

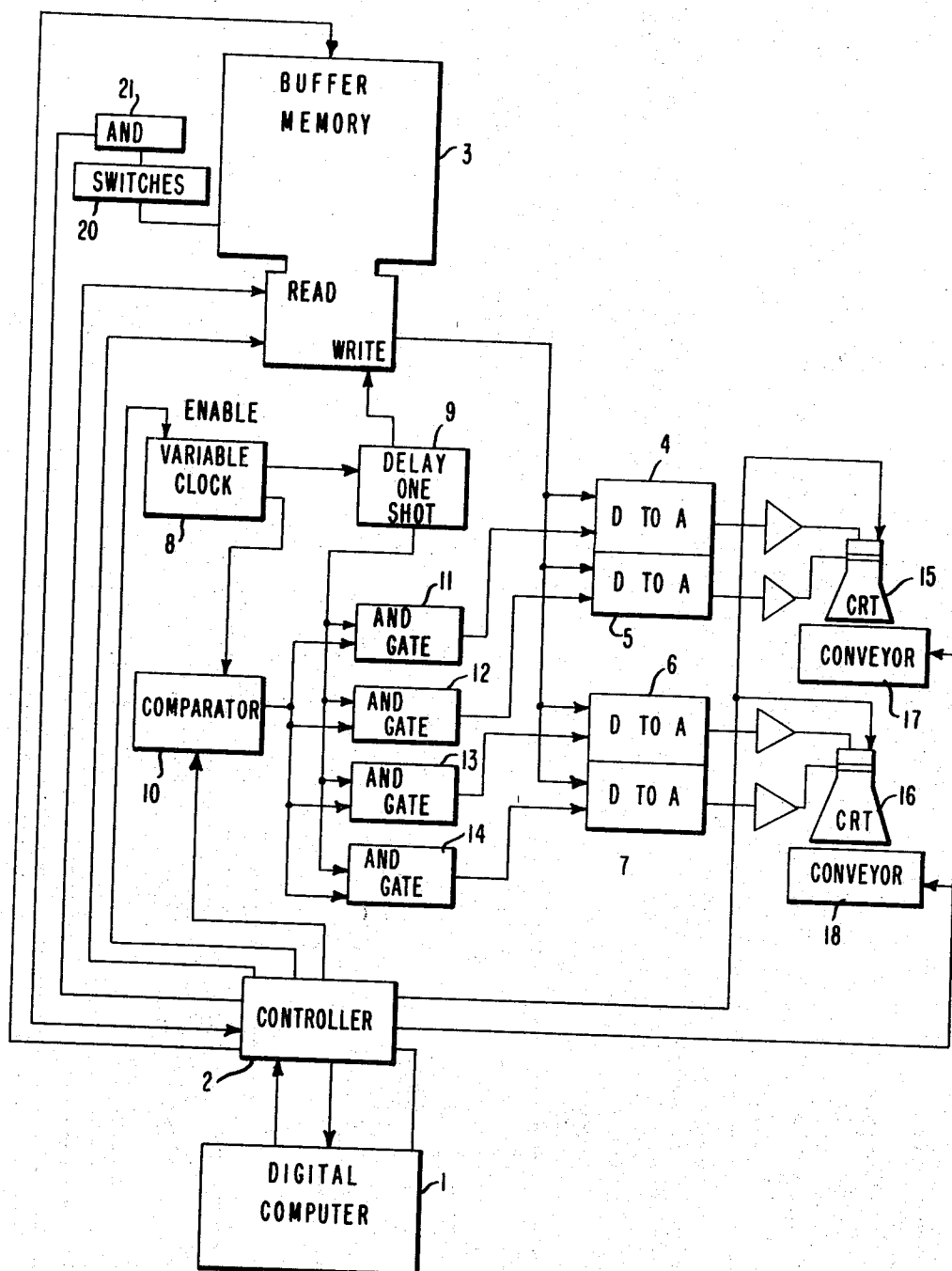
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HEXAARYLBIIIMIDAZOLE-COUMARIN COMPOSITIONS

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1

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HEXAARYLBIIMIDAZOLE-COUMARIN COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Photoactivatable compositions comprising, basically, a hexaarylbiimidazole and a selected substituted coumarin having absorption maximally in the near ultraviolet region. The basic composition can be combined with a leuco dye alone or with a leuco dye and a fixing system. The compositions may be employed with inert solvents, plasticizers and/or binders. A cathode ray tube print-out system is also described.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to photoactivatable compositions. More specifically, the invention concerns various near ultraviolet sensitive compositions containing a photodissociable hexaarylbiimidazole that absorbs radiation maximally in the ultraviolet at relatively short wavelengths, and a coumarin sensitizer (i.e., an energy-transfer agent) that absorbs radiation substantially in the ultraviolet at relatively long wavelengths.

Description of the prior art

Compositions of hexaarylbiimidazoles and leuco dyes are known to be photosensitive. They form colored images upon exposure to ultraviolet radiation. These images can be permanently fixed if a fixing system is added to the original composition. The biimidazole component, upon irradiation, photolyzes and dissociates to the colored triarylimidazolyl radical. This radical then oxidizes the leuco to its dye form, whereupon the dye form becomes fixed due to deactivation of the biimidazole by reaction with the fixing system. Thus, the entire sequence is dependent upon the photolization of the biimidazole. However, the hexaarylbiimidazoles in general absorb largely and maximally at ultraviolet (UV) wavelengths below 300 mμ. Thus, while any of the imaging compositions described above containing the biimidazole are sensitive to radiation over substantially the whole UV range, they respond most efficiently to radiation that corresponds to or substantially overlaps the region of maximum absorption; and it is not always practical to irradiate fully into this region. For example, in some imaging applications, it is desired to cover the photosensitive biimidazole-leuco dye imaging composition with a transparent film. Some film materials, such as "Mylar" and "Cronar" commercial polyesters, otherwise suitable, are not transparent below 300 mμ, and thus prevent such short wavelength activating radiation from reaching the biimidazole, with consequent loss in efficiency.

Further, many commercially important ultraviolet sources, such as cathode ray tubes widely useful in imaging devices that convert electrical to light energy and transmit such light as images to photosensitive surfaces (plates, papers, films), emit mainly in the near ultraviolet and above, owing in part to limitations in the available phosphors and in part to the screening by the fiber optic face plate of radiation below 300 mμ. Thus, imaging with

2

such radiation sources is not entirely satisfactory as to the imaging speeds and optical densities that the biimidazole/leuco dye systems can inherently provide.

Thus, as the activating radiation contain increasing proportions of visible components or as components closer to the UV region are filtered out, hexaarylbiimidazole photolysis, hence color formation from leuco dye, becomes less efficient as to the amount of energy utilized and the optical quality of the image produced.

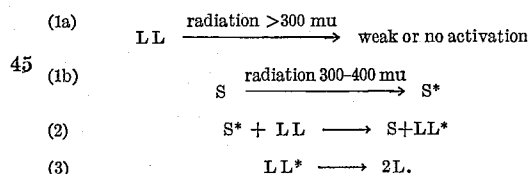
The present invention overcomes these deficiencies by enhancing the efficiency of the imaging systems described above in the near ultraviolet region of absorption through the use of selected coumarins.

SUMMARY OF THE INVENTION

This invention is based on the surprising discovery that substituted coumarins as defined below, which strongly absorb ultraviolet light at longer wavelengths than the biimidazoles, can transfer such absorbed longer wavelength light energy to the biimidazoles. By thus enhancing the spectral sensitivity of the biimidazoles at wavelengths they normally poorly absorb, the coumarins significantly enhance their utility as light screens and photooxidants.

While the sensitization mechanism is not known with certainty, it is considered that when compositions of this invention comprising a relatively short wavelength absorbing biimidazole and a relatively longer wavelength absorbing coumarin sensitizer as defined are irradiated with such relatively longer wavelength light in the range 300-400 mμ, the biimidazole is only weakly affected, i.e., a substantial proportion of the biimidazole molecules remain in the ground (unactivated) state. The sensitizer, however, responding directly, absorbs the light more fully and is activated to at least one excited energy transfer state. In such state, the activated coumarin transfers absorbed energy to the biimidazole, for example through collision or resonance interaction, and returns to the ground state, thus becoming available again for activation. The thus indirectly-activated biimidazole molecules dissociate into imidazolyl radicals.

The overall sensitization process can be represented as

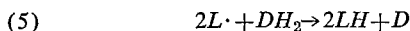


where C is the coumarin sensitizer; S* its activated energy transfer state; LL is the biimidazole (dimer), LL* its activated, dissociable state; and L is the resulting imidazolyl radical.

The subsequent fate of the inherently colored and energy-rich imidazolyl radicals and their utilization in accordance with the various embodiments of this invention depends on the substantial absence or presence of other substances that are reactive towards the radicals. Thus, in formulating light screens or windows containing biimidazole/sensitizer compositions of this invention, there will usually be employed other components, such as solvents, plasticizers, and binders that are substantially inert, i.e., resistant, to oxidation by the imidazolyl radicals. In such an embodiment, the sensitization process manifests itself as a color change, attributable to formation of the inherently color triarylimidazolyl radical (Equation 3). When the light source is removed, the color fades as the radicals dimerize (Equation 4) to the biimidazole:



The imidazolyl radicals are useful oxidants, as schematically illustrated in Equation 5:



where DH_2 for example is an oxidizable substance such as a leuco dye, D is the oxidation product (dye), and LH is the reduction product (a triarylimidazole in this instance).

Thus, the biimidazole/sensitizer combinations are particularly useful as photo-actuated photooxidants for a variety of substrates, including leuco dyes, and the biimidazole/sensitizer/leuco dye combinations constitute the basic ingredients of widely useful photo-actuated imaging systems, as more fully described below.

The basic composition then of this invention comprises:

(a) a hexaarylbiimidazole that absorbs in the ultraviolet principally at wavelengths below $300 m\mu$ and is dissociable to triarylimidazolyl radicals by such radiation, and

(b) a coumarin which has a light absorption maximum in the ultraviolet at wavelengths greater than $300 m\mu$ that is stronger than the absorption of the biimidazole at such wavelengths, and is capable of transferring the absorbed energy corresponding to such wavelengths to the biimidazole.

Other embodiments of the invention comprise the above basic composition in combination with other components of an imaging system. For example, another composition of the invention comprises a composition of (a) and (b) defined above, and (c) a leuco dye.

Still another composition of the invention comprises (a), (b) and (c) defined above, and (d) a fixing component, e.g., a redox couple defined further below.

It is understood that any of the above compositions of this invention can also contain solvents, plasticizers, polymeric binders, and/or carriers which do not affect the ultraviolet absorption or the imaging properties of the primary ingredients.

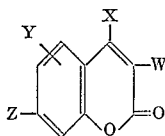
DESCRIPTION OF THE DRAWING

The drawing attached hereto schematically illustrates a digital computer output system which employs the compositions of this invention.

DETAILED DESCRIPTION OF THE INVENTION

(A) The coumarin component

The coumarins operable in the compositions of this invention are those of the formula



wherein

X and Y are each hydrogen, lower alkyl or lower alkoxy; Z is hydrogen, lower alkyl, lower alkoxy or dilower alkylamino;

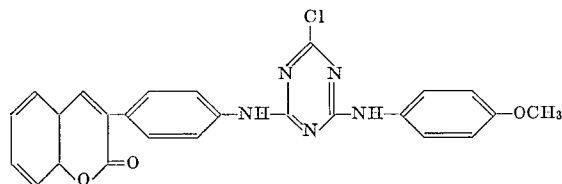
W is hydrogen, lower alkyl, phenyl containing a lower alkoxy group in the *o*- or *p*-position, and phenyl containing a substituted amino group in the *o*- or *p*-position; and wherein at least one of W and Z is other than hydrogen or lower alkyl. Stated differently, the coumarin must contain at least one of the dialkylamino, alkoxy, alkoxyphenyl or aminophenyl groups in the 3- or 7-position.

These coumarins absorb maximally in the $300\text{--}400 m\mu$ region, particularly in the $340\text{--}390 m\mu$ region.

The 7-diloweralkylamino-4-lower alkyl coumarins are a preferred subclass which include 7-dimethylamino-4-butyl coumarin, 7-diethylamino-4-ethyl coumarin, 7-dibutylamino-4-methyl coumarin, and the more preferred sensitizers 7-dimethylamino-4-methyl coumarin [avail-

able as "Calcofluor" White LD (λ max. $360 m\mu$ in EtOH, $\epsilon=20,700$)] and 7-diethylamino-4-methyl coumarin [available as "Calcofluor" White RW (λ max. $375 m\mu$ in EtOH, $\epsilon=22,000$)].

Another subclass encompasses the 7-lower alkoxy coumarins such as 7-methoxycoumarin, 7-ethoxycoumarin, 7-propoxycoumarin, 7-butoxycoumarin, 5,7-dimethoxycoumarin. Still another subclass includes the 3-(ortho- or para-alkoxyphenyl)coumarins such as 3-(*p*-methoxyphenyl)coumarin, 3-(*o*-methoxyphenyl)coumarin, 3-(*p*-ethoxyphenyl)-7-methylcoumarin, 3-(*p*-butoxyphenyl)coumarin, 3-(*p*-methoxy-5-methylcoumarin), and 3-(*o*-*p*-dimethoxyphenyl)coumarin. Still another substituted coumarin sensitizer is commercially available as "Tinopal" PG, which has the formula



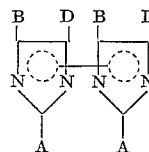
The quantity of coumarin sensitizer employed may vary widely. It will normally amount to .1 to 2 moles/mole of the biimidazole, and preferably about .4 to .6 moles per mole of biimidazole.

In contrast, other coumarins, such as coumarin, 3-carbethoxycoumarin, 6-chlorocoumarin, 7-hydroxy-4-methylcoumarin, and 6,7-dihydroxy-4-methylcoumarin, known as optical brighteners for other photochemical systems, are much less or not all effective to sensitize biimidazole photolysis and the imaging reaction.

It has also been found that 3,3'-diethylthiacyanine iodide (λ max. $428 m\mu$), itself a poor sensitizer for the biimidazole-leuco dye imaging system, is highly and synergistically effective in combination with a near-UV absorbing coumarin-type sensitizer, such as 7-diethylamino-4-methyl coumarin (λ max. $375 m\mu$), affording increased imaging speeds and higher optical densities, particularly when irradiated with phosphor emissions extending from the near UV into the visible, and peaking at $450 m\mu$.

(B) The hexaarylbiimidazole component

The hexaarylbiimidazoles are the 2,2',4,4',5,5'-hexaarylbiimidazoles that absorb ultraviolet light principally at wavelengths below $300 m\mu$ and primarily in the range of $250\text{--}275 m\mu$, and are thereby dissociated into the corresponding 2,4,5-triarylimidazolyl radicals. They can be represented by the formula



wherein A , B and D represent aryl groups which can be the same or different, carbocyclic or heterocyclic, unsubstituted or substituted with substituents that do not interfere with the dissociation of the biimidazole to the imidazolyl radical or with the oxidation of the leuco dye, and each dotted circle stands for four delocalized electrons (i.e., two conjugated double bonds) which satisfy the valences of the carbon and nitrogen atoms of the imidazolyl ring.

The aryl groups include one- and two-ring aryls, such as phenyl, biphenyl, naphthyl, furyl and thienyl. Suitable inert substituents on the aryl groups have Hammett sigma (para) values in the $-.5$ to 0.8 and are free of Zerewitinoff hydrogen, i.e., have no hydrogens reactive towards methyl magnesium iodide. Representative substituents and their sigma values (relative to $H=.00$), as given by

5

Jaffe, Chem. Rev. 53, 219-233 (1953) are: methyl (-0.17), ethyl (-0.15), t-butyl (-0.20), phenyl (0.22), trifluoromethyl (0.55), chloromethyl (0.18), cyanomethyl (0.01), 2-carboxyethyl (-0.07), butoxy (-0.32), phenoxy (-0.03), fluoro (0.34), chloro (0.37), bromo (0.39), iodo (0.35), methylthio (-0.05), methylsulfonyl (0.73), nitro (0.78), methoxycarbonyl (0.64), and cyano (0.63). Thus, the substituents may be halogen, cyano, lower hydrocarbyl (including alkyl, halo alkyl, cyanoalkyl, and aryl), alkoxy, aryloxy, alkylthio, arylthio, alkyl sulfonyl, arylsulfonyl, and nitro. In the foregoing list, alkyl groups referred to therein are preferably of 1-6 carbon atoms; while aryl groups referred to therein are preferably of 6-10 carbon atoms.

Preferably the aryl radicals are carbocyclic, particularly phenyl, and the substituents have Hammett sigma values in the range -0.4 to +0.4, particularly lower alkyl, lower alkoxy, Cl, F and Br groups.

In a preferred biimidazole class, the 2 and 2' aryl groups are phenyl rings bearing an ortho substituent having a Hammett sigma value in the range -0.4 to +0.4. Preferred such ortho substituents are fluorine, chlorine, bromine, lower alkyl and alkoxy groups; especially chloro.

Most preferably, the 2-phenyl ring carries only the above-described ortho group, and the 4- and 5-phenyl rings are either unsubstituted or substituted with lower alkoxy.

Representative hexaarylbiimidazoles which may be used in the practice of this invention are:

2,2'-bis(o-bromophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(p-bromophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(p-carboxyphenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetrakis(p-methoxyphenyl)biimidazole,
2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(p-chlorophenyl)-4,4',5,5'-tetrakis(p-methoxyphenyl)biimidazole,
2,2'-bis(p-cyanophenyl)-4,4',5,5'-tetrakis(p-methoxyphenyl)biimidazole,
2,2'-bis(2,4-dichlorophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(2,4-dimethoxyphenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(o-ethoxyphenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(m-fluorophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(o-fluorophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(p-fluorophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(o-hexoxyphenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(o-hexylphenyl)-4,4',5,5'-tetrakis(p-methoxyphenyl)biimidazole,
2,2'-bis(3,4-methylenedioxyphenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetrakis(m-methoxyphenyl)biimidazole,
2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetrakis[m-(beta-phenoxyethoxyphenyl)biimidazole,
2,2'-bis(2,6-dichlorophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(o-methoxyphenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(p-methoxyphenyl)-4,4'-bis(o-methoxyphenyl)-5,5'-diphenylbiimidazole,
2,2'-bis(o-nitrophenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(p-phenylsulfonylphenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(p-sulfamoylphenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-bis(2,4,6-trimethylphenyl)-4,4',5,5'-tetraphenylbiimidazole,
2,2'-di-4-biphenyl-4,4',5,5'-tetraphenylbiimidazole,
2,2'-di-1-naphthyl-4,4',5,5'-tetrakis(p-methoxyphenyl)biimidazole,

6

2,2'-di-9-phenanthryl-4,4',5,5'-tetrakis(p-methoxyphenyl)biimidazole,
2,2'-diphenyl-4,4',5,5'-tetra-4-biphenylbiimidazole,
2,2'-diphenyl-4,4',5,5'-tetra-2,4-xylylbiimidazole,
2,2'-di-3-pyridyl-4,4',5,5'-tetraphenylbiimidazole,
2,2'-di-3-thienyl-4,4',5,5'-tetraphenylbiimidazole,
2,2'-di-o-tolyl-4,4',5,5'-tetraphenylbiimidazole,
2,2'-di-p-tolyl-4,4',5,5'-di-o-tolyl-5,5'-diphenylbiimidazole,
2,2'-di-2,4-xylyl-4,4',5,5'-tetraphenylbiimidazole,
2,2',4,4',5,5'-hexakis(p-benzylthiophenyl)biimidazole,
2,2',4,4',5,5'-hexa-1-naphthylbiimidazole,
2,2',4,4',5,5'-hexaphenylbiimidazole,
2,2'-bis(2-nitro-5-methoxyphenyl)-4,4',5,5'-tetraphenylbiimidazole, and
2,2'-bis(o-nitrophenyl)-4,4',5,5'-tetrakis(m-methoxyphenyl)biimidazole.

The biimidazoles are conveniently obtained by known methods as more particularly described by Italian Patent 707,086 and by Hayashi et al., Bull. Chem. Soc. Japan, 33, 565 (1960). The preferred method, involving oxidative dimerization of the corresponding triarylhydrazine with ferricyanide in alkali, generally yields the 1,2'-biimidazoles, although other isomers, such as the 1,1',1,4', 2,2',2,4' and 4,4'-biimidazoles are sometimes also obtained admixed with the 1,2'-isomer. For the purposes of this invention, it is immaterial which isomer is employed so long as it is photodissociable to the imidazolyl radical as discussed above.

Biimidazoles useful in this invention are described in South African patent application 3627/63, published August 12, 1966, and in British Pat. 997,396, published July 7, 1965.

(C) The leuco dye component

The leuco dye component together with the basic composition forms one embodiment of this invention. By the term "leuco dye" is meant the colorless (i.e., the reduced) form of a dye compound which upon oxidation becomes colored. When present in the composition of this invention, it is oxidized to its colored form by the imidazolyl radical.

Leuco dyes which may be oxidized to color by triaryl-imidazolyl radicals generated by this invention include: aminotriarylmethanes, aminoxanthenes, aminothioxanthenes, amino-9,10-dihydroacridines, aminophenoxazines, aminophenothiazines, aminodihydrophenazines, aminodiphenylmethanes, leuco indamines, aminohydrocinnamic acids (cyanoethanes, leuco methines), hydrazines, leuco indigoid dyes, amino-2,3-dihydroanthraquinones, tetrahalo-p,p'-biphenols, 2(p-hydroxyphenyl)-4,5-diphenylimidazoles, phenethylamines, 10-acyl-aminodihydrophenazines, 10-acyl-aminophenothiazines, 10-acyl-aminophenoxazines; aminotriarylmethanes wherein the methane hydrogen has been replaced by alkylthio, benzylthio, 2-phenylhydrazino, or alkoxycarbonyl; aminotriarylmethanes wherein two aryl groups are substituted with a disubstituted amino and an alkyl group and the third aryl is p-alkylthio-, p-arylthio-, aralkylthiophenyl, 2-thienyl, 2-furyl, 3,4-methylenedioxyphenyl, 2-methoxy-4- (C₁ to C₈)alkoxyphenyl or 3,4-di(C₁ to C₈)alkoxyphenyl.

Leuco triarylmethane dyes that contain tertiary amino groups are preferred, particularly those wherein (1) at least two aryls are phenyls having (a) a para-R₁R₂ substituent, where R₁ and R₂ are C₁-C₁₀ alkyl, 2-hydroxyethyl, 2-cyanoethyl, benzyl or phenyl, and (b) an ortho C₁-C₆ alkyl, C₁-C₆ alkoxy, fluoro, chloro, or bromo-substituent, and (2) the third aryl, when different from the first two, is thienyl, furyl, phenyl or phenyl substituted with one or more C₁-C₆ alkyl, C₁-C₆ alkoxy, methylenedioxy, fluoro, chloro, bromo, amino, alkylamino, dialkylamino, alkylthio, hydroxy, carboxy, carbonamido, carbalkoxy, lower alkylsulfonyl, lower alkylsulfonamido, arylsulfonamido, nitro, or benzylthio groups. Representa-

tive aminotriarylmethanes that may be used in this invention follow:

bis(2-bromo-4-diethylaminophenyl)phenylmethane,
bis(2-butoxy-4-diethylaminophenyl)phenylmethane,
bis[4 - (2-cyanoethyl) (2 - hydroxyethyl)amino-o-tolyl]-
(p-benzylthiophenyl)methane,
bis[4 - (2-cyanoethyl) (2 - hydroxyethyl)amino-o-tolyl]-
2-thienylmethane,
bis(4-dibutylamino-o-tolyl)2-thienylmethane,
bis(4-diethylamino-2-ethylphenyl) (3,4 - methylenedioxy-
phenyl)-methane,
bis(4-diethylamino-2 - fluorophenyl) (p-benzylthiophenyl)
methane,
bis(4-diethylamino-2 - fluorophenyl) (3,4-methylenedioxy-
phenyl) methane,
bis(4 - diethylamino-2 - methoxyphenyl) (p-nitrophenyl)
methane,
bis(4 - diethylamino-1-naphthyl) (4-diethylamino-o-tolyl)
methane,
bis(4 - diethylamino-o-tolyl) (p-benzylthiophenyl) meth-
ane,
bis(4 - diethylamino-o-tolyl) (2,4-dimethoxyphenyl) meth-
ane,
bis(4-diethylamino-o-tolyl)2-furylmethane,
bis(4 - diethylamino-o-tolyl) (p-methoxyphenyl) methane,
bis(4 - diethylamino-o-tolyl) 3,4 - methylenedioxyphenyl)
methane,
bis(4 - diethylamino-o-tolyl) (p-methylthiophenyl) meth-
ane,
bis(4-diethylamino-o-tolyl) 1-naphthylmethane,
bis(4-diethylamino-o-tolyl) phenylmethane,
bis(4-diethylamino-o-tolyl) 2-thienylmethane,
tris(4-dimethylamino-2-chlorophenyl) methane,
bis(4 - dimethylamino-2,5-dimethylphenyl) phenylmeth-
ane,
bis(4 - dimethylamino-2-hexylphenyl) (p-butylthiophenyl)
methane,
bis(4 - dimethylamino-o-tolyl) (o-bromophenyl) methane,
bis[4 - (N-ethylanilino) -o-tolyl] (3,4 - dibutoxyphenyl)
methane,
bis(4 - ethylbenzylamino - o-tolyl)(p-methoxyphenyl)
methane,
bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl](p-
benzylthiophenyl) methane,
tris(4-diethylamino-o-tolyl) methane, and
tris(p-diethylamino-o-tolyl) methane.
bis(4-diethylamino-o-tolyl)-p-chlorophenyl methane
bis(4-diethylamino-o-tolyl)-p-bromophenyl methane
bis(4-diethylamino-o-tolyl)-p-fluorophenyl methane
bis(4-diethylamino-o-tolyl)-p-tolyl methane
bis(4 - diethylamino-o-tolyl)-4-methoxy-1-naphthyl meth-
ane
bis(4 - diethylamino-o-tolyl) - 3,4,5 - trimethoxyphenyl
methane
bis(4-diethylamino-o-tolyl)-p-hydroxyphenyl methane
bis(4 - diethylamino-o-tolyl) - 3-methylthienyl methane
5-[bis(4-diethylamino-o-tolyl)-methyl]-2,3-cresotic acid
4-[bis(4-diethylamino-o-tolyl)-methyl]-phenol
4-[bis(4-diethylamino-o-tolyl)-methyl]-acetanilide
4-[bis(4-diethylamino-o-tolyl)-methyl]-phenylacetate
4-[bis(4-diethylamino-o-tolyl)-methyl]-benzoic acid
4-[bis(4-diethylamino-o-tolyl)-methyl]-diphenyl sulfone
4-[bis(4 - diethylamino-o-tolyl)-methyl] - phenylmethyl
sulfone
4-[bis(4 - diethylamino-o-tolyl)-methyl] - methylsulfon-
anilide
4-[bis(4 - diethylamino-o-tolyl)-methyl] - p-tolylsulfon-
anilide
bis(4 - diethylamino-o-tolyl)-p-nitrophenyl methane

These amino substituted cationic dye precursors are generally employed in the color forming process as salts of strong acids, including Lewis acids, such as hydrochloric, hydrobromic, sulfuric, nitric, phosphoric, acetic, oxalic, p-toluenesulfonic, zinc chloride, zinc bromide, and

ferric chloride, the proportion of acid varying from 0.33 mole to 1 mole per amino group.

Representative leuco compounds of the other classes are as follows:

Aminoxanthenes

3-amino-6-dimethylamino-2-methyl-9-(o-chlorophenyl)
xanthene
3-amino-6-dimethylamino-2-methyl-9-phenylxanthene
3-amino-6-dimethylamino-2-methylxanthene
3,6-bis(diethylamino)-9-(o-chlorophenyl)xanthene
3,6-bis(diethylamino)-9-hexylxanthene
3,6-bis(diethylamino)-9-(o-methoxycarbonylphenyl)
xanthene
3,6-bis(diethylamino)-9-methylxanthene
3,6-bis(diethylamino)-9-phenylxanthene
3,6-bis(diethylamino)-9-o-tolylxanthene
3,6-bis(dimethylamino)-9-(o-chlorophenyl)xanthene
3,6-bis(dimethylamino)-9-ethylxanthene
3,6-bis(dimethylamino)-9-(o-methoxycarbonylphenyl)
xanthene
3,6-bis(dimethylamino)-9-methylxanthene.

Aminothioxanthenes

3,6-bis(diethylamino)-9-(o-ethoxycarbonylphenyl)
thioxanthene
3,6-bis(dimethylamino)-9-(o-methoxycarbonylphenyl)
thioxanthene
3,6-bis(dimethylamino)thioxanthene
3,6-dianilino-9-(o-ethoxycarbonylphenyl)thioxanthene

Amino-9,10-dihydroacridines

3,6-bis(benzylamino)-9,10-dihydro-9-methylacridine
3,6-bis(diethylamino)-9-hexyl-9,10-dihydroacridine
3,6-bis(diethylamino)-9,10-dihydro-9-methylacridine
3,6-bis(diethylamino)-9,10-dihydro-9-phenylacridine
3,6-diamino-9-hexyl-9,10-dihydroacridine
3,6-diamino-9,10-dihydro-9-methylacridine
3,6-diamino-9,10-dihydro-9-phenylacridine
3,6-bis(dimethylamino)-9-hexyl-9,10-dihydroacridine
3,6-bis(dimethylamino)-9,10-dihydro-9-methylacridine.

Aminophenoxazines

3,7-bis(dimethylamino)phenoxazine
3,7-bis(diethylamino)phenoxazine
3,7-bis(dibutylamino)phenoxazine
3-diethylamino-7-dimethylamino-2-methylphenoxazine
3-dimethylamino-7-dipropylaminophenoxazine
5-dimethylamino-9-diethylamino-12H-benzo[a]
phenoxazine
5-dibenzylamino-9-diethylamino-12H-benzo[a]
phenoxazine
5,9-bis(diethylamino)-12H-benzo[a]phenoxazine
Acylation gives the corresponding 10-acyl compounds.

Aminophenothiazines

3,7-bis(dimethylamino)phenothiazine
3,7-bis(dimethylamino)-4,6-dimethylphenothiazine
3,7-bis(diethylamino)-2,8-dimethylphenothiazine
3,7-bis(diethylamino)-4-nitrophenothiazine
3,7-bis(dibutylamino)phenothiazine
3-diethylamino-7-dimethylaminophenothiazine
3-dimethylamino-7-N-benzyl-N-methylaminopheno-
thiazine
3,7-bis(N-benzyl-N-ethylamino)phenothiazine
Acylation gives the corresponding 10-acyl compounds.

Aminodihydrophenazines

3,7-bis(benzylethylamino)-5,10-dihydro-5-phenyl-
phenazine
3,7-bis(diethylamino)-5-hexyl-5,10-dihydrophenazine
3,7-bis(dihexylamino)-5,10-dihydrophenazine
3,7-bis(dimethylamino)-5-(p-chlorophenyl)-5,10-dihydro-
phenazine
3,7-diamino-5-(o-chlorophenyl)-5,10-dihydrophenazine
3,7-diamino-5,10-dihydrophenazine

3,7-diamino-5,10-dihydro-5-methylphenazine
 3,7-diamino-5-hexyl-5,10-dihydrophenazine
 3,7-bis(dimethylamino)-5,10-dihydrophenazine
 3,7-bis(dimethylamino)-5,10-dihydro-5-phenylphenazine
 3,7-bis(dimethylamino)-5,10-dihydro-5-methylphenazine
 Acylation gives the corresponding 10-acyl compounds.

Aminodiphenylmethanes

1,4-bis[bis-(p-diethylaminophenyl)methyl]piperazine
 bis(p-diethylaminophenyl)anilinoethane
 bis(p-diethylaminophenyl)-1-benzotriazolylmethane
 bis(p-diethylaminophenyl)-2-benzotriazolylmethane
 bis(p-diethylaminophenyl)(p-chloroanilino)methane
 bis(p-diethylaminophenyl)(2,4-dichloroanilino)methane
 bis(p-diethylaminophenyl)(methylamino)methane
 bis(p-diethylaminophenyl)(octadecylamino)methane
 bis(p-dimethylaminophenyl)aminomethane
 bis(p-dimethylaminophenyl)anilinoethane
 1,1-bis(dimethylaminophenyl)ethane
 1,1-bis(dimethylaminophenyl)heptane
 bis(4-methylamino-m-tolyl)aminoethane.

Leuco indamines

4-amino-4'-dimethylaminodiphenylamine
 p-(p-dimethylaminoanilino)phenol

Aminohydrocinnamic acid (cyanoethanes, leuco methines)

4-amino- α,β -dicyanohydrocinnamic acid, methyl ester
 4-anilino- α,β -dicyanohydrocinnamic acid, methyl ester
 4-(p-chloroanilino)- α,β -dicyanohydrocinnamic acid, methyl ester
 α -cyano-4-dimethylaminohydrocinnamamide
 α -cyano-4-dimethylaminohydrocinnamic acid, methyl ester
 α,β -dicyano-4-diethylaminohydrocinnamic acid, methyl ester
 α,β -dicyano-4-dimethylaminohydrocinnamamide
 α,β -dicyano-4-dimethylaminohydrocinnamic acid, methyl ester
 α,β -dicyano-4-dimethylaminohydrocinnamic acid
 α,β -dicyano-4-dimethylaminohydrocinnamic acid, hexyl ester
 α,β -dicyano-4-ethylaminohydrocinnamic acid, methyl ester
 α,β -dicyano-4-hexylaminohydrocinnamic acid, methyl ester
 α,β -dicyano-4-methylaminocinnamic acid, methyl ester
 p-(2,2-dicyanoethyl)-N,N-dimethylaniline
 4-methoxy-4'-(1,2,2-tricyanoethyl)azobenzene
 4-(1,2,2-tricyanoethyl)azobenzene
 p-(1,2,2-tricyanoethyl)-N,N-dimethylaniline

Hydrazines

1-(p-diethylaminophenyl)-2-(2-pyridyl)hydrazine
 1-(p-dimethylaminophenyl)-2-(2-pyridyl)hydrazine
 1-(3-methyl-2-benzothiazolyl)-2-(4-hydroxy-1-naphthyl)hydrazine
 1-(2-naphthyl)-2-phenylhydrazine
 1-p-nitrophenyl-2-phenylhydrazine
 1-(1,3,3-trimethyl-2-indolyl)-2-(3-N-phenyl-carbamoyl-4-hydroxy-1-naphthyl)hydrazine

Leuco indigoid dyes

The leuco forms of indigoid dyes having CI numbers 73000, 73015, 73025, 73030, 73035, 73040, 73045, 73050, 73055, 73060, 73065, 73070, 73085, 73090, 73110, 73300, 73305, 73310, 73315, 73320, 73325, 73335, 73340, 73345, 73350, 73360.

Amino-2,3-dihydroanthraquinones

1,4-dianilino-2,3-dihydroanthraquinone
 1,4-bis(ethylamino)2,3-dihydroanthraquinone

Phenethylanilines

N-(2-cyanoethyl)-p-phenethylaniline
 N,N-diethyl-p-phenylethylaniline
 N,N-dimethyl-p-[2-(1-naphthyl)ethyl]aniline
 5 N,N-dimethyl-p-[2-(4-nitro-1-naphthyl)ethyl]aniline
 N,N-dimethyl-p-phenethylaniline
 N,N-dimethyl-p-[2-(4-methoxy-1-naphthyl)ethyl]aniline
 p-(p-methoxyphenethyl)aniline
 p-[2-(1-naphthyl)ethyl]aniline
 10 p-(p-nitrophenethyl)aniline
 p-phenethylaniline

Alkyl- and benzylthio derivatives of aminotriarylmethane

tris(p-dimethylaminophenyl)benzylthiomethane
 15 bis(p-dimethylaminophenyl)-p-dipropylaminophenyl-benzylthiomethane
 bis(p-dimethylaminophenyl)-p-propoxyphenylbenzylthiomethane
 bis(p-diethylaminophenyl)-p-cyanophenylbenzylthiomethane
 20 bis(p-diethylaminophenyl)-p-chlorophenylbenzylthiomethane
 bis(p-diethylaminophenyl)-p-fluorophenylbenzylthiomethane
 25 bis(p-diethylaminophenyl)-p-pentoxyphenylbenzylthiomethane
 bis(p-diethylaminophenyl)-p-carbamoylphenylbenzylthiomethane
 bis(p-diethylaminophenyl)-p-nitrophenylbenzylthiomethane
 30 bis(4-diethylamino-2-methoxyphenyl)-p-ethylphenyl-methylthiomethane
 bis(4-diethylamino-2-propoxyphenyl)-2-chloro-4-octylphenylethylthiomethane
 35 bis(p-diethylaminophenyl)-2,4-dimethoxyphenyl-propylthiomethane
 bis(p-diethylaminophenyl)-4-bromo-2-methoxyphenyl-butylthiomethane
 40 2-Phenylhydrazino derivatives of aminotriarylmethane
 1-tris(p-diethylaminophenyl)methyl-2-phenylhydrazine
 1-tris(4-diethylamino-2-chlorophenyl)methyl-2-phenylhydrazine
 1-tris(4-diethylamino-o-tolyl)methyl-2-phenylhydrazine
 45 1-[bis(p-dimethylaminophenyl)phenylmethyl]-2-phenylhydrazine
 1-[bis(4-dimethylamino-2-methoxyphenyl)-p-nitrophenylmethyl]-2-phenylhydrazine
 50 1-[bis(p-dipropylaminophenyl)-2,4-dichlorophenylmethyl]-2-phenylhydrazine

Alkoxy-carbonyl derivatives of aminotriarylmethane

tris(p-dimethylaminophenyl)ethoxycarbonylmethane
 55 (or ethyl tris(p-dimethylaminophenyl)acetate)
 tris(p-dibutylaminophenyl)pentoxycarbonylmethane
 tris(4-didodecylamino-o-tolyl)methoxycarbonylmethane
 tris[4-(N-ethyl-N-phenylamino)-2-ethylphenyl]ethoxycarbonylmethane
 60 tris[4-bis(2-methoxyethyl)amino-2-bromophenyl]-ethoxycarbonylmethane
 tris[4-bis(2-cyanoethyl)amino-2-chlorophenyl]-ethoxycarbonylmethane
 65 tris[4-bis(2-hydroxyethyl)amino-2-fluorophenyl]-ethoxycarbonylmethane
 tris(4-dibenzylamino-2-pentoxyphenyl)ethoxycarbonylmethane

70 Aminotriarylmethanes having specified aryl groups

Bis[4-(N-benzyl-N-ethylamino)-o-tolyl](p-benzylthiophenyl)methane
 Bis[4-bis(2-cyanoethyl)amino-o-tolyl](p-benzylthiophenyl)methane
 75

Bis[4-bis(2-ethoxyethyl)amino-o-tolyl](p-benzylthiophenyl) cyanomethane
 Bis[4-bis(2-hydroxyethyl)amino-2-ethylphenyl](p-benzylthiophenyl) methane
 Bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl](p-benzylthiophenyl) methane
 Bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl](p-benzylthiophenyl) methane
 Bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl](p-benzylthio-m-butylphenyl) methane
 Bis(4-diethylamino-o-tolyl) (p-benzylthiophenyl) cyanomethane
 Bis(4-diethylamino-o-tolyl) (p-phenylthiophenyl)-methane
 Bis(4-diethylamino-o-tolyl) [p-(o-tolylthio)phenyl]-methane
 Bis[4-bis(2-cyanoethyl)amino-o-tolyl] (3,4-dibutoxyphenyl) methane
 Bis[4-bis(2-cyanoethyl)amino-o-tolyl] 2-furylmethane
 Bis[4-bis(2-cyanoethyl)amino-o-tolyl] (3,4-dibutoxyphenyl) cyanomethane
 Bis[4-bis(3-hydroxypropyl)amino-o-tolyl] (2-methoxy-4-octyloxyphenyl) methane
 Bis[4-bis(2-methoxyethyl)amino-o-tolyl] (3,4-methylene-dioxyphenyl) methane
 Bis(4-dibenzylamino-o-tolyl) 2-thienylmethane
 Bis(4-dimethylamino-2-ethylphenyl) (3,4-methylene-dioxyphenyl) methane
 Bis(4-dimethylamino-2-ethylphenyl) 2-thienylcyano-methane
 Bis(4-dimethylamino-o-tolyl) (2,4-dimethoxyphenyl)-methane.

The leuco dyes are described in British Pat. 1,047,796, published Nov. 9, 1966; Italian Pat. 707,086, issued May 24, 1966 and in U.S. patent applications Ser. Nos. 363,638 and 363,639, both filed Apr. 29, 1964 and assigned to the assignee herein.

(D) The fixing component

The fixing component is so named because when present it fixes the colored form of the leuco dye permanently. The fixing component can be any material which will maintain the permanent image. For example, a redox system such as described in British Pat. 1,057,785 is useful. The component described therein comprises an oxidant and a reductant which react with each other when irradiated with actinic light of a different wavelength than that used to activate the coumarin. The reaction between the oxidant and reductant forms a reducing agent which reacts with and deactivates the biimidazole. Thus leuco image will remain stable. Other qualifications of this system are that it is unreactive at the wavelengths used to activate the coumarin and that it is unreactive with the leuco dye at any wavelength. Examples of the oxidant include quinones, ketones, phenazines, acridines, phenoxazinones, quinolines, phenanthrolines, isoquinolines, and anils. Examples of the reductant include ethers, esters, alcohols, compounds containing allylic or benzylic hydrogen, i.e., containing a methylene group attached to a carbon that is itself attached to another carbon by a double bond, acetals, aldehydes and amides. Specific examples of such compounds are found in said British Pat. 1,057,785 and are incorporated herein.

Another type of fixing agent is an organic progenitor of a reducing agent which forms a reducing agent upon heat treatment, but is otherwise inert to the biimidazole-leuco dye imaging system. The reducing agent so formed then reacts with and deactivates the biimidazole. Generally, the heat necessary to transform the progenitor will be between 80° C. and 160° C. Examples of such progenitors include acetals, orthoesters, carbonates and orthocarbonates of hydroquinones and phenols such as hydroquinone, phenylhydroquinone, t-butylhydroquinone, durohydroquinone, p-benzylhydroquinone, naphthylene-1,4-diol, 75

resorcinol, pyrogallol, 2,4,6-tri-tertbutylphenol, 2,6-di-tert-butyl-p-cresol, and 2,4,6-trimethylphenol; semicarbazones of aldehydes and ketones; Schiffs' bases of primary aromatic amines such as aniline and 1-naphthylamine; diketones which tautomerize to hydroquinones on heating such as 2,4-dihydro-1,4-naphthoquinone and 4 α ,5,8,8 α -tetrahydro-1,4-naphthoquinone. These and other heat-sensitive progenitors are described more fully in Manos U.S. Ser. No. 363,625, filed Apr. 29, 1964, and assigned to the assignee herein.

Still another type of fixing agent are diazonium compounds which, upon exposure to radiation of a wavelength different than that which energizes the biimidazole, yield a reducing agent directly. The reducing agent then reacts with and deactivates the biimidazole. Examples of diazonium compounds include diazotized

4-(p-tolylthio) o-anisidine
 2,4,5-trimethoxyaniline
 5-amino-2-diethylamino-p-anisic acid, methyl ester
 4-(p-tolylthio) o-anisidine
 4-(4-amino-3-butylphenyl) morpholine
 4-(4-amino-2,5-diethoxyphenyl) morpholine
 4-(4-amino-2,5-dibutoxyphenyl) morpholine
 4-(p-aminophenyl) morpholine
 4-amino-1-naphthol
 4-amino-7-methoxy-3-methyl-1-naphthol
 4-amino-3-methyl-1-naphthol
 N²,N²-dimethyl-1,2-naphthalenediamine
 N,N-diethyl-1,4-naphthalenediamine
 2-methyl-N¹-phenyl-1,4-naphthalenediamine
 4-amino-2,6-dimethoxyphenol
 N¹,N¹-diethyl-4-methyl-m-phenylenediamine
 4-methoxy-N³,N³-dimethyl-m-phenylenediamine
 N,N-diethyl-o-phenylenediamine
 N¹,N¹-diethyl-4-methyl-o-phenylenediamine
 N-methyl-N-phenyl-o-phenylenediamine
 p-phenylenediamine

These fixing agents are described in Cescon U.S. patent application Ser. No. 448,839, filed Apr. 16, 1965, and assigned to the assignee herein.

A preferred oxidant-reductant combination fixing agent comprises as oxidant pyrenequinone or phenanthrenequinone and as reductant a lower alkyl ester of nitrilotriacetic, nitrilo-tripropionic acid, dioxane, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, methoxyethyl terephthalate, cyclohexyl adipate, 1,3-cyclohexylene diacetate, or mixtures thereof. Preferably the reductant is a polyethylene glycol.

(E) Preferred composition ratios and other components

As previously stated, the basic composition, for sun-screen shields, etc., is preferably composed of .1 to 2 moles of coumarin to 1 mole of the biimidazole, and most preferably .4 to .6 moles of coumarin per mole of biimidazole.

For developing colored images through exposure to light, the biimidazole/near UV sensitizer/leuco dye combination will normally be employed in molar ratios 1/.1-2/.1-10, preferably 1/.4-.6/.5-2.

Amounts of the oxidant-reductant fixing system will range from molar ratios of 0.01:1 to 2:1 of oxidant to biimidazole, with 0.2:1 to 0.5:1 preferred. The reductant components can range from molar ratios of 11 to 40:1 of reductant to oxidant. Amounts of the organic progenitor fixing agent will range from molar ratios of 1:5 to 20:1 of progenitor to biimidazole. The diazonium fixing agent can range from ratios of 0.21 to 10:1 of agent to biimidazole.

Further, it will be normally advantageous to include other components in the imaging formulation, such as solvents, plasticizers and/or binders (0.5% by weight or more of each based on the total weight of imaging composition) to provide for intimate contact among the

biimidazole, coumarin, leuco dye, and fixing system, and to facilitate their application to substrates in coating applications.

Suitable solvents are those inert to the other ingredients of the composition and include amide such as N,N-dimethylformamide, N,N-dimethylacetamide; alcohols such as methanol, ethanol, 1-propanol, 2-propanol, butanol, ethylene glycol; ketones such as acetone, methyl ethyl ketone, 3-pentanone; halocarbons such as methylene chloride, chloroform, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane; polyethylene glycols; esters, e.g., ethyl acetate and ethyl benzoate; aryls such as benzene, o-dichlorobenzene and toluene; dimethylsulfoxide, pyridine, acetonitrile, tetrahydrofuran, dioxane, 1,1,2-trichloroethylene, 1-methyl-2-oxo-hexamethyleneimine, and mixtures thereof.

Suitable inert plasticizers include the polyethyleneglycols, such as the commercially available Carbowaxes, and related materials, such as substituted phenol-ethylene oxide adducts for example the products obtained from p-phenylphenol and 6 moles ethylene oxides, and from p-nonylphenol and 2 moles ethylene oxide, including commercially available materials such as the Igepal alkyl phenoxy polyoxyethylene ethanols.

Polymeric materials, particularly light-transparent and film-forming polymers, are useful as inert binders, and carriers for the essential ingredients described above; thus, bi-imidazole, leuco dye, sensitizer and polymer, with or without a mutual solvent, may be mixed, then sprayed, extruded, cast, pressed or otherwise formed into supported or unsupported films or shaped articles. Representative polymers are polyvinyl alcohol, ethyl cellulose, polyvinyl chloride, polystyrene, polyvinyl acetate, poly(methyl methacrylate), cellulose acetate, cellulose butyrate, copolymers of vinyl monomers, gelatin, and polyethylene. Other suitable inert materials which may be used include glasses, resins, and waxes.

Typical inert substrates include materials commonly used in the graphic arts and in decorative applications, such as paper ranging from tissue paper to heavy cardboard; films of plastics and polymeric materials such as regenerated cellulose, cellulose acetate, cellulose nitrate, polyester of glycol and terephthalic acid, vinyl polymers and copolymers, polyethylene, polyvinylacetate, polymethyl methacrylate, polyvinylchloride; textile fabrics; glass; wood and metals.

In addition, the spectral sensitivity of the compositions can be extended to the visible light range by incorporating therein, either in conjunction with the coumarin or alone, visible light-absorbing energy transfer agents such as phthalein dyes, e.g., fluoresceins, erythrosins, eosins and halofluoresceins; aminoacridine dyes such as 3,6-diaminoacridine hydrochloride, acriflavine and acridine orange; carbocyanine dyes such as 3,3'-diethyl oxacarbocyanine

iodide, 3,3'-diethyl-9-methyl oxacarbocyanine iodide, and 3,3',9-trimethyle thiocarbocyanine bromide; or cyanine dyes such as 1,1'-diethyl-2,2'-dyanine iodide, 1,1'-diethyl-4,4'-cyanine iodide, and 1,3',diethyl-4,2'-quinolyl thiacyanine iodide.

(F) Utility

The compositions of this invention are useful for light-actuated colored image formation and are used in a dry, non-silver photographic process capable of imaging in various colors and shades on various substrates, including fabrics, papers and similar fibrous sheet materials and films. Apparatus useful in conducting photographic dye-printing is described in U.S. Pats. 2,214,365 and 2,655,802. Even very soft paper, as for example tissue paper, which has been treated with a composition of this invention, can be readily printed by projecting the desired graphic pattern onto the treated paper and irradiating it to effect the color-forming reaction.

The imaging formulations are conveniently applied to the carrier substrates as solutions in volatile solvents such as those described above. They may be thus continuously coated on roll papers and films utilizing such typical devices for continuously laying down wet films as nip fed three roll reverse roll coating heads, gravure coaters, trailing blade coaters and Mayer bar coating heads (wherein the coating thickness is controlled by a threaded or a wire wound bar). The wet thickness is adjusted such that the dry thickness after solvent removal is in the desired range (about .1-1.5 mil, usually around .3-.5 mil on paper, .8-1.1 mil on film). After the solvent has been removed, as by radiant heating or forced air evaporation, the coated paper or film is wound up on rolls in the usual way.

Any convenient light source providing wavelengths in the near ultraviolet region of the spectrum that overlap the coumarins absorption bands may be used to activate the compositions for imidazolyl radical and image formation. The light may come from natural or artificial sources, may be monochromatic or polychromatic, incoherent or coherent (i.e. laser beams such as a pulsed nitrogen laser emitting at 337 mμ), and for high efficiency should correspond closely in wavelengths to the principal absorption bands of the coumarin sensitizers employed and should be sufficiently intense to activate a substantial proportion of the sensitizer molecules.

THE EXAMPLES

The following examples illustrate the compositions of this invention and their uses:

EXAMPLE 1

Ultraviolet light sensitive biimidazole compositions containing the following ingredients in parts by weight were prepared as solutions in acetone, a convenient carrier solvent:

Ingredient	Composition			Relative mole ratio o-C1HABI-1
	Control	A	G	
Acetone (solvent), grams	46	46	46	
Cellulose acetate butyrate (a thermoplastic resin binder)	6	6	6	
Polyethylene ether glycol, M.W. 550 (a plasticizer and the reductant of the fixing system)	3	3	3	
2-methoxyethyl phthalate (a plasticizer and a reductant of the fixing system)	1	1	1	
2,2'-bis(o-chlorophenyl)-4,4',4,5'-tetraphenyl-1,2'-biimidazole (o-C1HABI) λ_{max} 263 mμ (hexaarylbiimidazole)	.30	.30	.30	1.0
Tris(N,N-diethylamino-o-tolyl)methane (leuco dye)	.53	.53	.53	.67
p-Toluenesulfonic acid monohydrate (stabilizer for the reduced leuco dye)	.34	.34	.34	2.0
Pyrenequinone, mixed 1,6 and 1,8-isomers (oxidant of the fixing system)	.04	.04	.04	
7-dimethylamino-4-methylcoumarin λ_{max} 360 (sensitizer)		.16		1.0
7-diethylamino-4-methylcoumarin λ_{max} 375 (sensitizer)			.19	1.0

15

The solutions were applied to bleached-sulfite roll stock paper and the acetone allowed to evaporate to give coatings about 0.5 mil thick. Each paper was then irradiated by contact flashing with one flash from a Xenon flash lamp (HiCo Lite, emitting ultraviolet light above 200 mμ and approximating ordinary unfiltered sunlight), directly and through a filter system transmitting from 340 to 420 mμ with peak transmittance at 370 mμ, obtained by overlaying a Corning No. 7-54 filter (transmitting from 220 to 420 mμ) with a Corning No. 0-52 filter (transmitting

16

EXAMPLE 3

Imaging formulations were prepared as described in Example 1 except that (a) the quinone was omitted and (b) different coumarins, as identified below, were employed in amounts corresponding to 0.5 mole/mole o-CIHABI. Papers were coated with these formulations and imaged as described in Example 2 through filter system C except that a xenon arc lamp provided the radiation. The results are tabulated below:

Coumarin	Imaging results	
	Speed, sec.	O.D., 50 sec.
Composition:		
C..... 7-diethylamino, 4-methyl.....	2.2	1.21
D..... 5,7-dimethoxy.....	3.8	1.09
E..... "Tinopal" PG.....	2.9	0.99
Control 1..... None.....	5.0	1.01
Control 2..... 7-diethylamino-4-methyl-coumarin but no o-CIHABI.	No color formation	

from 340 mμ into the visible beyond 420 mμ). The results were as follows:

Composition:	Color formation	
	Unfiltered UV	Filtered UV
A.....	Intense.....	Medium.....
B.....	do.....	Medium-intense.....
Control.....	do.....	Faint green.....

The less intense color formation obtained with the filtered (i.e. near UV) radiation is attributed to the fact that the particular filter system employed shows only 70% transmittance at the 370 mμ peak. The results show, however, that the coumarins enhance the sensitivity of the imaging formulation to near UV radiation.

This example also demonstrates the conversion of the biimidazole to the imidazolyl radical through action of the coumarin, as evidenced by the further reaction of the radical with the leuco dye.

EXAMPLE 2

Photosensitive papers prepared as described in Example 1 were exposed to ultraviolet radiation from a medium pressure mercury lamp, through filter systems A, B, C described below:

Filter	Components	Remarks
A.....	Schott Filter UG-11.....	Transmits from 230 mμ to 420 mμ, with peak (90% transmission) at 320 mμ.
B.....	UG-11 over polyester film.....	The polyester transmits from 315 mμ into the visible; the combination from 315 mμ to 420 with peak (80% transmission) at 350 mμ.
C.....	UG-11 over Corning Filter No. 0-52.....	0-52 Cuts off light below 340 mμ; the combination transmits from 340 to 420 with peak (70% transmission) at 370 mμ.

Each sample was exposed for 50 seconds total, during which time the change in optical density was monitored with a reflectance sensitometer. The results are expressed below in terms of imaging speed, which is the time in seconds required to yield a 0.3 optical density increase, and the final optical density.

IMAGING RESULTS

Coumarin	Filter A		Filter B		Filter C	
	Speed	O.D.	Speed	O.D.	Speed	O.D.
Composition:						
A..... 7-Me ₂ N, 4-Me.....	3.5	1.03	6.4	0.89	11.5	0.58
B..... 7-Et ₂ N, 4-Me.....	3.0	1.12	5.7	0.89	9.5	0.76
Control..... None.....	4.0	1.13	9.8	0.75	24.3	0.42

The results, particularly with filter systems B and C, show that the coumarins significantly enhance the spectral sensitivity of the biimidazole/leuco dye imaging system to near ultraviolet radiation.

The results show (1) the coumarins are highly effective sensitizers in the near UV; with 7-diethylamino-4-methyl-coumarin more than doubling the speed and increasing the optical density 20%; (2) the coumarin alone, without the biimidazole is not a photooxidant for the leuco dye.

EXAMPLE 4

Imaging formulations were prepared as acetone solutions from the following ingredients, in parts by weight:

Ingredient	Composition		
	F	G	H
Acetone.....	46.0	46.0	48.8
Cellulose acetate butyrate.....	6.0	6.0	-----
p-Phenyl phenol-ethylene oxide adduct ¹	4.0	4.0	10.0
Polyethylene glycol.....	-----	-----	4.3
2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetrakis (m-methoxyphenyl)-1,2'-biimidazole.....	.62	.62	1.25
N,N'-tris(diethylamino-o-tolyl)methane.....	.30	-----	.30
p-Toluenesulfonic acid monohydrate.....	.34	-----	.29
7-diethylamino-4-methylcoumarin.....	.092	.092	.19
2-(4-hydroxy-3,5-dimethoxyphenyl)-4,5-bis(4-methoxyphenyl)imidazole ²	-----	.34	-----

¹ Produced from 1 mole of the phenol and 6 moles ethylene oxide; replacing this ingredient with the product obtained from p-nonylphenol and 2 moles ethylene oxide give substantially similar results.

² A Leuco dye, yielding a red oxocarylidene dye, as described in U.S. 3,297,710.

Appropriate controls were also prepared with no added coumarins. The solutions were applied to "Mylar" poly-

ester film and the acetone allowed to evaporate. The coated films were covered with a sharp cut off filter (Corning Filter No. 3-75), which transmits only 5% at 380 mμ, 40% at 400 mμ, and progressively more light at longer wavelengths, and irradiated by contact flashing as described in Example 1. In each example, the coatings con-

taining the coumarin sensitizer produced strongly colored images, whereas the controls formed substantially no color.

This example illustrates the use of cathode ray tubes as energy sources.

The formulation described in Example 4 as composition F (except that 36.8 instead of 46 parts acetone was employed) was coated on a bleached sulfite paper to a 0.5 mil thickness after acetone evaporation. A cathode ray tube with a P22B phosphor emitting from 390 to 550 m μ , with peaking at 450 m μ , and having a 1" x 2" standard television raster made up of a series of alphanumeric characters, was operated at a 20 kv. accelerating potential and an average raster current of 100 microamperes. Under such conditions, contacting the photosensitive paper with the cathode ray tube face produced a colored image having an optical density of at least 0.3 in 0.5 second.

EXAMPLE OF A CATHODE RAY TUBE PRINTOUT SYSTEM

Ultraviolet emitting cathode ray tubes for writing on photosensitive materials are particularly versatile light sources for use in imaging the subject compositions. These in general involve an ultraviolet emitting phosphor internal coating as the means for converting electrical energy to light energy and a fiber optic face plate as the means for directing the radiation to the photosensitive target. For purposes of this invention, the phosphors should emit strongly in the 320-420 m μ range so as to substantially overlap the near UV-absorption characteristic of the coumarin-containing compositions. Representative phosphors include the P4B (emitting at 300-550 m μ , peaking at 410 m μ), P16 (330-460, peaking at 380 m μ) and P22B (390-510, peaking at 450 m μ) types. (The Electronic Industries Association, New York, New York, assigns P-numbers and provides characterizing information on the phosphors; phosphors with the same P-number have substantially identical characteristics.)

In typical cathode ray tube printout systems, information to be recorded, which may originate from a computer, radar camera, infrared camera, TV camera or other central source, is fed to a command unit which in turn controls a function generator which transmits the information as signals (alpha-numerics, strokes, dots) that the cathodes ray tube can utilize and convert to a luminous pattern. For continuous imaging, a transport system conveys the photosensitive target (paper, cards or film) past the face of the tube and sends appropriate signals to the command unit to keep the imaging signals properly synchronized with the moving target. Such transport apparatus with auxiliary control and signal means is well known to the art and requires no further description. Related cathode ray tube printout systems are described in U.S. Pat. 3,289,196; 3,258,525; 3,235,658; 3,184,753; 3,041,947.

In such uses, the imaging compositions of this invention provide for high imaging speed, high resolution and good contrast in an essentially dry direct printout process. As the supports may vary widely, their use makes possible a multipurpose electronic information output system comprising a central electronic system feeding and operating a multiplicity of cathode ray tube printers, each capable of performing a separate function and of providing soft or hard copy.

The drawing schematically illustrates a digital computer output system, with a multiplicity of CRT image printers comprising: digital computer 1; device controller or command unit 2, to control the device from the computer and to inform the computer if the device needs servicing; buffer memory 3, to sequentially store binary information from 1 and subsequently pass this information on to digital-to-analog (D to A) converters (described below); variable clock 8 and delay one shot 9, to provide a time base and a strobe signal for transferring information from 3 to the D to A converters; comparator 10 and AND gates 11, 12, 13 and 14, to choose the proper D to A converter to receive the information from

3; D to A converters 4, 5, 6 and 7, to convert the digital information from 3 to analog voltages and amplify the voltages to drive the horizontal and vertical deflection systems of ultraviolet fiber optic cathodes ray tubes; cathode ray tubes 15 and 16 with UV-emitting phosphors and fiber optics; conveyors 17 and 18, to transport photosensitive paper and film (not shown), at the proper rates so that the resulting image is clear and distinct.

The digital output system operates in two major states; one, to read binary information with buffer memory 3; two, to write from 3 to cathodes ray tubes 15 and 16. To read into 3, computer 1 commands controller 2; memory 3 signals the need for more data to controller 2, which signals computer 1 with a pulse. When going into this state, controller 2 sends signals to blank CRT's 15 and 16 and stop conveyors 17 and 18; it puts the memory 3 into the read state by signalling to reset the address register to zero, then disengages clock 8 with a pulse and sets the counter in comparator 10 with a pulse. In the read state, controller 2 puts the data from 1 into proper sequence, so that the proper information gets to the D to A converters 4, 5, 6 and 7; it loads a flip-flop register in memory 3 with the data and reads the register in with a "read" pulse. When finished transferring the data, controller 2 unblanks CRT's 15 and 16 resets the address register in buffer 3 with a pulse, enables clock 8, starts conveyors 17 and 18 and controls their speed.

To write from buffer 3, controller 2 enables clock 8 with a second pulse, the clock being variable from 30 c.p.s. to 2 mc. and adjustable to the necessary flow of information to CRT's 15 and 16. Clock 8 relays the pulse to increment comparator 10, to cause a delayed-one-shot in 9, to read memory into buffer 3; such pulse (and each succeeding pulse) increments the memory address so that it can write sequentially one word into an output register. The address register flip-flops of the memory 3 are directed through switches 20 in series into AND gate 21 that allows a pulse to go to controller 2 when the memory is empty. The delayed pulse from 9, which passes through AND gates 11, 12, 13 and 14, strobes the buffered word into digital-to-analog converters 4, 5, 6 and 7, with comparator 10 logically ANDing the strobe signal into the proper converter. Thus, memory 3 presents the binary information to D to A's 4, 5, 6 and 7 which feed the signals to cathode ray tubes 15 and 16; which image the papers being conveyed past their faces by the conveyors 17 and 18.

The various components and associated electronics enumerated and referred to above, are known to those skilled in the art and available for use in digital computer/CRT printout systems, and need no further description.

If desired, additional CRT's can be added to the drawing system, each performing the same or different function. For example, a CRT with a 2" x 8" face plate images paper; while an identical CRT images cards; a third with a 1/4" x 1/4" face plate images 16 mm. film, e.g., at 36 frames/sec. for movies including alphanumeric and graphic movies, while a fourth with a 1/4" x 1/4" face plate images 35 mm. film for storage, blow back to large sizes, wall displays and read-only memories for the computer; all continuously generated by the computer. Thus the multiplicity of CRT's can replace a like multiplicity of the conventional peripheral readout equipments. Alternatively, ultraviolet lasers can be employed in place of the CRT's.

In other CRT printouts embodiment, an ordinary TV receiver is modified to accommodate a second CRT, in parallel with the viewing picture tube, but as a printing head, along with a photosensitive paper supply and a transport means for moving the paper past the printing face on demand. In operation, a TV station generates two different video signals; one, standard programming is displayed on the picture tube, the other—which may be different from the other in both information and format, and

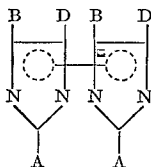
is generated by a TV camera or a computer character generator processing inputs from a wire service or other news source—is separated from the first and routed to the printing tube which delivers the hard copy as continuous tone images. To obtain high print rates from a raster display format, a band scan method is employed. In this method a small analog computer generates a long period ramp (a linear current waveform applied to the deflection yoke to move the cathode ray beam linearly across the tube face.) The vertical 60 c.p.s. ramp taken from the TV camera is mixed with the computer's ramp and a D.C. bias level. With the composite vertical waveform, the camera slowly scans the object at a rate, r . On the printing tube, the object appears to move slowly across the screen. At the printing tube face, the paper to be imaged is driven at a constant rate, r , equal to the scan rate. Hence, the relative motion is zero during the contact printing stage. Band scanning is useful with any raster display and it is not limited to TV raster displays; it is useful in general for imaging continuously moving paper, permits the use of relatively small (5" diameter or less) CRT's, and minimizes phosphor burning by minimizing the power density at the phosphor.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for obvious modifications will occur to those skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

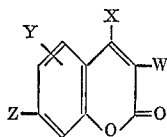
1. A photosensitive composition which comprises:

- (A) a hexaarylbiimidazole that absorbs in the ultraviolet principally at wave lengths below 300 mμ and is dissociable to triarylimidazolyl radicals by radiation of such wave lengths, and is represented by the structural formula



wherein A, B and D each represent phenyl, biphenyl, naphthyl, furyl or thienyl which can contain substituents having Hammett sigma values in the range -0.5 to $+0.8$ and having no hydrogens reactive toward methyl magnesium iodide, and

- (B) a coumarin which has a light absorption maximum in the ultraviolet at wave lengths greater than 300 mμ, that is stronger than the absorption of the biimidazole at such wave lengths, and is capable of transferring the absorbed energy corresponding to such wavelengths to the biimidazole, and which has the formula



wherein

- X and Y are each hydrogen, lower alkyl or lower alkoxy; Z is hydrogen, lower alkyl, lower alkoxy or dilower alkylamino; W is hydrogen, lower alkyl, phenyl containing a lower alkoxy group in the o or p-position, or phenyl containing a substituted amino group in the o or p-position; and wherein at

least one of W and Z is other than hydrogen or lower alkyl.

2. The composition of claim 1 which contains additionally an oxidizable leuco dye selected from the group consisting of aminotriarylmethanes, aminoxanthenes, aminothioxanthenes, amino-9,10-dihydroacridines, aminophenoxazines, aminophenothiazines, aminodihydrophenazines, aminodiphenylmethanes leuco indamines, aminohydrocinnamic acids, hydrazines, leuco indigoid dyes, amino-2,3-dihydroanthraquinones, tetrahalo-p,p'-biphenols, 2(p-hydroxyphenyl)-4,5-diphenylimidazoles, phenethylanilines, 10-acyl-aminodihydrophenazines, 10-acyl-aminophenothiazines, 10-acyl-aminophenoxazines, and aminotriarylmethanes wherein the methane hydrogen has been replaced by alkylthio, benzylthio, 2-phenylhydrazino or alkoxycarbonyl.

3. The composition of claim 2 which contains additionally an image fixing system comprising

- (A) a photooxidant which is activatable at wavelengths different from those required to activate the coumarin-biimidazole system, does not photooxidize leuco dye to dye, and is reducible in its photoactivated state to a second reductant, said photooxidant being selected from the class consisting of quinones, ketones, phenazines, acridines, phenoxazinones, quinolines, phenanthrolines, isoquinolines, and anils, and

- (B) a first reductant which is a reductant for the photooxidant but not for the photoactivated biimidazole, said first reductant reducing the photoactivated photooxidant to the second reductant, said first reductant being selected from the class consisting of ethers, esters, alcohols, acetals, aldehydes, amides, and compounds containing allylic or benzylic hydrogen.

4. The composition of claim 2 wherein the leuco dye is a triarylmethane wherein at least two of the aryl groups are phenyl having a para- R_1R_2N substituent in which R_1 and R_2 are C_1 - C_{10} alkyl, 2-hydroxyethyl, 2-cyanoethyl, benzyl or phenyl, and having an ortho C_1 - C_6 alkyl, C_1 - C_6 alkoxy, fluoro, chloro, or bromo substituent, and the third aryl group can be the same as the first two or can be thienyl, furyl, phenyl or substituted phenyl.

5. The composition of claim 1 wherein the coumarin is a 7-diloweralkylamino-4-lower alkyl coumarin.

6. The composition of claim 1 wherein the coumarin is a 7-lower alkoxy coumarin.

7. The composition of claim 1 wherein the coumarin is 7-diethylamino-4-methyl coumarin.

8. The composition of claim 1 wherein the A, B and D groups contain substituents having Hammett sigma values in the range -0.4 to $+0.4$.

9. The composition of claim 8 wherein each A is a phenyl ring bearing an ortho substituent selected from fluorine, chlorine, bromine, lower alkyl and lower alkoxy.

10. The composition of claim 9 wherein each B and D group is a phenyl ring.

11. The composition of claim 4 wherein the coumarin is 7-diethylamino-4-methyl coumarin; the biimidazole is 2-(o-chlorophenyl)-4,5-bis(m-methoxyphenyl) imidazolyl dimer and the leuco dye is an acid salt of trist(N,N-diethylamino-o-tolyl)methane.

12. A coating composition comprising the composition of claim 4 dissolved in an "inert solvent."

13. A coating composition comprising the composition of claim 4 and an inert substrate.

14. The composition of claim 3 where the photooxidant is "a quinone" and the first reductant is an "ether having abstractable hydrogen," an ester having abstractable hydrogen, a lower alkyl nitrilotriacetate or a lower alkyl nitrilotripropionate.

15. The composition of claim 14 wherein the photooxidant is pyrenequinone or phenanthraquinone and the first reductant is a polyalkylene glycol or an aryl phenoxy polyoxyethylene ethanol.

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21

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22

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