United States Patent [11] **3,630,736**

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Continuation-in-part of application Ser. No. 728,781, May 31, 1968, now Patent No. 3,445,234, which is a continuation-in-part of application Ser. No. 426,421, Jan. 18, 1965, now abandoned, which is a continuation-in-part of application Ser. No. 234,538, Oct. 31, 1962, now abandoned. This application May 19, 1969, Ser. No. 826,009

The portion of the term of the patent subsequent to May 20, 1986, has been disclaimed.

[54] LEUCO DYE/HEXAARYLBIIMIDAZOLE COMPOSITIONS AND PROCESSES

17 Claims, No Drawings

[52] U.S. Cl. **96/48,** 96/90
[51] Int. Cl. **G03c 5/24**
[50] Field of Search 96/48, 90

[56] **References Cited**

UNITED STATES PATENTS

3,445,234	5/1969	Cescon et al.	96/90

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ABSTRACT: Process for deactivating selected photosensitive, color-forming compositions against color formation by removing solvent from the compositions until they are substantially dry, and maintaining such dry compositions at a temperature below the activation temperature of the compositions; especially compositions comprising an admixture of selected hexaarylbiimidazoles and selected leuco dyes dispersed in a thermoplastic binder.

LEUCO DYE/HEXAARYLBIIMIDAZOLE COMPOSITIONS AND PROCESSES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 728,781, filed May 31, 1968, now U.S. Pat. No. 3,445,234, which is a continuation-in-part of now-abandoned application Ser. No. 426,421, filed Jan. 18, 1965, which is a continuation-in-part of now-abandoned application Ser. No. 234,538, filed Oct. 31, 1962.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is directed to a process for temporarily deactivating photosensitive color-forming compositions and to certain compositions useful in the process.

2. Description of the Prior Art

Hexaarylbiimidazole/leuco dye compositions have been found to be of use in photographic applications because of their ability to rapidly form permanent colored images upon exposure to photoirradiation, particularly ultraviolet light. However, since they are photosensitive in the ultraviolet and visible light wavelength regions and form color upon exposure to such light, it is difficult to prevent color formation in such compositions upon exposure to ambient room light, sunlight, or daylight, and thus it is difficult to handle the compositions.

It has been found, however, that such compositions can be temporarily deactivated to permit handling in the presence of room light, sunlight, or daylight by essentially freeing them of solvent and maintaining them at a temperature below their activation temperatures.

SUMMARY OF THE INVENTION

Accordingly, the process of this invention is a process for deactivating a photosensitive color-forming composition comprising an admixture of

a. a 2,2′,4,4′,5,5′-hexaarylbiimidazole wherein each aryl group contains up to 26 carbon atoms and is selected from carbocyclic and heterocyclic aromatic systems, and

b. at least one dye in the leuco form oxidizable to a differently colored compound, with the proviso that when the resultant dye is cationic, there is also present an acid which forms a salt with the leuco form of the dye, and

c. optionally, a binder within which (a) and (b) are dispersed;

which process comprises removing solvent that was employed in the preparation of the composition, followed by maintaining the composition at a temperature below its activation temperature. The solvent should be removed at least to the extent that the amount of color formed on irradiation is significantly less than the amount formed on irradiation in the presence of gross amounts of solvent.

Preferred compositions are those in which components (a) and (b) are dispersed in a binder.

DESCRIPTION OF THE INVENTION

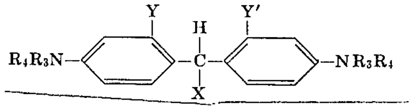
A. The Leuco Dye

This component of the photosensitive color-forming compositions described herein is the reduced form of the dye having one or two hydrogen atoms, or other removable group, the removal of which together with an additional electron in certain cases produces the dye. Since the leuco form of the dye is essentially colorless, or in some instances it may be of a different color or of a less intense shade than the parent dye, it provides a means of producing an image when the leuco form is oxidized to the dye. This oxidation is accomplished by having present in intimate admixture with the leuco form of the dye a dimer of a 2,4,5-triarylimidazolyl radical (i.e., a hexaarylbiimidazole). The dimer of the imidazolyl radical is activated by light, normally ultraviolet wavelengths from about 2,000 A. to about 4,200 A., and when irradiated with such light, it splits into free imidazolyl radicals. These free radicals react with the leuco form of the dye to produce a colored image against a background of unirradiated and, therefore, unchanged material.

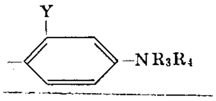
A large number of dyes in the leuco form have been found to be readily converted to the parent dye by free 2,4,5-triarylimidazolyl radicals by the above-described mechanism and are well adapted to provide new and useful image-forming compositions. Dyes in the leuco form which are operative according to the 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, phenethylanilines, 10-acylaminophenoxazines, 10-acylaminophenothiazines, 10-acylaminodihydorphenazines; or alkylthio, benzylthio-, 2-phenylhydrazino- and alkoxycarbonyl-derivatives of triphenylmethane, and the like. These classes of leuco dyes are described in greater detail in Cescon & Dessauer U.S. application Ser. No. 728,781, filed May 13, 1968; Cescon, Dessauer & Looney U.S. Pat. No. 3,423,427; Cescon, Dessauer & Looney U.S. application Ser. No. 290,583, filed June 26, 1963. Read U.S. Pat. No. 3,395,018 and Read U.S. Pat. No. 3,390,997 disclosed the leuco dyes having removable groups other than hydrogen.

The preferred leucos are the aminotriarylmethanes. Preferably the aminotriarylmethane is one wherein at least two of the aryl groups are phenyl groups having (a) an R_1R_2N substituent in the position para to the bond to the methane carbon atom wherein R_1 and R_2 are each groups selected from hydrogen, C_1 to C_{10} alkyl, 2-hydroxyethyl, 2-cyanoethyl, benzyl or phenyl, and (b) a group ortho to the bond to the methane carbon atom which is selected from lower alkyl, lower alkoxy, fluorine, chlorine, bromine, or butadienylene which when joined to the phenyl group forms a naphthalene ring; and the third aryl group, when different from the first two, is selected from thienyl, furyl, oxazylyl, pyridyl, thiazolyl, indolyl, indolinyl, benzoxazolyl, quinolyl, benzothiazolyl, phenyl, naphthyl, or such aforelisted groups substituted with lower alkyl, lower alkoxyl, methylenedioxy, fluoro, chloro, bromo, amino, lower alkylamino, lower dialkylamine, lower alkylthio, hydroxy, carboxy, carbonamido, lower carbalkoxy, lower alkylsulfonyl, lower alkylsulfonamido, C_6 to C_{10} arylsulfonamido, nitro or benzylthio. Preferably the third aryl group is the same as the first two.

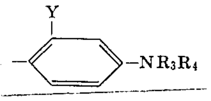
Particularly preferred aminotriarylmethanes have the following structural formula:



wherein R_3 and R_4 are selected from lower alkyl (preferably ethyl) or benzyl, Y and Y′ are lower alkyl (preferably methyl) and X is selected from



p-methoxyphenyl, 2-thienyl, phenyl, 1-naphthyl, 2,3-dimethoxyphenyl, 3,4-methylene-dioxyphenyl, or p-benzothiophenyl. Preferably X is selected from



phenyl, 1-naphthyl, or p-benxothiophenyl.

Specific examples of the leuco dyes include:

a. Aminotriarylmethanes

bis(4-amino-2-butylphenyl)(p-dimethylaminophenyl)methane
bis(4-amino-2-chlorophenyl)(p-aminophenyl)methane
bis(4-amino-3-chlorophenyl)(o-chlorophenyl)methane
bis(4-amino-3-chlorophenyl)phenylmethane
bis(4-amino-3,5-diethylphenyl)(o-chlorophenyl)methane
bis(4-amino-3,5-diethylphenyl)(o-ethoxyphenyl)emthane
bis(4-amino-3,5-diethylphenyl)(p-methoxyphenyl)methane
bis(4-amino-3,5-diethylphenyl)phenylmethane
bis(4-amino-3-ethylphenyl)(o-chlorophenyl)methane
bis(p-aminophenyl)(4-amino-m-tolyl)methane
bis(p-aminophenyl)(o-chlorophenyl)methane
bis(p-aminophenyl)(p-chlorophenyl)methane
bis(p-aminophenyl)(2,4-dichlorophenyl)methane
bis(p-aminophenyl)(2,5-dichlorophenyl)methane
bis(p-aminophenyl)(2,6-dichlorophenyl)methane
bis)p-aminophenyl)pehnylmethane
bis(4-amino-o-tolyl)(p-chlorophenyl)methane
bis(4-amino-o-tolyl)(2,4-dichlorophenyl)methane
bis(p-anilinophenyl)(4-amino-m-tolyl)methane
bis(4-benzylamino-2-cyanophenyl)(p-aminophenyl)methane
bis(p-benzylethylaminophenyl)(p-chlorophenyl)methane
bis(p-benzylethylaminophenyl)(p-diethylaminophenyl)methane
bis(p-benzylethylaminophenyl)(p-dimethylaminophenyl)methane
bis(4-benzylethylamino-o-tolyl)(p-methoxyphenyl)methane
bis(p-benzylethylaminophenyl)-phenylmethane
bis(4-benzylethylamino-o-tolyl)(o-chlorophenyl)methane
bis(4-benzylethylamino-o-tolyl)(p-diethylaminophenyl)methane
bis(4-benzylethylamino-o-tolyl)(4-diethylamino-o-tolyl)methane
bis(4-benzylethylamino-o-tolyl)(p-dimethylaminophenyl)methane
bis[2-chloro-4-(2-diethylaminoethyl)ethylaminophenyl](o-chloro-phenyl)methane
bis[p-bis(2-cyanoethyl)aminophenyl]phenylmethane
bis[p-(2-cyanoethyl)ethylamino-o-tolyl](p-dimethylaminophenyl)methane
bis[p-(2-cyanoethyl)methylaminophenyl](p-diethylaminophenyl)methane
bis(p-dibutylaminophenyl)[p-(2-cyanoethyl)methylaminophenyl]methane
bis(p-dibutylaminophenyl)(p-diethylaminophenyl)methane
bis(4-diethylamino-2-butoxyphenyl)(p-diethylamino-phenyl)methane
bis(4-diethylamino-2-fluorophenyl)o-tolylmethane
bis(p-diethylaminophenyl)(p-aminophenyl)methane
bis(p-diethylaminophenyl)(4-anilino-1-naphthyl)methane
bis(p-diethylaminophenyl)(m-butoxyphenyl)methane
bis(p-diethylaminophenyl)(o-chlorophenyl)methane
bis(p-diethylaminophenyl)(p-cyanophenyl)methane
bis(p-diethylaminophenyl)(2,4-dichlorophenyl)methane
bis(p-diethylaminophenyl)(4-diethylamino-1-naphthyl)methane
bis(p-diethylaminophenyl)(p-diemthylaminophenyl)methane
bis(p-diethylaminophenyl)(4-ethylamino-1-naphthyl)methane
bis(p-diethylaminophenyl)2-naphthylmethane
bis(p-diethylaminophenyl)(p-nitrophenyl)methane
bis(p-diethylaminophenyl)2-pyridylmethane
bis(p-diethylamino-m-tolyl)(p-diethylaminophenyl)methane
bis(4-diethylamino-o-tolyl)(o-chlorophenyl)methane
bis(4-diethylamino-o-tolyl)(p-diethylaminophenyl)methane
bis(4-diethylamino-o-tolyl)(p-diphenylaminophenyl)methane

bis(4-diethylamino-o-tolyl)phenylmethane
bis(4-diemthylamino-2-bromophenyl)phenylmethane
bis(p-dimethylaminophenyl)(4-anilino-1-naphthyl)methane
bis(p-dimethylaminophenyl)(p-butylaminophenyl)methane
bis(p-dimethylaminophenyl)(p-sec. butylethylamino-phenyl)methane
bis(p-dimethylaminophenyl)(p-chlorophenyl)methane
bis(p-diemthylaminophenyl)(p-diethylaminophenyl)methane
bis(p-dimethylaminophenyl)(4-dimethylamino-1-naphthyl)methane
bis(p-dimethylaminophenyl)(6-dimehtylamino-m-tolyl)methane
bis(p-dimethylaminophenyl)(4-dimethylamino-o-tolyl)methane
bis(p-dimethylaminophenyl)(4-ethylamino-1-naphthyl)methane
bis(p-dimethylaminophenyl)(p-hexyloxyphenyl)methane
bis(p-dimethylaminophenyl)(p-methoxyphenyl)methane
bis(p-dimethylaminophenyl)(5-methyl-2-pyridyl)methane
bis(p-dimethylaminophenyl)2-quinolylmethane
bis(p-dimethylaminophenyl)o-tolylmethane
bis(p-dimethylaminophenyl)(1,3,3-trimethyl-2-indolinylidene-methyl)methane
bis(4-dimethylamino-o-tolyl)(p-aminophenyl)methane
bis(4-dimethylamino-o-tolyl)(o-bromphenyl)methane
bis(4-dimethylamino-o-tolyl)(o-cyanophenyl)methane
bis(4-dimethylamino-o-tolyl)(o-fluorophenyl)methane
bis(4-dimethylamino-o-tolyl)1-naphthylmethane
bis(4-dimethylamino-o-tolyl)phenylmethane
bis(p-ethylaminophenyl)(o-chlorophenyl)methane
bis(4-ethylamino-m-tolyl)(o-methoxyphenyl)methane
bis(4-ethylamino-m-tolyl)(p-methoxyphenyl)methane
bis(4-ethylamino-m-tolyl)(p-dimethylaminophenyl)methane
bis (4-ethylamino-m-tolyl)(p-hydroxyphenol)methane
bis[4-ethyl(2-hydroxyethyl)amino-m-tolyl](p-diethylaminophenyl)methane
bis[p-(2-hydroxyethyl)aminophenyl](o-chlorophenyl)methane
bis[p-(bis(2-hydroxyethyl)aminophenyl](4-diethylamino-o-tolyl)methane
bis[p-(2-methoxyethyl)aminophenyl]phenylmethane
bis(p-methylaminophenyl)(o-hydroxyphenyl)methane
bis(p-propylaminophenyl)(m-bromophenyl)methane
tris(4-amino-o-tolyl)methane
tris(4-anilino-o-tolyl)methane
tris(p-benzylaminophenyl)methane
tris[4-bis(2-cyanoethyl)amino-o-tolyl]methane
tris[p-(2-cyanoethyl)ethylaminophenyl]methane
tris(p-dibutylaminophenyl)methane
tris(p-di-n-butylaminophenyl)methane
tris(4-diethylamino-2-chlorophenyl)methane
tris(p-diethylaminophenyl)methane
tris(4-diethylamino-o-tolyl)methane
tris(p-dihexylamino-o-tolyl)methane
tris(4-diemthylamino-o-toly)methane
tris(p-hexylaminophenyl)methane
tris[p-bis(2-hydroxyethyl)aminophenyl]methane
tris(p-methylaminophenyl)methane
tris(p-dioctadecylaminophenyl)methane
tris(4-diethylamino-2-fluorophenyl)methane
tris(4-dimethylamino-2-fluorophenyl)methane
bis(2-bromo-4-diethylaminophenyl)phenylmethane,
bis(2-butoxy-4-diethylaminophenyl)phenylmethane,
bis(4-diethylamino-o-tolyl)(p-methoxyphenyl)methane,
bis(4-diethylamino-2-methoxyphenyl)(p-nitrophenyl)methane,
bis(4-diethylamino-1-naphthyl)(4-diethylamino-o-tolyl)methane,
bis(4-diethylamino-o-tolyl)1-naphthylmethane,
bis(4-diethylamino-o-tolyl)phenylmethane,
tris(4-dimethylamino-2-chlorophenyl)methane,
bis(4-dimethylamino-2,5-dimethylphenyl)phenylmethane,
bis(4-dimethylamino-o-tolyl)(o-bromophenyl)methane,
bis(4-ethylbenzylamino-o-tolyl)(p-methoxyphenyl)methane,
tris(p-dicotylamino-o-tolyl)methane,
bis(4-diethylamino-o-tolyl)-4-methoxy-1-naphthyl methane
bis(4-diethylamino-o-tolyl)-3,4,5-trimethoxyphenyl methane
bis(4-diethylamino-o-tolyl)-p-hydroxyphenol 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]-methylsulfonanilide
4-[bis(4-diethylamino-o-tolyl)-methyl]-p-tolylsulfonanilide
bis(4-diethylamino-o-tolyl)-p-nitrophenyl methane
bis(4-diethylamino-o-tolyl)(2-diethylamino-4-methyl-5-thiazolyl)methane
bis(4-diethylamino-o-tolyl)(2-diethylamino-5-methyl-6-benzoxazolyl)methane
bis(4-diethylamino-o-tolyl)(2-diethylamino-5-methyl-6-benzothiazolyl)methane
bis(4-diethylamino-o-tolyl)(1-ethyl-2-methyl-3-indolyl)methane
bis(4-diethylamino-o-tolyl)(1-benzyl-2-methyl-3-indolyl)methane
bis(4-diethylamino-o-tolyl)(1-ethyl-2-methyl-5-methoxyl-3-indolyl)methane
bis(1-o-xylyl-2-methyl-3-indolyl)(4-diethylamino-o-tolyl)methane
bis(4-diethylamino-o-tolyl)(1-ethyl-5-indolinyl)methane
bis(1-isobutyl-6-methyl-5-indolinyl)(4-diethylamino-o-tolyl)methane
bis(4-diethylamino-o-tolyl)(8-methyl-9-julolindinyl)methane
bis(4-diethylamino-2-acetamidophenyl)(4-diethylamino-o-tolyl)methane
4-[bis(4-diethylamino-o-tolyl)methyl]-N-ethylacetanilide
bis[4-(1-phenyl-2,3-dimethyl-5-pyrazolinyl)](4-diethylamino-o-tolyl)methane
bis(4-diethylamino-o-tolyl)(7-diethylamino-4-methyl-3-coumarinyl)methane
bis(4-diethylamino-o-tolyl)(4-acrylamidophenyl)methane
bis(4-diethylamino-o-tolyl)(p-benzylthiophenyl)methane
bis(4-diethylamino-o-tolyl)(4-isopropylthio-3-methylphenyl)methane
bis(4-diethylamino-o-tolyl)(4-chlorobenzylthiophenyl)methane
bis(4-diethylamino-o-tolyl)(2-furyl)methane
bis(4-diethylamino-o-tolyl)(3,4-methylenedioxyphenyl)methane
bis(4-diethylamino-o-tolyl)(3,4-dimethoxyphenyl)methane
bis(4-diethylamino-o-tolyl)(3-methyl-2-thienyl)methane
bis(4-diethylamino-o-tolyl)(2,4-dimethoxyphenyl)methane
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-methylene-dioxyphenyl)methane,
bis(4-diethylamino-2-fluorophenyl)(p-benzylthiophenyl)methane,
bis(4-diethylamino-2-fluorophenyl)(3,4-methylene-dioxyphenyl)methane,
bis(4-diethylamino-o-tolyl)(p-methylthiophenyl)methane,
bis(4-diethylamino-o-tolyl)2-thienylmethane,
bis(4-dimethylamino-2-hexylphenyl)(p-butylthiophenyl)methane,
bis[4-(N-ethylanilino)-o-tolyl](3,4-dibutoxyphenyl)methane,
bis[4-bis(2-hydroxyethyl)amino-2-fluorophenyl](p-benzylthiophenyl)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-1naphthyl methane,
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.

b. Aminoxanthenes

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

In addition to the above-listed aminoxanthenes the leuco forms of the xanthene dyes identified by the following Color Index numbers may be used, 45000, 45005, 45010, 45015, 45050, 45070, 45090, 45095, 45100, 45105, 45150.

c. 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

d. 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.

Also included are the leuco forms of the acridine dyes having CI numbers 46000, 46005B, 46010, 46015, 46020, 46025, 46030, 46035, 46040, 46055, 46060, 46065, 46070, 46075, 46080.

e. Aminophenoxazines

3,7-bis(diethylamino)phenoxazine
9-dimethylamino-benzo[a]phenoxazine
and the leuco forms of phenoxazine dyes having CI numbers 51000, 51180, 51185, 51190, 51195.

f. Aminophenothiazines

3,7-bis(benzylamino)phenothiazine and the leuco form of phenothiazine dyes having CI numbers 52000, 52010, 52015, 52020, 52025, 52030, 52035, 52050.

g. Aminodihydorphenazines

3,7-bis(benzylethylamino)-5,10-dihydro-5-phenylphenazine
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-dihydrophenazine
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(diemthylamino)-5,10-dihydro-5-methylphenazine

Also included are the leuco forms of the phenazine dyes having CI numbers 50035, 50040, 50045, 50200, 50205, 50206, 50210, 50216, 50220, 50225, 50235, 50240.

h. Aminodiphenylmethanes

1,4-bis[bis-p(diethylaminophenyl)methyl]piperazine
bis(p-diethylaminophenyl)anilinomethane
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-dimethylaminiphenyl)anilinomethane
1,1-bis(dimethylaminophenyl)ethane
1,1-bis(dimethylaminophenyl)heptane
bis(4-methylamino-m-tolyl)aminoethane.

i. Leuco indamines

4-amino-4′-dimethylaminodiphenylamine
p-(p-dimethylaminoanilino)phenol
and the leuco forms of indamine and indophenol dyes having CI numbers 49400, 49405, 49410, 49700.

j. Aminohydrocinnamic acids (cyanoethanes, leuco methines)
4-amino-α, β-dicyanohydrocinnamic acid, methyl ester
4-anilino-α, β-dicyanohydrocinnamic acid, methyl ester
4-(p-chloroanilino)-αβ-dicyanohydrocinnamic acid, methyl ester
α-cyano-4-dimethylaminohydrocinnamamide
α-cyano-4-dimethylaminohydrocinnamic acid, methyl ester
α, β-dicyano-4-diethylaminohydrocinnamic acid, methyl ester
αβ-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
αβ-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
and substituted hydrocinnamic acids which are the leuco forms of dyes having CI numbers 48000, 48001, and 48005.

k. 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-indolinyl)-2-(3-N-phenylcarbamoyl-4-hydroxy-1-naphthyl)hydrazine

l. 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.

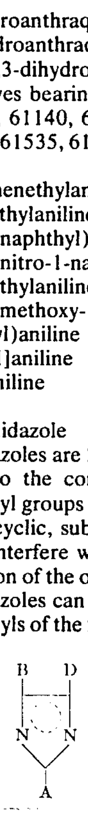
m. Amino-2,3-dihydroanthraquinones
1,4-dianilino-2,3-dihydroanthraquinone
1,4-bis(ethylamino)-2,3-dihydroanthraquinone
and leuco forms of dyes bearing CI numbers 61100, 61105, 61107, 61116, 61120, 61140, 61500, 61505, 61510, 61515, 61520, 61525, 61530, 61535, 61540, 61565, 61650.

o. Phenethylanilines
N-(2-cyanoethyl)-p-phenethylaniline
N,N-diethyl-p-phenylethylaniline
N,N-dimethyl-p-[2-(1-naphthyl)ethyl]aniline
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
p-(p-nitrophenethyl)aniline
p-phenethylaniline

B. The Hexaarylbiimidazole

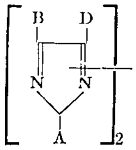
The hexaarylbiimidazoles are 2,4,5-triarylimidazolyl dimers that are dissociable to the corresponding triarylimidazolyl radicals wherein the aryl groups may be the same or different, carbocyclic or heterocyclic, substituent free or bearing substituents that do not interfere with the dissociation step and the subsequent oxidation of the oxidizable substrate.

The hexaarylbiimidazoles can be represented as the dimers of 2,4,5-triarylimidazolyls of the formula



wherein A, B, and D are aryl radicals, as previously defined.

The hexaarylbiimidazoles can also be represented by the formula



wherein A, B, and D stand for aryl radicals described above. Upon dissociation, the dimer forms the corresponding 2,4,5-triarylimidazolyl radical. The B and D groups can normally carry 0–3 substituents, the A-group 0–4 substituents.

The aryl groups include one- and two-ring aryls, such as phenyl, biphenyl, naphthyl, pyridyl, furyl and thienyl. Suitable inert substituents on the aryl groups have Hammett sigma (para) values in the −0.5 to 0.8 range and are other than hydroxyl, sulfhydryl, amino, alkylamino or dialkylamino. Preferably, these inert substituents are free of Zerewitinoff hydrogen i.e., have no hydrogens reactive towards methyl magnesium iodide. Representative substituents and their sigma values, (relative to H=0.00), as given by Jaffe, Chem. Rev. 53, 219–233 (1953) are: methyl (−0.17), ethyl (−0.15), t-butyl (−0.20), phenyl (0.01), butoxy (−0.32), phenoxy (−0.03), fluoro (0.06), chloro(0.23), bromo (0.23), iodo (0.28), methylthio (−0.05), nitro (0.78), ethoxycarbonyl (0.52), and cyano (0.63). The foregoing substituents are preferred; however, other substituents which may be employed include trifluoromethyl (0.55), chloromethyl (0.18), carboxyl (0.27), cyanomethyl (0.01), 2-carboxyethyl (−0.07), and methylsulfonyl (0.73). Thus the substituents may be halogen, cyano, lower hydrocarbyl (including alkyl, halo alkyl, cyanoalkyl, hydroxyalkyl and aryl), lower alkoxy, aryloxy, lower alkylthio, arylthio, sulfo, alkyl sulfonyl, arylsulfonyl, and nitro, and lower alkylcarbonyl. In the foregoing list, alkyl groups referred to therein are preferably of one to six carbon atoms; while aryl groups referred to therein are preferably of six to 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, chloro, fluoro, bromo and benzo 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 ortho substituents are fluorine, chlorine, bromine, methyl and methoxy groups; especially chloro. Such dimers tend less than other dimers to form color when the light-sensitive compositions are applied to and dried on substrates at somewhat elevated temperatures, e.g., in the range 70°–100° C.

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 dimers of the imidazolyl radicals other than those given in the examples which fall within the scope of the invention are listed below, in terms of the substituents of the aryl groups when aryl is phenyl and in terms of other aryl groups than phenyl, by way of illustrating the activatable imidazolyl dimers which may be employed in the composition.

I. PHENYL SUBSTITUTED IMIDAZOLYL RADICALS

Substituents of phenyl rings attached at—		
2-position	4-position	5-position
o-Acetoxy		
o-Benzyl		
o-Benzylthio	o-Benzylthio	o-Benzylthio.
p-[4,5-bis(p-methoxyphenyl)-2-imidazolyl].		
o-Bromo	p-Bromo	
Do	o-Methoxy	o-Methoxy.
2-bromo-4-phenyl		
o-n-Butoxy		
N-butylacetamido		
o-Butylthio		
p-t-Butylthio		
o-Butyryloxy		

I. PHENYL SUBSTITUTED IMIDAZOLYL RADICALS—Continued

Substituents of phenyl rings attached at—		
2-position	4-position	5-position
o-Chloro		
Do	o-Chloro	o-Chloro.
Do	p-Chloro	
Do	do	p-Chloro.
Do	3,4-dichloro	
Do	p-Methoxy	
Do	m-Pentyloxy	
Do	m-Pentyloxy	m-Pentyloxy.
Do	m-Methoxy	m-Methoxy.
Do	p-Propionyloxy	
2-Chloro-4-phenyl		
2-Chloro-4-methoxy		
p-Chloro	p-Chloro	p-Chloro.
o-Cyano		
Do	p-t-Butyl	
Do	do	p-t-Butyl.
Do	p-Cyano	0-Cyano.
Do	p-Methoxy	p-Methoxy.
2,3-dibromo		
2,4-dibromo		
2,6-dibutyl		
o-Dibutylsulfamoyl		
2,4-dichloro	o-Bromo	
2,6-dichloro		
2,6-dichloro	p-Butoxy	p-Butoxy.
3,4-dichloro	2,4-dimethoxy	
2,4-dicyano	p-Cyano	p-Cyano.
2,6-dicyano		
3,5-dicyano-4-methoxy		
p-(2,2-dicyanovinyl)		
2,4-diethoxy		
o-Diethylsulfamoyl		
2,5-difluoro	p-Cyano	
2,5-difluoro	do	p-Cyano.
2,3-dimethoxy		
2,4-dimethoxy	o-Chloro	
Do	o-Chloro	o-Chloro.
Do	2,4-dimethoxy	
Do	do	2,4-dimethoxy.
Do	o-Methoxy	
Do	p-Methoxy	
Do	do	p-Methoxy.
Do	m-Phenylthio	
Do	do	m-Phenylthio.
3,4-dimethoxy	o-Cyano	
Do	2,4-dipentyl	2,4-dipentyl.
2,4-dimethoxy		
o-Dimethylcarbamoyl		
2,4-dipentyl	2,4-dipentyl	2,4-dipentyl.
p-(4,5-diphenyl-2-imidazolyl)		
p-[4-(4,5-diphenyl-2-imidazolyl) phenyl].		
2,4-dipropoxy		
2,4-dinaphthylthio		
2-nitro	m-Methoxy	m-Methoxy.
2-nitro-5-methoxy		
2,4-dipropoxy	o-Diethylcarbamoyl.	
o-dipropylcarbamoyl		
p-Ethoxy		
Do	p-Diethylsulfamoyl.	
o-Ethoxycarbonyl		
o-Ethyl		
o-N-ethylbutyramido		
o-Ethylthio		
o-N-ethylvaleramido	p-t-Pentyl	p-t-Pentyl.
o-Fluoro	o-Methoxy	o-Methoxy.
p-Hexyloxy	p-Methoxycarbonyl.	p-Methoxycarbonyl.
o-Methoxy		
Do	p-Chloro	
Do	o-Methylthio	o-Methylthio.
Do	p-Nitro	
Do	do	p-Nitro.
Do	p-Phenylsulfonyl	
Do	do	p-Phenylsulfonyl.
p-Methoxy	p-Benzylthio	p-Benzylthio.
Do	m-Butyryloxy	m-Butyryloxy.
Do	2-chloro-4,5-dimethoxy.	2-chloro-4,5-dimethoxy.
Do	m-Dimethylcarbamoyl.	
o-Methoxycarbonyl		
Do	p-N-ethylphenyl sulfamoyl.	
p-Methoxycarbonyl		
4-methoxy-3-nitro		
2-methoxy-4-phenyl		
o-Methyl	p-Benzoyloxy	p-Benzoyloxy.
Do	o-Methyl	o-Methyl.
m-N-methylacetamido	p-Methoxy	p-Methoxy.
o-N-Methylacetamido	o-N-ethylbutyramido.	o-N-ethylbutyramido.
Do	o-N-methylacetamido.	
Do	do	o-N-Methylacetamido.
o-N-Methylpropionamido		
o-Methylthio		
p-Methylthio	p-Methoxy	p-Methoxy.
Do	p-Methylthio	
Do	do	p-Methylthio.
o-1-naphthyl	p-Phenoxy	
o-2-naphthyl		
m-Nitro	2,4-dimethoxy	2,4-dimethoxy.
Do	2,4-dimethylthio	
o-t-Pentyl		
p-Pentyl		
o-Pentyloxy		
p-Pentyloxy		
o-Pentyloxycarbonyl		
o-Phenoxy		
Do	3,4,5-trimethoxy	3,4,5-trimethoxy.
p-Phenoxy	p-Methoxy	
m-Phenyl	p-Phenyl	p-Phenyl.
o-Phenyl		
Do	p-Methoxycarbonyl.	p-Methoxycarbonyl.
Do	m-Pentyloxycarbonyl.	
Do	do	m-Pentyloxycarbonyl.
Do	p-Phenyl	p-Phenyl.
p-Phenyl	do	Do.
p-Phenyldydroazonomethyl		
o-Phenylthio	p-1-naphthylthio	p-1-Naphthylthio.
p-Phenylthio	p-Methoxy	p-Methoxy.
o-Propoxy		
2,4,6-tribromo		
2,4,6-tributyl		
2,4,6-tri-methyl		
2,3,5-trichloro		
2,4,6-trichloro		
Do	o-Butylthio	
2,4,6-tricyano	p-Cyano	p-Cyano.
2,4,6-triethoxy		
p-Trifluoromethoxy		
2,3,4-trimethoxy		
2,4,6-trimethoxy		
3,4,5-trimethoxy		
3,4,5-trimethyl	3,4,5-trimethyl	3,4,5-trimethyl.
2,4,6-tripropoxy		
	o-t-Butoxy	
	p-Butoxy	
	4-t-butoxy-2-methoxy.	
	p-t-Butyl	
	p-t-Butylthio	p-t-Butylthio.
	o-Chloro	2,5-dimethoxy.
	2-chloro-4-methoxy.	
	2-cyano-2,4-dimethoxy.	
	2,3-dichloro	2,4-dimethylthio.
	2,4-dimethoxy	
	do	2,4,5-trimethoxy.
	2,5-dimethyl	2,5-dimethyl.
	2,5-dipentyl	
	o-Methoxy	o-Methoxy.
	do	p-Methoxy.
	4-methoxy-3-nitro	2-methoxy-4-methyl.
	o-Methyl	2,4,5-trimethoxyl
	p-Methyl	
	p-Methylthio	
	do	p-Methylthio.
	p-Pentyl	
	p-t-Pentyloxy	p-t-Pentyloxy.
	2,4-5-trimethoxy	p-Methoxy.
	2,4,5-trimethyl	

II. Other ring groups than phenyl in imidazolyl radical

2-position	4-position	5-position
2,4-dipentylphenyl	2-naphthyl	2-naphthyl.
p-Methoxyphenyl	do	Do.
o-Methoxycarbonyl phenyl	do	Phenyl.
(1-methoxy-2-naphthyl)	Phenyl	Do.
(3-methoxy-2-naphthyl)	do	Do.
1-naphthyl	do	Do.
o-Pentyloxycarbonyl phenyl	2-naphthyl	2-naphthyl.
3-pyridyl	Phenyl	Phenyl.

The above dimers of 2,4,5-triarylimidazolyl radicals which provide light-activated components for the invention compositions are characterized by the property of dissociating into two triarylimidazolyl free radicals when illuminated with ultraviolet light of the aforementioned wavelength. Such a dissociation may be detected, and the existence of the free radicals discerned, by electron paramagnetic resonance, by ultraviolet spectra, and by visible spectra.

The triarylimidazoles which are intermediates for the biimidazoles or dimers of the 2,4,5-triarylimidazolyl radicals are prepared as follows:

A. By refluxing, in glacial acetic acid containing ammonium acetate, benzil, a related compound such as a binaphthoyl or a naphthylphenylglyoxal, or an appropriately substituted compound of the benzil type with an aromatic aldehyde such as benzaldehyde, naphthaldehyde, a phenanthraldehyde or with picolinaldehyde, a nicotinaldehyde, a thiophenecarboxaldehyde or a suitably substituted aldehyde of these types. The reaction product is precipitated by drowning the reaction mass, e.g., in water or in an ammonium hydroxide solution, and is recovered by filtration. The product can then be purified by recrystallization from a solvent. This procedure is described by Davidson et al., J. Org. Chem. 2, 319 (1937).

B. By refluxing a benzoin and one of the above-mentioned aldehydes in methanol in the presence of copper acetate and ammonia. This is an adaptation of the procedure of Wiedenhagen et al., Ber. 70, 570 (1937).

C. By heating a benzil or above-named related compound with an aforementioned aldehyde at 180° to 190° C. in formamide solution as disclosed in Belgian Pat. 589,417.

The intermediate triarylimidazole is dissolved in ethanol containing potassium hydroxide and then oxidized to the corresponding biimidazole or dimer of the triarylimidazolyl radical by treatment with aqueous potassium ferricyanide. The desired product precipitates from the reaction mixture, is isolated by filtration, and is washed free from ferricyanide with water. This procedure is described by Hayashi et al., Bull. Chem. Soc. Japan, 33, 565 (1960). The triarylimidazole may also be oxidized by agitating a benzene or chloroform solution of the imidazole with lead dioxide (PbO_2) or by passing a saturated solution of the imidazole in benzene through a column packed with PbO_2 and diatomaceous earth.

These dimers exist in isomeric forms which are differentiated by the manner in which the radicals composing the dimers are linked together and which exhibit different spectral and thermotropic properties.

The preferred method, involving oxidative dimerization of the corresponding triarylimidazole 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 triaryl imidazolyl radicals which are the effective oxidizing agents of the invention compositions.

C. The Leuco Dye/Hexaarylbiimidazole Admixture

THe hexaarylbiimidazoles are phototropic, i.e., they change color upon exposure to suitable radiation and return to their original color after the radiation source is removed. They may by virtue of this property contribute some color to the image that is produced when a leuco dye composition containing a biimidazole is irradiated. This color is, however, fugitive. It fades at varying rates depending upon the substituent group in the biimidazole, and is not relied upon to color the image produced by radiation. The leuco dye component provides the permanent colored image when reacted upon by the free radicals of the biimidazole when the biimidazole is activated, e.g., by ultraviolet light. The primary purpose of the biimidazole, then, is to furnish a photosensitive material which, upon radiation, is activated to react with the leuco dye to develop color in accordance with the pattern of an irradiated area.

The hexaarylbiimidazoles are also thermally dissociable to triarylimidazolyl radicals and thus their combinations with leuco dyes are also thermally activatable for color formation. Therefore, for use in the processes of this invention, the compositions must be maintained below the decomposition (dissociation) temperature of the biimidazole. In this regard, preferred biimidazoles are those having ortho-substituted phenyl groups at the 2 and 2′ positions, the substituents being ortho to the point of attachment to the imidazole ring; and preferred leuco dyes are triarylmethanes wherein at least two of the aryls are p-substituted aminophenyl groups having a selected substituent ortho to the methane carbon, as defined earlier.

The leuco form of the dye and the dimer of the 2,4,5-triarylimidazolyl radical may be mixed in mole ratios within the range from about 10:1 (leuco dye:dimer) to about 1:10. In the presence of a small quantity of solvent, including moisture, such mixtures will produce on substrates a permanent image when irradiated with ultraviolet light. The preferred ratio range is 2:1 to 1:2, while the preferred ratio is about 1:1.

D. Acids for Leuco Dye Salt Formation

With the leuco form of dyes which have amino or substituted amino groups within the dye structure and which are characterized as cationic dyes, an amine salt-forming mineral acid, organic acid, or an acid from a compound supplying acid is employed. The amount of acid usually varies from 0.33 mole to 1 mole per mole of amino nitrogen in the dye. The preferred quantity of acid is about 0.5 to 0.9 mole per mole of amino nitrogen. Acid in an amount in excess of that required to form a salt with the amino nitrogen should be avoided because excess acid reduces the reactivity of the light-activated biimidazole and renders the composition less light sensitive. Representative acids which form the required amine salts are hydrochloric, hydrobromic, sulfuric, nitric, phosphoric, acetic, oxalic, p-toluenesulfonic, trichloroacetic, trifluoroacetic and perfluoroheptanoic acid. Other acids such as acids in the "Lewis" sense or acid sources which may be employed in the presence of water or moisture include zinc chloride, zinc bromide, and ferric chloride.

With the leuco form of dyes which produce dyes by the removal of two hydrogen atoms, acid is not needed and in most cases should be avoided to prevent desensitizing the light-sensitive composition.

E. Binders

Polymeric binders may also be present in the light-sensitive compositions to thicken them or adhere them to substrates. Binder can also serve as a matrix for the color-forming composition and the mixture may be cast, extruded, or otherwise formed into unsupported imageable films. Light-transparent and film-forming polymers, are preferred. Examples are ethyl cellulose, polyvinyl alcohol, polyvinyl chloride, polystyrene, polyvinyl acetate, poly(methyl methacrylate), cellulose acetate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, chlorinated rubber, copolymers of the above vinyl monomers, and gelatin. Binder or matrix amounts vary from about 0.5 to about 200 parts, preferably 3 to 15 parts, by weight per part of combined weight of aminotriarylmethane and photooxidant. In general, from 0.5 to 10 parts are used as adhesive or thickener, while higher amounts are used to form the unsupported films.

Preferred binders are those which aid in maintaining the deactivated state by being solids which are sufficiently rigid to prevent the biimidazole/leuco dye molecules from diffusing together, but which soften or melt on heating sufficiently to permit the hexaarylbiimidazole and leuco dye components to move and react together to induce color formation. Such binders are normally solvent-soluble, substantially amorphous thermoplastic polymers. Preferably the binder is one that has a glass transition temperature (T_g) below the dissociation temperature of the biimidazole. Such binders include poly(vinylacetate) 30° C., poly(n-propyl acrylate) 35° C., poly(chlorotrifluoroethylene) 45° C., poly(ethyl methacrylate) 65° C., poly(vinyl chloride) 82° C., polystyrene 100° C., poly(methyl methacrylate) 105° C., poly(methacrylonitrile) 120° C., polyvinylformal 105° C., poly(vinylacetal) 82° C., poly(vinyl butyral) 49° C., cellulose triacetate 105° C., cellulose acetate butyrate 50° C., ethyl cellulose 43° C., ethylene/vinyl acetate copolymers 28° to 85° C., cellulose acetate butyrate 135° C., 25 percent ethyl acrylate/75 percent methyl methacrylate copolymer 59° C., 2 percent methyl acrylate/31 percent 2-ethylhexylacrylate/67 percent methyl methacrylate copolymer 52° C., 0.5 percent methyl acrylate/39.5 percent methyl methacrylate/60 percent n-butyl methacrylate copolymer 57° C., poly(n-butyl methacrylate) 22° C., and poly(vinyl pyrrolidone) 86° C.

T_g may vary with polymer average molecular weight and molecular weight distribution. The binder composition may also contain inert infusible filler such as titanium dioxide, organophilic colloidal silica, bentonite, powdered glass, and also heat-absorbing materials to facilitate the heat-activation step such as graphite and flake metal, in minor, noninterfering amounts. Preferably they are polymethylmethacrylate, copolymer of methyl acrylate/2-ethylhexyl acrylate/methyl methacrylate, copolymer of methyl acrylate/methyl methacrylate/n-butyl methacrylate, copolymer of ethyl acrylate/methyl methacrylate, or poly(vinyl acetate), cellulose acetate butyrate.

F. The Process

Solvents inert toward the leuco dye or salt thereof when used, the hexaarylbiimidazole, and the binder when present, are conveniently employed to dissolve these components, mix them and provide fluid homogeneous media for application to substrates.

In general, a solvent should dissolve all components, i.e., the leuco dye, biimidazole and binder, if employed, but be inert to the photosensitive materials. It should also be inert to and wet but not dissolve the substrate to which the photosensitive materials are applied.

To obtain the final deactivated coating, in accordance with the invention, the solvent must be removed substantially completely as by evaporation, or otherwise prevented from performing its plasticizing, fluidizing function, as by freezing, such that the image-forming capability is substantially diminished upon subsequent irradiation.

For deactivation by solvent evaporation the solvent quantity is ordinarily substantially removed, e.g., to 0.5 percent by weight of the composition or less. In heating for solvent evaporation, at atmospheric or reduced pressures, temperatures are generally kept below 150° C., preferably below 100° C., and the solvents are chosen accordingly. Volatile solvents such as methanol, ethanol, acetone, and the like may be removed from the compositions and from cellulosic substrates readily and substantially completely enough to reduce the photosensitivity of the composition to the desired low levels by simple drying at ordinary temperatures. On the other hand N,N-dimethylformamide, N,N-diethylacetamide, and dimethylsulfoxide tend to be so strongly held that prolonged heating under vacuum is often necessary for their complete removal. Other volatile solvents which may be used include 1-propanol, 2-propanol, n-butanol, methyl acetate, ethyl acetate, benzene, toluene, methyl ethyl ketone, 3-pentanone, methylene chloride, chloroform, 1,1,2-trichloroethane, tetrahydrofuran, dioxane, and mixtures thereof in various proportions as may be required to dissolve the various components selected for use in the composition. For deactivation by freezing any solvent (plasticizer), volatile or nonvolatile, may be used that crystallizes or solidifies to a rigid mass such as a hard glass.

G. Other Ingredients in the Compositions

The compositions may also contain sensitizers that extend the spectral sensitivity of the imaging system to longer wavelengths. Sensitizers include (a) hydroxyphthalein dyes such as fluorescein, the eosins, the phloxines, the erythrosins, rose bengal, and others disclosed in U.S. application Ser. No. 654,720, filed July 20, 1967, and assigned to the assignee herein, (b) acridine dyes, particularly 3,6-bis(alkylamino)acridines such as 3,6-bis(dimethylamino)acridine hydrochloride, 3,6-bis(diethylamino)acridine hydrochloride, 2,7-dimethyl-3,6-bis(ethylamino)acridine hydrochloride, 2,7-dimethyl-3,6-bis(diethylamino)acridine hydrochloride, 3,6-bis(dimethylamino)-10-methyl acridinium methanesulfonate and others disclosed in U.S. application Ser. No. 654,721, filed July 20, 1967 and assigned to the assignee herein, (c) carbocyanine dyes such as 3,3′-diethyl oxacarbocyanine iodide, 3,3′-diethyl-9-methyl oxacarbocyanine iodide, 3,3′-9-trimethyl oxacarbocyanineiodide 3,3′-diethyl-4,5,4′,5′-dibenzoxacarbocyanine p-toluene sulfonate, 3,3′-diethyl oxaselenacarbocyanine iodide, 3,3′-di-n-butyl-9-methylthiacarbocyanine iodide, 3,3′-diethyl thiaselenacarbocyanine iodide, and 3,3′-diethyl selenacarbocyanine iodide, and others disclosed in U.S. application Ser. No. 654,676, filed July 20, 1967, and assigned the the assignee herein, (d) coumarins such as 7-dimethylamino-4-methylcoumarin, 7-dimethylamino-4-butylcoumarin, 7-diethylamino-4-ethylcoumarin, and others disclosed in U.S. application Ser. No. 622,526, filed Mar. 13, 1967, and assigned to the assignee herein, and (e) aminophenylketones such as p-dimethylaminobenzophenone, p,p-bis(dimethylamino)-benzophenone, p,p′-bis(diethylamino)benzophenone and others disclosed in U.S. application Ser. No. 654,677, filed July 20, 1967, and assigned to the assignee herein. For sensitized imaging, sensitizers of classes (a), (b), and (c) above are generally used in amounts ranging from about 0.01 to 0.1 mole, preferably 0.01–0.05 mole, per mole of the biimidazole; those of classes (d) and (e) above in amounts ranging from about 0.1 to 2 moles, preferably 0.4 to 0.6 mole, per mole of the biimidazole.

H. Preparation of Compositions

A common procedure is to dissolve a leuco dye ranging in concentration from about 0.5 percent by weight to the solubility limit in a volatile solvent, and to add a hexaarylbiimidazole in an amount equivalent on a molar basis to the leuco dye. Optionally, a binder or a sensitizer as described above may also be added to the solution. The leuco dye selected depends upon the color and quality of the image desired. Two or more leuco dyes may be used in combination to obtain a particular color or shade of color or to provide a neutral gray or black image.

In applying a solution to paper, films, fabrics, or to the surfaces of rigid substrates such as glass, wood, or metals the solution may be sprayed, brushed, applied by a roller or an immersion coater, flowed over the surface, picked up by immersion or spread by other means. Complete coverage of the substrate may be attained or a pattern of the light-sensitive composition may be printed on the substrate. In impregnating paper, for instance, such concentrations of solution and pickup by the paper are made so as to provide from about 0.01 mg./in.^{2} to about 5.0 mg./in.^{2} of leuco dye and the equivalent amount of biimidazole activator. Images of greater and lesser intensity of color are provided by the application of greater and lesser amounts of leuco dye to the substrate. For coating roll papers and films there may be used 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 0.1–1.5 mil, usually around 0.3–0.5 mil on paper, 0.8–1.1 mil on film).

The substrates bearing the solution of the leuco dye and biimidazole, and optionally the binder, may be dried simply by allowing the solvent to evaporate at room temperature. They also may be dried under vacuum at room temperature by forced air solvent evaporation, or at elevated temperatures, as by radiant heating at atmospheric or reduced pressures, as discussed under solvents.

In use, the compositions are usually coated upon inert substrates, materials commonly used in the graphic arts and in decorative applications. These include 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, polymethylmethacrylate, polyvinylchloride; textile fabrics; glass, wood and metals. Opaque as well as transparent substrates can be used. Substrates which bear the photosensitive components as a coating on the reverse side of the substrate, i.e., on the side away from the ultraviolet light source used for image formation, must be transparent not only in the visible region but transparent to a portion of the ultraviolet range useful for image formation.

I. USE

The photosensitive color-forming capabilities of the deactivated compositions can be restored by (a) adding a small amount of solvent, described above, followed by exposure to photoradiation or (b) by heating to melting or softening followed by exposure to photoradiation, or (c) by heating to above the thermal dissociation temperature of the biimidazole.

Any convenient source of activating light may be used to activate the light-sensitive composition and induce the formation of an image. In general, light sources that supply radiation in the region between about 2,000 A. and about 4,200 A. are useful in producing images with the leuco dyehexaarylbiimidazole-solvent compositions on numerous substrates. Among the light sources which have been employed are sunlamps, electronic flashguns, germicidal lamps, ultraviolet lamps providing specifically light of short wavelength (2,537 A.) and lamps providing light of long wavelength (2,537 A.). Visible light sources may be used when the compositions also contain sensitizers that are responsive to visible light and transfer adsorbed energy to the biimidazole. The light exposure time will vary from a fraction of a second to several minutes depending upon the intensity of the light, its distance from the light-sensitive composition, and nature and amount of the light-sensitive composition available, and the intensity of color in the image desired. There may also be used coherent light beams, for example, pulsed nitrogen lasers, argon ion lasers and ionized Neon II lasers, whose emissions fall within or overlap the ultraviolet absorption bands of the triarylimidazolyl dimer.

The compositions and methods of this invention are broadly useful for optical printing and anywhere it is desirable to capture images as in photography, patternmaking reproducing written, printed, drawn, or typed mater, and recording radiation signals as line graphics, alphanumerics or other characters. The applied heat and light radiations can be passed through stencils, negatives or transparencies including halftone and continuous tone negative and positives in contact with or projected onto the radiation-sensitive image-fix composition; or, the activating and imaging radiations can be reflected for impingement on the radiation-sensitive material from printed or typed copy or objects that are opaque or transmit radiation poorly. Multiple copies can be made using a single imaging exposure by stacking radiation-transparent assemblies comprising the imaging composition coated on a transparent substrate such as UV-transparent film, paper or glass and maintaining the assembly at the activating temperature while irradiating. The ultimately desired dye optical density pattern can be constructed stepwise, according to one or more patterns, by exposing previously unexposed areas to suitable heat and light radiation and/or by reexposing previously underexposed areas (i.e., areas wherein the maximum obtainable optical density has not yet been fully developed) to one or more additional heat and light exposures. Such "add on" capability and versatility of the invention compositions is particularly useful in recording information and creating electronically generated displays and graphics.

J. Examples

EXAMPLE 1

Seven hundred fifty milligrams of polymethylmethacrylate was dissolved under agitation with warming in excess acetone. This solution was combined with 0.9 ml. of a 0.1 molar tris(2-methyl-4-diethylamino-phenyl)methane solution in acetone, 0.6 ml. of a 0.3 molar p-toluene-sulfonic acid solution in acetone, and 1.8 ml. of a 0.05 molar 2,2'-(o-chlorophenyl)-4,4',5,5'-tetrakis(m-methoxyphenyl)biimidazole solution in acetone. The resulting solution was then concentrated to a volume of about 15 ml., cast to a 5 mil wet thickness on 5 mil thick Mylar polyester film, allowed to air-dry for 5 minutes, then heated for 1 minute under an IR lamp to complete the acetone evaporation.

The coated film was substantially colorless in room daylight. After contact-flashing with a xenon lamp five times consecutively at 25° C. it was still substantially colorless. It was then heated on a hotplate to about 105° C. and again contact-flashed five times, whereupon it developed a strong blue color.

The xenon flashlamp used above is available as HiCo light and emits ultraviolet and visible light approximating sunlight at a high intensity of about 1×10^5 milliwatts/cm.^{2} for about 0.001-second flash duration.

EXAMPLE 2

The following composition:

Ingredient	Quantity
Acetone	10 milliliters
2,2'-(o-chlorophenyl)-4,4',5,5'-tetrakis(m-methoxyphenyl)biimidazole	0.624 gram
tris(2-methyl-4-diethylaminophenyl)-methane	0.300 gram
p-Toluenesulfonic acid monohydrate	0.342 gram

was coated on Whatman No. 1 filter paper. One-third of the coated area, while still wet, was flashed once with the xenon lamp described in example 1. The reflectance optical density of the blue color that developed on irradiation was 1.11. The coated paper was then dried in an oven at 45° C. for 5 minutes. One-half of the previously unexposed coated area was then flashed once with the xenon lamp; the resulting optical density was 0.47. The remaining unexposed, but dried portion of the coated paper was then moistened with acetone and flashed once with the xenon lamp. The resulting optical density was 1.15.

EXAMPLES 3–9

The following compositions can be deactivated against color formation by heating below 100° C., and optionally, applying a vacuum. They can be reactivated by adding a small amount of solvent.

EXAMPLE 3

Tris(4-diethylamino-o-tolyl)methane trihydrochloride
2,2'-Bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole
Benzene/N,N-dimethylformamide or ethanol or acetone solvent

EXAMPLE 4

Bis(4-dimethylamino-o-tolyl)pehnylmethane dihydrochloride
2,2'-Bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole
Benzene/N,N,-dimethylformamide enzene/N,N-dimethylformamide solvent

EXAMPLE 5

Tris(4-diethylamino-o-tolyl)methane trihydrochloride
2,2',4,4',5,5'-hexaphenylbiimidazole
Benzene/N,N-dimethylformamide solvent

EXAMPLE 6

Tris(4-diethylamino-o-tolyl)methane trihydrochloride
Bis(4-diemthylamino-o-tolyl)methane dihydrochloride
2,2',Bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl biimidazole
Benzene/N,N-dimethylformamide solvent

EXAMPLE 7

Tris(4-diethylamino-o-tolyl)methane trihydrochloride
Bis(4-dimethylamino-o-tolyl)methane dihydrochloride
4,4'-dihydroxy-3,3',5,5'-tetrabromobiphenyl
2,2'-Bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl biimidazole
Benzene/N,N-dimethylformamide solvent

EXAMPLE 8

Tris(4-diethylamino-o-tolyl)methane trihydrochloride
2,2′-bis(p-chlorophenyl)-4,4′,5,5′-tetrakis(p-methoxy-phenyl)biimidazole
Acetone

EXAMPLE 9

Tris(2-methyl-4-diethylaminophenyl)methane tritoluenesulfate
2,2′-(o-chlorophenyl)-4,4′,5,5′-tetrakis(m-methoxyphenyl)biimidazole
Acetone
Polymethylmethacrylate or polyvinyl acetate or ethyl acrylate/methyl methacrylate copolymer

EXAMPLE 10

Example 1 was repeated with the following materials: 170 mg. of polymethacrylate in excess acetone, 0.5 ml. of dimethyl phthalate, 0.9 ml. of 0.1 molar tris(2-methyl-4-diethylaminophenyl)methane in acetone, 1.2 ml. of 0.3 molar p-toluenesulfonic acid in acetone, and 3.6 ml. of 0.05 molar 2,2′-(o-chlorophenyl)-4,4′,5,5′-tetrakis(m-methoxyphenyl)biimidazole in acetone. The acetone solution was concentrated to 10 ml. coated to a 5 mil thickness on 1.0 mil thick polyester film, and allowed to air-dry overnight at about 25° C. in the dark.

A section of the air-dried film was contact-flashed three times with the xenon lamp at room temperature. Only a faint blue color developed. Another section was heated to 105° C. and contact flashed twice. A deep blue color developed. Blue, room temperature-stable, positive prints were obtained on contact flashing through a silver negative at 105° C.

EXAMPLE 11

A coating solution was prepared from the ingredients tabulated below:

Ingredient	Quantity, g.
Acetone	24.0
poly(methylmethacrylate) as "Lucite" 140, T_g = about 100° C.	5.2
2,2′-(o-chlorophenyl)-4,4′,5,5′-tetrakis(m-methoxyphenyl)biimidazole	0.56
p-Chlorophenyl-bis(2-methyl-4-diethylaminophenyl)methane	0.16
p-Toluenesulfonic acid monohydrate	0.14

The solution was coated on film as described in example 1 and allowed to air-dry for 2 hours. Contact flashing five times with the xenon lamp through a silver negative produced no color at room temperature but produced a dark green print at 100° C.

EXAMPLES 12–15

Coating compositions were prepared from the following:

Ingredient	% by Weight
Acetone	83.
Binder as described below	14.
2,2′-(o-chlorophenyl)-4,4′,5,5′-tetrakis(m-methoxyphenyl) biimidazole	1.5
tris(2-methyl-4-diethylaminophenyl)-methane	0.70
p-Toluenesulfonic acid monohydrate	0.80

The solutions were coated on bleached sulfite paper at 50° C. to evaporate the acetone and give 0.6 mil thick dry coatings having a dry coating weight of 0.9 lb./100 ft.^{2}

Samples of the coated papers were irradiated through a stencil with the high-intensity UV xenon lamp (one flash) at

50° C. and at 100° C. The results are tabulated below:

Example	Binder[1]	Image, optical density at— 50°	100°
12	Poly(methyl methacrylate)	0.28	0.46
13	2% methyl acrylate/31% 2-ethylhexyl acrylate/67% methyl methacrylate copolymer.	0.20	0.61
14	0.5% methyl acrylate/39.5% methyl methacrylate/60% n-butyl methacrylate.	0.18	0.54
15	The polymer of Example 6 plus 7-diethylamino-4-methyl coumarin, 0.22% by wt. of the coating composition as sensitizer.	0.17	1.11

[1] The co-polymer compositions are in percent by weight.

The unexposed areas of the imaged papers developed little or no color on subsequent exposure to the xenon lamp at room temperature. In addition, all the above coated papers were found to have a high degree of stability towards ambient light at room temperatures as determined by exposure to fluorescent desk lamps and low-intensity ultraviolet from a Blacklight Blue Lamp.

EXAMPLES 16–19

Coated papers were prepared as described in examples 12–15 using binders as tabulated below. Samples of the coated papers were irradiated under the tabulated conditions with a Blacklight Blue Lamp emitting low-intensity ultraviolet light (0.75 milliwatts/cm.^{2}). The exposure results are expressed below as increase in reflectance optical density (O.D.) over the unexposed material.

		O.D. increase		
Example	Binder	25° (40 sec.)	50° (40 sec.)	65° (10 sec.)
16	Poly(methyl methacrylate)	0.05	0.12	
17	25% ethyl acrylate/75% methyl methacrylate copolymer.	0.07		0.26
18	Poly(vinyl acetate)	0.05	0.35	0.35
19	Cellulose acetate butyrate, filtered grade EAB 531-1.	0.07	0.07	

EXAMPLE 20

The following coating composition was prepared:

Ingredient	% by Weight
Acetone	82.9
Polyvinylacetate (Tg = 30° C.)	13.96
2,2′-(o-chlorophenyl)-4,4′,5,5′- tetrakis(m-methoxyphenyl)biimidazole	1.43
Tris(2-methyl-4-diethylaminophenyl) methane	0.70
p-Toluenesulfonic acid monohydrate	0.80
7-Diethylamino-4-methyl coumarin	0.22

The solution was coated on bleached sulfite paper at 50° C. to evaporate the acetone and give a 0.6 mil thick dry coating having a dry coating weight of 0.9 lb./100 ft.^{2}.

Samples of the coated paper were irradiated at 25°, 50° and 75° C. with a Blacklight Blue Lamp (low-intensity UV, 0.75 milliwatts/cm.^{2}) for 10 seconds, with the following results expressed as increase in reflectance optical density (O.D.).

Temp., °C.	O.D. Increase
25	0.03 (substantially, colorless)
50	0.34 (blue)
75	0.55 (deeper blue)

EXAMPLES 21–22

Coating compositions were prepared as described in examples 12–15 except that tris(4-dimethylaminophenyl)methane (Crystal Violet) and tris(2-fluoro-4-diethylaminophenyl)methane (F-dye) were employed as the leuco dye.

The compositions were coated on "Mylar" polyester film as described in example 1. Samples of the coated films were exposed to Black Lamp Blue Light irradiation at the temperatures and times tabulated below, with the following results expressed as increase in the transmission optical density over the unexposed film.

		O.D. Increase		
Example	Leuco Dye	25° 40 Sec.	50° 10 Sec.	50° 40 Sec.
21	Crystal Violet	0.19	0.21	0.36
22	F-Dye	—	0.07	0.26

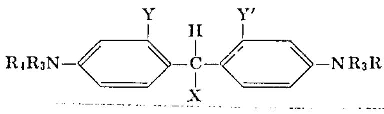
The preceding representative examples may be varied within the scope of the present total specification disclosure, as understood and practiced by one skilled in the art, to achieve essentially the same results.

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.

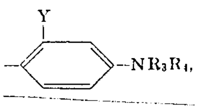
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Process for deactivating a photosensitive color-forming composition against color formation which comprises
   a. removing essentially all solvent from a composition comprising an admixture of
      1. a 2,2',4,4',5,5'-hexaarylbiimidazole wherein each aryl group contains up to 26 carbon atoms and is selected from carbocyclic and heterocyclic aromatic systems, and
      2. at least one dye in the leuco form oxidizable to a differently colored compound, with the proviso that when the resultant dye is cationic, there is also present an acid which forms a salt with the leuco form of the dye,
   b. and maintaining the composition at a temperature below its thermal color-forming activation temperature.

2. The process of claim 1 wherein
   the 2,2',4,4',5,5'-hexaarylbiimidazole is a hexaphenylbiimidazole in which the 2 and 2' phenyl groups each contain one ortho substituent selected from lower alkyl, lower alkoxy, chloro, fluoro or bromo, and wherein the 4,4',5,5-phenyl groups are either unsubstituted or each contain one to three lower alkoxy groups;
   the dye in the leuco form is a strong acid salt of an aminotriarylmethane dye of the formula



wherein R_3 and R_4 are each lower alkyl or benzyl, Y and Y' are each lower alkyl and X is

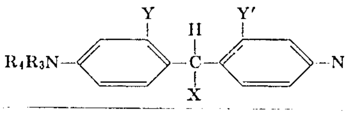


p-methoxyphenyl, 2-thienyl, phenyl, 1-naphthyl, 2,3-dimethoxyphenyl, 3,4-methylenedioxyphenyl, or benzylthiophenyl;

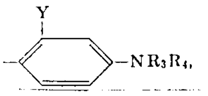
and the solvent is removed by evaporation.

3. Process for preparing and deactivating a photosensitive color-forming composition against color formation which comprises
   a. preparing a composition comprising
      1. a 2,2',4,4',5,5'-hexaarylbiimidazole wherein each aryl group contains up to 26 carbon atoms and is selected from carbocyclic and heterocyclic aromatic systems, and
      2. at least one dye in the leuco form having one or two removable hydrogen atoms, the removal of which forms a differently colored compound, with the proviso that when the leuco form has only one removable hydrogen and the resultant dye is cationic there is also present an acid which forms a salt with the leuco form of the dye, by intimately mixing components (1) and (2) together in a volatile carrier solvent;
   b. coating a substrate with the solution prepared in step (a);
   c. evaporating the solvent essentially completely, and
   d. maintaining the coated composition at a temperature below its thermal color-forming activation temperature.

4. The process of claim 3 wherein
   the 2,2',4,4',5,5'-hexaarylbiimidazole is a hexaphenylbiimidazole in which the 2 and 2' phenyl groups each contain one ortho substituent selected from lower alkyl, lower alkoxy, chloro, fluoro or bromo, and wherein the 4,4',5,5'phenyl groups are either unsubstituted or each contain one to three lower alkoxy groups;
   the dye in the leuco form is a strong acid salt of an aminotriarylmethane dye of the formula



wherein R_3 and R_4 are each lower alkyl or benzyl, Y and Y' are each lower alkyl and X is



p-methoxyphenyl, 2-thienyl, phenyl, 1-naphthyl, 2,3-dimethoxyphenyl, 3,4-methylenedioxyphenyl, or benzylthiophenyl;

and wherein the substrate is film or paper.

5. A composition consisting essentially of
   1. a 2,2',4,4',5,5'-hexaarylbiimidazole wherein each aryl group contains up to 26 carbon atoms and is selected from carbocyclic and heterocyclic aromatic systems, and
   2. at least one dye in the leuco form that is oxidizable to a differently colored compound, with the proviso that when the resultant dye is cationic there is also present an acid which forms a salt with the leuco form of the dye, and
   3. a light transparent film-forming polymeric binder within which components (1) and (2) are dispersed.

6. The composition of claim 5 wherein
   the hexaarylbiimidazole is a hexaphenylbiimidazole in which the phenyl groups can contain noninterfering substituents which have Hammett sigma values in the -0.5 to $+0.8$ range;
   the dye in the leuco form is selected from aminotriarylmethanes, aminoxanthanes, 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-acylaminophenoxazines, 10-acylaminophenothiazines, 10-acylaminodihydrophenazines, alkylthiotriphenylmethanes, benzylthiotriphenylmethanes, 2-phenylhydrazinotriphenylmethanes or alkoxycarbonyltriphenylmethanes;
   and the said binder is sufficiently rigid at room temperature to prevent movement of components (1) and (2) but softens on heating sufficiently to permit movement of components (1) and (2) dispersed therein at a temperature below the thermal color-forming activation temperature of the composition.

7. The composition of claim **6** wherein

in the hexaphenylbiimidazole the 2 and 2′ phenyl groups each bear one ortho substituent selected from fluorine, chlorine, bromo, methyl and methoxy; and the 4,4′,5 and 5′ phenyl groups are each either unsubstituted or bear one substituent selected from lower alkyl, lower alkoxy, chloro, fluoro, bromo or benzo,

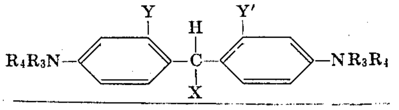
the dye in the leuco form is a strong acid salt of an aminotriarylmethane in the leuco form wherein at least two of the aryl groups are phenyl groups having (a) an R_1R_2N substituent in the position para to the bond to the methane carbon atom wherein R_1 and R_2 are each groups selected from hydrogen, C_1 to C_{10} alkyl, 2-hydroxyethyl, 2-cyanoethyl, benzyl or phenyl, and (b) a group ortho to the bond to the methane carbon atom which is selected from lower alkyl, lower alkoxy, fluorine, chlorine, bromine, or butadienylene which when joined to the phenyl group forms a naphthalene ring; and the third aryl group, when different from the first two, is selected from thienyl, furyl, oxazylyl, pyridyl, thiazolyl, indolyl, indolinyl, benzoxazolyl, quinolyl, benzothiazolyl, phenyl, naphthyl, or such aforelisted groups substituted with lower alkyl, lower alkoxyl, methylenedioxy, fluoro, chloro, bromo, amino, lower alkylamino, lower dialkylamino, lower alkylthio, hydroxy, carboxy, carbonamido, lower carbalkoxy, lower alkylsulfonyl, lower alkylsulfonamido, C_6 to C_{10} arylsulfonamido, nitro or benzylthio,

and the inert binder is a thermoplastic binder within which components (1) and (2) are dispersed, said binder having a glass transition temperature above 25° C. but below the decomposition temperature of components (1) and (2).

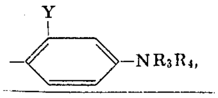
8. The composition of claim **7** wherein

in the hexaphenylbiimidazole, the 2 and 2′ phenyl groups each contain one ortho substituent selected from lower alkyl, lower alkoxy, chloro, fluoro or bromo; and the 4,4′,5 and 5′ phenyl groups are either unsubstituted or each contain one to three lower alkoxy groups;

the dye in the leuco form is a strong acid salt of an aminotriarylmethane dye of the formula



wherein R_3 and R_4 are each lower alkyl or benzyl, Y and Y′ are each lower alkyl and X is



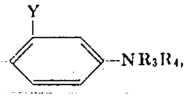
p-methoxyphenyl, 2-thienyl, phenyl, 1-naphthyl, 2,3-dimethoxyphenyl, 3,4-methylenedioxyphenyl, or benzylthiophenyl;

and wherein the binder is a thermoplastic polymer.

9. The composition of claim **8** wherein

in the hexaphenylbiimidazole, the 2 and 2′ phenyl each contain an ortho chloro group; and the 4,4′,5 and 5′ phenyl groups are either unsubstituted or each contain one meta methoxy group;

in the strong acid salt of an aminotriarylmethane R_3 and R_4 are lower alkyl, Y and Y′ are lower alkyl, and X is



or p-chlorophenyl;

and the inert binder is selected from polymethyl methacrylate, methyl acrylate/2-ethylhexyl acrylate/methyl methacrylate copolymer, methyl acrylate/methyl methacrylate/n-butyl methacrylate copolymer, ethyl acrylate/methyl methacrylate copolymer, polyvinyl acetate or cellulose acetate butyrate.

10. The composition of claim **9** wherein

the hexaphenylbiimidazole is 2,2′-(o-chlorophenyl)-4,4′,5,5′-tetrakis(m-methoxyphenyl)biimidazole;

the aminotriarylmethane is tris(2-methyl-4-diethylaminophenyl)methane, and

the binder is polymethylmethacrylate or polyvinyl acetate.

11. The process of claim **1** wherein said composition contains a light transparent film-forming polymeric binder within which components (1) and (2) are dispersed.

12. The process of claim **2** wherein said composition contains a light transparent film-forming polymeric binder within which components (1) and (2) are dispersed.

13. The process of claim **3** wherein said composition contains a light transparent film-forming polymeric binder within which components (1) and (2) are dispersed.

14. The process of claim **4** wherein said composition contains a light transparent film-forming polymeric binder within which components (1) and (2) are dispersed.

15. An image-forming product comprising a supporting base carrying the composition of claim **5**.

16. Paper treated with the composition of claim **5**.

17. Film treated with the composition of claim **5**.

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