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Hazy et al.

[11] **3,907,569**

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[54] **ULTRAVIOLET HOLDBACK OF NONSILVER PHOTOSENSITIVE SYSTEMS BY INCORPORATING THEREIN CERTAIN ORGANIC ADDITIVES**

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[52] **U.S. Cl.** ..... **96/90 R**; 96/115 P

[51] **Int. Cl.**[2] **G03C 1/52**

[58] **Field of Search** ..... 96/90 R, 90 PC, 88, 115 P

[56] **References Cited**

UNITED STATES PATENTS

3,351,467	11/1967	Sprague et al.	96/90 R
3,502,476	3/1970	Itano et al.	96/90 R
3,510,304	5/1970	Fichter et al.	96/90 R
3,527,639	9/1970	Moraw	96/90 R
3,533,792	10/1970	Petro et al.	96/90 R
3,560,216	2/1971	Hori et al.	96/90 R
3,579,342	5/1971	Strilko	96/90 R
3,620,748	11/1971	Fichter	96/90 R
3,642,479	2/1972	Allan et al.	96/90 R
3,708,297	1/1973	Poot	96/90 R
3,712,817	1/1973	Hazy	96/90 R

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[57] **ABSTRACT**

A non-silver, photosensitive composition comprising: at least one aminoaryl ethylene color forming compound and at least one activator for said color forming compound, wherein the composition includes in addition at least one organic compound the addition of which produces imagery having improved ultraviolet holdback, such compounds being selected from the group consisting of heterocyclic compounds, quinone compounds, multifunctional aromatic hydroxy compounds and aromatic carbonyl containing compounds.

9 Claims, No Drawings

ULTRAVIOLET HOLDBACK OF NONSILVER PHOTOSENSITIVE SYSTEMS BY INCORPORATING THEREIN CERTAIN ORGANIC ADDITIVES

This invention relates to photosensitive compositions and to photosensitive films based on such compositions. More particularly, it relates to improved ultraviolet holdback characteristics obtained from such photosensitive compositions by the incorporation therein of certain organic compounds as described below. The improved ultraviolet holdback of said compositions makes them especially suitable for use in the preparation of intermediate masters for duplication purposes and for photomasks. Some of these compounds improve photosensitive compositions even further, giving the additional advantage of being particularly useful for the production of see-through masks, since they increase the ultraviolet holdback with little or no increase in visible density so that the resulting mask retains transparency to visible radiation.

The importance of this invention will be apparent from the fact that in a significant portion of the photographic processing requiring the need for duplication of information that may be available from a negative taken in a camera, in which relatively large numbers of such duplicates are required, ultraviolet light sources are commonly used in the printers involved in such duplication in view of the high density of illumination that can be packed in the small space in contradistinction to substantially lower levels of illumination that may be provided by visible light sources. Since ultraviolet is the commonly used source of illumination for duplication purposes and since duplicates may be made from duplicates, the sensitometric properties of the photographic system in the ultraviolet are important and particularly with regard to the amount of optical ultraviolet density that can be achieved in the material on suitable exposure to ultraviolet light. Intermediate masters exhibiting such high optical density in the image area, even though the density in the visible may be very low, are then suitable for use as "stencils" to enable one to copy information onto a material which again will require the use of ultraviolet light for exposure purposes, but in which the visible density is very high. In reality, this is a process of multigeneration and the improved ultraviolet holdback described in this specification is of fundamental importance in order to achieve the design purpose.

Compounds useful in the practice of this invention fall into the following general classes: heterocyclic compounds, materials containing quinone structures, multifunctional aromatic hydroxy compounds and aromatic carbonyl containing compounds.

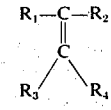
The photosensitive compositions to which the present invention is particularly applicable include nonsilver photosensitive compositions comprising an aminoaryl ethylene color forming compound and an activator, usually an organic halogen compound or a sulfur containing compound as described in the following U.S. Pat. Nos. among others:

Ethylene Compounds	3,510,304; 3,533,792
Organic Halogen Compounds	3,042,515; 3,147,117
Sulfur Containing Compounds	3,285,744
Sulfur and Halogen Containing Compounds	3,113,024

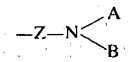
The disclosures of said patents are intended to be incorporated herein by reference. The compounds enumerated below are representative of specific compounds within the above classes and are intended to be illustrative and are not to be considered a complete listing of all of those which are suitable for the present invention:

1. Color Forming Compounds

Suitable color forming compounds useful in the practice of this invention are ethylene compounds as described in U.S. Pat. Nos. 3,510,304 and 3,533,792 which may be represented by the formula



wherein R_1 and R_2 are each a monovalent radical represented by the formula



in which Z is selected from the group consisting of phenyl, naphthyl and diphenyl, and in which A and B are each selected from the group consisting of H and alkyl and wherein R_3 and R_4 are each selected from the group consisting of H, alkyl and aryl.

2. Activators

a. Organic Halogen Compounds

The organic halogen compounds which are suitable in the light sensitive compositions to which the present invention is applicable include those represented by the general formula A—C—X_3 wherein A represents halogen (Cl, Br or I), H, alkyl, substituted alkyl including halogen substituted alkyl, aryl, substituted aryl, aroyl, and arylalkyl and wherein 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. Preferred compounds are halogen substituted alkanes, e.g., CBr_4, CHI_3, C_2HBr_5, CI_4 etc., and α,α,α-tribromoacetophenone.

b. Sulfur Containing Compounds

The sulfur containing compounds which are suitable in the photosensitive compositions to which the present invention is applicable are those represented by either the formula R—SH or the formula R—S—S—R wherein each R represents an aryl or heterocyclic ring. Suitable compounds include 2-mercaptobenzothiazole, 5-methoxy-2-mercaptobenzothiazole, 1-phenyl-5-mercaptotetrazole and pentachlorobenzenethiobis(dimethyl-thiocarbonyl) disulfide.

c. Sulfur and Halogen Containing Compounds

Activator compounds containing both halogen and sulfur and which are suitable for the present invention include the sulfonyl and sulfenyl halides described in U.S. Pat. No. 3,113,024, e.g., 2,4-dinitrobenzenesulfonyl chloride, p-chlorobenzenesulfonyl chloride, o-nitrobenzenesulfenyl chloride and pentachlorobenzenesulfenyl chloride.

3. Binder

As described in the above noted patents, the photo-

sensitive compositions are preferably formulated with a film forming binder and are cast as a thin film from solution usually as a thin coating on a suitable substrate. Among the binders which can be used are solutions of polystyrene, copolymers of styrene and acrylonitrile, polyphenylene oxide, polycarbonate, polyvinylbutyral, suitable combinations of the above, and others such as those described in U.S. Pat. Nos. 3,100,703 and 3,147,117. The compositions have been utilized without a binder, for example, when imbibed in a paper or other porous substrate.

4. Additional Constituents

Many additional compounds which have been added to the aforementioned photosensitive compositions for specific benefits are fully described in the above noted patents, including compounds to sensitize the compositions to certain wavelengths of light, stabilizers to permit storage of the compositions, additives to modify the color of the image produced by exposure to light, and additives which facilitate fixing of the compositions after exposure. The present invention is applicable to compositions including one or more of such additives.

5. Organic Compounds Producing Imagery Having Improved Ultraviolet Holdback

The organic compounds producing imagery having improved ultraviolet holdback, the use of which comprises the present invention, may be selected from the following general classes: heterocyclic compounds, quinone compounds, multifunctional aromatic hydroxy compounds and aromatic carbonyl compounds. Examples of heterocyclic materials which have been found suitable include: acridine, phenothiazine, acridan, carbazole, N-vinylcarbazole and benzoflavine. Quinone compounds which are useful for the present invention include: 1,2-naphthoquinone, 2-amino-1,4-naphthoquinone, 1,4-diamino-9,10Anthraguinone, 1,-4-diamino-2,3-dichloro-9,10-anthraquinone and 2,3-dichloro-1,4-naphthoquinone. The aromatic hydroxy compounds which are suitable include 1,2,4-trihydroxybenzene and 1,4,9,10-tetrahydroxy-9,10-dihydroanthracene. Suitable carbonyl compounds include acetanilide, phenyl acetate and N-acetyl-N'-phenylhydrazine. Other compounds suitable for the practice of this invention include those which have structures fitting more than one of the outlined classes as, for example: 1-amino-4-hydroxy9,10-anthraquinone, 1-amino-4-benzamido-9,10-anthraquinone, 1,4-dihydroxy-9,10-anthraquinone, 2-hydroxy-3-naphthoic acid anilide, 2-hydroxycarbazole-3-carboxylic acid P-chloroanilide and 2-hydroxy-α-benzocarbazole-3-carboxylic acid p-methoxyanilide.

Proportions

Suitable proportions of the U.V. holdback compounds range from 0.02 part to up to 2 parts by weight of compound, for each part by weight of the color forming compound in the composition and depends to some extent on the solubility of the particular compound in the binder-solvent used. The proportions of other constituents are as described in U.S. Pat. Nos. 3,510,304 and 3,533,792, for example.

Base

The formulations employed in this invention can be applied to any suitable substrate such as cellulose acetate, polyesters such as polyethylene terephthalate as defined by the trade names Mylar (E.I. duPont) and Celanar (Celanese Corporation), paper, cloth, glass, etc.

Fixing

Fixing of the exposed photosensitive compositions employed in this invention is accomplished by heat or by solvent wash as described in the patents noted above.

EXAMPLES

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

EXAMPLE 1

A solution of 130 mg of 1,1-bis(4-dimethylaminophenyl)-ethylene, 50 mg of 2,6-di-t-butyl-p-cresol, 10 mg of triphenyl stibene, 280 mg of iodoform, 100 mg of triethylamine, 75 mg of methyl oleate and 3 mg of 1,2-naphthoquinone in 6 cc of a 10 percent solution of polyphenylene oxide in 1:1 chloroform-chlorobenzene was coated 0.003 inch (wet thickness) on a polyester substrate and dried for 2 minutes at 90°C. The resulting film was exposed to a high pressure mercury arc lamp through an Eastman No. 2 step wedge and given a maximum exposure of 90 mj/cm². The film was fixed by heating to 160°C for 2 minutes and gave a net maximum optical density (over base plus fog) of 1.40 when read with a U.V. densitometer using a filter which transmitted only 366.0 nm radiation. An otherwise identical film was prepared, but without the naphthoquinone. Maximum optical density over base plus fog after identical processing was 0.82.

EXAMPLE 2

A film was prepared as described in example 1 using a solution of 130 mg of 1,1-bis(4-dimethylaminophenyl)-ethylene, 50 mg of 2,6-di-t-butyl-p-cresol, 10 mg of triphenyl stibene, 200 mg of iodoform and 3 mg of 1,2-naphthoquinone in 6 cc of a 10 percent solution of polycarbonate in 3:1 methylene chloride-chlorobenzene. Exposure and processing as described in Example 1 produced a net D_{max} (read through a 366.0 nm filter) of 2.51. The same film without 1,2-naphthoquinone produced only a net D_{max} of 1.05.

EXAMPLE 3

To 6 cc of a 10 percent solution of polyvinylbutyral in 3:1 methylene chloride-chlorobenzene was added 130 mg of 1,1-bis(4-dimethylaminophenyl)-ethylene, 50 mg of 2,6-di-t-butyl-p-cresol, 10 mg of triphenyl stibene, 280 mg of iodoform and 3 mg of 1,2-naphthoquinone. This solution was cast as a film upon a polyester substrate and allowed to dry. Exposure of 360 mj/cm² and fixing as described in Example 1 gave a net D_{max} (366.0 nm filter) of 2.70 while a film made without 1,2-naphthoquinone gave a net D_{max} of 0.46.

EXAMPLES 4–8

A film was prepared from a solution containing 140 mg of 1,1-bis(4-dimethylaminophenyl)-ethylene, 500 mg of carbon tetrabromide, 50 mg of 2,6-di-t-butyl-p-cresol, 10 mg of triphenyl stibene and 100 mg of triethylamine in 6 cc of a 10% solution of polystyrene in 3:2 toluene – methyl ethyl ketone. This film was exposed and fixed as described in Example 1. Identical films were then prepared, except that each contained one compound representative of the materials useful for

this invention, and these films were exposed and processed identically. The maximum density over base plus fog was read for each film through both a visible filter and a 366 nm filter. The data thus obtained are shown in Table I. Examination of the data shown in Table I will illustrate the usefulness of these additives for the production of see-through masks, since the ultraviolet holdback has been significantly improved with little or no enhancement of visible imagery.

EXAMPLE 9

A film was cast on polyethylene terephthalate from a solution consisting of 30 mg of 1,1-bis(4-dimethylaminophenyl)-ethylene, 100 mg of 2-mercaptobenzothiazole, 35 mg of carbon tetrabromide, 64 mg of triethylamine, 1 cc of acetone and 6 cc of 18 percent polystyrene in 2:1 toluene-ethylene dichloride. The film was dried at room temperature for 10 minutes and then was exposed to a General Electric Sunlamp. The density thus produced was 0.10 over base plus fog when read with a visible filter and the value obtained when read through a 366 nm filter was 0.55 over base plus fog. An otherwise identical film was prepared, except that 100 mg of phenoxazine was added to the coating solution. This film gave 0.34 net density (visible) and 1.07 net density at 366 nm.

TABLE I

Effect of Additives on Optical Density of Films Containing Carbon Tetrabromide as Activator

Example No.	Additive	Amount (mg)	net D_{max} visible	net D_{max} (366 nm)
Control	None	—	0.74	0.98
4	Acridine	100	0.84	2.25
5	Phenothiazine	100	1.05	2.14
6	1,2-Naphthoquinone	10	0.46	1.35
7	Acridan	75	0.87	2.48
8	N-Vinylcarbazole	100	0.29	2.16

EXAMPLES 10–32

A film was cast from a solution containing 70 mg of 1,1-bis(4-dimethylaminophenyl)-ethylene, 50 mg of 2,6-di-t-butyl-p-cresol, 10 mg of triphenyl stibene, 420 mg of iodoform, 100 mg of triethylamine and 6 cc of 15 percent polystyrene in 3:2 toluene - methyl ethyl ketone. This film was exposed to a medium pressure mercury arc lamp and given an exposure of 360 mj/cm². The film was fixed by heating to 160°C for 2 minutes and the net D_{max} was read through a 366.0 nm filter and a visible filter. Identical films were then prepared, except that each contained one compound representative of the materials useful for this invention, and these films were exposed and processed identically. Table II describes the results obtained. It should be noted that many of the films described in Table II gave an increased density of 366 nm without proportionate increase in visible density, so that these compositions would be especially suitable for the production of see-through masks.

EXAMPLE 33

A film was prepared from a solution of 30 mg of 1,1-bis(4-dimethylaminophenyl)-ethylene, 50 mg of 2,6-di-t-butyl-p-cresol, 100 mg of 4-nitrobenzenesulfonyl chloride, 200 mg of triethylamine and 6 cc of 18% polystyrene in 2:1 toluene – ethylene dichloride. After drying at room temperature for 10 minutes, the film was exposed to a sunlamp to give 0.14 net density (visible) and 0.60 net density (366 nm). An otherwise identical film was prepared, except that 50 mg of phenoxazine was added to the coating solution. This film produced 0.16 net density (visible) and 0.84 net density (366 nm).

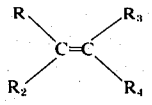
TABLE II

Effect of Additives on Optical Density of Films Containing Iodoform as Activator

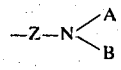
Example No.	Additive	Amount (mg)	net D_{max} (Visible)	net D_{max} (366 nm)
Control	None	—	2.03	1.54
10	Benzoflavine	10	2.38	1.62
11	Carbazole	10	2.34	1.73
12	N-Vinylcarbazole	100	1.03	2.79
13	Acridan	100	0.44	1.77
14	Acridine	100	1.50	2.20
15	1-Amino-4-hydroxy-9,10-anthraquinone	10	1.95	2.00
16	1,4-Diamino-9,10-anthraquinone	10	2.28	1.90
17	1-Amino-4-benzamido-9,10-anthraquinone	100	2.17	2.02
18	1,4-Diamino-2,3-dichloro-9,10-anthraquinone	10	2.50	1.73
19	1,4-Dihydroxy-9,10-anthraquinone	10	2.31	1.71
20	2-Amino-1,4-naphthoquinone	10	2.25	2.14
21	2-Hydroxy-3-naphthoic acid anilide	10	2.66	1.68
22	2-Hydroxycarbazole-3-carboxylic acid p-chloroanilide	10	2.88	2.36
23	2-Hydroxy-α-benzocarbazole-3-carboxylic acid p-methoxyanilide	10	2.45	1.68
24	Phenoxazine	100	1.70	2.02
25	Phenothiazine	100	1.56	1.82
26	Acetanilide	100	1.83	1.60
27	Phenyl acetate	100	2.21	1.74
28	N-Acetyl-N'-phenylhydrazine	10	2.70	1.92
29	1,2,4-Benzenetriol	10	2.58	2.16
30	1,4,9,10-Tetrahydroxy-9,10-dihydroanthracene	10	0.92	2.64
31	2,3-Dichloro-1,4-naphthoquinone	10	2.01	2.20
32	1,2-Naphthoquinone	3	2.13	2.74

We claim:

1. In a non-silver photosensitive composition comprising: (**1**) at least one color forming compound represented by the general formula



wherein each of R and R_2 is a monovalent radical represented by the formula



in which Z is selected from the group consisting of phenyl, naphthyl, and diphenyl and each of A and B is selected from the group consisting of H and alkyl; and each of R_3 and R_4 is selected from the group consisting of H, alkyl and aryl; and

2. at least one activator for said color forming compound, said activator being selected from the group consisting of (a) organic halogen compounds represented by the general formula Q—C—Hal_3 wherein Q is selected from the group consisting of H, Cl, Br, I, alkyl, substituted alkyl, aryl, substituted aryl, aroyl, and arylalkyl; and each Hal represents a halogen atom selected from the group consisting of Cl, Br or I; (b) sulfur containing compounds represented by either R—SH or R—S—S—R wherein each R represents an aryl or heterocyclic ring; and (c) compounds containing both halogen and sulfur selected from the group consisting of sulfonyl and sulfenyl halides;

the improvement which consists in the incorporation in said composition of (3) at least one organic compound which produces imagery having improved ultraviolet holdback, said compound being selected from the group consisting of heterocyclic compounds selected from the group consisting of acridine, phenothiazine, acridan, carbazole, N-vinylcarbazole, and benzolflavine; quinone compounds selected from the group consisting of naphthoquinones and 9,10 anthraquinones; and multifunctional aromatic hydroxy compounds selected from the group consisting of 1,2,4-trihydroxybenzene and 1,4,9,10-tetrahydroxy-9,10-dihydroanthracene.

2. The composition of claim **1** in which the relative proportions of said color forming ethylene compound and said compound producing imagery having improved U.V. holdback is between 50:1 and 1:2.

3. The composition of claim **1** in which the color forming compound is 1,1-bis(4-dimethylaminophenyl)-ethylene and the ultraviolet holdback compound is a quinone.

4. The composition of claim **3** wherein the quinone is a naphthoquinone.

5. The composition of claim **4** in which the naphthoquinone is 1,2-naphthoquinone.

6. A photosensitive member comprising a support and a coating therein comprising the composition of claim **1**.

7. The composition of claim **1** wherein the U.V. holdback compound is acridan.

8. The composition of claim **1** wherein the U.V. holdback compound is an anthraquinone.

9. The composition of claim **1** wherein the U.V. holdback compound is acridine.

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