

July 27, 1971

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3,595,657

NON-SILVER DIRECT POSITIVE DYE BLEACH-OUT SYSTEM USING  
INDIGOID DYES AND COLORLESS ACTIVATORS

Filed Oct. 3, 1968

2 Sheets-Sheet 1

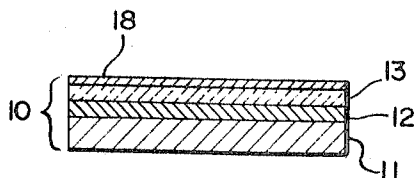


FIG. 1

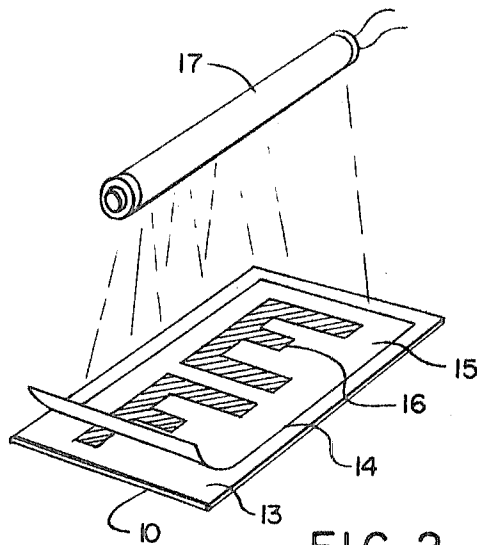


FIG. 2

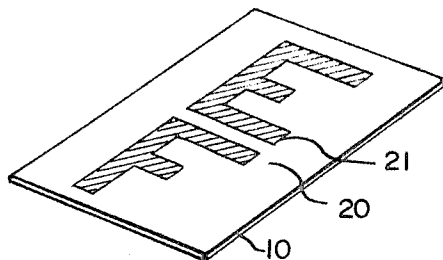


FIG. 3

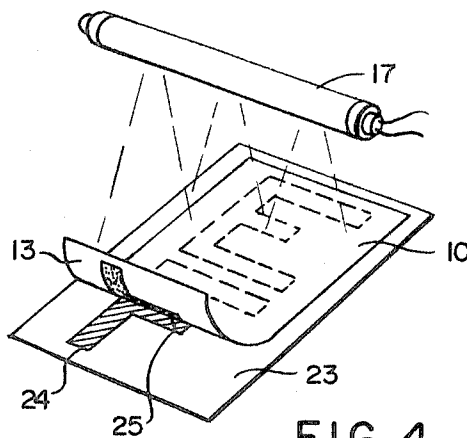


FIG. 4

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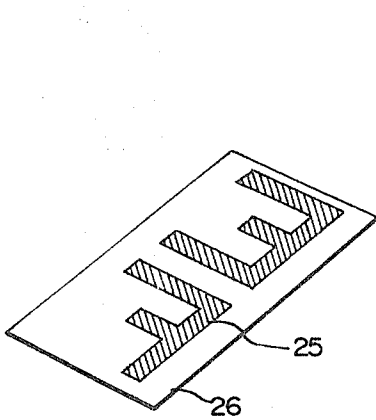


FIG. 5

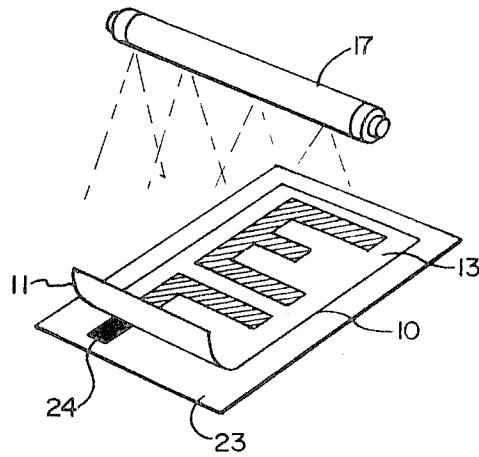


FIG. 6

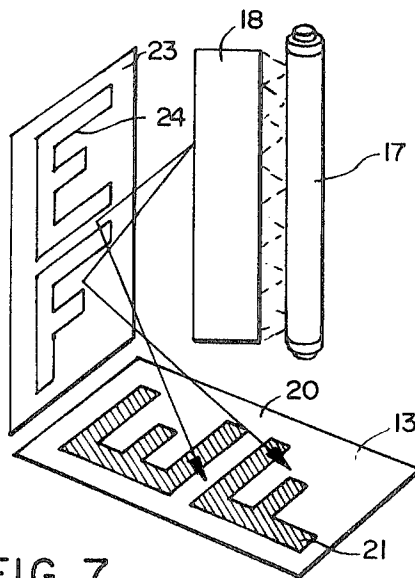


FIG. 7

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3,595,657

## NON-SILVER DIRECT POSITIVE DYE BLEACH-OUT SYSTEM USING INDIGOID DYES AND COLORLESS ACTIVATORS

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Int. Cl. G03c 5/24, 1/72

U.S. Cl. 96—48

13 Claims

### ABSTRACT OF THE DISCLOSURE

A direct positive bleach-out photographic system suitable for photography and photocopy work. An indigoid dye and activator, supported in a binder, form the photosensitive system which is bleached out when exposed to ultraviolet light.

### CROSS REFERENCES TO RELATED APPLICATIONS

In four copending applications we have disclosed four other direct positive bleach-out systems. These applications are Ser. No. 764,766 filed Oct. 3, 1968 directed to a combination of indigoid dyes and colored activators; Ser. No. 764,661 filed Oct. 3, 1968 directed to a combination of polymethine dyes and essentially colorless activators; Ser. No. 764,662 filed Oct. 3, 1968 directed to a combination of polymethine dyes and colored activators; and Ser. No. 764,762 filed Oct. 3, 1968 directed to a combination of stable free radical dyes and essentially colorless activators.

This invention relates to a photographic method and article and more particularly to a direct positive bleach-out photographic system suitable for photography to produce black-and-white and monochrome prints and transparencies, for photocopying to make black-and-white and monochrome copies and to processes and articles which involve as at least one step or product the making of a photographic copy.

There is, of course, a large body of prior art concerned with the general fields of photography and photocopying. This body of prior art includes the use of silver halide emulsions with their attendant darkroom processing techniques, the employment of photoconductive particles or films with accompanying formation of electrostatic latent images and subsequent toning and fixing, and the formation of vesicular images in water-insensitive photographic materials. However, since these prior art techniques are completely distinguishable from that of the present invention, they need not be discussed. Rather, the prior art which is pertinent to this invention is set forth in a series of United States Patents (see for example USP 3,102,027, 3,104,973, 3,114,635, 3,154,416 and 3,155,509) describing a so-called "bleach-out" system employing a light-sensitive combination of a dye and an activator. Exposure of these light-sensitive materials effects bleaching of the dyes in those areas exposed to light of a predetermined wavelength range. The unexposed areas remain the color of the original dye, thus forming a contrast which gives rise to a copy or photograph.

Bleach-out systems of this type have certain marked advantages, among which may be listed the absence of graininess, the elimination of darkroom procedures and rapidity of access. However, the prior art systems, although realizing these advantages at least in part, possess certain inherent disadvantages. The light-sensitive systems of this prior art show a marked tendency to develop color in the bleached areas during use or storage even in the absence of light, thus causing eventual obliteration of

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the copy. Most of these prior art systems cannot be fixed satisfactorily.

It would, therefore, be desirable to have a positive bleach-out photographic system which retained all the advantages inherent in such a system and which at the same time is capable of overcoming at least some of the more restrictive disadvantages associated with the prior art systems.

It is therefore a primary object of this invention to provide a light-sensitive, positive bleach-out photographic system which is capable of providing a sharp, positive grainless copy of rapid access which exhibits improved stability. It is yet another object to provide such a system which can be made extremely light-fast, which is flexible with respect to the manner in which it may be exposed, to the type of processing to which it is subjected and to the type of final product achieved.

It is another primary object of this invention to provide a method of photography or photocopying which is capable, through the choice of dyes and structure of the light-sensitive system, of producing prints or transparencies in black-and-white or monochrome which are extremely light-fast and which may be applied to cloth as well as paper substrates.

It is another primary object of this invention to provide photosensitive articles of the character described and methods of using them which are simple to formulate and use and which may be relatively inexpensive. Other objects of the invention will in part be obvious and will in part be apparent hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the article possessing the features, properties, and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings in which:

FIG. 1 is a cross section of the light-sensitive system of this invention applied to a substrate to form a photosensitive sheet;

FIG. 2 illustrates the step of exposing the photosensitive sheet of FIG. 1 to a negative for copying by direct contact;

FIG. 3 illustrates the formation of the image made by the exposure illustrated in FIG. 2;

FIG. 4 illustrates the use of the photosensitive article of this invention to make a reverse copy of an opaque original by the reflux technique;

FIG. 5 illustrates the copy made by the exposure illustrated in FIG. 4;

FIG. 6 illustrates the use of the photosensitive article of this invention to make a right-reading copy of an opaque original by the reflux technique; and

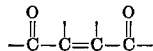
FIG. 7 illustrates the use of the photosensitive article of this invention to make a right-reading copy of an opaque original by the projection technique.

The photosensitive positive bleach-out system of this invention may be defined as one which comprises an indigoid dye such as an indigo, thioindigo or selenoindigo dye, or a combination of such dyes and an activator which is a compound or mixture of compounds capable of initiating the photopolymerization of a vinyl monomer. More specifically, these activators are compounds which form free radicals when exposed to a predetermined wavelength range of the electromagnetic spectrum. In the case of the systems of this invention this wavelength range generally encompasses that normally designated as the ultraviolet. However, some of the systems are sensitive to gamma rays and X-rays.

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The bleach-out dyes usable in the photosensitive system of this invention may be generally defined as the indigoid dyes which include the indigo and indirubin dyes. These dyes have long been known as very intense, stable, and extremely light-fast dyes. The indigoid dyes moreover, offer a wide range of colors as well as the possibility of a one-dye black, this latter being particularly attractive for a photocopy system.

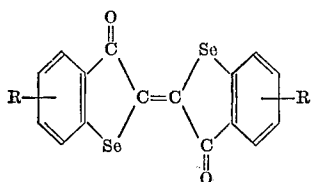
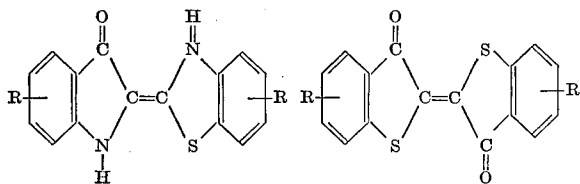
The term "indigoid" dye as used hereinafter is meant to include all those dyes generally considered by those skilled in the art to fall within the general class of dyes having as their chromophoric structure the conjugated grouping



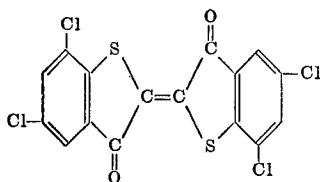
which is reducible to the substantive leuco form. A substantial body of art exists on the synthesis, classification, and naming of these indigoid dyes. (See for example "The Chemistry of Synthetic Dyes" by K. Venkataraman, Academic Press, Inc., New York, 1952, pp. 1003-1045; and "Colour Index" second edition, 1956, volume 3 published in the United States by the American Association of Textile Chemists and Colourists pp. 3547-3567.)

There are a number of ways in which the indigoid dyes may be classified and described. The following brief description represents one way of grouping these dyes in subclasses better to illustrate the various structures possible. These subclasses and the examples given are meant to be illustrative and not limiting.

(1) Symmetrical derivatives of indigo, thioindigo and selenoindigo represented as

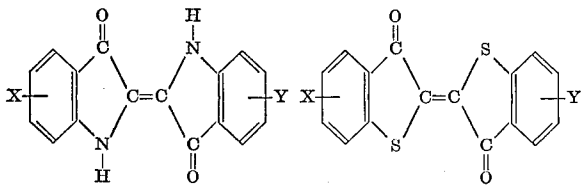


wherein R may be one or more of the following: lower alkyl, lower alkoxy, Cl, Br, NH<sub>2</sub>, NaSO<sub>3</sub>, aryl and substituted aryl. An example of this subclass is

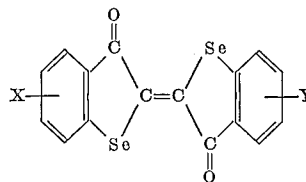


which is known as C.I. Vat. Blue 41 and is reddish blue in color.

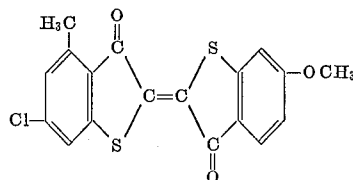
(2) Asymmetrical derivatives of indigo, thioindigo or selenoindigo represented as



## 4

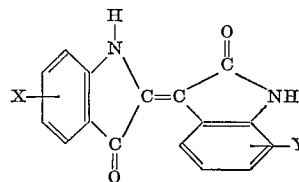


wherein X and Y are different and may be one or more of the following: lower alkyl, lower alkoxy, Cl, Br, NH<sub>2</sub>, NaSO<sub>3</sub>, aryl, and substituted aryl. An example of this subclass is

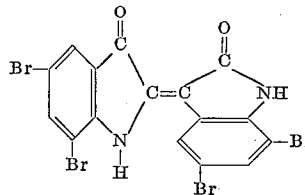


which is known as C.I. Vat Red 6 and is bright red in color.

(3) Indirubins represented as

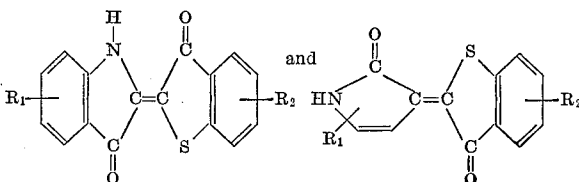


wherein X and Y have the same meaning as above. An example of this subclass of indigoid dye is

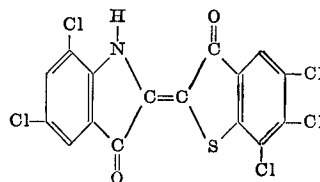


which is known as Ciba Heliotrop B and is magenta red in color.

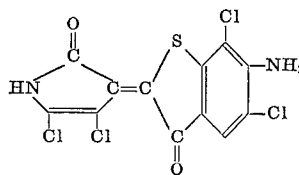
(4) Indigos and indirubins wherein one imino group is replaced by sulfur represented as



wherein R<sub>1</sub> and R<sub>2</sub> may be the same or different and are one or more of the following: lower alkyl, lower alkoxy, Cl, Br, NH<sub>2</sub>, NaSO<sub>3</sub>, aryl and substituted aryl. Two examples of this subclass of indigoid dyes are



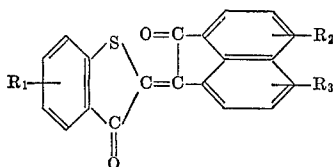
which is known as C.I. Vat Violet 5 and is bluish violet in color; and



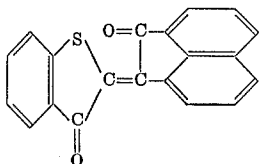
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which is known as Algol Brown GN and is dull yellowish orange in color.

(5) Dyes containing one ketone-bearing heterocyclic grouping connected by means of a double bond to a carbon alpha to a keto or oxo group in an aromatic system as represented by



wherein  $R_1$ ,  $R_2$ , and  $R_3$ , which may be the same or different, are one or more radicals which may be lower alkyl or halide. An example of this subclass of indigoid dyes is

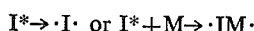


which is known as Ciba Scarlet G, C. I. 1228 and is scarlet in color.

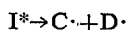
The final choice among these various dyes will depend upon the image color desired, the rapidity of access needed, the activator used and the substrate employed. The proper combination of dye and activator to meet performance requirements for the photosensitive system is well within the ability of one skilled in the art.

The activators suitable for use with these dyes are those compounds which are capable, through the formation of free radicals, of initiating photopolymerization of vinyl monomers.

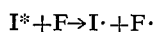
Free radical formation by these activators may be by one of several well-known mechanisms which may be summarized as diradical formation



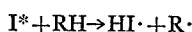
homoclytic cleavage



electron transfer



hydrogen transfer



(See for example Photographic Science and Engineering 7:360 (1963) "Image-Forming Systems Based on Photopolymerization")

A number of diverse compounds are known in the art which meet the requirements for the activators of this invention and the following list is given as illustrative of a number of different classes; and it is not meant to be limiting:

(1) carbonyl compounds:

polynuclear quinones (phenanthrenequinone)

$\alpha$ -ketones (benzil)

$\alpha$ -hydroxyketones (benzoin)

acyloin ethers (benzoin methyl ether)

$\alpha$ -alkyl substituted aromatic acyloins ( $\alpha$ -methyl benzoin);

(2) azo and diazo compounds:

diazonium chloride of p-aminodiphenylamine

$\alpha$ -azobis (1-cyclohexanecarbonitrile)

(3) organic sulfur compounds:

disulfides (dibenzyl disulfide)

mercaptans (2-mercaptobenzothiazole)

metal mercaptides (mercuric phenylmercaptide)

o-alkyl xanthene esters (carbalkoxymethylene bis (n-propyl xanthene)

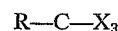
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thiuram derivatives (tetramethylthiuram disulfide)  
sulfenates (ethyl-2-benzothiazylsulfenate)

(4) peroxides:

di-tertiarybutyl peroxide  
hydrogen peroxides

(5) organic halogen compounds of the formula



wherein R is H, Cl, Br, alkyl, substituted alkyl, aryl or substituted aryl and X is Cl, Br or I.

carbon tetrabromide

$\alpha, \alpha, \alpha$ -tribromoacetophenone

bromoform

hexachloroethane

iodoform

(6) miscellaneous redox systems:

salts of iron, cobalt and nickel

$\beta$ -naphthol

persulfates

alkali metal salts of anthraquinone sulfonic acid

salts of heavy metals including zinc and silver

divalent tin salts (stannous chloride)

metal alkyls (tetraethyl lead)

inorganic sulfides, selenides and tellurides

uranyl salts of mono- and

dicarboxylic acids.

(See for example Jaromir Kosar "Light-Sensitive Systems" John Wiley and Sons, Inc., N.Y., 1965, chapter 5, and U.S. Pats. 2,880,152, 3,065,160 and 3,099,558 for further descriptions of one or more classes of these activators.)

In forming the photosensitive system of this invention, the mole ratio of activator to dye may range from about 20-to-1 to about 500-to-1, with about 100-to-1 being typical and generally preferred. The activator-dye ratio employed will, of course, depend upon the activator-dye system as well as upon the performance characteristics desired from the photosensitive system.

In compounding the photosensitive composition, it may also be desirable to incorporate one or more additives. For example, such additives may include, but are not limited to, plasticizers, agents to control the coating properties, and compounds capable of color filtering.

The photosensitive system (dye plus activator) is affixed to a substrate through a film-forming binder. This is most conveniently done by forming a solution of the binder along with any additives such as plasticizers, etc., in a suitable solvent and then adding the dye and activator to the solution under conditions of temperature and exposure to light which will not effect any premature bleaching of the dye. The film-forming binder must not, of course, have any adverse effects on the ability of the desired electromagnetic radiation to bleach the dye.

The role of the binder in forming a suitable photosensitive system is not completely understood; but it appears that it is desirable to use a binder having the structure



incorporated therein where X is an electronegative element. Perhaps such binders donate a hydrogen atom, a possibility if the C—H bond is of a type which is relatively easily broken. A suitable binder can be easily chosen as a result of simple experimentation with the desired dye-activator combination. If oxygen enters into the activation process when the photosensitive system is exposed, then it is preferable that the binder be oxygen-permeable.

A number of film-forming resins may be used as the binder; and the preferred one nitrocellulose applied as a solution in acetone. Other suitable binders include, but are not limited to ethyl cellulose, Carbowax 6000 (a polyethyl-

ene glycol sold by Union Carbide and Carbon Corporation) cellulose acetate butyrate, polyvinyl acetate, polymethyl methacrylate and polyvinyl chloride. Solvents will be chosen which are compatible with these binders, and typical solvents include, but are not limited to, acetone, toluene, methylene chloride, and mixed solvents such as toluene/tetrahydrofuran and benzene/acetone. The performance of the photosensitive system deposited in binders other than nitrocellulose may be enhanced in some systems if a precoat intermediate layer of nitrocellulose or other binder is interposed between the substrate and the photosensitive layer. The reason for this enhancement is not understood but may be evidence by an increase in bleaching speed.

The concentration of the dye and activator in the solution of the film-forming material will be governed by the final coating weight desired and the technique used to apply the coating solution to the substrate surface. The coating weight in turn will generally determine both the image quality and speed of the photosensitive system. In general, the lighter the coating weight the higher will be the resolution and the faster will be the bleaching. The optimum coating weight will also depend upon the extinction coefficient of the photosensitive system and will generally range between about  $1 \times 10^{-5}$  to about  $1 \times 10^{-3}$  gram dye per square centimeter.

Typically, the concentration of the dye in the coating solution may range from about 0.01 gram per 100 milliliters to the limit of solubility of the dye in the solution. The amount of activator present will, of course, be governed by the selected mole ratio of activator to dye as defined above.

The thickness of the liquid coating at the time of application to the substrate may vary over a wide range and will be governed by the final coating weight desired, the solids concentration of the coating solution and the method by which the coating is accomplished.

The coating composition may be applied to the substrate by any suitable, well-known coating technique including roller coating, spraying, brushing, knife coating, and the like. Coating and drying must, of course, be accomplished under conditions which will not cause any premature bleaching of the dye.

The substrate material will, of course, be chosen to give the characteristics desired in the final photograph or photocopy and such materials are well known in the art. Thus, for example, if prints or photocopies are desired, the substrate will be an opaque paper material, typically a photographic print paper. If on the other hand the final product is to be a transparency, then the substrate will be a transparent film, typically of a synthetic resin. The substrate may be flexible or nonflexible as desired, and if a protective or barrier film is interposed between the substrate and the photosensitive film, little attention need be given to the chemical characteristics of the substrate.

The interposition of an intermediate layer between the substrate and the photosensitive film may be desirable for one or more of a number of reasons. This intermediate layer may be a coating of the same film-forming material used for forming the photosensitive layer or it may be formed of any other suitable type of material. It may serve as a barrier to prevent unwanted chemical components of the substrate from making contact with the photosensitive layer. The intermediate layer may also be used to enhance the physical properties of the substrate such as to render it smooth, make it more adhesive to the coating solution, or prevent curl of the substrate. The intermediate layer may also be used to enhance the optical properties of the photosensitive layer. As examples we may cite antihalation layers which are well known in the art and/or a layer of a material capable of absorbing light within a given wavelength range.

FIG. 1 illustrates, in diagrammatic cross section, a photosensitive article constructed in accordance with this invention. Such an article normally takes the form of sheet

10 formed of a substrate 11, an intermediate layer 12, and a photosensitive layer 13. The article of FIG. 1 would be particularly suitable for making black and white or monochrome copies or transparencies, depending on the characteristics of the substrate 11. Thus, if the substrate 11 is an opaque sheet, the final result will be a photocopy or a print, while if the substrate 11 is, for example, a transparent film, the final copy will be a transparency. As explained above, the intermediate layer 12 is optional and may be used to perform one or more of several functions. Similarly, the photosensitive layer 13 may be covered, such as with an anti-abrasion coating 18.

FIG. 2 illustrates the manner in which a photosensitive sheet such as that shown in FIG. 1 may be used to form a copy of a transparency having a light or transparent background 15 and indicia 16. The photosensitive sheet 10 with the photosensitive layer 13 in contact with the transparency 14 is exposed to a suitable light source, in this example a source 17 of ultraviolet light. The ultraviolet light from source 17 will, of course, be transmitted through the light or colorless areas 15 to strike the photosensitive layer 13 and to bleach-out those areas which are thus exposed. However, since the ultraviolet light is not transmitted through the dark or black areas of indicia 16, these areas remain the color of the original dye of the photosensitive system since no bleaching of these areas occurs. The result is the copy illustrated in FIG. 3 wherein the numeral 20 designates the bleached or light areas corresponding to the light areas of the transparency and the dark areas 21 corresponding directly to the indicia on the transparency.

The production of a reverse-reading copy of an opaque master is illustrated in FIGS. 4 and 5. The photosensitive sheet is placed such that the photosensitive layer 13 contacts the opaque master formed of white background areas 23 and dark indicia 24. Exposure to the ultraviolet light 17 will result in its reflection from the white background 23 against the photosensitive layer to produce a bleached area 26 (FIG. 5) and unbleached areas 25. The photosensitive sheet used may have a transparent substrate, in which case the copy of FIG. 5 may be reversed and used as negative in the manner shown in FIGS. 2 and 3. Thus a right-reading copy may be made as a second step.

FIGS. 6 and 7 illustrate diagrammatically two ways in which right-reading copies may be made directly either by the reflex technique (FIG. 6) or the projection technique (FIG. 7). In FIG. 6 the photosensitive sheet is placed with the substrate surface in contact with the opaque master. Under these circumstances, some definition of outline is lost, but it is satisfactory for some purposes. In FIG. 7 the ultraviolet light from source 17 is directed through suitable well-known projection optics indicated generally at 18 to strike the original and to be reflected from the white or light areas 23 onto the photosensitive layer 13. Although this technique is optically feasible it will normally not be employed in photocopying due to the cost of the optical system required in the employment of ultraviolet light. Finally, right-reading copies may be made using optical reversal systems which are known in the photocopy art.

It may be desirable to fix the image after it is formed by exposure of the photosensitive system. Fixing may be accomplished by one of several techniques. If oxygen is involved in the image formation, an anti-oxidant overcoat may be applied to the photosensitive layer. The activator may be quenched by application of a suitable quenching agent, e.g., diphenylamine to quench biacetyl activators. Carbonyl activators may be destroyed by the application of suitable reducing agents. Finally, the activator may be photoreduced such as the photoreduction of aromatic ketones by amines. (See for example JACS 90:165 (1968).)

If the copy can be stored in a dark environment and exposed only periodically, then fixing is not necessary.

The following examples, which are meant to be illustrative and not limiting, are given further to describe the invention.

#### Example 1

Sufficient acetone was added to a mixture of 10 g. nitrocellulose (Hercules RS5-6 seconds wet with 30% by weight isopropyl alcohol) and 5 g. of dibutylphthalate (plasticizer) to make 100 g. of a standard binder solution. A casein-coated, smooth finish paper was coated with a 2-mil wet thickness film of this standard binder solution and dried. This precoated paper was used in all of the following examples.

A dye solution was formed by dissolving 0.058 gram of thioindigo in 50 ml. of warmed chloroform. 5 ml. of this dye solution was mixed with 15 ml. of the standard binder solution and then 0.408 g. of benzoin was added (molar ratio of activator to dye was 100:1) to form the photosensitive coating solution. This coating solution was coated at a 6-mil thickness on the precoated paper and air dried.

The photosensitive sheet was exposed for 5 minutes through a 21-step Kodak Photographic Step Tablet (No. 2 with a density range 0.05 to 3.05) and a glass plate to a 275-watt General Electric sunlamp at a distance of 10 inches. In the use of this standard device for measuring photosensitivity the number of steps which have a discernible lower density than the unexposed portion of the photosensitive layer is a measure of its photosensitivity. This means, of course, that the greater the number of steps, the greater is the sensitivity of the system. This exposure of the photosensitive system of this example gave 12 discernible steps and the image was pink on a white background.

When this formulation was repeated using 10 ml. of the binder solution and eliminating the benzoin activator, no bleaching occurred. Likewise when 0.640 g.  $\text{CBr}_4$  was added to a mixture of 10 ml. of the coating solution and 5 ml. of the dye solution no bleaching occurred. Thus benzoin is clearly an activator for the thioindigo.

It should be noted that the film base for the Step Tablet used had a transmission of about 50% at 360 millimicrons wavelength and considerably less than 50% below 360 millimicrons so that in using the Step Tablet the radiation to which the photosensitive system was exposed approached the visible spectra range. This means that these systems should be generally much faster when exposed to the optimum radiation wavelength range. However, the Step Tablet is a standard, reproducible method of evaluating photosensitivity and was therefore used.

#### Example 2

The formulation of Example 1 was repeated, except that 0.404 g. of benzil replaced the benzoin as activator and 2.5 ml. of methanol was added. Seven steps were obtained upon exposure, the bleaching being from pink to pale yellow.

#### Example 3

A dye solution was made by dissolving 0.0672 g.  $\text{N,N'}$ -diacetylindigo in 50 ml. methylene chloride. 5 ml. of this dye solution and 2.5 ml. methylene chloride were used in place of the dye solution of Example 1. The photosensitive coating was applied to paper, dried and exposed as in Example 1 and gave 8 steps, the images being magenta on an off-white background.

#### Example 4

5 ml. of a dye solution, made by dissolving 0.058 g.  $\text{N,N'}$ -dimethylindigo in 50 ml. acetone, and 2.5 ml. of acetone were added to 15 ml. of the standard binder solution along with 0.408 g. of benzoin. This photosensitive system was coated on paper, dried and exposed as in Example 1. Fifteen steps were bleached from cyan to ivory. When the benzoin activator was omitted from the coating solution, no detectable bleaching occurred

under the tablet, but slight bleaching occurred in other areas not covered by the transparency.

#### Example 5

The dye solution of Example 4 was replaced with one formed by dissolving 0.058 g.  $\text{N}$ -methyl indigo in 50 ml. acetone. Seventeen steps were bleached from blue to white; while in a control coating containing no benzoin only three steps were detected.

#### Example 6

A dilute solution of Vat Black 1, a black indigoid dye, in methylene chloride was concentrated by partial evaporation of the solvent. To this concentrated solution were added several grains of benzoin and sufficient standard binder solution to make a coatable liquid which was coated onto a 6-mil wet thickness of casein-coated paper which did not have a nitrocellulose precoat. After drying, the photosensitive coated paper was exposed through a silver transparency to light from a 275-watt reflector sunlamp at a distance of 10 inches for 5 minutes. The image was gray on white.

#### Example 7

The standard binder solution of Example 1 was replaced in the photosensitive system of Example 4 by the following binder solutions (all percent are by weight):

	Percent
Ethyl cellulose in toluene	10
Cellulose acetate butyrate in acetone	5
Polyethylene glycol in methylene chloride	15
Polyvinyl acetate in acetone	10
Polymethyl methacrylate in acetone	10
Polyvinyl chloride in 20/80 toluene/tetrahydrofuran	10
Polystyrene in 50/50 acetone/benzene	5

The papers on which these photosensitive coatings were applied were first given a precoat of the same binder used in the photosensitive coatings. All exposures of the photosensitive sheets were carried out as described in Example 1. Each of these binders were acceptable for forming a photosensitive system; however, those with a cellulosic base were preferred.

#### Example 8

0.663 g. of carbon tetrabromide was dissolved in a mixture of 5 ml. of the dye solution of Example 4, 2.5 ml. of acetone and 15 ml. of the standard binder solution. The photosensitive coating composition was applied to the nitrocellulose precoated paper and exposed as in Example 1 using the Step Tablet. Eight steps were bleached.

#### Example 9

A mixture of 0.23 g. of allylthiourea and 0.037 g. of citric acid was used in place of the carbon tetrabromide activator of Example 8. Exposure as in Example 1 gave 5 discernible steps.

The use of the indigoid dyes in a bleach-out system provides the possibility of forming intensely colored, light-fast images not only in a layer of a photosensitive coating applied to the usual substrates, e.g., films or papers but also within the substrate itself. Thus cloth or fabric may be impregnated with the photosensitive composition to form dye images in situ in the fabric. Indigoid dyes also provides the possibility of making a one-dye black system.

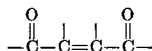
It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method and in the article set forth without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. A photosensitive composition which bleaches to form an image upon exposure to ultraviolet radiation

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alone, comprising in combination an indigoid dye having the conjugated grouping



and an activator in a binder, said activator being essentially colorless, capable of forming free radicals when exposed to ultraviolet radiation in the presence of said dye, capable of initiating photopolymerization of vinyl monomers and being a carbonyl, azo, diazo, organic sulfur-containing, or peroxide compound.

2. A photosensitive composition in accordance with claim 1, wherein said indigoid dye is a symmetrical derivative of indigo, thioindigo or selenoindigo.

3. A photosensitive composition in accordance with claim 1 wherein said indigoid dye is an asymmetrical derivative of indigo, thioindigo or selenoindigo.

4. A photosensitive composition in accordance with claim 1 wherein said indigoid dye is an indirubin.

5. A photosensitive composition in accordance with claim 1 wherein said carbonyl compound is an  $\alpha$ -diketone or  $\alpha$ -hydroxyketone.

6. A photosensitive composition in accordance with claim 1 wherein the mole ratio of activator to dye ranges between about 20-to-1 to about 500-to-1.

7. A photosensitive composition in accordance with claim 1 wherein said binder incorporates the structure



wherein X is an electronegative element.

8. A photosensitive composition in accordance with claim 1 wherein said binder is nitrocellulose, ethyl cellulose, cellulose acetate butyrate, polyethylene glycol, polyvinyl acetate, polymethyl methacrylate, polyvinyl chloride or polystyrene.

9. A photosensitive article suitable for exposure to ultraviolet energy alone for forming an image by direct bleach-out, comprising in combination:

(a) a substrate; and

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(b) at least one layer of a photosensitive composition affixed to said substrate in a binder, said photosensitive composition comprising in combination

(1) an indigoid dye, and

(2) an activator which is essentially colorless, is capable of forming free radicals when exposed to ultraviolet radiation in the presence of said dye and is a carbonyl, azo, diazo, organic sulfur-containing, or peroxide compound.

10. A photosensitive article in accordance with claim 9 wherein said substrate is a fabric.

11. A photosensitive article in accordance with claim 9 further characterized by having an intermediate coating layer interposed between said substrate and said layer of said photosensitive composition.

12. A method of forming an image of a master by direct bleach-out, characterized by exposing a photosensitive system in association with said master to ultraviolet radiation, said photosensitive system comprising in combination an indigoid dye and an activator incorporated in a binder and being affixed to a substrate, said activator being capable of forming free radicals when exposed to said radiation and being a carbonyl, azo, diazo, organic sulfur-containing, or peroxide compound.

13. A method in accordance with claim 12 wherein said activator is a carbonyl compound and said image is fixed by the step of destroying said activator by applying to said image a reducing agent for said carbonyl compound.

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