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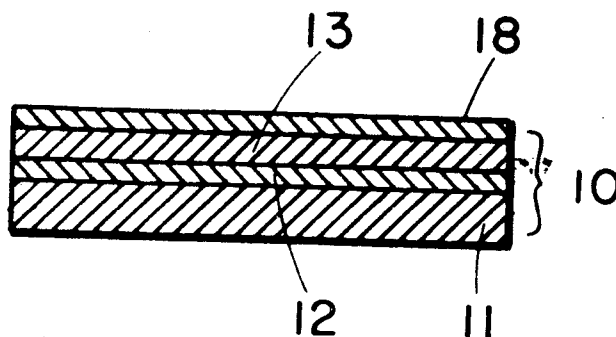
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[54] **PHOTOSENSITIVE ARTICLE AND METHOD OF**
USING SAME INCORPORATING LEUCO DYE
PRECURSORS AND QUINONE ACTIVATORS
 27 Claims, 4 Drawing Figs.

[52] U.S. Cl. 96/90,
 96/27, 96/48
 [51] Int. Cl. G03c 1/52
 [50] Field of Search. 96/88, 90,
 27, 48

ABSTRACT: A direct printout photographic system suitable for photocopy work, particularly for microfilm blowups. A leuco base of a di- or triarylmethane, xanthene, thioxanthene, selenaxanthene, anthracene or acridine dye and a quinone activator, supported in a binder or distributed within a portion of a substrate, form the photosensitive system which is activated when exposed to a range of electromagnetic radiation extending from the ultraviolet through the visible spectrum. The system is adaptable to making monochrome and black-and-white prints and transparencies.



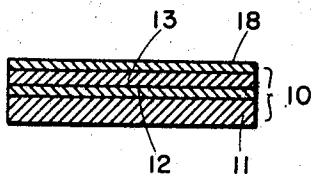


Fig. 1

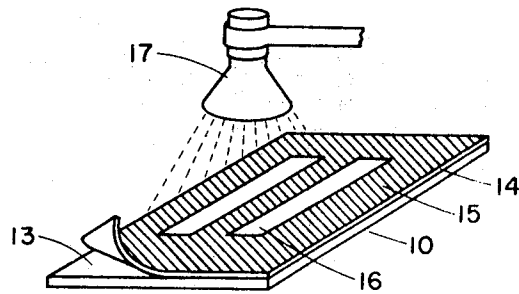


Fig. 2

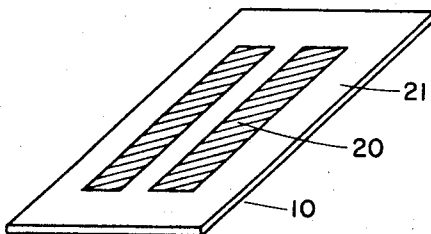


Fig. 3

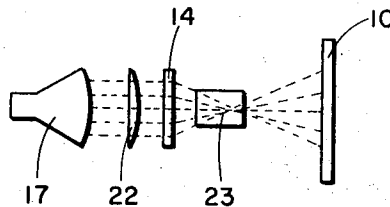


Fig. 4

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PHOTOSENSITIVE ARTICLE AND METHOD OF USING SAME INCORPORATING LEUCO DYE PRECURSORS AND QUINONE ACTIVATORS

CROSS-REFERENCE TO RELATED APPLICATIONS

In two copending applications we have disclosed two other printout systems. These applications are Ser. No. 832,540 filed May 8, 1969 directed to combinations of di- or triaryl-methane, xanthene, thioxanthene, selenaxanthene, anthracene and acridine dye precursors with halogen-substituted fluorescein dyes as activators; and Ser. No. 823,065 filed May 8, 1969 directed to combinations of leucoesters of indigoid dyes and activators.

This invention relates to a photographic method and article and more particularly to a direct printout photographic system suitable for making black-and-white and monochrome copies from negatives and to processes and articles which involve as at least one step or product the making of a photographic copy from a negative. The system of this invention is particularly suitable for making microfilm blowup copies.

There is, of course, a large body of prior art concerned with the general fields of producing positive prints or transparencies from negatives or transparencies. This body of prior art includes the use of silver halide emulsions with their attendant darkroom processing techniques as well as several negative diazo processes, some of which require development with ammonia. However, since these prior art techniques are completely distinguishable from that of the present invention, they need only be considered with regard to their use in microfilm blowup processes. The prior art which is more closely associated with this invention is set forth in a series of U.S. Patents, among which may be listed U.S. Pat. Nos. 3,113,024, 3,121,632, 3,121,633, 3,140,948, 3,140,949, 3,272,635, 3,284,205, 3,285,744, 3,342,595, 3,342,602, 3,351,467, and 3,377,167. These patents describe a number of photosensitive printout systems employing a light-sensitive combination of leucobases of dyes and a number of different activators. Exposure of these light-sensitive materials activates the leucobases to form the dyes in those areas exposed to light of a predetermined wavelength range. The unexposed areas remain unchanged, thus forming a contrast which gives rise to a copy or photograph. It is necessary, subsequent to exposure, to destroy, remove or inactivate the leucobases in the unexposed areas.

Printout systems of this type have certain marked advantages, among which may be listed the absence of graininess, the elimination of one or more developing steps and rapidity of access. However, the prior art systems, although realizing these advantages at least in part, possess certain inherent disadvantages. As activators for the dye precursors, the prior art uses colorless components such as sulfur-containing compounds as organic sulfonyl halides, mercapto compounds, disulfides, thiourea or acyclic thioacetanilides; organic $>C=O$ containing compounds such as alkyl, aryl, alkyl, aryl, acyclic and heterocyclic ketones; carboxylic aliphatic and aromatic acids; carboxylic acid anhydrides; and nitrogen-containing compounds as benzotriazoles and heterocyclic ketimides. Some of these activators used in the prior art give rise to relatively slow systems and some are suitable for use over a very limited wavelength range.

Since the photosensitive systems of this invention are particularly suited for making enlarged prints of microfilms, a very brief description of the prior art systems used for this purpose is in order. These include a wet diazo process which requires the use of ammonia, a dry diazo process which is relatively slow, a process based upon the use of a silver halide using a stabilization paper and involving wet processing which is expensive, a process requiring a silver nitrate bath, and several other processes based upon the formation of electrostatic or electromagnetic images which must be toned. None of these prior art processes combines all of the desired features (rapidity of access, ease of handling, elimination of noxious and/or toxic fumes, dry processing and low cost) which are sought in a system for producing microfilm blowups.

It would, therefore, be desirable to have a printout 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, printout photographic system which is capable of providing a sharp, grainless copy of rapid access. It is another object of this invention to provide a light-sensitive system of the character described which can be chosen to give a very rapid access. It is yet another object to provide such a system which is particularly suitable for microfilm blowup prints.

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 and monochrome.

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 an enlarged 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;

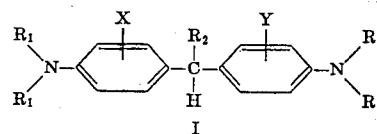
FIG. 3 illustrates the formation of the image made by the exposure illustrated in FIG. 2; and

FIG. 4 is a diagram illustrating the formation of a copy by projection.

The photosensitive printout system of this invention may be defined as one which comprises a leuco base of a class of dyes which includes di- and triarylmethanes, xanthenes, thioxanthenes, anthracenes and acridines, and a quinone as the activator. More specifically, these activators are quinones which are capable of acting in the role of an effective oxidizing agent when exposed to a predetermined wavelength range of the electromagnetic spectrum. This wavelength range extends from the ultraviolet through the visible spectrum, not all combinations of dye precursor and activator being sensitive over the entire range. Many of the photosensitive systems are rapidly imaged when exposed to intense ultraviolet radiation.

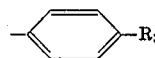
The dye precursors usable in the photosensitive system of this invention may be defined as leuco bases of certain dyes, namely those generally referred to as the di- or triarylmethanes, the xanthenes, thioxanthenes and selenaxanthenes, the dihydroanthracenes and the acridines.

The leuco bases of the di- and triarylmethane dyes may be represented by the general formula I



wherein R₁ is H, alkyl, aralkyl or aryl and may be the same or different

R₂ is H, aryl, alkyl, or



wherein

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R_3 is H or

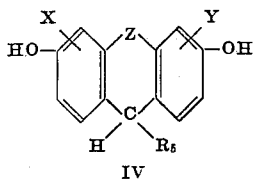
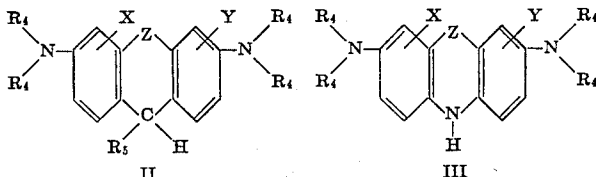


R_1 being the same as defined

X and Y are H or water-solubilizing functional groups such as SO_3Na , OH, OCH_3 , NHSO_2R_1 and the like.

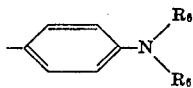
The leuco bases of this group of dyes give rise, upon oxidation, to a wide range of colors. Typical leuco bases of this group include, but are not limited to leuco crystal violet, leuco opal blue, leuco malachite green, leuco rosaniline, leuco pararosaniline, p,p',p''-trimethyl leuco opal blue, p,p',p''-trichloro leuco opal blue and p,p'-bis(dimethylamino)diphenyl methane.

A second group of dyes, the leuco bases of which are suitable as dye precursors for the photosensitive system of this invention, may be considered to be generally similar in structure to the diaryl methanes and are characterized by the presence of one or more bridging atoms to join the two phenyl groupings. Such leuco dye bases may be represented by one of three general formulas II, III or IV:



wherein:

R_4 is H, lower alkyl, or aryl and may be the same or different
 R_5 is H, alkyl, aryl or



wherein

R_6 is H, alkyl, aralkyl or aryl
 X and Y are the same as in formula I
 Z is $>\text{O}$, $>\text{S}$, $>\text{Se}$, $>\text{NH}$ or



where R_7 is H or alkyl.

When in formula II Z is O, the leuco dye base is a xanthene; when Z is S, the leuco dye base is a thioxanthene; and when Z is



the leuco base is a dihydroanthracene.

The following dyes may be cited as exemplary of this group. This list is illustrative and not meant to be limiting:

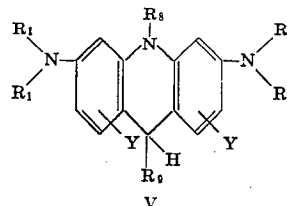
- 3,6-bis(dimethylamino)-9-(p-dimethylaminophenyl) xanthene
- 3,6-bis(diethylamino)-9-(p-dimethylaminophenyl) xanthene
- 3,6-bis(diethylamino)-9-(p-diethylaminophenyl) xanthene
- 3,6-bis(dimethylamino)-9-(p-dimethylaminophenyl) thioxanthene
- 2,7-bis(dimethylamino)-10-p-dimethylaminophenyl-9,10-dihydro-9,9-dimethylanthracene

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2,7-bis(dimethylamino)-9,10-dihydro-9,9-dimethyl anthracene

2,7-bis(dimethylamino)-10-ethyl-9,10-dihydro-9,9-dimethyl anthracene.

- 5 The leuco bases of a final group of dyes, the acridines, may be used as the dye precursors. They may be represented by the general formula V:



where R_1 has the same meaning as in formula I

R_8 and R_9 are H, alkyl, aryl or substituted aryl

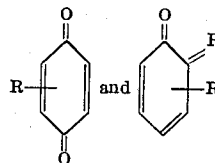
Y is H, halogen or alkyl

The acridines include, but are not limited to, chrysaniline, benzoflavine, acridine orange R, and flaveosine.

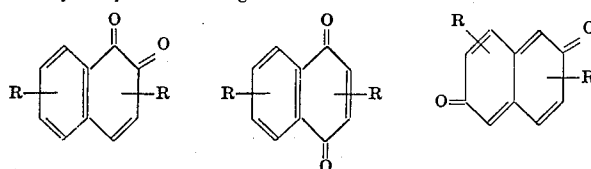
The final choice among these various dye precursors will depend upon the color of the print desired, the rapidity of access required and the activator used.

The activators for the photosensitive systems of this invention are quinones which are compounds having two intracyclic carbonyl groups attached to intracyclic carbon atoms in a conjugated carbocyclic ring system. Some of these quinones are in themselves colored.

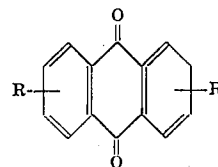
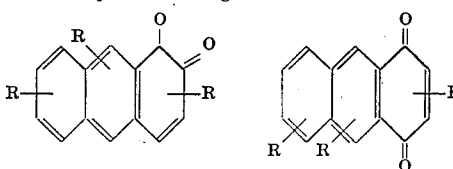
The quinones suitable for the practice of this invention include the benzoquinones of the general formulas



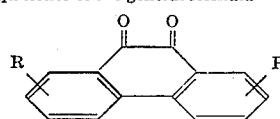
the naphthoquinones of the general formulas



the anthraquinones of the general formulas

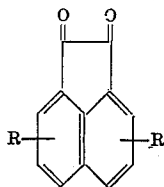


the phenanthrenequinones of the general formula

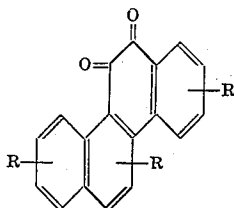


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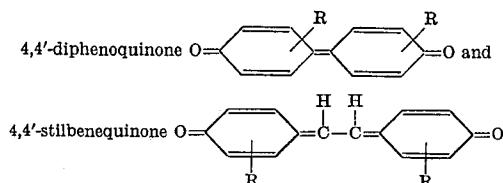
the acenaphthenequinones of the general formula



and the chrysenequinones of the general formula



In addition, quinones in which the conjugated system has been extended may be used. Exemplary of this type of quinone are



In all of these quinone compounds R may be H, alkyl, aryl, halogen, aralkyl, $-NR'_2$ (where R' is H, alkyl or aryl), SO_3Na and the like.

As examples of quinone activators we may cite the following:

9,10-anthraquinone
1-chloroanthraquinone
2-chloroanthraquinone
2-methylanthraquinone
2-ethylanthraquinone
2-t-butylanthraquinone
octamethylanthraquinone
1,4-dimethylanthraquinone
1,4-naphthoquinone
9,10-phenanthrenequinone
1,2-benzanthraquinone
2,3-benzanthraquinone
2,3-dimethylanthraquinone
2-phenylanthraquinone
2,3-diphenylanthraquinone
3-chloro-2-methylanthraquinone
sodium salt of anthraquinone alpha-sulfonic acid
cetenequinone
7,8,9,10-tetrahydronaphthacenequinone
1,2,3,4-tetrahydrobenz anthracene-7,12-dione

In forming the photosensitive system of this invention, the mole ratio of activator to dye precursor may range from about 0.01-to-1 to about 100-to-1, with about 2-to-1 being typical and generally preferred. The activator-dye precursor ratio employed will, of course, depend upon the activator-dye precursor system as well as upon the performance characteristics desired from the photosensitive system. For colored activators it will generally be desirable to use the minimum amount of activator compatible with the access speed required since this minimizes the amount of obscuring color contributed by the activator which may have to be removed or decolorized in one of several ways to be described.

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 for the binder, agents to control the coating properties, and compounds capable of color filtering. In addition, encapsulated fixing precursors may be included for thermal or mechanical release (e.g., application of heat or pressure to break the capsules) after exposure. Inasmuch as activation of

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the system is by oxidation, it may also be desirable to include inhibitors and stabilizers such as free radical traps and antioxidants. Many free radical traps and antioxidants are known, among which may be listed phenols, aromatic amines, sulfur compounds and polyfunctional acids. Specific compounds which are illustrative of such a class of additives include, but are not limited to, 2-t-butyl-4-hydroxyanisole, 3-t-butyl-4-hydroxyanisole, propyl gallate, 2,6-di-t-butyl-p-cresol, zinc dimethyldithiocarbamate and zinc dibutylphosphorodithioate.

The photosensitive system (dye precursor plus activator) will generally be 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 activation of the dye precursor. The film-forming binder must not, of course, have any adverse effects on the ability of the desired electromagnetic radiation to generate the dye.

A number of film-forming resins may be used as the binder; and the preferred one is nitrocellulose applied as a solution in acetone. Other suitable binders include, but are not limited to, polystyrene, ethyl cellulose, Carbowax 6,000 (a polyethylene glycol sold by Union Carbide and Carbon Corporation), cellulose acetate butyrate and polyvinyl acetate. The solvent system chosen must also be a solvent for the activator and must, of course, be compatible with the binder. Typical solvents include, but are not limited to, acetone, toluene, methylene chloride, and mixed solvents such as toluene/tetrahydrofuran and benzene/acetone.

It is also within the scope of this invention to apply a solution of the dye precursor and activator (with any desired additives) to a substrate such as an absorptive paper without a binder, relying on at least the surface of the paper to contain and hold the photosensitive system.

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 influence the image quality and it may have some control over the speed of the photosensitive system. In general, the heavier the coating weight the greater will be the intensity of the copy. The optimum coating weight will also depend upon the solubility of the dye precursor and the extinction coefficient of the photosensitive system. It may be desirable in the case of difficultly soluble dye precursors to apply more than one coat to the substrate. A preferred final coating weight range is between about 1×10^{17} to 1×10^{12} grams of dye precursor/square centimeter.

The concentration of the dye precursor in the coating solution will depend upon the coating technique used and the final coating weight desired; while 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 also be governed by the final coating weight desired, the solids concentration of the coating solution and the method by which the coating is accomplished. These parameters may readily be balanced and determined for any given system.

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 activation of the dye precursor.

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 with satisfactory dimensional stability and reflection characteristics. 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 or to prevent undesirable absorption of the coating solution by the substrate. The intermediate layer may also be used to enhance the physical properties of the substrate such as to render it smooth or to make it more adhesive to the coating solution. 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 somewhat 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 antiabrasion 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 negative 14 having a dark or opaque background 15 (indicated by crosshatching) and light or transparent indicia 16, an arrangement such as would be found in a microfilm. The photosensitive sheet 10 with the photosensitive layer 13 in contact with the negative 14 is exposed to a suitable light source, in this example a source 17 of visible light. The visible light from source 17 will, of course, be transmitted through the light or transparent indicia areas 16 to strike the photosensitive layer 13 and to activate the dye precursor in those areas which are thus exposed. However, since the visible light is not transmitted through the dark or opaque areas of background 15, the dye precursor in these areas remains unactivated. The result is the copy illustrated in FIG. 3 wherein the numeral 20 designates the activated or colored indicia areas corresponding to the light or transparent areas of the negative. The light, unactivated areas 21 correspond directly to the opaque background 15 of the negative. As will be described in the examples, it is necessary to fix the dye precursor in the unactivated areas 21 to render it insensitive to light. Since the activator may be colored, it may also be desirable to remove or decolorize it.

Because the photosensitive system of this invention is free of any graininess and may be compounded to have a very rapid access time, it is particularly suited for making enlarged copies from microfilms without loss of definition. The projection optics for achieving such enlargements are well known and not part of this invention. A suitable arrangement is, however, represented diagrammatically in FIG. 4. Radiation from light source 17 is directed by means of a lens 22 (or other optical device) through the microfilm 14 (in negative form) containing an image and then through a projection lens or lenses 23 onto the photosensitive sheet 10. The extent to which the original image is enlarged is well within the skill of the optical apparatus designer.

Since the exposed photosensitive sheet or surface contains areas having inactivated dye precursors and activators, and since these dye precursors are gradually or even relatively rapidly activated by ambient light, it is necessary to fix the

photocopy or transparency by removing or inactivating the dye precursors in those areas. It may also be desirable to remove or decolorize the activators in the same areas to minimize or eliminate any color contributions which they make to the background (unexposed) areas of the copy.

In fixing the copy, that part of the dye precursor which has not been activated may be removed, destroyed or inactivated. Removal is most conveniently achieved by a solvent rinse, the solvent serving to wash out the dye precursor. The solvent must, of course, be a nonsolvent for the dye so that the dye image is not removed. A typical solvent rinse for a leuco base dye precursor is a suitably balanced mixture of acetone, toluene and petroleum ether.

Destruction of the dye precursor may be accomplished through a chemical reaction which converts the dye precursor to a colorless, light-insensitive compound or which converts it to a compound removable or inactivatable by heat. Inactivation may be achieved through inhibition, such as by the use of an antioxidant or an oxygen-barrier overcoat. The chemical reactant or reactants or inhibiting agents may be incorporated directly into the photosensitive layer at the time of its application to a substrate or applied subsequent to exposure. It may be material which requires some heat to effect the necessary chemical reaction or inhibition, or it may be encapsulated, in which case the capsules may be broken either by pressure or by heat.

A number of antioxidants are known in the art, examples having been given in connection with the discussion on additives. As oxygen barriers we may apply a binder coating containing an inhibitor to the exposed photosensitive sheet. Typical inhibitors include ascorbic acid, 1-phenyl-3-pyrazolidone, 2,6-di-t-butyl-p-cresol, 2,6-di-t-butylphenol, N,N'-diphenyl-p-phenylenediamine, ferric chloride, cobalt chloride, cobalt naphthenate and cobaltous thiocyanate.

If the activator itself is colored it may be desirable to remove or decolorize it. This may be accomplished by solvent removal using either the same or different solvent used to remove the dye precursor. Any solvent used must, of course, be a nonsolvent for the dye image formed. Destruction of the activators may be through reaction with a reducing agent encapsulated in the photosensitive coating composition or applied subsequent to exposure or through bleaching after the dye precursor has been fixed by one of the methods described. The steps of fixing the dye precursor and of removing or decolorizing the activator may be combined. It will generally be preferably, especially where the photosensitive product is to be used in more-or-less automatic equipment, to choose a fixing technique which is rapid and "dry" (i.e., which does not require the use of any externally applied liquid).

The following examples, which are meant to be illustrative and not limiting, are given further to describe the invention. All of the steps in the following examples were carried out under subdued light.

EXAMPLE 1

Sufficient acetone was added to a mixture of 10 g. of nitrocellulose (Hercules RS5-6 seconds wet with 30 percent by weight isopropyl alcohol) and 5 g. of dibutylphthalate (plasticizer) to make 100 g. of a standard binder solution. To 0.1 g. leuco crystal violet (dye precursor) dissolved in 8 ml. of the standard binder solution and 4 ml. of acetone was added 0.146 g. of 2-t-butyl-anthraquinone. The solution was coated at 6-mil wet thickness on a smooth paper, dried and exposed to three different light sources for 1 minute through a Kodak No. 2 silver step tablet (density range 0.05 to 3.05). In the use of this standard device for measuring photosensitivity the number of steps which have a discernible higher 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. The number of steps which could be distinguished from the background is given for each of the three light sources including a control which contained no activator.

Type of light source	Distance from source to photosensitive surface inches	Number of steps discernible	
		With activator	Without activator
275-watt sunlamp (ultra-violet).....	10	14	11
500-watt photo flood lamp (visible).....	10	15	7
750-watt tungsten lamp through series of projection lenses.....	24	13	9

After exposure, the image was fixed by three 1-minute solvent rinses with a 1:1:4 (by volume) mixture of acetone:toluene:petroleum ether.

The speed of the photosensitive system of this example was determined for light having a wavelength of 4,000 Å. The light source was a 750-watt tungsten projection lamp having a suitable interference filter interposed between it and a transparent polyester film coated with the photosensitive system. The intensity of the exposure source was measured with a pre-calibrated thermopile in conjunction with a microvoltmeter, first in the absence of any coated film and then for a series of coated films, each being exposed for a longer period than the preceding film. The diffuse densities of each of the exposed films were measured on a calibrated transmission densitometer.

From a plot of diffuse density vs. log exposure a point was determined at which the density of the exposed film was 1.0 density unit above the density of the base plus fog. The reciprocal of the exposure (expressed as ergs/cm.²) at that point was taken as the speed of the photosensitive film. When the light striking the photosensitive system had a wavelength of 4,000 Å. this measured speed was 5.3×10^{17} (erg/cm.²)⁻¹ and of 6,000 Å. it was 3.6×10^{18} (erg/cm.²)⁻¹. These speeds compare favorably with a fast diazo system.

EXAMPLE 2

The photosensitive composition of example 1 (containing activator) was coated at 6-mil wet thickness on paper over a 2-mil binder precoat, dried and exposed to a 275-watt sunlamp at a distance of 6 inches. Exposure through a silver transparency for 3 seconds yielded a pale blue image on a white background; while exposure for 10 seconds yielded a deep blue image on a white background. Fixing was done as in example 1.

EXAMPLE 3

A 5 percent solution of cellulose acetate butyrate in acetone was substituted for the standard solution of cellulose nitrate of example 1 and an exposure was made through the step tablet. The images obtained were essentially identical to those of example 2 and eight steps were identifiable.

EXAMPLE 4

A photosensitive composition was formulated by mixing 3 ml. of acetone, 8 ml. of the standard binder solution, 0.1 g. of leuco crystal violet and 0.012 g. of 1-(N-methylamino)anthraquinone activator. This solution was coated to a 6-mil wet thickness on a paper having a dried 2-mil standard binder precoat. The photosensitive coating was exposed through the step tablet to the 275-watt sunlamp at a distance of 10 inches for 35 seconds. Twelve steps were discernible. When a comparable control coating which did not contain any activator was made, coated and exposed in an identical manner for 30 seconds, 9 steps were identifiable. Fixing was done as in example 1.

EXAMPLE 5

A photosensitive composition was formulated by mixing 4 ml. of acetone, 8 ml. of standard binder solution, 0.01 g. of 3,6-bis(dimethylamino)-9-(p-dimethylaminophenyl)xanthene and 0.146 g. of p-naphthoquinone. The resulting solution was coated to a 6-mil wet thickness on a paper having

a dried 2-mil standard binder precoat. The photosensitive system was exposed through the step tablet to the 275-watt sunlamp at a distance of 10 inches for 35 seconds, and 14 steps were identifiable. Fixing was done as in example 1.

5 When a photosensitive coating was prepared and exposed in an identical manner but with no quinone activator, five steps were discernible.

It will thus be seen that the photosensitive systems of this invention provide direct printout copies relatively rapidly and through the use of activators which are not noxious to handle. Moreover, the systems are not subject to graininess and are adaptable to making relatively inexpensive blowups of microfilms.

We claim:

15 1. A photosensitive composition which prints out to form an image upon exposure to electromagnetic radiation, comprising in combination a dye precursor which is a leuco base of a di- or triarylmethane, xanthene, thioxanthene, selenaxanthene, anthracene or acridine dye and an activator which is a quinone having two intracyclic carbonyl groups attached to intracyclic carbon atoms in a conjugated carbocyclic ring system and which is selected from the group consisting of benzoquinone, mono substituted benzoquinones, naphthoquinone, mono- and disubstituted naphthoquinones, anthraquinone, mono- di- and trisubstituted anthraquinones, phenanthrenequinone, mono- and disubstituted phenanthrenequinones, acenaphthenequinone, mono- and disubstituted acenaphthenequinones, chrysenequinone, mono- and disubstituted chrysenequinones, 4,4'-diphenoquinone, mono- and disubstituted 4,4'-diphenoquinones, 4,4'-stilbenequinone, and mono- and disubstituted 4,4'-stilbenequinones wherein the substituents in the substituted quinones may be alkyl, aryl, halogen, aralkyl, —SO₃Na or —NR₂ wherein R is H, alkyl or aryl.

35 2. A photosensitive composition in accordance with claim 1 wherein said dye precursor is leuco crystal violet.

3. A photosensitive composition in accordance with claim 1 wherein said dye precursor is 3,6-bis(dimethylamino)-9-(p-dimethylaminophenyl) xanthene.

40 4. A photosensitive composition in accordance with claim 1 wherein said dye precursor is leucopararosaniline.

5. A photosensitive composition in accordance with claim 1 wherein said activator is 2-t-butylanthraquinone.

6. A photosensitive composition in accordance with claim 1 wherein said activator is 1-(N-methylamino)anthraquinone.

7. A photosensitive composition in accordance with claim 1 which is activated by ultraviolet radiation.

8. A photosensitive composition in accordance with claim 1 which is activated by visible light.

50 9. A photosensitive composition in accordance with claim 1 wherein the mole ratio of activator to dye precursor ranges between about 0.01-to-1 to about 100-to-1.

10. A photosensitive composition in accordance with claim 1 wherein said composition is incorporated in a binder.

55 11. A photosensitive composition in accordance with claim 10 including a plasticizer for said binder.

12. A photosensitive composition in accordance with claim 10 wherein said binder is nitrocellulose.

60 13. A photosensitive composition in accordance with claim 10 wherein said binder is ethyl cellulose.

14. A photosensitive composition in accordance with claim 10 wherein said binder is cellulose acetate butyrate.

15. A photosensitive composition in accordance with claim 1 including one or more additives serving as color filters, oxidation inhibitors and stabilizers or fixing agents for said dye precursor.

16. A photosensitive composition in accordance with claim 15 wherein said additive is contained within capsules which may be broken by heating or through pressure.

70 17. A photosensitive article suitable for exposure to radiant energy for forming an image by direct printout, comprising in combination

- a substrate; and
- at least one layer of a photosensitive composition affixed to said substrate in a binder, said photosensitive composition

tion comprising in combination

1. a dye precursor which is a leuco base of a di- or triarylmethane, xanthene, thioxanthene, selenaxanthene, anthracene or acridine dye; and

2. an activator for said dye precursor which is a quinone having two intracyclic carbonyl groups attached to intracyclic carbon atoms in a conjugated carbocyclic ring system and which is selected from the group consisting of benzoquinone, monosubstituted benzoquinones, naphthoquinone, mono- and disubstituted naphthoquinones, anthraquinone, mono-, di- and trisubstituted anthraquinones, phenanthrenequinone, mono- and disubstituted phenanthrenequinones, acenaphthenequinone, mono- and disubstituted acenaphthenequinones, chrysenequinone, mono- and disubstituted chrysenequinones, 4,4'-diphenoquinone, mono- and disubstituted 4,4'-diphenoquinones, 4,4'-stilbenequinone, and mono- and disubstituted 4,4'-stilbenequinones wherein the substituents in the substituted quinones may be alkyl, aryl, halogen, aralkyl, SO_3Na or NR_2 wherein R is H, alkyl or aryl.

18. A photosensitive article in accordance with claim 17 wherein said substrate is an opaque paper.

19. A photosensitive article in accordance with claim 17 wherein said substrate is an essentially transparent film.

20. A photosensitive article in accordance with claim 17 further characterized by having an intermediate coating layer interposed between said substrate and said layer of said photosensitive composition, said coating layer serving as a chemical barrier, as a modifier of the physical properties of said substrate, or as a modifier of the optical properties of said photosensitive composition.

21. A method of forming an image of a transparency by direct printout, characterized by exposing a photosensitive article through said transparency to electromagnetic radiation of a predetermined wavelength range and fixing the image in the resulting print, said photosensitive article comprising in combination a dye precursor which is a leuco base of a di- or triarylmethane, xanthene, thioxanthene, selenaxanthene,

anthracene or acridine dye and an activator which is a quinone having two intracyclic carbonyl groups attached to intracyclic carbon atoms in a conjugated carbocyclic ring system and which is selected from the group consisting of benzoquinone, monosubstituted benzoquinones, naphthoquinone, mono- and disubstituted naphthoquinones, anthraquinone, mono-, di- and trisubstituted anthraquinones, phenanthrenequinone, mono- and disubstituted phenanthrenequinones, acenaphthenequinone, mono- and disubstituted acenaphthenequinones, chrysenequinone, mono- and disubstituted chrysenequinones, 4,4'-diphenoquinone, mono- and disubstituted 4,4'-diphenoquinones, 4,4'-stilbenequinone, and mono- and disubstituted 4,4'-stilbenequinones wherein the substituents in the substituted quinones may be alkyl, aryl, halogen, aralkyl, SO_3Na or NR_2 wherein R is H, alkyl or aryl.

22. A method in accordance with claim 21 wherein said transparency is placed in contact with said photosensitive article.

23. A method in accordance with claim 21 wherein optical elements adapted to project and enlarge an image are placed between said transparency and said photosensitive article, whereby the image of said transparency is optically projected as an enlargement onto said photosensitive article.

24. A method in accordance with claim 21 wherein said fixing comprises removing at least the dye precursor which was not activated to form said image.

25. A method in accordance with claim 24 wherein said removing comprises washing said print with a liquid which is a solvent for said dye precursor and a nonsolvent for the dye image formed.

26. A method in accordance with claim 21 wherein said fixing comprises destroying the dye precursor which was not activated to form said image with a reactant capable of converting said dye precursor to a colorless, light-insensitive compound.

27. A method in accordance with claim 21 wherein said fixing comprises applying an oxygen-barrier overcoat to said print.

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