PATENT SPECIFICATION

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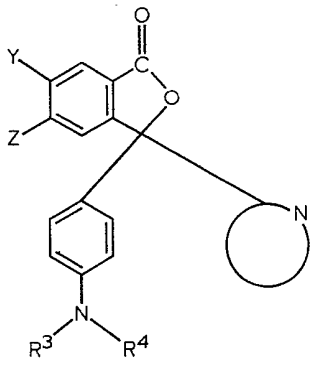
(54) 3-ARYL-3-HETERYLPHTHALIDES AND PREPARATIONS THEREOF

(71) We, STERLING DRUG INC., a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 90 Park Avenue, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

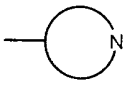
This invention relates to 3-aryl-3-heteroarylphthalides and 3,3-bis(heteroaryl)phthalides useful as color precursors, particularly in the art of carbonless duplicating as, for example, in pressure-sensitive systems, in thermal marking systems and in hectographic or spirit-reproducing copying systems; to substituted 2-(indolylcarbonyl)benzoic acids and 2-(pyrrolylcarbonyl)benzoic acids useful as intermediates to the subject phthalide color precursors; to processes for preparing said phthalides and benzoic acids; and to pressure-sensitive duplicating systems, thermal marking systems and hectographic copying systems containing the same.

Several classes of organic compounds of widely diverse structural types are known to be useful as colorless precursors for carbonless duplicating systems. Among the more important classes, there may be named phenothiazines, for example, benzoyl leuco methylene blue; phthalides with which this invention is concerned, for example, crystal violet lactone; fluorans, for example, 2′ - anilino - 6′ - diethylaminofluoran and 2′ - dibenzylamino - 6′ - diethylaminofluoran; and various other types of colorless precursors currently employed in commercially accepted carbonless copy systems. Typical of the many such systems taught in the prior art are those described in U.S. Patents 2,712,507, 2,800,457 and 3,041,289. Many of the color formers in the prior art suffer one or more disadvantages such as low tinctorial strength, poor light stability, low resistance to sublimation, low susceptibility to copiability of the color-developed form in standard copying machines, for example, a Xerox (Registered Trade Mark) copier, and low solubility in common organic solvents, the latter disadvantage thus requiring the use of specialized and expensive solvents in order to obtain microencapsulated solutions of sufficient concentration for use in pressure-sensitive copying systems.

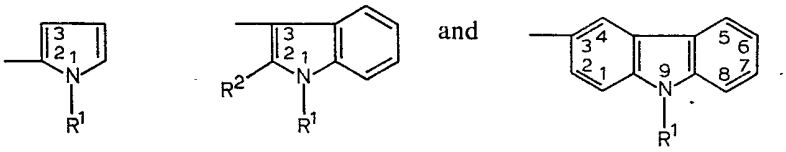
U.S. Patent 3,491,112 discloses in most pertinent part a series of normally colorless phthalides stated to be useful as color formers in pressure-sensitive copying paper which are represented by the structural formula



wherein

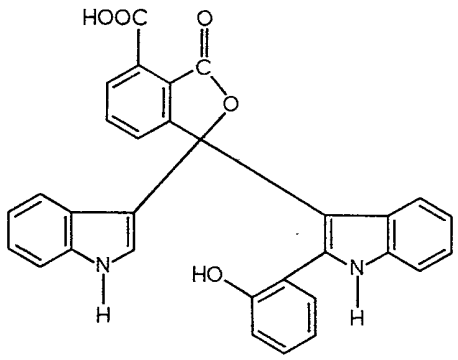


is a heterocyclic radical selected from the group consisting of



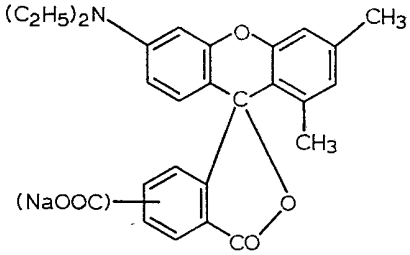
in which R_1 and R_2 are C_1 to C_4 alkyl, phenyl and hydrogen; Z and Y are hydrogen and dialkylamino in which alkyl is C_1 to C_4 alkyl with the proviso that only one Z and Y can be said dialkylamino while the other is hydrogen; and R_3 and R_4 are C_1 to C_4 alkyl.

U.S. Patent 3,779,753 discloses the phthalide having the formula



which is stated to be useful as an optical filter agent "in photographic processes" to protect a selectively exposed photosensitive material from further exposure during processing in the presence of incident light.

British Patent 1,427,318 discloses the interaction of trimellitic anhydride and *m*-diethylaminophenol to obtain a mixture of 4 - diethylamino - 2 - hydroxybenzophenone - 2',4' - dicarboxylic acid and the corresponding 2',5'-dicarboxylic acid isomer. The isomeric mixture is then interacted with 3,5-dimethylphenol in the presence of sulfuric acid followed by treatment with sodium hydroxide to obtain the compound having the structure



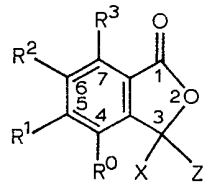
which is stated to be useful as a color former in a spirit reproducing process.

U.S. Patent 3,509,174 discloses 1,2-dimethyl-3-(2-carboxybenzoyl-indole which is stated to be an intermediate to a series of 3,3-bis(3-indolyl)phthalides useful as color formers in pressure-sensitive copying paper.

The present invention provides novel 3-aryl-3-heteroarylphthalides among 3-aryl-3-indolylphthalides, 3-aryl-3-pyrrolylphthalides, 3-aryl-3-carbozolylphthalides and 3,3-bis(heteroaryl)phthalides, particularly 3,3-bis(indolyl)phthalides, which are useful as color formers in pressure-sensitive duplicating systems, in thermal marking systems and in hectographic or spirit-reproducing systems. The compounds develop colored images of good to excellent tinctorial strength, and have the advantages of improved light stability, high resistance to sublimation and

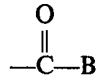
enhanced solubility in common organic solvents. Certain species are also soluble in water and lower alcohols and are therefore of particular utility as color formers in hectographic or spirit-reproducing copying systems.

One aspect of the present invention resides in the novel phthalides, which are particularly useful as colorless precursors in the art of carbonless duplicating, thermal marking and hectograph duplicating, which are 3-X-3-Z-4-R°-5-R¹-6-R²-7-R³ phthalides having the formula

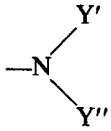


(I)

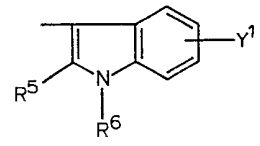
wherein R^0, R^1, R^2 and R^3 each represent hydrogen or halo or when R^0, R^3 and one of R^1 and R^2 are each hydrogen, the other of R^1 and R^2 represents nitro, amino, acetamido, dialkylamino wherein alkyl is non-tertiary C_1 to C_4 alkyl or



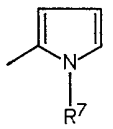
in which B represents —OY or



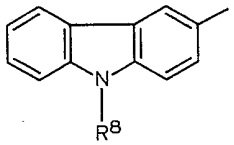
wherein Y is hydrogen, an alkali metal cation, an ammonium cation, a C_1 to C_{18} mono-, di- or trialkylammonium cation, C_1 to C_{18} alkyl, C_2 to C_{18} alkenyl, benzyl or benzyl substituted in the benzene ring thereof by C_1 to C_{12} alkyl, halo or C_1 to C_8 alkoxy; Y′ is hydrogen or C_1 to C_{18} alkyl; Y″ is hydrogen, C_1 to C_{18} alkyl or C_4 to C_{12} N,N-dialkylaminoalkyl; X represents a monovalent radical having the formula



A

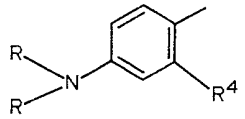


B or

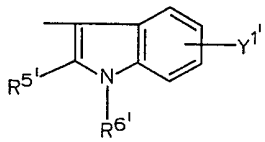


C

Z represents a monovalent radical having the formula



D or



E

where, in the above, R represents non-tertiary C_1 to C_4 alkyl, benzyl or benzyl substituted in the benzene ring by one or two of halo or C_1 to C_3 alkyl, when X has the Formula B or C, R^4 represents acetamido, dialkylamino in which alkyl is non-tertiary C_1 to C_4 alkyl, and when one of R^1 or R^2 represents any of said carboxy or said carbonyl substituents, R^4 further represents hydrogen, C_1 to C_3 alkyl, C_1 to C_4 alkoxy or halo, and when X has the Formula A, one of R^1 and R^2 must represent one of said carboxy or said carbonyl groups and R^4 represents hydrogen, acetamido, dialkylamino in which alkyl is non-tertiary C_1 to C_4 alkyl, C_1 to C_3 alkyl, C_1 to C_4 alkoxy or halo, R^5 and $R^{5'}$ represent hydrogen, C_1 to C_3 alkyl or phenyl, R^6 and $R^{6'}$ represent hydrogen, C_1 to C_{18} alkyl, C_2 to C_4 alkenyl, benzyl or benzyl substituted in the benzene ring by one or two of halo or C_1 to C_3 alkyl, R^7 and R^8 represent hydrogen, C_1 to C_3 alkyl or phenyl, and Y^1 to $Y^{1'}$ represent no or one or

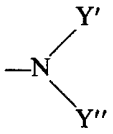
two C_1 to C_3 alkyl, C_1 to C_3 alkoxy, halo or nitro substituents in the benzenoid portion of the indolyl radical with the provisos (i) that X and Z can both simultaneously represent monovalent indolyl moieties only when one of R^1 and R^2 represent said

and (ii) X represents a pyrrolyl or a carbazolyl moiety only when Z represents a 2-R^4-4-N-$(R)_2$-phenyl moiety. The Y^1 and Y^2 substituents referred to throughout are preferably at the 5- or 6-position of the indole ring.

In a particular embodiment in accordance with the above invention of Formula I, Z is a radical of Formula D above and X is a radical of Formula A, B or C above (referred to as Formulas III, IV and V, respectively).

In a second particular embodiment in accordance with the above invention of Formula I, X is a radical of Formula A above and Z is a radical of Formula E above (referred to as Formula VI) wherein the indolyl radicals A and E can be the same or different; R^0 and R^3 and at least one of R^1 and R^2 represent hydrogen and the other represents

in which B represents —OY or



wherein Y is hydrogen, an alkyl metal cation, and ammonium cation, a C_1 to C_{18} mono-, di- or trialkylammonium cation, C_1 to C_{18} alkyl, C_2 to C_{18} alkenyl, benzyl or benzyl or benzyl substituted in the benzene ring thereof by C_1 to C_{12} alkyl, halo or C_1 to C_8 alkoxy; Y′ is hydrogen or C_1 to C_{18} alkyl; Y″ is hydrogen, C_1 to C_{18} alkyl or C_4 to C_{12} N,N-dialkylaminoalkyl; and R^5, $R^{5'}$, R^6, $R^{6'}$, Y^1 and $Y^{1'}$ each have the same respective meanings given in relation to Formula I.

The invention also deals with a pressure-sensitive carbonless duplicating system, thermal marking system or hectographic copy system containing as a color-forming substance a 3-X-3-Z-4-R^0-5-R^1-6-R^2-7-R^3-phthalide according to Formula I, as defined above, and particularly a pressure-sensitive transfer sheet, adapted for use with a receiving sheet having an electron accepting layer, comprising a support sheet coated on one side with a layer of pressure-rupturable microcapsules, said microcapsules containing a liquid solution of a color forming substance comprising at least one compound having Formula I. The invention also deals particularly with a heat responsive record material comprising a support sheet coated on one side with a layer containing a mixture comprising at least one color-forming compound having Formula I and an acidic developer arranged such that application of heat will produce a mark-forming reaction between the color-forming compound and the acidic developer.

Preferred embodiments above-described are those wherein the color-forming component comprises a 3 - [2 - R^4 - 4 - $N(R)_2$ - phenyl] - 3 - (1 - R^5 - 2 - R^6 - 5/6 - Y^1 - 3 - indolyl) - 4 - R^0 - 5 - R^1 - 6 - R^2 - 7 - R^3 - phthalide wherein R, R^0, R^1, R^2, R^3, R^4, R^5, R^6 and Y^1 have the same respective meanings given in relation to Formula III or a 3 - (1 - R^5 - 2 - R^6 - 5/6 - Y^1 - 3 - indolyl) - 3 - (1 - $R^{5'}$ - 2 - $R^{6'}$ - 5/6 - $Y^{1'}$ - 3 - indolyl) - 4 - R^0 - 5 - R^1 - 6 - R^2 - 7 - R^3 - phthalide wherein R^0, R^1, R^2, R^3, R^5, R^6, $R^{5'}$, $R^{6'}$, Y^1 and $Y^{1'}$ have the same respective meanings given in relation to Formula VI.

A further particular aspect of the invention resides in a hectographic or spirit reproducing copying system comprising a transfer sheet coated on one side with a layer containing a color-forming substance comprising a compound according to Formula I wherein R^0, R^3 and one of R^1 and R^2 are each hydrogen, the other of R^1 and R^2 represents

wherein Y is hydrogen, an alkali metal cation, an ammonium cation or a C_1 to C_{18} mono-, di- or trialkylammonium cation.

As used herein the term "halo" includes chloro, fluoro, bromo and iodo. Chloro is the preferred halo substituent because of the relatively low cost and ease of preparation of the required chloro-substituted intermediates and because the other halogens offer no particular advantages over chloro. However the other above-named halo substituents are also satisfactory.

The terms "C_1 to C_4 alkoxy" and "dialkylamino in which alkyl is non-tertiary C_1 to C_4 alkyl" denote saturated, acyclic groups which may be straight or branched as exemplified by methoxy, ethoxy, propoxy, isopropoxy, butoxy, *sec*-butoxy, isobutoxy, *tert*-butoxy, dimethylamino, diethylamino, ethylmethylamino, dipropylamino, dibutylamino, isobutylmethylamino, and the like.

As used herein the terms "C_1 to C_3 alkyl", "C_1 to C_{12} alkyl" and "C_1 to C_{18} alkyl" denote saturated monovalent straight or branched aliphatic hydrocarbon radicals including methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *tert*-butyl, amyl, 1-methylbutyl, 3-methylbutyl, hexyl, isohexyl, heptyl, isoheptyl, octyl, isooctyl, 2-ethylhexyl, nonyl, 3-ethylheptyl, n-decyl, n-undecyl, *n*-dodecyl, *n*-tridecyl, *n*-tetradecyl, *n*-pentadecyl, *n*-hexadecyl, *n*-heptadecyl, *n*-octadecyl, 1,3,5-trimethylhexyl, 1,5-dimethyl-4-ethylhexyl, 5-methyl-2-butyl-hexyl, 2-propylnonyl, 2-butyloctyl, 2-pentylnonyl, 1,2-dimethylhexadecyl, and the like.

As used herein the term "alkali metal cation" includes lithium, sodium and potassium cations.

The term "C_1 to C_{18} alkylammonium cation" includes ammonium cations substituted by from 1 to 3 alkyl groups as above described. The alkyl groups can be the same or different provided the ammonium cation contains no more than 18 carbon atoms. As examples there can be named methylammonium, *t*-butylammonium, *t*-octylammonium, *n*-dodecylammonium, *n*-octadecylammonium, di-*n*-butylammonium, di-*n*-nonylammonium, isopropyl-*n*-butylammonium, dimethyl-*n*-butylammonium, triethylammonium, N-ethyl-N,N-diisopropylammonium, tributylammonium, di-*n*-butyl-n-octylammonium and the like.

The terms "C_1 to C_8" alkoxy and "C_1 to C_{18} alkoxy" includes saturated, acyclic, straight or branch-chained groups such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, *sec*-butoxy, isobutoxy, *tert*-butoxy, *n*-pentyloxy, *n*-hexyloxy, *n*-heptyloxy, *n*-octyloxy, *n*-nonyloxy, *n*-decyloxy, *n*-undecyloxy, *n*-dodecyloxy, *n*-tridecyloxy, *n*-tetradecyloxy, *n*-pentadecyloxy, *n*-hexadecyloxy, *n*-heptadecyloxy, *n*-octadecyloxy, 1-methylpentyloxy, 2,2-dimethylbutyloxy, 2-methylhexyloxy, 1,4-dimethylpentyloxy, 3-ethylpentyloxy, 2-methylheptyloxy, 1-ethylhexyloxy, 2-propylpentyloxy, 2-methyl-3-ethylpentyloxy, 1,3,5-trimethylhexyloxy, 1,5-dimethyl-4-ethylhexyloxy, 5-methyl-2-butylhexyloxy, 2-propylnonyloxy, 2-butyloctyloxy, 1,1-dimethylundecyloxy, 2-pentylnonyloxy, 1,2-dimethyltetradecyloxy, 1,1-dimethylpentadecyloxy and the like.

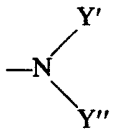
The term "C_1 to C_{12} N,N-dialkylaminoalkyl" includes branched and straight chain alkyl groups which can be the same or different provided the total number of carbon atoms is not less than four nor more than twelve. As examples there can be named 2-dimethylaminoethyl, diethylaminomethyl, 3-dimethylaminopropyl, 1-dimethylamino-2-propyl, 3-diethylaminopropyl, 1-diethylamino-2-propyl, 2-dipropylaminoethyl, 2-di-*i*-propylaminoethyl, 3-dipropylaminopropyl, 3-dimethylaminopropyl, 4-diethylamino-*n*-butyl, 3-dibutylaminopropyl, 4-dimethylamino-*n*-butyl, 5-diethylaminopentyl, 5-dipropylaminopentyl, 6-dimethylamino-*n*-hexyl, 6-diethylamino-6-ethylhexyl, 4-dibutylamino-*n*-butyl, 8-dimethylamino-*n*-octyl, 8-diethylamino-*n*-octyl, 10-dimethylamino-*n*-decyl, 5-dipropylamino-2-pentyl and the like.

As used herein, the term "C_2 to C_{18} alkenyl" means a monovalent aliphatic radical possessing a single double bond, for example, ethenyl (or vinyl), 2-propenyl (or allyl), 1-methylethenyl (or isopropenyl), 2-methyl-2-propenyl, 2-methyl-1-propenyl, 2-butenyl, 3-butenyl, 1-pentenyl, 2-pentenyl, 3-methyl-2-butenyl, 2-methyl-1-butenyl (isoamylenyl), 3-methyl-1-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 2-heptenyl, 1-octenyl, 1-hexadecenyl, 9-octadecenyl, 9-decenyl, 1-methyl-4-butenyl, 4-pentenyl, 1-ethyl-1-propenyl, 1-ethyl-3-propenyl, 10-undecenyl and the like.

Anhydrides of alkanoic acids of two to five carbon atoms include acetic anhydride, propionic anhydride, butyric anhydride, isobutyric anhydride, valeric anhydride, isovaleric anhydride, α-methylbutyric anhydride, pivalic anhydride and the like. Acetic anhydride is preferred because of its low cost and high reactivity, however the other above-named anhydrides are also satisfactory.

The novel compounds of Formula I hereinabove are essentially colorless in the depicted form. When contacted with an acidic medium, for example silica gel or one of the types ordinarily employed in pressure-sensitive carbonless duplicating systems such as silton clay of phenolic resins the compounds of Formula I develop an orange-red through green to a blackish-purple colored image of good to excellent tinctorial strength, and possessing excellent light stability, resistance to sublimation and xerographic copiability. The compounds are thus highly suitable for use as colorless precursors, that is color-forming substances in pressure-sensitive carbonless duplicating systems. The darker violets and bluish-black colors can be used alone as color formers to produce images which are readily copiable, whereas the reds, greens and blue colors can be used as toners in admixture with other color formers to produce images of a neutral shade which desirably are readily copiable by xerographic means. Moreover, the compounds of Formula I, in particular those wherein one of R^1 and R^2 represents

in which B represents —OY or



wherein Y is C_1 to C_{18} alkyl, C_1 to C_{18} alkenyl, benzyl or benzyl substituted in the benzene ring thereof by C_1 to C_{12} alkyl, halo or C_1 to C_8 alkoxy; Y′ is hydrogen or C_1 to C_{18} alkyl; Y″ is hydrogen, C_1 to C_{18} alkyl or C_4 to C_{12} N,N-dialkylaminoalkyl have enhanced solubility in common and inexpensive organic solvents such as odorless mineral spirits, kerosene, vegetable oils and the like; and those wherein one of R^1 and R^2 is an alkali-metal cation, an ammonium cation or a C_1 to C_{18} mono-, di- or trialkylammonium cation salt or the carboxy group are soluble in water and lower-alkanols thereby avoiding the need for more expensive, specialized solvents such as polyhalogenated or alkylated biphenyls which have ordinarily been used to prepare microencapsulated solutions of the color formers of the prior art.

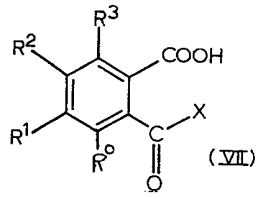
The compounds of this invention may be incorporated in any of the commercially accepted systems known in the carbonless duplicating art. A typical technique for such application is as follows. Solutions containing one or more colorless precursor compounds of Formula I, optionally in admixture with other color formers, in suitable solvents are microencapsulated by well-known procedures for example as described in U.S. Patent 3,649,649. The microencapsules are coated on the reverse side of a transfer sheet with the aid of a suitable binder and the coated transfer sheet is then assembled in a manifold with the microcapsule coated side in contact with a receiving sheet coated with an electron accepting substance, for example, silton clay or a phenolic resin. Application of pressure to the manifold such as that exerted by a stylus, typewriter or other form of writing or printing causes the capsules on the reverse side to rupture. The solution of the color former released from the ruptured microcapsules flows to the receiving sheet and on contact with the acidic medium thereon forms orange-red to violet-black colored images of good tinctorial strength. It is, of course, obvious that variants of this mode of application can be utilized. For example, the receiving sheet in a manifold can alternatively be coated with the subject compounds and the acidic developing agent can be contained in microcapsules applied to the reverse side of the top sheet in the manifold; or the receiving sheet can be coated with a mixture containing both the acidic developing agent and the microencapsulated color former.

It has also been found that when the compounds of Formula I are intimately

mixed with an acidic developer of the type generally employed in thermal papers such as described in U.S. Patent 3,539,375, that is, papers which produce a colored image when contacted with a heated stylus or heated type, for example, bisphenol A, heating of the mixture produces a colored image of varying shades from orange-red to violet-black depending on the particular compound of the invention employed. The ability of the compounds of Formula I to form a deep color when heated in admixture with an acidic developer such as bisphenol A, makes them useful in thermal paper marking systems, either where an original or a duplicate copy is prepared by contacting the thermal paper with a heated stylus or heated type in any of the methods generally known in the art.

The compounds of this invention which are soluble in water and lower-alkanols may be incorporated in any of the commercial hectographic or spirit-reproducing copying systems such as described in British Patent 1,427,318. In such systems a transfer sheet coated on one side with a layer containing one or more water- or lower alkanol-soluble color formers of Formula I is placed with its coated surface against one surface of a master paper which is then typed, written or marked on, causing transfer of the coating as a substantially colorless reverse image to the master paper at the points where the transfer sheet and master paper at the points where the transfer sheet and master paper have been pressed together. The master paper is then brought into contact with a succession of sheets of paper moistened with a suitable spirit-reproducing fluid such as ethanol. The fluid dissolves a part of the color former and transfer it to each paper sheet where it combines with an electron-accepting substance, to give a orangish-red to violet-black colored image which duplicates the original typing or writing on the master paper.

The 3-X-3-Z-4-R^0-5-R^1-6-R^2-7-R^3-phthalides of Formula I wherein R^0, R^1, R^2 and R^3 each represent hydrogen or halo, or when R^0, R^3 and one of R^1 and R^2 are each hydrogen the other represents nitro, dialkylamino wherein alkyl is non-tertiary C_1 to C_4 alkyl, or carboxy are obtained by interacting approximately an equimolar quantity of the appropriate 2-(X-carbonyl)-3-R^0-4-R^1-5-R^2-6-R^3-benzoic acid of the formula



(VII)

wherein R^0, R^1, R^2 and R^3 are as defined above, X represents a monovalent radical having the Formula A or B above in which R^5 represents hydrogen, C_1 to C_3 alkyl or phenyl, R^6 represents C_4 to C_{18} alkyl, C_2 to C_4 alkenyl, benzyl or benzyl substituted in the benzene ring by one or two of halo or C_1 to C_3 alkyl or represents hydrogen or C_1 to C_3 alkyl only when Y^1 is other than hydrogen and/or when one of R^1 and R^2 is amino or carboxy; R^7 represents hydrogen, C_1 to C_3 alkyl or phenyl; and Y^1 represents no or one or two C_1 to C_3 alkyl, C_1 to C_3 alkoxy, halo or nitro substituents in the benzenoid portion of the indolyl radical, with the appropriate 3-R^4-N,N-$(R)_2$-aniline or a 1-$R^{6'}$-2-$R^{5'}$-$Y^{1'}$indole wherein R, R^4, $R^{5'}$, $R^{6'}$ and $Y^{1'}$ are as defined above. (The compounds of Formula VII when X are radicals A and B will be referred to herein as Formulas VIII and IX, respectively). The compounds of formula VII and the process for their preparation are described in Divisional Application No. 8013346. Serial No. 1,600,663. The reaction is conveniently carried out in the presence of an anhydride of an alkanoic acid having from 2 to 5 carbon atoms, for example, acetic anhydride at a temperature in the range of 10 to 140°C. for from approximately thirty minutes to eighteen hours. The 3-X-3-Z-4-R^0-5-R^1-6-R^2-7-R^3-phthalide thus obtained can be isolated by filtration if it is insoluble in the reaction medium or by dilution of the reaction medium with a miscible solvent in which the product is insoluble, for example, a lower-alkanol or low molecular weight hydrocarbon, for example, isopropyl alcohol or hexane to effect precipitation of the phthalide. Alternatively, the reaction mixture can be poured into an aqueous base or an aqueous base added to the reaction mixture, for example, dilute ammonium hydroxide, sodium hydroxide or sodium carbonate and the phthalide extracted with an organic solvent, for example, benzene or toluene followed by evaporation of the organic solvent leaving the product as residue. The

phthalide once isolated can be purified by conventional means such as trituration or recrystallization from a suitable solvent. In a second alternative method, the reaction mixture can be added to an aqueous acid, for example, dilute hydrochloric acid and the pH adjusted by the addition of a dilute alkali, for example, dilute aqueous ammonium hydroxide or an alkaline salt, for example, sodium acetate and the product filtered or extracted as described above.

The 3-(1-R^6-2-R^5-5/6-Y^1-3-indolyl)-3-(1-$R^{6'}$-2-$R^{5'}$-5/6-$Y^{1'}$-3-indolyl)-4-R^0-5-R^1-6-R^2-7-R^3-phthalides of Formula VI in which the indole moieties are the same can be prepared by interacting a corresponding 3-R^0-4-R^1-5-R^2-6-R^3-phthalic anhydride, e.g., trimellitic anhydride with approximately two molecular proportions of the appropriate 1-R^6-2-R^5-Y^1-indole. The reaction is conveniently carried out in the presence of an anhydride of an alkanoic acid having from two to five carbon atoms, for example acetic anhydride at a temperature in the range of 10 to 140°C., but more desirably, at a temperature in the range of 75 to 140°C. to obtain the desired 3-(1-R^6-2-R^5-5/6-Y^1-3-indolyl)-3-(1-$R^{6'}$-2-2$R^{5'}$-5/6-$Y^{1'}$-3-indolyl)-5/6-carboxyphthalide. The phthalides are isolated in a manner similar to that indicated in the first mode of synthesis described above.

The 3-X-3-Z-5/6-aminophthalides of Formula I can be prepared by reducing the corresponding 3X-3-Z-5/6-nitrophthalide. The reduction is conveniently carried out in an acidic medium, for example, hydrochloric acid using a metal salt reducing agent, for example, stannous chloride at a temperature in the range of 0 to 80°C., but more desirably at a temperature in the range of 50—80°C. The desired phthalide is collected by filtration and purified by conventional means for example recrystallization from a suitable solvent after an aqueous alkali extraction.

The 3-X-3-Z-5/6-acetamidophthalide according to Formula I can be conveniently obtained by interacting the appropriate compound of Formula VII, wherein one of R^1 and R^2 is amino and the other and each of R^0 and R^3 are hydrogens, with approximately an equimolar quantity of an appropriate 3-R^4-N,N-$(R)_2$-aniline or a 1-$R^{6'}$-2-$R^{5'}$-$Y^{1'}$-indole in the presence of at least two molecular proportions of acetic anhydride. The product is isolated by adding water and dilute alkali to the reaction mixture and the product extracted with an organic solvent, for example, benzene or toluene followed by evaporation of the organic solvent leaving the phthalide as a crystalline material.

The 3-X-3-Z-5/6-COOY-phthalides of Formula I in which Y is a C_1 to C_{18} alkyl, a C_2 to C_{18} alkenyl, a benzyl or a benzyl substituted in the benzene ring thereof by C_1 to C_{12} alkyl, halo or C_1 to C_8 alkoxy are obtained by interacting a 3-X-3-Z-5/6-COOH-phthalide with an appropriate alkylating agent, for example, dimethyl sulfate, diethyl sulfate or Y-halogen, e.g., ethyl iodide, butyl bromide, allyl chloride, octyl bromide, hexadecyl bromide or benzyl bromide, in an inert diluent, for example, acetone, N,N-dimethylformamide or hexamethylphosphoramide in the presence of an alkali metal salt, particularly an alkali metal hydroxide or carbonate, for example, sodium hydroxide, sodium carbonate, potassium hydroxide or potassium carbonate. The reaction is conveniently carried out at a temperature in the range of 10° to 100°C. for approximately one to three hours. The 3-X-3-Z-5/6-COOY-phthalide thus obtained is isolated by adding the reacting mixture to water with subsequent extraction into and subsequent isolation from an aromatic solvent, for example, benzene or toluene. The organic layer is separated, dried over a suitable drying agent, followed by evaporation of the organic solvent leaving the phthalide as a residue. The product once isolated can be purified by conventional means such as trituration or recrystallization from a suitable solvent.

The 3-X-3-Z-5/6-CON'Y''-phthalides of Formula I are obtained by amidating the corresponding 3-X-3-Z-5/6-COOH-phthalide or the appropriate corresponding carboxylic functional derivative thereof, 3-X-3-Z-5/6-COOY-phthalide, with the appropriate Y'Y''NH amine, for example, 3-(di-*n*-butylamino)propylamine. The reaction is conveniently carried out optionally in the presence of an inert diluent or in the absence of an inert diluent at a temperature in the range of 90 to 150°C. for approximately five hours. The phthalide thus obtained can be isolated by adding the reaction mixture to water and the product extracted with an organic solvent, for example, benzene or toluene. The organic layer is separated and evaporated or distilled in vacuum to leave the product as a residue or oil.

The 3-X-3-Z-5/6-COOY-phthalides wherein the Y is an alkali metal cation, an ammonium cation or a mono-, di- or trialkylammonium cation are obtained by interacting the appropriate 3-X-3-Z-5/6-COOH-phthalide with approximately an equimolar quantity of an appropriate alkali metal salt, for example, sodium hydroxide, potassium hydroxide or lithium hydroxide, ammonium hydroxide or a

suitable primary amine, for example, 1,1,3,3-tetramethylbutylamine. The reaction is conveniently carried out in an inert diluent, for example, acetone at a temperature in the range of 10 to 50°C. for approximately five minutes to one hour. The phthalide thus obtained is isolated by dilution of the reaction medium with a miscible solvent in which the product is insoluble, for example, low molecular weight hydrocarbons such as hexane in order to effect precipitation of the product. The phthalide once isolated can be purified by conventional means such as trituration or recrystallization from a suitable solvent.

Both the known and the novel 2-X-carbonyl-3-R^0-4-R^1-5-R^2-6-R^3-benzoic acids of Formula VII are prepared in similar fashion, by interacting a 3-R^0-4-R^1-5-R^2-6-R^3-phthalic anhydride with a 1-R^6-2-R^5-Y^1-indole, a 1-R^7-pyrrole, or a 9-R^8-carbazole wherein R^0, R^1, R^2, R^3, R^5, R^6, R^7, R^8 and Y^1 each have the same meanings given in relation to Formula VII usually in the presence of a Lewis acid, for example, aluminum chloride or zinc chloride, and with a diluent such as benzene, toluene, xylene, chlorobenzene, 1,2-dichloroethane or *o*-dichlorobenzene at a temperature of about 0 to 150°C. The reaction is conveniently carried out in toluene in the presence of aluminum chloride at about 0 to 25°C. Alternatively, the more reactive indoles can be interacted in the absence of a Lewis acid by simply heating the reactants together in an inert solvent at about 80 to 150°C. The 2-(X-carbonyl)-3-R^0-4-R^1-5-R^2-6-R^3-benzoic acids in which Lewis acids are used in their preparation are isolated by adding water to the reaction mixture or the reaction mixture to water or dilute mineral acid, for example, hydrochloric acid and subsequently separating the organic layer. The product is extracted from the organic layer with a dilute aqueous alkali solution and precipitated by the addition of a mineral acid, for example, hydrochloric acid. The benzoic acid is collected by filtration and may be purified by conventional means but is generally dried and used as is. Alternatively, in the case where the more reactive indoles are utilized, it is preferable not to use a Lewis acid and the 2-(X-carbonyl)-3-R^0-4-R^1-5-R^2-6-R^3-benzoic acids are obtained by cooling the reaction mixture to ambient temperature and collecting the product by filtration. The product once isolated can be purified by conventional means but preferably the benzoic acid is dried and used as is.

The 2-(X-carbonyl)-5/6-aminobenzoic acids of Formula VII are obtained by reducing the corresponding 2-(X-carbonyl)-5/6-nitrobenzoic acid. The reduction is conveniently carried out in an acidic medium, for example, hydrochloric acid using a metal salt reducing agent, for example, stannous chloride at a temperature in the range of 0 to 80°C., but preferably at a temperature in the range of 50—80°C. The desired benzoic acid is collected by filtration and purified if desired by conventional means but preferably it is dried and used as is.

It will, of course, be appreciated that reaction of an unsymmetrically substituted phthalic anhydride with an indole, pyrrole or carbazole can produce isomers or a mixture of isomers of 2-(heteroarylcarbonyl)benzoic acids. For example, reaction of a 4-substituted phthalic anhydride with an indole, pyrrole or carbazole can produce either a 4- or 5-substituted 2-(heteroarylcarbonyl)benzoic acid or a mixture thereof. Similarly a 3-substituted phthalic anhydride can produce either a 3- or a 6-substituted 2-(heteroarylcarbonyl-benzoic acid or a mixture of these. The mixtures of isomeric 2-(heteroarylcarbonyl)benzoic acids can be separated by conventional means such as fractional crystallization or chromatography. Alternatively, the isomeric mixtures can be reacted directly with appropriate 3-R^4-N,N-$(R)_2$-anilines or 1-$R^{6'}$-2-$R^{5'}$-5/6-$Y^{1'}$-indoles to produce isomeric mixtures of phthalides of Formula I. Thus, reaction of a mixture of 4- and 5-substituted 2-(heteroarylcarbonyl)benzoic acids with a 3-R^4-N,N-$(R)_2$-aniline or a 1-$R^{6'}$-2-$R^{5'}$-5/6-$Y^{1'}$-indole will produce a mixture of 5- and 6-substituted phthalides. The mixtures of phthalides can, if desired, be separated by conventional means or simply and preferably used as mixtures in the practice of this invention. Throughout this application where the possibility of different isomeric products being formed is present, the nomenclature 4/5, 5/6 and so forth is adopted meaning the product obtained or claimed is a mixture of the isomers.

Indoles, the substituted indoles, pyrrole, the substituted pyrroles, carbazole and the substituted carbazoles required as intermediates for the preparation of the carbonyl-benzoic acid intermediates of Formula VII, VIII and IX and for the final products of Formulas I, III, IV, V and VI form an old and well-known class of compounds which are readily obtained by conventional procedures well known in the art. The following compounds are exemplary of indoles, pyrroles and carbazoles useful in the practice of this invention: indole, 1-methylindole, 2-methylindole, 1,2-dimethylindole, 1-ethyl-2-methylindole, 2-phenylindole, 1-

propyl-2-methylindole, 1-benzyl-2-methylindole, 1-butyl-2-methylindole, 1-octyl-2-methylindole, 2-ethyl-5-methylindole, 1-benzyl-5-fluoroindole, 1-methyl-6-nitroindole, 5-methoxy-1-butylindole, 1-allyl-2-methylindole, 1,2-dimethyl-6-nitroindole, 1-(4-chlorobenzyl)-2-methyl-5-nitroindole, 2-ethylindole, 2-ethyl-1-methylindole, 1-isopropylindole, 2-isopropylindole, 1-methyl-5-bromo-6-nitroindole, 2,5,6-trimethylindole, 1-isobutyl-2-methylindole, 6-bromo-2-methylindole, 1-hexylindole,1-(2,5-dimethylbenzyl)-2-methylindole, 2-propylindole, 6-chloro-2-phenylindole, 1-(2-ethylhexyl)-2-methylindole, 1-(2,6-dichlorobenzyl)-2-methylindole, 1-vinyl-2-methylindole, 2-ethyl-6-methylindole, 6-fluoro-1-benzylindole, 1-(4-bromobenzyl)-2-isopropylindole, 1-(3-chlorobenzyl)-2-ethylindole, 5-chloro-1-benzylindole, 1-(2-fluorobenzyl)-2-methylindole, 5-iodo-1-(1-methylhexyl)-indole, 5,6-dimethoxyindole, 1-(2-methylbenzyl)-2-methylindole, 5,6-dichloro-2-phenylindole, 1-isoamylindole, 1-[3-(2-methyl)-1-propenyl]-2-methoxyindole, pyrrole, N-methylpyrrole, N-ethylpyrrole, N-propylpyrrole, N-isopropylpyrrole, N-phenylpyrrole, carbazole, 9-methylcarbazole, 9-ethylcarbazole, 9-propylcarbazole, 9-isopropylcarbazole, and 9-phenylcarbazole.

The 3-R^4-N,N-$(R)_2$-anilines, which are required for interaction with the 2-(X-carbonyl)-3-R^0-4-R^1-5-R^2-6-R^3-benzoic acids of Formula VII to obtain the 3-X-3-[2-R^4-4-N$(R)_2$-phenyl]-4-R^0-5-R^1-6-R^2-7-R^3-phthalides of Formula II form an old and well-known class of compounds readily obtained by conventional procedures well known in the art. The following anilines exemplify compounds falling within the ambit of the formula Z-H which are useful in the practice of the step in the processes of this invention for producing the aforesaid phthalides of Formula II: N,N,N′,N′-tetramethyl-*m*-phenylenediamine, N,N-dibutylaniline, N,N-diethyl-3-ethoxyaniline, N,N-diethyl-*m*-anisidine, N,N-dimethylaniline, N-benzyl-N-ethylaniline, N,N-diethyl-*m*-toluidine, N,N-diethylaniline, N-ethyl-N-methylaniline, N-benzyl-N-methylaniline, N-benzyl-N-propylaniline, N,N-dimethyl-3-bromoaniline, N,N,N′,N′-tetraisopropyl-*m*-phenylenediamine, N,N-dibutyl-3-fluoroaniline, N,N-diethyl-2-methoxy-3-chloroaniline, N-benzyl-N-methyl-3-ethylaniline, N,N,N′,N′-tetra-*sec*-butyl-*m*-phenylenediamine, N-benzyl-N-butyl-3-iodoaniline, N,N-diisopropyl-3-chloroaniline, N-benzyl-N-*sec*-butylaniline, N,N-di-*sec*-butylaniline, N,N-diethyl-3-isopropylaniline, N,N-diisobutylaniline, N,N-diethyl-2-propoxyaniline, N,N-dipropylaniline, N-isopropyl-N-methylaniline, N-methyl-N-propylaniline, N,N,N′,N′-tetrabutyl-*m*-phenylenediamine, N,N-dipropyl-*o*-anisidine, N-isobutyl-N-ethylaniline, N,N,N′,N′-tetraethyl-*m*-phenylenediamine, N-propyl-N-ethylaniline,N,N-diethyl-2-ethoxyaniline, N-benzyl-N-*sec*-butyl-2-propoxyaniline, and N,N-dimethyl-*m*-toluidine.

The molecular structures of the compounds of this invention were assigned on the basis of the modes of synthesis, elemental analysis and study of their infrared, nuclear magnetic resonance, and mass spectra.

The following examples will further illustrate the invention without, however, limiting it thereto.

Example 1

A. To a mixture of 8.17 g (0.05 mole) of N-ethylcarbazole and 3.7 g (0.025 mole) of phthalic anhydride in 112 g of chlorobenzene, 6.65 g (0.05 mole) of aluminum chloride was added in small increments at ambient temperature after which the mixture was warmed in the range of 50—70°C for two hours. The reaction mixture was poured onto ice and rendered acidic by the addition of 10 percent hydrochloric acid. The chlorobenzene layer was separated and steam, distilled to remove the chlorobenzene. The residue was extracted with 10 percent aqueous sodium hydroxide, filtered to remove the insolubles and then acidified with dilute hydrochloric acid. The solid which separated was collected by filtration, washed with water and dried to obtain *2-[(9-ethyl-3-carbazolyl)carbonyl]benzoic acid* (Formula VII: R^0=R^1=R^2=R^3=H; R^8=CH_2CH_3) melting over the range 120—130°C.

B. A mixture of 3.43 g. (0.01 mole) or 2-[(9-ethyl-3-carbazolyl)carbonyl]benzoic acid, 1.80 g. (0.011 mole) of N,N,N′,N′-tetramethyl-*m*-phenylenediamine and 4.0 ml. of acetic anhydride was interacted with stirring at room temperature overnight. The reaction mixture was then diluted with ethanol and the precipitate which separated was filtered and washed with ethanol. The filter cake was then reslurried in methanol, filtered and washed successively with methanol and diethylether. The material was dried *in vacuo* to yield *3-[2,4-bis(dimethylamino)phenyl]-3(9-ethyl-3-carbazoyl)phthalide* (Formula V:

$R^0=R^1=R^2=R^3=H$; $R=CH_3$; $R^4=N(CH_3)_2$; $R^8=CH_2CH_3$) which melted over the range 134—142°C. A significant infrared absorption maximum appeared at 1753 cm^{-1} (C=O; s). A toluene solution of this product spotted on silica gel developed a bordeaux-colored image.

Example 2

A. To a mixture of 2.96 g. (0.02 mole) of phthalic anhydride and 5.72 g. (0.04 mole) of N-phenylpyrrole in 50 ml. of chlorobenzene, maintained at 0—5°C. in an ice bath, 810 g. (0.06 mole) of aluminum chloride was added in small portions. The reaction mixture was held at 0—5°C. for approximately two hours. The reaction was allowed to warm to room temperature and then set aside overnight at ambient temperature. The reaction mixture was worked up in a manner similar to that described in part A of Example 1 to obtain *2-[(1-phenyl-2-pyrrolyl)carbonyl]benzoic acid* (Formula IX: $R^0=R^1=R^2=R^3=H$; $R^7=C_6H_5$) which melted over the range 159—168°C.

B. A mixture of 2.91 g. (0.01 mole) of 2-[(1-phenyl-2-pyrrolyl)carbonyl]benzoic acid prepared in part A above, 2.34 g. (0.017 mole) or 84.6 percent active N,N,N′,N′-tetramethyl-*m*-phenylenediamine in 4.0 ml. of acetic anhydride was interacted in a manner similar to that described in Example 1, part B to obtain 2.61 g. of *3-[2,4-bis(dimethylamino)phenyl]-3-(1-phenyl-2-pyrrolyl)phthalide* (Formula IV: $R^0=R^1=R^2=R^3=H$; $R=CH_3$; $R^4=N(CH_3)_2$; $R^7=C_6H_5$); a peach-colored powder melting at 193—194°C. The infrared spectrum showed a maximum at 1760 cm^{-1} (C=O; s). A toluene solution of this product spotted on silica gel developed an immediate orange-red-colored image.

Example 3

A. Proceeding in a manner similar to that described in part A of Example 2, 14.8 g (0.1 mole) of phthalic anhydride, 16.2 g (0.2 mole) of N-methylpyrrole and 39.0 g (0.3 mole) of aluminum chloride were interacted in 50 ml of chlorobenzene to obtain *2-[(1-methyl-2-pyrrolyl)carbonyl]benzoic acid* (Formula IX: $R^0=R^1=R^2=R^3=H$; $R^7=CH_3$) melting at 165—167°C. A significant absorption maximum appeared at 1710 cm^{-1} (C=O; s).

B. A mixture of 4.58 g (0.02 mole) or 2-[(1-methyl-2-pyrrolyl)carbonyl]benzoic acid, from part A above, 3.61 g (0.022 mole) of N,N,N′,N′-tetramethyl-*m*-phenylenediamine and 3.0 ml of acetic anhydride was interacted in a manner similar to that described above in Example 1, part B to obtain 1.92 g of *3-[2,4-bis(dimethylamino)phenyl]-3-(1-methyl-2-pyrrolyl)phthalide* (Formula IV: $R^0=R^1=R^2=R^3=H$; $R=R^7=CH_3$; $R^4=N(CH_3)_2$), a tan powder melting at 148—150°C. A toluene solution of this product spotted on silica gel developed an intense red-colored image.

Example 4

A. A stirred solution of 48.0 g (0.250 mole) of trimellitic anhydride and 45.0 g (0.314 mole) of 1-ethyl-2-methylindole in 350 ml of ethylene dichloride was heated at reflux for a period of approximately two hours, and then allowed to cool to ambient temperature. The solid, which separated, was collected by filtration, washed with 200 ml of ethylene dichloride and dried *in vacuo* at 60°C to obtain 66.0 g of *4/5-carboxy-2-[(1-ethyl-2-methyl-3-indolyl)carbonyl]benzoic acid* (Formula VIII: $R^1=R^2=H/COOH$; $R^0=R^3=Y^1=H$; $R^5=CH_3$; $R^6=CH_2CH_3$), a yellowish-orange solid melting over the range 198—201°C. Infrared maxima appeared at 1730 (C=O; s) and 1700 cm^{-1} (C=O; vs). The nuclear magnetic resonance spectrum was in agreement with the assigned structure.

B. A stirred mixture of 17.5 g (0.05 mole) of the 4/5-carboxy-2-[(1-ethyl-2-methyl-3-indolyl)carbonyl]benzoic acid, prepared as described in part A above, 8.5 g (0.052 mole) of N,N,N′,N′-tetramethyl-*m*-phenylenediamine and 25 ml of acetic anhydride was heated at 50°C for a period of two hours and then allowed to cool to ambient temperature. After the addition of 25 ml of isopropyl alcohol, the resulting mixture was poured into water with vigorous stirring. The solid which separated was collected by filtration, washed with water and dried *in vacuo* at 60°C to obtain 22.0 g of *3-[2,4-bis(dimethylamino)-phenyl]-3-(1-ethyl-3-methyl-3-indolyl)-5/6-carboxyphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOH$; $R^4=N(CH_3)_2$; $R^6=CH_2CH_3$) as a dark purple solid melting over the range 149—151°C. Infrared maxima appeared at 1775 (C=O; s) and 1720 cm^{-1} (C=O; s).

C. Three milliliters of dimethyl sulfate was added to a refluxing mixture of 3.0 g of the 3-[2,4-bis(dimethylamino)-phenyl]-3-(1-ethyl-2-methyl-3-indolyl)-5/6-

carboxyphthalide prepared as described in part B above, 3.0 g of potassium carbonate and 100 ml of acetone. The reaction mixture was heated at reflux for a period of two hours and was then poured into water and the aqueous mixture extracted with toluene. The toluene extract was washed successively with water and saturated salt solution and then evaporated to dryness. The residue was triturated with ligroin (b.p. 60—90°C) and the solid separated and dried to obtain 1.0 g of *3-[2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOCH_3$; $R^4=N(CH_3)_2$; $R^6=CH_2CH_3$), a light purple solid melting over the range of 72—85°C. Infrared maxima appeared at 1760 (C=O; s) and 1730 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 511 (M^+) and at 452 ($M^+—CO_2CH_3$). A toluene solution of the produce spotted on silica gel, an acidic clay or a phenolic resin developed a grape-colored image.

Example 5

To a stirred mixture of 6.38 g (0.013 mole) of 3-[2,4-bis(dimethylamino)phenyl]-3-(1-ethyl-2-methyl-3-indolyl)-5/6-carboxyphthalide, prepared as described above in part B of Example 4, 150 ml of hexamethylphosphoramide and 10 ml of 25 percent aqueous sodium hydroxide, there was added 7.0 ml of ethyl iodide. The mixture was stirred at room temperature for a period of two hours. The reaction mixture was then drowned in water and the aqueous mixture was extracted with toluene. The toluene layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was triturated with ligroin (b.p. 60—90°C) and the separated solid collected and dried to obtain 0.92 g of *3-[2,4-bis(dimethylamino)phenyl]-3-(1-ethyl-2-methyl-3-indolyl)-5/6-ethoxycarbonylphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOCH_2CH_3$; $R^4=N(CH_3)_2$; $R^6=CH_2CH_3$), a light brown powder melting over the range 88—97°C. Infrared maxima appeared at 1765 (C=O; s) and 1725 cm^{-1} (C=O; s). The nuclear magnetic resonance spectrum was in agreement with the assigned structure. Analysis by mass spectrum showed m/e peak at 525 (M^+). A toluene solution of the product spotted on silica gel, and acidic clay or a phenolic resin developed a grape-colored image.

Example 6

Following a procedure similar to that described above in part C of Example 4 but substituting dimethylformamide for acetone and *n*-octyl bromide for dimethyl sulfate, there was obtained *3-[2,4-bis(dimethylamino)phenyl]-3-(1-ethyl-2-methyl-3-indolyl)-5/6-n-octyloxycarbonylphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COO(CH_2)_7CH_3$; $R^4=N(CH_3)_2$; $R^6=CH_2CH_3$) as a light brown oil. Infrared maxima appeared at 1770 (C=O; s) and 1730 cm^{-1} (C=O; s). A benzene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a grape-colored image.

Example 7

Following a procedure similar to that described above in Example 6 except that α-bromotoluene was used in place of *n*-octyl bromide, there was obtained 2.52 g of *3-[2,4-bis(dimethylamino)phenyl]-3-(1-ethyl-2-methyl-3-indolyl)-5/6-phenylmethoxycarbonylphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOCH_2C_6H_5$; $R^4=N(CH_3)_2$; $R^6=CH_2CH_3$), a light purple powder melting over the range 72—78°C. Infrared maxima appeared at 1770 cm^{-1} (C=O; s), analysis by mass spectrum showed m/e peaks at 587 (M^+) and 543 ($M^+—CO_2$). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a grape-colored image.

Example 8

A. A mixture of 35 g (0.10 mole) of 4/5-carboxy-2-[(1 ethyl-2-methyl-3-indolyl)carbonyl]benzoic acid prepared as described in Example 4, part A above, 20 g (0.103 mole) of N,N-diethyl-*m*-phenetidine and 60 ml of acetic anhydride was stirred at room temperature for a period of approximately eighteen hours. After the addition of 100 ml of isopropyl alcohol, the resulting mixture was poured into water with vigorous stirring. The solid which separated was collected by filtration, washed with water and dried to obtain 53.4 g of *3-(2-ethoxy-4-diethylaminophenyl)-3-(1-ethyl-2-methyl-3-indolyl)-5/6-carboxyphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOH$; $R^4=OC_2H_5$; $R^5=CH_3$), a dark blue solid melting over the range of 130—144°C. Infrared maxima appeared at 1765 (C=O; s) and

1725 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 526 (M^+) and 481 (M^+—CO_2H).

B. Employing a procedure similar to that described in part C of Example 4, but interacting 5.0 g (0.0095 mole) of 3-(2-ethoxy-4-diethylaminophenyl)-3-(1-ethyl-3-methyl-3-indolyl)-5/6-carboxyphthalide prepared as described in part A of this example with dimethyl sulfate instead of 3-[2,4-bis(dimethylamino)phenyl]-3-(1-ethyl-2-methyl-3-indolyl)-5/6-carboxyphthalide, there was obtained 4.9 g of *3-(2-ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOCH_3$; $R^4=OC_2H_5$; $R^5=CH_3$), a light green-colored solid melting over the range 96—103°C. Infrared maxima appeared at 1765 (C=O; s) and 1730 cm^{-1} (C=O; s). The nuclear magnetic resonance spectrum was in agreement with the assigned structure. Analysis of mass spectrum showed m/e peaks at 540 (M^+), 496 (M^+—CO_2) and 418 (M^+—$COOCH_3$). A toluene solution of the product spotted on silica gel, and acidic clay or a phenolic resin developed a deep blue-colored image which had a good lightfastness.

Example 9

When diethyl sulfate was substituted for dimethyl sulfate for interaction with 3-(2-ethoxy-4-diethylaminophenyl)-3-(1-ethyl-2-methyl-3-indolyl)-5/6-carboxyphthalide according to the procedure described in part B of Example 8, there was obtained 1.5 g of *3-(2-ethoxy-4-diethylaminophenyl)-3-(1-ethyl-2-methyl-3-indolyl)-5/6-ethoxycarbonylphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOCH_2CH_3$; $R^4=OC_2H_5$; $R^5=CH_3$), a light yellow solid melting over the range 141—148°C. Infrared maxima appeared at 1750 (C=O; s) and 1732 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 554 (M^+), 510 (M^+—CO) and 481 (M^+—$CO_2C_2H_5$). A toluene solution of the product spotted on silica gel, and acidic clay or a phenolic resin developed a deep blue-colored image which had a good lightfastness.

Example 10

Following a procedure similar to that described above in Example 8, part B, 5.0 g (0.0095 mole) of 3-(2-ethoxy-4-diethylaminophenyl)-3-(1-ethyl-2-methyl-3-indolyl)-5/6-carboxyphthalide prepared as described in Example 8, part A was interacted with 2.0 g (0.0117 mole) of α-bromotoluene to obtain 3.4 g of *3-(2-ethoxy-4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - phenylmethoxycarbonylphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOCH_2C_6H_5$; $R^4=OC_2H_5$; $R^5=CH_3$), a light yellow solid melting over the range 82—87°C. Infrared maxima appeared at 1765 (C=O; s) and 1725 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 616 (M^+) and 572 (M^+—CO_2). A toluene solution of the product spotted on silica gel, and acidic clay or a phenolic resin developed a deep blue-colored image which has good lightfastness.

Example 11

When *n*-octyl bromide was substituted for α-bromotoluene for interaction with 3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6-carboxyphthalide according to the procedure described in Example 10, there was obtained *3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - n - octoxycarbonylphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COO$-*n*-$(CH_2)_7CH_3$; $R^4=OC_2H_5$; $R^5=CH_3$), a light blue solid melting over the range 134—162°C. A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a deep blue-colored image which had good lightfastness.

Example 12

Substituting 1-bromohexadecane for *n*-octyl bromide for interaction with 3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide according to the procedure described in Example 11, there was obtained 7.1 g of *3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - hexadecanoxycarbonylphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H/COO(CH_2)_{15}CH_3$; $R^4=OC_2H_5$; $R^5=CH_3$), a light brown oil. Infrared maxima appeared at 1765 (C=O; s) and 1725 cm^{-1} (C=O; s). The nuclear magnetic resonance spectrum was in agreement with the assigned structure. Analysis by mass spectrum showed m/e peaks at 750 (M^+) and 706 (M^+—

CO_2). A benzene solution of the product spotted on silica gel, an acidic clay or phenolic resin developed a deep blue-colored image which has a good lightfastness.

Example 13

To a stirred solution of 5.3 g of 3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in Example 8, part A, in 25 ml of acetone there was added 2.6 g of 1,1,3,3-tetramethylbutylamine. The mixture was stirred at ambient temperature for approximately ten minutes and then 160 ml of *n*-hexane was added. The supernatant liquid was decanted and the insoluble, brown, gummy residue triturated with *n*-hexane to obtain 6.2 g of *1,1,3,3 - tetramethylbutylammonium salt of 3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula III: $R^0=R^3=Y^1=H$; R

$$R^1=R^2=H/COO\overset{\ominus}{N}\overset{\oplus}{H}_3C(CH_3)_2CH_2C(CH_3)_2CH_3;$$

$R=R^6=C_2H_5$; $R^4=OC_2H_5$; $R^5=CH_3$), a beige-colored solid melting over the range of 80—105°C with decomposition. Infrared spectral analysis showed significant maxima in the range from 2350 cm^{-1} to 2150 cm^{-1}, and a strong absorption at 1760 cm^{-1} (C=O; s). The assigned structure was corroborated by a concordant nuclear magnetic resonance spectrum. A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a deep blue-colored image which had good lightfastness. This product is also a water-soluble color-former.

Example 14

A. Following a procedure similar to that described in part A of Example 8 but interacting N,N-dimethylaniline instead of N,N-diethyl-*m*-phenetidine, with 4/5 - carboxy - 2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl]benzoic acid, there was obtained *3 - (4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=R^4=Y^1=H$; $R^1=R^2=H/COOH$; $R^6=C_2H_5$), a blue-colored solid melting over the range 141—160°C. Infrared maxima appeared at 1770 (C=O; s) and 1730 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 454 (M^+), 410 ($M^+—CO_2$) and 409 ($M^+—COOH$).

B. employing a procedure similar to that described in part C of Example 4, but substituting 3 - (4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in part A above for 3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide for interaction with dimethylsulfate, there was obtained *3 - (4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=R^4=Y^1=H$; $R^1=R^2=H/COOCH_3$; $R^6=C_2H_5$), a light yellow solid melting over the range 101—110°C. Infrared maxima appeared at 1760 (C=O; s) and 1730 cm^{-1} (C=O; s). The nuclear magnetic resonance spectrum was in agreement with the assigned structure. Analysis by mass spectrum showed m/e peaks at 468 (M^+), 424 ($M^+—CO_2$) and 409 ($M^+—COOCH_3$). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a blue-colored image had good lightfastness.

Example 15

Proceeding in a manner similar to that described above in Example 23, 3 - (4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in Example 14, part A, was interacted with diethyl sulfate to obtain *3 - (4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - ethoxycarbonylphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=R^4=Y^1=H$; $R^1=R^2=H/COOC_2H_5$; $R^6=C_2H_5$), a light green solid melting over the range 114—131°C. Infrared maxima appeared at 1765 (C=O; s) and 1725 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 482 (M^+), 438 ($M^+—CO_2$) and 409 ($M^+—CO_2C_2H_5$). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a blue-colored image which had good lightfastness.

Example 16

When α-bromotoluene was substituted for diethyl sulfate in Example 15, there was obtained *3 - (4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) -*

5/6 - phenylmethoxycarbonylphthalide (Formula III: $R=R^5=CH_3$; $R^0=R^3=R^4=Y^1=H$; $R^1=R^2=H/COOCH_2C_6H_5$; $R^6=C_2H_5$), a light green-colored solid melting over the range 93—98°C. Infrared maxima appeared at 1770 (C=O; s) and 1728 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 544 (M^+) and 500 ($M^+—CO_2$). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a blue-colored image which had good lightfastness.

Example 17

A. Following a procedure similar to that described in part A of Example 8, but using 15 g of N,N-diethylaniline instead of N,N-diethyl-*m*-phenetidine for interaction with 4/5-carboxy-2-[(1-ethyl-2-methyl-3-indolyl)carbonyl]benzoic acid, there was obtained *3 - (4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=R^4=Y^1=H$; $R^1=R^2=H/COOH$; $R^5=CH_3$), a blue solid melting over the range 169—182°C. Infrared maxima appeared at 1765 (C=O; s) and 1730 cm^{-1} (C=O; s), the nuclear magnetic resonance spectrum was in agreement with the assigned structure.

B. Proceeding in a manner similar to that described in part C of Example 4, but using 3 - (4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in part A above in place of 3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide for interaction with dimethyl sulfate, there was obtained *3 - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=R^4=Y^1=H$; $R^1=R^2=H/COOCH_3$; $R^5=CH_3$); a light green solid melting over the range 114—128°C. Infrared maxima appeared at 1765 (C=O; s) and 1730 cm^{-1} (C=O; s). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a blue-colored image which had good lightfastness.

Example 18

A. Employing a procedure similar to that described in part A of Example 8, but using *m*-chloro-N,N-dimethylaniline instead of N,N-diethyl-*m*-phenetidine for interaction with 4/5 - carboxy - 2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl]benzoic acid, there was obtained *3 - (2 - chloro - 4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOH$; $R^4=Cl$; $R^6=C_2H_5$), as a greenish-blue solid melting over the range 130—142°C. Infrared maxima appeared at 1770 (C=O; s) and 1725 cm^{-1} (C=O; m).

B. Proceeding in a manner similar to that described in part C of Example 4, but using 3 - (2 - chloro - 4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in part A above instead of 3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide for interaction with dimethyl sulfate, there was obtained *3 - (2 - chloro - 4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6-methoxycarbonylphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOCH_3$; $R^4=Cl$; $R^6=C_2H_5$), as a light blue solid melting over the range 168—193°C. Infrared maxima appeared at 1770 (C=O; s) and 1730 cm^{-1} (C=O; s). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a pale green-colored image.

Example 19

A. Following a procedure similar to that described in part A of Example 8, but using N,N-*m*-diethyltoluidine instead of N,N-diethyl-*m*-phenetidine for interaction with 4/5 - carboxy - 2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl]benzoic acid, there was obtained *3 - (2 - methyl - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOH$; $R^4=R^5=CH_3$), a turquoise-colored solid melting over the range 146—162°C. Infrared maxima appeared at 1765 (C=O; s) and 1720 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 496 (M^+), 452 ($M^+—CO_2$) and 451 ($M^+—COOH$).

B. Employing a procedure similar to that described in part C of Example 4, but using 2 - (2 - methyl - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in part A above instead of 3 - [2,4 - bis)dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide, there was obtained *3 - (2 - methyl - 4 -*

diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOCH_3$; $R^4=R^5=CH_3$), a light yellow solid melting over the range 113—120°C. Infrared maxima appeared at 1770 (C=O; s) and 1730 cm^{-1} (C=O; s). The nuclear magnetic resonance spectrum was in agreement with the assigned structure. Analysis by mass spectrum showed m/e peaks at 510 (M^+) and 495 (M^+—$COOCH_3$) A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a turquoise-colored image which has good lightfastness.

Example 20

Proceeding in a manner similar to that described above in Example 9, 3 - (2 - methyl - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in Example 19, part A was interacted with diethyl sulfate to obtain *3 - (2 - methyl - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - ethoxycarbonylphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOC_2H_5$; $R^4=R^5=CH_3$), a tan solid melting over the range 89—144°C. Infrared maxima appeared at 1765 (C=O; s) and 1725 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 524 (M^+), 480 (M^+—CO_2) and 451 (M^+—$CO_2C_2H_5$). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a turquoise-colored image which had good lightfastness.

Example 21

When α-bromotoluene was substituted for diethyl sulfate in Example 20 for interaction with 3 - (2 - methyl - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in Example 19, part A, there was obtained *3 - (2 - methyl - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - phenylmethoxycarbonylphthalide* (Formula III: $R=R^6=C_2H_5$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOCH_2C_6H_5$; $R^4=R^5=CH_3$), a light yellow solid melting over the range 92—98°C. Infrared maxima appeared at 1765 (C=O; s) and 1725 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 586 (M^+) and 542 (M^+—CO_2). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a turquoise-colored image having good lightfastness.

Example 22

A. Following a procedure similar to that described in part A of Example 8, but using N,N-di-*n*-butylaniline instead of N,N-diethyl-*m*-phenetidine for interaction with 4/5 - carboxy - 2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl]benzoic acid, there was obtained *3 - (4 - di - n - butylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula III: $R=CH_2(CH_2)_2CH_3$; $R^0=R^3=R^4=Y^1=H$; $R^1=R^2=H/COOH$; $R^5=CH_3$; $R^6=C_2H_5$), as a blue-colored solid melting over the range 81—94°C. Infrared maxima appeared at 1760 (C=O; s) and 1725 cm^{-1} (C=O; m).

B. Employing a procedure similar to that described in part C of Example 4 but using 3 - (4 - di - n - butylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in Part A above instead of 3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide for interaction with dimethyl sulfate, there was obtained *3 - (4 - di - n - butylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula III: $R=CH_2(CH_2)_2CH_3$; $R^0=R^3=R^4=Y^1=H$; $R^1=R^2=H/COOCH_3$; $R^5=CH_3$; $R^6=C_2H_5$), a light yellow solid melting over the range 72—94°C. Infrared maxima appeared at 1765 (C=O; s) and 1728 cm^{-1} (C=O; s). Analysis by mass spectrum showed m/e peaks at 552 (M^+), 508 (M^+—CO_2) and 493 (M^+—CO_2CH_3). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a blue-colored image which had good lightfastness.

Example 23

A. Following a procedure similar to that described in part A of Example 8, but using N,N-dimethyl-*m*-anisidine instead of N,N-diethyl-*m*-phenetidine for interaction with 4/5 - carboxy - 2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl]benzoic acid, there was obtained *3 - (2 - methoxy - 4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula III: $R=R^5=CH_3$; $R^0=R^3=Y^1=H$; $R^1=R^2=H/COOH$;

R^4=OCH_3; R^6=C_2H_5), a deep blue solid melting over the range 128—133°C. Infrared maxima appeared at 1760 (C=O; s) and 1730 cm^{-1} (C=O; m). Analysis by mass spectrum showed m/e peaks at 484 (M^+), 440 (M^+—CO_2) and 439 (M^+—COOH).

B. Employing a procedure similar to that described in Part C of Example 4, but using 3 - (2 - methoxy - 4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in part A above instead of 3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide for interaction with dimethyl sulfate, there was obtained *2 - (2 - methoxy - 4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula III: R=R^5=CH_3; R^0=R^3=Y^1=H; R^1=R^2=H/$COOCH_3$; R^4=OCH_3; R^6=C_2H_5), as a light blue solid melting over the range 131—135°C. Infrared maxima appeared at 1760 (C=O; s) and 1730 cm^{-1}(C=O; s). Analysis by mass spectrum showed m/e peaks at 498 (M^+), 454 (M^+—CO_2) and 439 (M^+—CO_2CH_3). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a deep blue-colored image which had good lightfastness.

Example 24

A. Proceeding in a manner similar to that described in part A of Example 8, but using 3-*n*-butoxy-N,N-diethylaniline instead of N,N-diethyl-*m*-phenetidine for interaction with 4/5 - carboxy - 2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl]benzoic acid, there was obtained *3 - (2 - n - butoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6-carboxyphthalide* (Formula III: R=R^6=C_2H_5; R^0=R^3=Y^1=H; R^1=R^2=H/COOH; R^4=$OCH_2(CH_2)_2CH_3$; R^5=CH_3), a deep blue solid melting over the range 113—125°C. Infrared maxima appeared at 1760 (C=O; s) and 1725 cm^{-1} (C=O; m). Analysis by mass spectrum showed a m/e peak at 510 (M^+—CO_2).

B. Following a procedure similar to that described in part C of Example 4, but using 3 - (2 - *n* - butoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in part A above instead of 3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide for interaction with dimethyl sulfate, there was obtained *3 - (2 - n - butoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula III: R=R^6=C_2H_5; R^0=R^3=Y^1=H; R^1=R^2=H/$COOCH_3$; R^4=$OCH_2(CH_2)_2CH_3$; R^5=CH_3), a light green oil. Infrared maxima appeared at 1765 (C=O; s) and 1730 cm^{-1} (C=O; s). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin developed a deep blue-colored image which had good lightfastness.

Example 25

A. A stirred mixture of 19.2 g 0.10 mole) of trimellitic anhydride, 35 g (0.22 mole) of 1-ethyl-2-methylindole and 75 ml of acetic anhydride was heated at reflux for approximately one hour, then cooled slightly below reflux after which there was slowly added 100 ml of methanol. The resulting solution was cooled to ambient temperature and slowly poured with stirring into a mixture of ice and water. The solid that formed was collected by filtration and dried *in vacuo* at 60°C to obtain *3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula VI: R^1=R^2=H/COOH; R^5=$R^{5'}$=CH_3; R^6=$R^{6'}$=CH_2CH_3; R^0=R^3=Y^1=$Y^{1'}$=H), as deep red solid melting over the range of 110—119°C. Infrared maxima appeared at 1760 (C=O; s) and 1720 cm^{-1} (C=O; m). The nuclear magnetic resonance spectrum was in accord with the assigned structure.

B. Following a procedure similar to that described above in part C of Example 4, but using 3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described above in part A of this example instead of 3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide for interaction with dimethyl sulfate, there was obtained *3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula VI: R^1=R^2=H/$COOCH_3$; R^0=R^3=Y^1=$Y^{1'}$=H; R^5=$R^{5'}$=CH_3; R^6=$R^{6'}$=CH_2CH_3), a tan solid melting over the range of 226—229°C with decomposition. Infrared maxima appeared at 1765 (C=O; s) and 1735 cm^{-1} (C=O; s). The nuclear magnetic resonance spectrum was concordant with the assigned structure. Mass spectrum analysis showed m/e peaks at 506 (M^+). 462 (M^+—CO_2) and 447 (M^+—CO_2CH_3). An acetone solution of the product spotted on silica gel, an acidic clay or a

phenolic resin developed a deep red-colored image which had good xerographic copiability and good lightfastness.

Example 26

A stirred mixture of 3.0 g (0.006 mole) of 3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide prepared as in Example 25, part B and 35 ml of 3 - (di - *n* - butylamino)propylamine was heated at 125—130°C for approximately five hours and then allowed to cool to ambient temperature. The brown solution was poured into a mixture of water and toluene and the toluene layer was separated, washed with water and concentrated under reduced pressure. The excess amine was removed by vacuum distillation. There was thus obtained *3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - (3 - N,N - di - n - butylamino)propylaminocarbonylphthalide* (Formula VI: $R^1=R^2=H/CONH(CH_2)_3N(n\text{-}C_4H_9)_2$; $R^5=R^{5'}=CH_3$; $R^6=R^{6'}=C_2H_5$; $R^0=R^3=Y^1=Y^{1'}=H$), as a light brown oil. Infrared maxima appeared at 1770 (C=O; s) and 1650 cm^{-1} (C=O; s). The nuclear resonance spectrum was concordant with the assigned structure. When a soy oil solution of the product was spotted on silica gel, an acidic clay or a phenolic resin, a dark red-colored image developed which had good light fastness.

Example 27

A. Following a procedure similar to that described in Example 4, part B above, for interacting 10.6 g of 4/5 - carboxy - 2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl]benzoic acid, prepared as described in Example 4, part A, and 7.0 g of 1 - *n* - butyl - 2 - methylindole, there was obtained 16 g of *3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 3 - (1 - n - butyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula VI: $R^1=R^2=H/COOH$; $R^5=R^{5'}=CH_3$; $R^6=C_2H_5$; $R^{6'}=n\text{-}C_4H_9$; $R^0=R^3=Y^1=Y^{1'}=H$), a deep red solid melting over the range of 128—138°C with decomposition. Infrared maxima appeared at 1762 (C=O; s) and 1738 cm^{-1} (C=O; s).

B. Employing a procedure similar to that described above in part B of Example 25, except that 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 3 - (1 - *n* - butyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described above in part A of this Example was used in place of 3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide, there was obtained *3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 3 - (1 - n - butyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula VI: $R^1=R^2=H/COOCH_3$; $R^5=R^{5'}=CH_3$; $R^6=C_2H_5$; $R^{6'}=n\text{-}C_4H_9$; $R^0=R^3=Y^1=Y^{1'}=H$), a light orange solid melting over the range of 82—94°C. Significant infrared maxima appeared at 1765 (C=O; s) and 1730 cm^{-1} (C=O; s). Mass spectral analysis showed m/e peaks at 534 (M^+) and 490 ($M^+—CO_2$). A toluene solution of the product spotted on silica gel, an acidic clay or a phenolic resin deveoped a deep red-colored image which possessed good lightfastness.

Example 28

A. Proceeding in a manner similar to that described in Example 27, part A above, but using 1-allyl-2-methylindole instead of 1-*n*-butyl-2-methylindole for interaction with 4/5 - carboxy - 2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl]benzoic acid, there was obtained *3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 3 - (1 - allyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula VI: $R^1=R^2=H/COOH$; $R^5=R^{5'}=CH_3$; $R^6=C_2H_5$; $R^{6'}=CH_2—CH=CH_2$; $R^0=R^3=Y^1=Y^{1'}=H$), a deep red solid melting at 135°C with decomposition. Significant infrared maxima appeared at1765 (C=O; s) and 1730 cm^{-1} (C=O; m).

B. When 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 3 - (1 - allyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide prepared as described in part A of this example was substituted for 3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide in the procedure described in part B of Example 25, there was obtained *3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 3 - (1 - allyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide* (Formula VI: $R^1=R^2=H/COOCH$; $R^5=R^{5'}=CH_3$; $R^6=C_2H_5$; $R^{6'}=CH_2—CH=CH_2$; $R^0=R^3=Y^1=Y^{1'}=H$), an orange solid melting over the range of 152—164°C. Infrared spectral analysis showed maxima at 1760 (C=O; s) and 1732 cm^{-1} (C=O; s). Nuclear magnetic resonance analysis was in accord with the assigned structure. Analysis by mass spectrum showed m/e peaks at 518 (M^+), 474 ($M^+—CO_2$) and 459 ($M^+—COOCH_3$). A toluene solution of the product spotted on silica gel, an acid clay or a phenolic resin developed a deep red-colored image which had good lightfastness.

Example 29

Employing a procedure similar to that described in Example 4, part B above, for interacting 4/5 - carboxy - 2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl]benzoic acid, prepared as described in Example 4, part A and 1-ethyl-2-methylindole, there was obtained *3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula VI: $R^1=R^2=H/COOH$; $R^5=R^{5'}=CH_3$; $R^6=R^{6'}=CH_2CH_3$; $R^0=R^3=Y^1=Y^{1'}=H$). Proceeding in a manner similar to that described in Example 25, Part B, the following esters of the thus prepared 3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide of Formula VI ($R^0=R^3=Y^1=Y^{1'}=H$; $R^5=R^{5'}=CH_3$; $R^6=R^{6'}=CH_2CH_3$; $R^1/R^2=H/COOH$) above were prepared by esterification employing the appropriate dialkyl sulfate or organic halide. A toluene solution of these individual esters, when spotted on silica gel, and acidic clay or a phenolic resin, each developed a deep red-colored image which had good lightfastness. The infrared analyses, nuclear magnetic resonance analyses and mass spectral analyses obtained for the products of Examples 30 to 35 inclusive were concordant for the assigned structure given in those examples.

Example 30

3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - ethoxycarbonylphthalide (Formula VI: $R^1=R^2=H/COOC_2H_5$; $R^5=R^{5'}=CH_3$; $R^6=R^{6'}=CH_2CH_3$; $R^0=R^3=Y^1=Y^{1'}=H$) was obtained as a pale yellow solid melting over the range of 176—179°C.

Example 31

3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - n - butoxycarbonylphthalide (Formula VI: $R^1=R^2=H/COO(CH_2)_3CH_3$; $R^5=R^{5'}=CH_3$; $R^6=R^{6'}=CH_2CH_3$; $R^0=R^3=Y^1=Y^{1'}=H$) was obtained as a light orange solid melting at 88°C with decomposition.

Example 32

3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - n - octyloxycarbonylphthalide (Formula VI: $R^1=R^2=H/COO(CH_2)_7CH_3$; $R^5=R^{5'}=CH_3$; $R^6=R^{6'}=CH_2CH_3$; $R^0=R^3=Y^1=Y^{1'}=H$) was obtained as an orange oil.

Example 33

3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - phenylmethoxycarbonylphthalide (Formula VI: $R^1=R^2=H/COOCH_2C_6H_5$; $R^5=R^{5'}=CH_3$; $R^6=R^{6'}=CH_2CH_3$; $R^0=R^3=Y^1=Y^{1'}=H$) was obtained as a light orange solid melting over the range of 94—100°C. with decomposition.

Example 34

3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - allyloxycarbonylphthalide (Formula VI: $R^1=R^2=H/COOCH_2CH=CH_2$; $R^5=R^{5'}=CH_3$; $R^6=R^{6'}=CH_2CH_3$; $R^0=R^3=Y^1=Y^{1'}=H$) was obtained as a light orange solid melting over the range of 75—87°C.

Example 35

3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - n - hexadecyloxycarbonylphthalide (Formula VI: $R^1=R^2$—$H/COO(CH_2)_{15}CH_3$; $R^5=R^{5'}=CH_3$; $R^6=R^{6'}=CH_2CH_3$; $R^0=R^3=Y^1=Y^{1'}=H$) was obtained as a dark red oil. Infrared maxima appeared at 1770 (C=O; s) and 1730 cm^{-1} (C=O; s).

Example 36

A. To a stirred suspension of 9.66 g. (0.017 mole) of tetrachlorophilic anhydride and 13.4 g. (0.034 mole) of 80 percent active 1-ethyl-2-methylindole in 30 ml of benzene maintained at 0—5°C. by means of an ice bath, 10.6 g. (0.079 mole) of aluminum chloride was added in small increments. The reaction mixture was then maintained at 0 to 5°C. for an additional twenty minutes, allowed to warm to room temperature and stirred overnight. The mixture was transferred to a beaker and triturated successively with hexane, 10 percent hydrochloric acid, and lastly with 5 percent aqueous sodium hydroxide which had been heated to 70°C. The residual oil was filtered, acidified with dilute hydrochloric acid and allowed to stand overnight. On standing, the oil gave way to a solid which was collected by filtration, washed with water and dried to yield 6.8 g. of *2 - [(1 - ethyl - 2 - methyl - 3 - indolyl)carbonyl] - 3,4,5,6 - tetrachlorobenzoic acid* (Formula VIII:

$R^0=R^1=R^2=R^3=Cl$; $R^5=CH_3$; $R^6=CH_3CH_2$; $Y^1=H$), an off white solid melting at 214—216°C. Analysis by mass spectrum showed m/e peaks at 443 (M^+, Cl=35) and 398 (M^+—COOH).

B. A suspension of 2.0 g. (0.015 mole) of *m*-amino-N,N-dimethylaniline in 10 ml. of acetic anhydride was heated to 80—90°C. for approximately thirty minutes and then cooled to room temperature. 4.43 Grams (0.01 mole) of 2 - [(1 - ethyl-2-methyl-3-indolyl) - carbonyl - 3,4,5,6-tetrachloro benzoic acid, prepared as described in part A above was added and the resulting mixture was heated at 60—70°C. for approximately thirty minutes. After cooling, the reaction mixture was poured into 100 ml. of 10 percent hydrochloric acid and the mixture made alkaline with 10 percent aqueous sodium hydroxide with the addition of ice. The solid which separated was collected by filtration and dried to obtain *3 - [2 - acetamido - 4 - dimethylaminophenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 4,5,6,7 - tetrachlorophthalide* (Formula III: $R^0=R^1=R^2=R^3=Cl$; $R=R^5=CH_3$;

$R^6=CH_2CH_3$; $Y^1=H$) which developed a bluegreen color when spotted on silica gel in the form of a toluene solution.

Example 37

A. Using a procedure similar to the one described in part A of Example 4, 48.0 g (0.25 mole) of trimellitic anhydride and 32.8 g (0.25 mole) of 2-methylindole were interacted in 250 ml of ethylene dichloride to obtain 66.1 g of *4/5 - carboxy - 2 - [(2 - methyl - 3 - indolyl)carbonyl]benzoic acid* (Formula VIII: $R^1=R^2=H/COOH$; $R^0=R^3=R^6=Y^1=H$; $R^5=CH_3$) melting at 237—241°C.

B. A procedure similar to that described in part B of Example 4 above, was followed for interacting 10 g (0.023 mole) of 4/5 - carboxy - 2 - [(2 - methyl - 3 - indolyl)carbonyl]benzoic acid, prepared as described in part A above, and 8.0 g (0.06 mole) of 2-methylindole in the presence of 50 ml of acetic anhydride. There was thus obtained *3,3 - bis(2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula VI: $R^1=R^2=H/COOH$; $R^0=R^3=R^6=R^{6'}=Y^1=Y^{1'}=H$; $R^5=R^{5'}=CH_3$), a pink solid melting over the range of 145—165°C.

Example 38

A. Proceeding in a similar fashion to the one described in part A of Example 3, 28.6 g (0.01 mole) of tetrachlorophthalic anhydride, 16.2 g (0.2 mole) of N-methylpyrrole and 40 g (0.3 mole) of aluminum chloride were interacted in 50 ml of dry chlorobenzene to obtain *2 - [(1 - methyl - 2 - pyrrolyl)carbonyl] - 3,4,5,6 - tetrachlorobenzoic acid* (Formula IX: $R^0=R^1=R^2=R^3=Cl$; $R^7=CH_3$) having a melting point of 203—205°C.

B. Employing the procedure of part B of Example 3 hereinabove, 3.70 g (0.01 mole) of 2 - [(1 - methyl - 2 - pyrrolyl)carbonyl] - 3,4,5,6 - tetrachlorobenzoic acid, prepared as described in part A above, and 2.0 g (0.012 mole) of N,N,N',N'-tetramethyl-*m*-phenylenediamine were interacted in the presence of 10 ml of acetic anhydride to obtain *3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - methyl - 2 - pyrrolyl) - 4,5,6,7 - tetrachlorophthalide* (Formula IV: $R^0=R^1=R^2=R^3=Cl$; $R=R^7=CH_3$; $R^4=N(CH_3)_2$).

Example 39

To a stirred solution of 5.3 g of 3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide, prepared as described in example 8, part A, in 25 ml of acetone, there was added 30 ml of a 0.5 N methanolic sodium hydroxide solution. The mixture was stirred for approximately fifteen minutes at ambient temperature and concentrated to a syrup under vacuum. A small portion of fresh acetone was added to the syrup and the dark blue crystals which formed were collected by filtration. A small portion of hexane was added to the crystals resulting in a gummy residue. The residue was then triturated with more hexane to obtain a bright blue powder which was collected by filtration and dried to yield 4,8 g of the *sodium salt of 3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide* (Formula III: $R^0=R^3=Y^1=H$; $R^1=R^2=H/COO^{\ominus}Na^{\oplus}$; $R=R^6=C_2H_5$; $R^4=OC_2H_5$; $R^5=CH_3$), a bright

blue colored powder melting over the range 82—95°C. Infrared spectral analysis showed significant maxima at 1752 (C=O, s) and 1735 cm^{-1} (C=O, s).

By following procedures similar to those described in the foregoing examples but employing the appropriate 2 - [(1 - R^6 - 2 - R^5 - 5/6 - Y^1 - 3 - indolyl)carbonyl]- 3 - R^0 - 4 - R^1 - 5 - R^2 - 6 - R^3 - benzoic acids of Formula VIII and appropriately substituted 3 - R^4 - N,N - $(R)_2$ - anilines there will be obtained the 3 - [2 - R^4 - 4 - $N(R)_2$ - phenyl] - 3 - (1 - R^6 - 2 - R^5 - 5/6 - Y^1 - 3 - indolyl) - 4 - R^0 - 5 - R^1 - 6 - R^2 - 7 - R^3 - phthalides of Formula III, Examples 40—50, presented in Table A hereinbelow.

TABLE A
Phthalides of Formula III

Ex.	R	R^0	R^1	R^2	R^3	R^4	R^5	R^6	Y^1
40	$C_6H_5CH_2$	H	H/COONHC$_8$H$_{17}$	H/COONHC$_8$H$_{17}$	H	OC_3H_7	H	$C_6H_5CH_2$	5-F
41	CH_3	H	H/COO-*i*-C$_3$H$_7$	H/COO-*i*-C$_3$H$_7$	H	Cl	C_2H_5	H	5,6-Cl_2
42	4-Cl-$C_6H_4CH_2$	H	H/COO$^{\ominus}$K$^{\oplus}$	H/COO$^{\ominus}$K$^{\oplus}$	H	C_3H_7	CH_3	2-CH_3-1-C_3H_4	H
43	4-CH_3—$C_6H_4CH_2$	H	H/COON$(C_2H_5)_2$	H/COON$(C_2H_5)_2$	H	OC_4H_9	H	*i*-C_5H_{11}	H
44	2-F-$C_6H_4CH_2$	H	H/COO$^{\ominus}$N$H_4^{\oplus}$	H/COO$^{\ominus}$N$H_4^{\oplus}$	H	Br	C_2H_5	H	5-CH_3
45	C_2H_5	H	H/COON$(CH_2)_8$-CH$(CH_3)_2$	H/COON$(CH_2)_8$-CH$(CH_3)_2$	H	OCH_3	C_3H_7	H	H
46	$C_6H_4CH_2$	H	H/COOCH$_2$C$_6$H$_4$Cl	H/COOCH$_2$C$_6$H$_4$Cl	H	I	CH_3	H	5,6$(CH_3)_2$
47	CH_3	H	H/COONC$_6$H$_{13}$	H/COONC$_6$H$_{13}$	H	O-*i*-C_3H_7	CH_3	H	6-Br
48	*n*-C_4H_9	H	H/COO$^{\ominus}$N$^{\oplus}$HCH$_3$-C$_{14}$H$_{29}$	H/COO$^{\ominus}$N$^{\oplus}$HCH$_3$-C$_{14}$H$_{29}$	H	C_2H_5	CH_3	2-F-$C_6H_4CH_2$	H
49	C_2H_5	H	H/COOCH$_2$C$_6$H$_3$-$(CH_3)_2$	H/COOCH$_2$C$_6$H$_3$-$(CH_3)_2$	H	OC_4H_9	H	CH_3	5-Br-6-NO_2
50	$C_6H_5CH_2$, CH_3	H	H/COONHC$_2$H$_4$N-$(CH_3)_2$	H/COONHC$_2$H$_4$N-$(CH_3)_2$	H	C_2H_5	CH_3	C_2H_5	H

By following procedures similar to those described in the foregoing examples but employing the appropriate 2 - (1 - R^7 - 2 - pyrrolyl)carbonyl - 3 - R^0 - 4 - R^1 - 5 - R^2 - 6 - R^3 - benzoic acids of Formula IX and appropriately substituted 3 - R^4 - N,N - $(R)_2$ - anilines there will be obtained the 3 - [2 - R^4 - 4 - N$(R)_2$ - phenyl] - 3 - (1 - R^7 - 2 - pyrrolyl) - 4 - R^0 - 5 - R^1 - 6 - R^2 - 7 - R^3 - phthalides of Formula IV, Examples 51—62, presented in Table B hereinbelow.

TABLE B

Phthalides of Formula IV

Ex.	R	R^0	R^1	R^2	R^3	R^4	R^7
51	n-C_4H_9	H	H	$N(C_2H_5)_2$	H	$N(n\text{-}C_4H_9)_2$	C_6H_5
52	2,4-Cl_2-$C_6H_3CH_2$	H	$H/COO^{\ominus}Li^{\oplus}$	$H/COO^{\oplus}Li^{\oplus}$	H	OC_4H_9	C_2H_5
53	C_2H_5	H	Br	H	H	$N(C_2H_5)_2$	$i\text{-}C_3H_7$
54	$i\text{-}C_3H_7$	Br	Br	Br	Br	$N(i\text{-}C_3H_7)_2$	C_2H_5
55	4-Br$C_6H_4CH_2$	H	$H/COOC_{10}H_{21}$	$H/COOC_{10}H_{21}$	H	Cl	CH_3
56	2-F-$C_6H_4CH_2$	H	$H/COONHC_{12}H_{23}$	$H/COONHC_{12}H_{23}$	H	OCH_3	$n\text{-}C_3H_7$
57	2,5-$(CH_3)_2C_6H_3CH_2$	H	$H/COON(n\text{-}C_4H_9)_2$	$H/COON(n\text{-}C_4H_9)_2$	H	I	C_6H_5
58	$C_6H_5CH_2$, $s\text{-}C_4H_9$	H	$H/COO^{\ominus}\overset{\oplus}{N}H_3C_{18}H_{37}$	$H/COO^{\ominus}\overset{\oplus}{N}H_3C_{18}H_{37}$	H	C_3H_7	C_2H_5
59	C_2H_5	Cl	Cl	Cl	Cl	$N(C_2H_5)_2$	$i\text{-}C_3H_7$
60	$C_6H_4CH_2$	H	NO_2	H	H	$NHCOCH_3$	C_6H_5
61	$n\text{-}C_3H_7$	H	$NHCOCH_3$	H	H	Br	C_2H_5
62	CH_3	H	$H/COONHC_2H_4\text{-}N(i\text{-}C_3H_7)_2$	$H/COONHC_2H_4\text{-}N(i\text{-}C_3H_7)_2$	H	CH_3	CH_3

By following procedures similar to those described in the foregoing examples but employing the appropriate 2 - (9 - R^8 - 3 - carbazolyl)carbonyl - 3 - R^0 - 4 - R^1 - 5 - R^2 - 6 - R^3 - benzoic acids and appropriately substituted 3 - R^4 - N,N - $(R)_2$ - anilines there will be obtained the 3 - [2 - R^4 - 4 - $N(R)_2$ - phenyl] - 3 - (9 - R^8 - 3 - carbazolyl) - 4 - R^0 - 5 - R^1 - 6 - R^2 - 7 - R^3 - phthalides of Formula V, Examples 63—73, presented in Table C hereinbelow.

TABLE C
Phthalides of Formula V

Ex.	R	R^0	R^1	R^2	R^3	R^4	R^8
63	$C_6H_5CH_2$	H	H/COOH	H/COOH	H	Cl	*i*-C_3H_7
64	*n*-C_3H_7	Cl	Cl	H	Cl	$N(n\text{-}C_3H_7)_2$	C_6H_5
65	$C_6H_5CH_2$, C_2H_5	H	H/COO-*n*-C_4H_9	H/COO-*n*-C_4H_9	H	H	C_2H_5
66	3-Cl-$C_6H_4CH_2$	H	H/$COO^{\ominus}Na^{\oplus}$	H/$COO^{\ominus}Na^{\oplus}$	H	I	*n*-C_3H_7
67	*i*-C_4H_9	H	H/$COONHC_{16}H_{33}$	H/$COONHC_{16}H_{33}$	H	$NHCOCH_3$	CH_3
68	C_2H_5	Br	Br	Br	Br	$N(C_2H_5)_2$	*i*-C_3H_7
69	2,5-$(CH_3)_2C_6H_3CH_2$	H	H/$COOC_2H_3$	H/$COOC_2H_3$	H	O-*i*-C_3H_7	C_2H_5
70	2-F-$C_6H_4CH_2$	H	H/$COO^{\ominus}\overset{\oplus}{N}H_3C_6H_{13}$	H/$COO^{\ominus}\overset{\oplus}{N}H_3C_6H_{13}$	H	Br	C_2H_5
71	2,6-$Cl_2C_6H_3CH_2$	H	H/$COON(C_{18}H_{37})_2$	H/$COON(C_{18}H_{37})_2$	H	C_3H_7	*i*-C_3H_7
72	4-Cl-$C_6H_8CH_2$	H	H/$COOC_{12}H_{25}$	H/$COOC_{12}H_{25}$	H	Cl	CH_3
73	*n*-C_3H_7	H	H/$COONHC_3H_7N(CH_3)_2$	H/$COONHC_3H_7N(CH_3)_2$	H	CH_3	C_6H_5

By following procedures similar to those described in the foregoing examples but employing the appropriate 2 - [(1 - R^6 - 2 - R^5 - 5/6 - Y^1 - 3 - indolyl)carbonyl] - 3 - R^0 - 4 - R^1 - 5 - R^2 - 6 - R^3 - benzoic acids of Formula VIII and appropriately substituted 1 - $R^{6'}$ - 2 - $R^{5'}$ - 5/6 - $Y^{1'}$ - indoles there will be obtained the 3 - (1 - R^6 - 2 - R^5 - 5/6 - Y^1 - 3 - indolyl) - 3 - (1 - $R^{6'}$ - 2 - $R^{5'}$ - 5/6 - $Y^{1'}$ - 3 - indolyl) - 4 - R^0 - 5 - R^1 - 6 - R^2 - 7 - R^3 - phthalides of Formula VI, Examples 74—87, presented in Table D hereinbelow.

TABLE D
Phthalides of Formula VI

Ex.	R^0	R^1/R^2	R^3	R^5	R^6	Y^1	$R^{5'}$	$R^{6'}$	$Y^{1'}$
74	H	$H/COO^{\ominus}K^{\oplus}$	H	H	H	H	H	C_4H_9	OCH_3
75	H	$H/COOC_{18}H_{37}$	H	H	$C_6H_4CH_2$	5-F	C_6H_5	H	H
76	H	$H/COONHC_6H_{13}$	H	H	CH_3	6-NO_2	C_2H_5	H	CH_3
77	H	$H/COO^{\ominus}\overset{\oplus}{N}H(CH_3)_3$	H	i-C_3H_7	H	H	H	CH_3	5-Br, 6-NO_2
78	H	$H/COONH_2$	H	CH_3	H	6-Br	CH_3	2,5-$(CH_3)_2C_6H_3CH_2$	H
79	H	$H/COOC_{14}H_{29}$	H	CH_3	2-$(C_2H_5)C_6H_{12}$	H	CH_3	C_2H_3	H
80	H	$H/COON(CH_3)_2$	H	i-C_3H_7	4-$BrC_6H_4CH_2$	H	H	H	5,6-$(CH_3)_2$
81	H	$H/COO(CH_2)_8CH(CH_3)_2$	H	H	i-C_5H_{11}	H	C_6H_5	H	5,6-$(Cl)_2$
82	H	$H/COO^{\ominus}\overset{\oplus}{N}H_4$	H	CH_3	2-CH_3-$C_6H_4CH_2$	H	H	1-CH_3-C_6H_{12}	5-I
83	H	$H/COOCH_2C_6H_4Cl$	H	CH_3	3-(2-CH_3)-1-C_3H_3	H	CH_3	2,5-$(CH_3)_2C_6H_3CH_2$	H
84	H	$H/COOCH_2C_6H_3(CH_3)_2$	H	CH_3	i-C_4H_9	H	CH_3	$C_{18}H_{37}$	H
85	H	H/COO[3-(2-CH_3)-1C_3H_3]	H	CH_3	H	5,6-$(CH_3)_2$	C_2H_5	3-Cl-$C_6H_4CH_2$	H
86	H	$H/COOC_6H_{13}$	H	CH_3	2-F-$C_6H_4CH_2$	H	CH_3	CH_3	6-NO_2
87	H	$H/COONHC_6H_{12}N(CH_3)_2$	H	C_2H_5	H	CH_3	CH_3	C_2H_5	H

Example 88

The use of the compounds of Formulas I through VI and described in Examples 1 through 87 as color forming components in pressure sensitive microencapsulated copying systems is similarly illustrated with reference to the product of Example 9.

A. A mixture of 196 ml of distilled water and 15.0 g of pigskin gelatin was stirred at approximately 50°C for approximately 45 minutes. There was then added to the mixture a warmed (approximately 50°C) solution of 49.0 g of alkylated biphenyls and 1.0 g of 3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - ethoxycarbonylphthalide prepared as described above in Example 9. The resulting solution was stirred for approximately fifteen minutes. A second solution of 81.0 ml of distilled water and 5.0 g of carboxymethylcellulose was then prepared and warmed to approximately 50°C for approximately one hour.

B. The two solutions, the first containing water, gelatin,alkylated biphenyls and the product, and the second containing water with carboxymethylcellulose were mixed by means of an Eppenbach Homo-Mixer (Gifford-Wood Co., Hudson, N.Y.). The pH was adjusted to 6.5 by the addition of approximately 0.7 ml of 20 percent aqueous sodium hydroxide. To the resultant mixture was added over a period of two to three minutes 650 ml of distilled water which had been heated to 50°C. With the stirrer running at an applied voltage of between 35 to 40 volts there was slowly added sufficiently ten percent aqueous acetic acid to set the pH at 4.5, this being the point where coacervation was initiated. Four drops of 2-ethylhexanol were added to suppress foaming. After approximately twenty minutes an external ice/water bath was placed around the reactor containing the suspension. Cooling was continued and at approximately 15°C, 10.0 ml of glutaraldehyde was added over a period of five minutes. When the internal temperature reached 10°C, the Eppenbach Homo-Mixer was replaced with a conventional blade type laboratory agitator and the thus prepared suspension of microcapsules was stirred an additional three hours during which period the temperature was allowed to warm to room temperature.

C. The microcapsule suspension prepared as described in part B above was coated on paper sheets to a thickness of approximately 0.0015 inch and the coated paper air dried. The paper thus coated with the microencapsulated colorless precursor was assembled as the top sheet in a manifold system by positioning the coated side in contact with the coated side of a commercially available receiving sheet coated with a color developer of the electron accepting type. More specifically, papers coated with a phenolic resin and with an acidic clay were employed in this test. An image was then drawn with a stylus on the top sheet bearing the microencapsulated colorless precursor on its reverse side causing the affected microcapsules to rupture thus allowing the solution of the colorless precursor held by said microcapsules to flow into contact with the color developing substance on the receiving sheet whereupon a deep blue-colored image promptly formed. The developed image exhibited good lightfastness when exposed to daylight or to a daylight fluorescent lamp for extended periods.

When evaluated in a duplicating system prepared and tested as described above, the product of Example 15, 3 - (4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - ethoxycarbonylphthalide, produced a blue-colored developed image; the product of Example 20, 3 - (2 - methyl - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - ethoxycarbonylphthalide, produced a turquoise-colored developed image; and the product of Example 25B, 3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide, produced a deep red-colored developed image.

Example 89

When evaluated in a carbonless duplicating system by proceeding in a manner similar to that described in Example 88 above, except that soy oil was used in place of alkylated biphenyls, the product of Example 6, 3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - *n* - octyloxycarbonylphthalide, produced a grape-colored developed image; and the product of Example 32, 3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - *n* - octyloxycarbonylphthalide, produced a deep red-colored developed image.

Example 90

Following a procedure similar to that described in Example 88 but using kerosene instead of alkylated biphenyls for evaluation in a carbonless duplicating

system, the product of Example 12, 3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - hexadecyloxycarbonylphthalide, produced a deep blue-colored developed image.

Example 91

The utility of the phthalides of Formulas I to IV whose preparations are described in the foregoing examples as color forming components in thermal marking systems is illustrated by the incorporation and testing of the compound of Example 8B, 3 - (2 - ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide in a thermal sensitive marking paper. The test paper was prepared by a procedure similar to that described in U.S. Patent 3,539,375.

A. A mixture of 2.0 g of 3-(2-ethoxy-4-diethylaminophenyl)-3-(1-ethyl-2-methyl-3-indolyl)-5/6-methoxycarbonylphthalide, 8.6 g of a ten percent aqueous solution of polyvinyl alcohol (approximately 99 percent hydrolyzed), 3.7 g of water and 31.6 g of 1/16 inch diameter zirconium grinding beads was charged into a container which was placed in a mechanical shaker. Shaking was effected for one hour. The zirconium beads were then removed by straining the mixture through a No. 40 sieve.

B. Similarly, a mixture of 9.8 g of 4,4'-isopropylidine diphenol (Bisphenol A), 42.0 g of ten percent aqueous polyvinyl alcohol solution (approximately 99 percent hydrolyzed), 18.2 g of water and 221.2 g of 1/16 inch diameter zirconium grinding beads was charged into a container which was placed in a mechanical shaker. After shaking was effected for one hour, the zirconium beads were removed by straining through a No. 40 sieve.

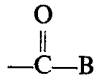
C. A coating composition was prepared by mixing 2.1 g of the slurry from A and 47.9 g of the slurry from B. The mixture was then uniformly coated on sheets of paper at thicknesses of approximately 0.003 inch and the coated sheets air-dried. The coated paper was tested by tracing a design on the coated side of the paper placed on a smooth flat surface with a stylus heated to approximately 125°C. A deep blue-colored image corresponding to the traced design promptly developed.

When evaluated in thermal marking paper prepared and tested as described above, the product of Example 25B, 3,3 - bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/5 - methoxycarbonylphthalide, produced a violet-colored image; the product of Example 7, 3 - [2,4 - bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - phenylmethoxycarbonylphthalide, produced a grape-colored image; the product of Example 14B, 3 - (4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide, produced a blue-colored image; and the product of Example 19B, 3 - (2 - methyl - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide, produced a turquoise-colored image.

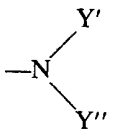
WHAT WE CLAIM IS:—

1. A compound of the Formula I (herein) wherein:

R^0, R^1, R^2 and R^3 each represent hydrogen or halo, or when R^0, R^3 and one of R^1 and R^2 are each hydrogen, the other of R^1 and R^2 represents nitro, amino, acetamido, dialkylamino wherein alkyl is non-tertiary C_1 to C_4 alkyl, or



in which B represents —OY or



wherein Y is hydrogen, an alkali metal cation, an ammonium cation, a C_1 to C_{18} mono- di- or trialkylammonium cation, C_1 to C_{18} alkyl, C_2 to C_{18} alkenyl, benzyl or benzyl substituted in the benzene ring thereof by C_1 to C_{12} alkyl, halo or C_1 to C_8 alkoxy; Y' is hydrogen or C_1 to C_{18} alkyl; Y'' is hydrogen, C_1 to C_{18} alkyl or C_4 to C_{12} N,N-dialkylaminoalkyl;

X represents a monovalent radical having the Formula A, B or C (herein),

Z represents a monovalent radical having the Formula D or E (herein), in which

R represents non-tertiary C_1 to C_4 alkyl, benzyl or benzyl substituted in the benzene ring by one or two of halo or C_1 to C_3 alkyl,

when X has the Formula B or C, R^4 represents acetamido, dialkylamino in which alkyl is non-tertiary C_1 to C_4 alkyl, and when one of R^1 or R^2 represents any of said carboxy or said carbonyl substituents, R^4 further represents hydrogen, C_1 to C_3 alkyl, C_1 to C_4 alkoxy or halo, and when X has the Formula A, one of R^1 and R^2 must represent one of said carboxy or said carbonyl groups and R^4 represents hydrogen, acetamido, dialkylamino in which alkyl is non-tertiary C_1 to C_4 alkyl, C_1 to C_3 alkyl, C_1 to C_4 alkoxy or halo,

R^5 and $R^{5'}$ represent hydrogen, C_1 to C_3 alkyl or phenyl;

R^6 and $R^{6'}$ represent hydrogen, C_1 to C_{18} alkyl, C_2 to C_4 alkenyl, benzyl or benzyl substituted in the benzene ring by one or two of halo or C_1 to C_3 alkyl,

R^7 and R^8 represent hydrogen, C_1 to C_3 alkyl or phenyl, and

Y^1 and $Y^{1'}$ represent no or one to two C_1 to C_3 alkyl, C_1 to C_3 alkoxy, halo or nitro substituents in the benzenoid portion of the indolyl radical with the provisos (i) that X and Z can both simultaneously represent monovalent indolyl moieties only when one of R^1 and R^2 represents said

and (ii) X represents a pyrrolyl or a carbazolyl moiety only when Z represents a 2-R^4-4-N-$(R)_2$-phenyl moiety.

2. 3 - [2,4 - Bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - *n* - octyloxycarbonylphthalide.

3. 3 - (2 - Ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - ethoxycarbonylphthalide.

4. 3 - (4 - Dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5 - 5/6 - methoxycarbonylphthalide.

5. 3 - (2 - Methyl - 4 - dimethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide.

6. 3 - (2 - Ethoxy - 4 - diethylaminophenyl) - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - hexadecyloxycarbonylphthalide.

7. 3 - [2,4 - Bis(dimethylamino)phenyl] - 3 - (1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide.

8. 3 - [2,4 - Bis(dimethylamino)phenyl] - 3 - (1 - phenyl - 2 - pyrrolyl)phthalide.

9. 3 - [2,4 - Bis(dimethylamino)phenyl] - 3 - (9 - ethyl - 3 - carbazolyl)phthalide.

10. A compound according to claim 1, wherein X is a radical of Formula A and Z is a radical of Formula E.

11. 3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - carboxyphthalide.

12. 3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - ethoxycarbonylphthalide.

13. 3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - *n* - octyloxycarbonylphthalide.

14. 3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - *n* - hexadecyloxycarbonylphthalide.

15. 3 - (1 - Ethyl - 2 - methyl - 3 - indolyl) - 3 - (1 - *n* - butyl - 2 - methyl - 3 - indolyl) - 5/6 - methoxycarbonylphthalide.

16. 3,3 - Bis(1 - ethyl - 2 - methyl - 3 - indolyl) - 5/6 - [3 - N,N - di - *n* - butylamino)propylaminocarbonyl]phthalide.

17. A process for preparing a compound according to claim 1, which comprises interacting a compound of the Formula VII (herein) with approximately one molecular proportion of a 3 - R^4 - N,N - $(R)_2$ - aniline or a 1 - $R^{6'}$ - 2 - $R^{5'}$ - $Y^{1'}$ - indole in the presence of an anhydride of an alkanoic acid having from 2 to 5 carbon atoms, wherein R^0, R^1, R^2 and R^3 each represent hydrogen or halo, or when R^0, R^3 and one of R^1 and R^2 are each hydrogen, the other of R^1 and R^2 represents nitro, dialkylamino wherein alkyl is non-tertiary C_1 to C_4 alkyl, or carboxy; and R, R^4, R^5, $R^{5'}$, R^6, $R^{6'}$, R^7, X, Y^1 and $Y^{1'}$ each have the same respective meanings given in claim 1.

18. A process for preparing a compound according to claim 1, wherein X is a

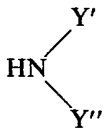
radical of the Formula A and Z is a radical of Formula E and A and E are the same which comprises interacting a 3 - R^0 - 4 - R^1 - 5 - R^2 - 6 - R^3 - phthalic anhydride with approximately two molecular proportions of an 1 - R^6 - 2 - R^5 - Y^1 - indole, wherein R^0, R^1, R^2, R^3, R^4, R^5, R^6 and Y^1 each have the same respective meanings given in claim 1.

19. A process for preparing a compound according to claim 1, wherein one of R^1 and R^2 is amino which comprises reducing the corresponding compound of Formula I wherein one of R^1 and R^2 is nitro.

20. A process for preparing a compound according to claim 1, wherein one of R^1 and R^2 is acetamido which comprises interacting a compound of Formula (VII) herein where one of R^1 and R^2 is amino and the other of R^1 and R^2 and each of R^0 and R^3 are hydrogen, with approximately one molecular proportion of a 3 - R^4 - N,N - $(R)_2$ - aniline or a 1 - $R^{6'}$ - 2 - $R^{5'}$ - $Y^{1'}$ - indole in the presence of at least two molecular proportions of acetic anhydride wherein R^4, $R^{5'}$, $R^{6'}$, X and $Y^{1'}$ each have the same respective meanings given in claim 1.

21. A process for preparing a compound according to claim 1, in which one of R^1 and R^2 is COOY and Y is C_1 to C_{18} alkyl, C_1 to C_{18} alkenyl, benzyl or benzyl substituted in the benzene ring thereof by C_1 to C_{12} alkyl, halo or C_1 to C_8 alkoxy which comprises esterifying the corresponding compound of Formula I where one of R^1 and R^2 is COOH with a corresponding alkylating agent.

22. A process for preparing a compound according to claim 1, in which one of R^1 and R^2 is CON(Y')(Y'') which comprises amidating the corresponding compound of Formula I in which one of R^1 and R^2 is COOY with a corresponding compound of the formula



23. A process for preparing a compound according to claim 1, in which one of R^1 and R^2 is COOY wherein Y is an alkali metal cation, an ammonium cation, or a C_1 to C_{18} mono, di- or trialkylammonium cation, which comprises reacting a corresponding compound of Formula I wherein one of R^1 and R^2 is COOH with a corresponding alkali metal or ammonium salt or a primary amine.

24. A process for preparing a compound according to claim 1, substantially as herein described with reference to the Examples 1—34 and 36—87.

25. A process for preparing a compound according to claim 1, substantially as herein described with reference to Example 35.

26. A compound as claimed in any of claims 1 to 16, when prepared by the process according to any one of claims 17 to 25.

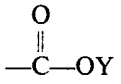
27. A compound according to claim 1, substantially as herein described with reference to Examples 1—34 and 36—87.

28. A compound according to claim 1, substantially as herein described with reference to Example 35.

29. A pressure-sensitive carbonless duplicating system, thermal marking system or hectographic copying system containing as a color-forming substance a compound according to any one of claims 1 to 16 and 26 to 28.

30. A thermal marking system according to claim 29, comprising a support sheet coated on one side with a layer containing a mixture of the color-forming substance and an acidic developer arranged such that application of heat will produce a mark-forming reaction between the color-forming substance and the acidic developer.

31. A hectographic copying system comprising a support sheet coated on one side with a layer containing a color-forming substance comprising a compound according to claim 1, wherein R^0, R^3 and one of R^1 and R^2 are each hydrogen and the other of R^1 and R^2 represents



wherein Y is an alkali metal cation, an ammonium cation or a C_1 to C_{18} mono-, di- or trialkylammonium cation.

32. A pressure-sensitive carbonless duplicating system, thermal marking system or hectographic copying system according to claim 29, substantially as herein described with reference to the Examples 88—91.

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