon atom to which two or three aryl groups are attached as in the di- and tri-aryl methane derivatives, or which forms a portion

of a heterocyclic ring in a fused ring compound such as the xanthenes, thioxanthenes, acridines, anthracenes, and the like.

Within the context of the term leuco compound is included the alkyl and allyl ethers of the compounds given in the preceding paragraph.

Styryl and cyanine dye bases suitable for the present invention are described in United States Patents 3,100,703; 3,102,810; and 3,095,303 and suitable merocyanine dye bases are described in United States Patent 3,109,736.

The disclosure of each of these patents are incorporated herein by reference.

II. ACTIVATORS

The color forming compounds described above may be activated by suitable compounds as described in United States Patents 3,147,107; 3,102,810; and 3,113,024; and United States Patent 3,285,744. The incorporation of these applications by reference is intended to include the disclosures therein.

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—X_3 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. CBr_4, CHI_3, C_2HBr_5, etc. and α,α,α-tribromoacetophenone.

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 R_1—SH or R_1—S—S—R_1 wherein each R_1 represents an aryl or heterocyclic ring. Suitable compounds include 2-mercaptobenzothiazole, 5-methoxy-2-mercaptobenzothiazole, 1 - phenyl - 5 - mercaptotetrazole, pentachlorothiobenzene and bis(dimethylthiocarbamyl) disulfide.

Activator compounds containing both halogen and sulfur and which are suitable for the present invention include the sulfonyl and sulfenyl halides described in United States Patent 3,113,024, e.g. 2,4-dinitrobenzene sulfonyl chloride, p-chlorobenzenesulfonyl chloride, o-nitrobenzenesulfenyl chloride and pentachlorobenzenesulfenyl chloride.

III. THE N→O COMPOUNDS

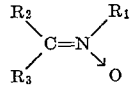
N→O compounds useful in the present invention are those described in the application Serial No. 544,395 filed April 22, 166, and are those represented by one of the following formulas:

R—N→O and R_1N→O

wherein, as described in the above noted pending application, R represents an organic moiety such that the compound R—N→O is an N-oxide selected from the group consisting of tertiary amine oxides, nitrones and dinitrones and R′ represents the atoms of carbon, oxygen, nitrogen or sulfur necessary to complete a five or six membered heterocyclic ring or a fused ring.

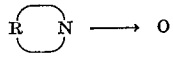
The R—N→O compounds include N→ oxides of tertiary amines and nitrones and dinitrones. The N-oxides of the tertiary amines may be prepared as described in Witman United States Patent 3,047,579 and include trialkylamine oxides, such as trimethyl-, triethyl-, methyl diethyl-, tripropyl-, tributyl-, etc.,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



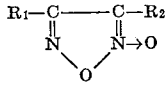
where R_1, R_2 and R_3 can be hydrogen, alkyl, substituted alkyl, alkenyl, aryl and substituted aryl. Examples of nitrones suitable for the present invention include α-N-diphenylnitrone, αα-diphenyl-N-methylnitrone, N-ethylnitrone, Δ'-tetrahydropyridine-N-oxide, 4,5,5-trimethyl-Δ'-pyrroline-N-oxide, N-methylcyclopentanone ketonitrone, N-phenylfluorenone ketonitrone 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 azoxypyridine-N-oxides, pyridylcarbinol-N-oxides, vinylpyridine-N-oxides, N,N - dimethylaminostyrylpyridine-N-oxides, quinoline - N - oxide and substituted compounds 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 furoxanes which may be represented by the formula



wherein R_1 and R_2 can be alkyl or substituted alkyl, aryl or substituted aryl, amino, halogen, nitro, carboxyl, oxygen (as ether), either symmetrical or unsymmetrical and both R_1 and R_2 can be part of a ring system. Examples of furoxane suitable for the present invention include: diphenylfuroxan, dibenzoylfuroxan, amino(phenyl)furoxan, benzofuroxan, cyclohexenefuroxan, naphthofuroxan and derivatives thereof.

IV. BINDER

The photosensitive formulations employed in this invention can be applied to any suitable substrate as described in the above noted patents and applications.

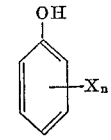
One convenient method of preparing photographic film and paper is to dissolve all of the constituents in a single solvent and then cast the solution onto an inert base such as glass or a synthetic resin polymer such as Mylar or to dip an absorbent material such as paper into such a solution. Once the solvent which is preferably a volatile solvent has evaporated the resultant film is suitable for exposure. It will be understood that if desired a film forming binder may be included in the formulation in order to produce a self-sustaining film, strippable from the glass base or other inert support.

V. TRIARYL COMPOUND OF GROUP V–B ELEMENTS

An optional additional substituent which is very useful in the composition of this invention is a triaryl compound of Sb, As, Bi or P, triphenylstilbene being a particularly preferred compound.

VI. STABILIZER

All of the foregoing constituents are known in one or another of the above noted patents. The present invention is directed to the addition of a compound which enhances the shelf life and gives clean background when the film has been exposed and developed. This constituent may be represented by the general structure



wherein X may represent one or more hydroxyl groups or amino groups or alkyl or allyl groups and *n* is an integer not less than 1 and not more than 5. When *n* is greater than 1, all of the X's used need not be the same. Examples of such compounds are: p-aminophenol; catechol; 2,4-di-tert-pentyl phenol; 2,5-bis(1,1-dimethylpropyl)hydroquinone; 2-6-di-tert - butyl-p-cresol; 2,6-di-tert-butyl phenol; para, tertiary butyl phenol; tert-butyl hydroxy anisole; etc.

Compositions of this invention should be prepared from pure starting materials. Commercially available materials may be further purified if necessary. For many compositions preparation under yellow bug lights or Wratten OA safelight filters are satisfactory. For others it is necessary to prepare the composition under red photographic safelights or in total darkness where the composition is sufficiently sensitive to be fully panchromatic.

After preparation the composition is coated on film supports such as Mylar, cellulose acetate or the like. Coatings on paper are made on paper whose surface has been subbed with polyvinyl alcohol, gelatin or any hydrophilic colloid. Coatings on paper without the hydrophilic surface have also worked reasonably well. The coatings are dried for 1 to 10 minutes in air and stored in a closed container at room temperature or under refrigeration until ready to be exposed.

The coated film or paper is exposed photographically to radiation from a tungsten lamp, an ultraviolet lamp or a photoflood lamp at a distance of about 12 inches. The time required for a latent image or printout image to form varies depending on the composition of the photosensitive mixture, and the intensity of exposing light.

The resulting latent image or printout image can be photodeveloped or intensified respectively, by exposure to an infrared lamp or by exposure to filtered light which passes radiation of suitable wave length to increase the image density. The resulting exposed and developed print is fixed by heating in a forced draft oven at about 100–200° C. for approximately 2 to 5 minutes. Placing the exposed and developed print on a heated surface at about 100–200° C. for approximately 30 seconds will also render the print fixed and permanent. Washing the exposed and developed print in a suitable mixture of solvents, such as 1 part acetone to 4 parts of petroleum ether is another useful means of fixing the images formed by the compositions described herein, but this fact is mentioned only for informational purposes since one of the novel features of this invention is its ability to be fixed by heat alone.

COMPOSITION RANGES

Constituents	Parts by weight
(I) Color forming compound	1 part by weight (total).
(II) Activator:	
Organic halogen compound	5–500 parts per part of I.
Sulfonyl and sulfenyl halides	1–100 parts per part of I.
Mercapto compounds	Do.
(III) N→O compound	1–50 parts per part of I.
(IV) Binder	2–20 parts per part of I.
(V) Triaryl compound of Group VB elements.	1–50 parts per part of I.
(VI) Stabilizer	Do.

EXAMPLE 1

Leuco opal blue—25 mg.
2–6-di-tert-butyl-p-cresol—50 mg.
4-picoline-N-oxide—5 mg.
Triphenylstilbene—10 mg.
Iodoform—200 mg.
10% Polystyrene (Dow 700) dissolved in benzene—3 cc.
Acetone—1 cc.
Benzene—1 cc.

The constituents listed were dissolved in a mixture of acetone and benzene in the order listed. The resulting composition was coated on baryta photographic paper having a polyvinyl alcohol coating on the surface. The coated product was then dried in air. Exposure of the coating to a 35-mm projector (15×enlargement) for 3–5 seconds produced a latent image. Development was done with an infrared lamp. The print was fixed by placing the paper on a hot-plate at 150° C. for 30 seconds. Using the Eastman Kodak model 101 sensitometer for one minute exposure, eight steps of the step wedge are visible after development.

EXAMPLE 2

Example 1 was repeated using 2-6-di-tert-butyl phenol in place of 2-6 di-tert-butyl-p-cresol. Similar results were obtained.

EXAMPLE 3

Example 1 was repeated using leuco crystal violet in place of leuco opal blue in the initial formulation. Similar results were obtained.

EXAMPLE 4

A composition comprising

4-(p-dimethylaminostyryl)quinoline—25 mg.
Leuco malachite green—50 mg.
2-6-di-tert-butyl-p-cresol—50 mg.
4-picoline-N-oxide—5 mg.
Iodoform—200 mg.
10% Polystyrene (Dow 700) dissolved in benzene—4 cc.

was prepared as a solution in benzene. The resulting composition was coated on a sheet of Mylar polyester and air dried. Exposure of the coating to model 101 sensitometer for ten seconds produced seventeen steps after development using a Corning 2408 glass filter. The print was fixed by washing in solution of 1 part acetone and 4 parts petroleum ether. The print can be heat fixed but the dye base causes the unexposed areas to be colored. Omitting the monohydric phenol compound from the composition gave thirteen steps and higher fog, when processed in the identical manner.

EXAMPLE 5

Example 4 was repeated using 2-6-di-tert-butyl phenol in place of 2-6-di-tert-butyl-p-cresol and similar results were obtained.

EXAMPLE 6

A solution of the following was prepared as in Example 1:

4-(p-dimethylaminostyryl)-quinoline—40 mg.
4-picoline-N-oxide—5 mg.
2-6-di-tert-butyl-p-cresol—50 mg.
Iodoform—200 mg.
10% polystyrene (Dow 700) dissolved in benzene—4 cc.

The resulting composition was coated on a film of Mylar polyester and dried. Exposure of the resulting product was made using a model 101 sensitometer for ten seconds. There were nineteen steps visible after development using a Corning 2408 glass filter. Identical processing of the same composition without the 2-6-di-tert-butyl-p-cresol produced eleven steps and a high fog.

EXAMPLE 7

Similar results were obtained when the 2-6-di-tert-butyl-p-cresol in Example 6 was replaced with 2-6-di-tert-butyl-phenol.

EXAMPLE 8

2-[3-(3-ethyl - 2(3H) - benzothiazolylidene) - propenyl]-quinoline—25 mg.
4-picoline-N-oxide—5 mg.
2-6-di-tert-butyl-p-cresol—50 mg.
Iodoform—200 mg.
10% polystyrene (Dow 700) dissolved in benzene—4 cc.

The above ingredients were dissolved as in the previous examples and the resulting composition was coated on Mylar film and air dried. Exposure was made on Eastman Kodak model 101 sensitometer for ten seconds. There were nine steps visible after development with a General Electric infrared lamp. Only five steps were visible in an otherwise identical coating without the 2-6-di-tert-butyl-p-cresol, processed in the same way.

EXAMPLE 9

3-ethyl-5-[3-ethyl-2(3H)-benzothiazolylidene)-ethylidene]-2-(2-quinolylmethylene)-4-thiazolindone—25 mg.
4-picoline-N-oxide—5 mg.
2-6-di-tert-butyl-p-cresol—50 mg.
Iodoform—200 mg.
10% polystyrene Dow 700 (methylene chloride)—4 cc.

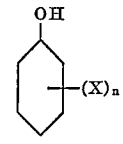
The above constituents were dissolved. The resulting solution was coated on a sheet of Mylar polyester and dried. Exposure was made on Eastman Kodak model 101 sensitometer for 60 seconds. Addition of 2-6-di-tert-butyl-p-cresol gave three more steps than a control composition from which it was absent.

EXAMPLE 10

The addiiton of small amounts of 4-(p-dimethylamine-styryl)-quinoline to the formulation of Example 1 prior to the application of same to the baryta paper gave a noticeable increase in speed and density.

What is claimed is:

1. In a photosensitive composition comprising:
(a) at least one color-forming compound selected from the group consisting of leuco diphenylmethane and leuco triphenylmethane color-forming compounds and dye bases selected from the group consisting of cyanine, styryl and merocyanine dye bases;
(b) at least one activator for accelerating the change in said color-forming 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→O compound in sufficient amount to further accelerate the color-forming change in said product directly as a result of said exposure to said dose of radiation;
the improvement which comprises: the addition to said composition of at least one stabilizer represented by the general formula



wherein each X is selected from the group consisting of OH, NH_2, alkyl and allyl; and *n* is an integer of at least 1 and not more than 5, and the several X's may be different from one another when *n* is greater than 1.

2. The composition of claim 1 supported as a thin layer.

3. The composition of claim 1 in which for each part

by weight of color-forming leuco compound or dye base there are between 5 and 500 parts by weight of activator, between 1 and 50 parts of organic N→O compound and between 1 and 50 parts by weight of phenolic stabilizer.

4. The composition of claim **1** dispersed in a film forming binder.

5. The composition of claim **1** including in addition at least one triaryl compound of an element selected from the group consisting of Sb, Bi, As and P.

6. The composition of claim **1** wherein N→O compound is 4-picoline-N-oxide.

7. The composition of claim **1** wherein the stabilizer is 2,6-di-tert-butyl-p-cresol.

8. The composition of claim **1** wherein the stabilizer is 2,6-di-tert-butyl phenol.

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