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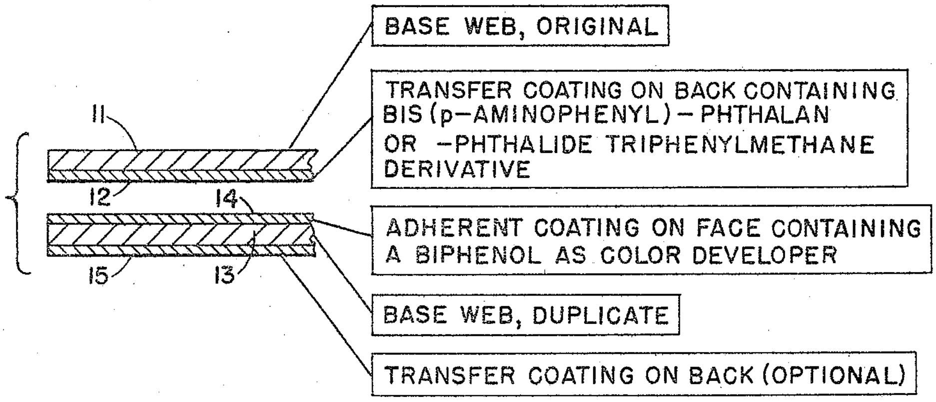

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3,244,550

MANIFOLD SHEETS COATED WITH LACTONE AND RELATED CHROMOGENOUS COMPOUNDS AND REACTIVE PHENOLICS AND METHOD OF MARKING

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This invention relates to arrangements and methods for producing dark-colored marks from colorless materials, which ordinarily appear white, or from materials which are only lightly colored. These materials usually are incorporated in coatings on webs, the coatings conveniently being on paper rolls, ribbons, or sheets. As used in the present specification and in the appended claims, both achromatic colors, that is, grays and black, and chromatic colors are included; dark-colored materials may be dark gray or black; or they may be chromatic colors likewise of low brilliance, such as dark blues, greens, purples, red, and browns whether or low or high saturation, or even vivid colors of high saturation and high brilliance, such as bright blues, greens, and reds. All of these colors are distinguished markedly from colorless materials, or from lightly colored materials having white or light gray colors or having pastel shades of high brilliance but low saturation.

The use of dyes and pigments in making multiple copies of correspondence, business documents, multiple forms and records, and the like always has been a source of some annoyance due to the tendency of the colored materials to smudge and to soil the skin and clothing of the user. A common example is carbon paper; another is the use of dyes on the master sheets or in the printing solutions employed in office duplicating systems. Considerable success has been achieved in making carbon paper less susceptible to casual transfer of the coloring agents, as by covering the transfer layer with a thin wax coating, or by binding a colored transfer vehicle within a layer from which only substantial pressure causes it to be extruded, but smudging and soiling still can occur during handling. Likewise some duplicating systems have been made cleaner by using diazo substances having little coloring or staining power until brought into contact with a diazo coupler, but difficulty in providing proper conditions for the diazo coupler reaction has limited their use, and the colored marks are less intense than those produced by the standard duplicating master sheets using the highly colored triphenylmethane dyes.

Another system proposed early in the development of the art involves the transfer by writing or typing pressures of one color reagent from a sheet or coating, which replaces a carbon sheet, to the face of a duplicate sheet carrying a complementary color reagent. Use of materials such as ferric sulfate on one surface and tannic acid on the other were proposed, such that deposits of a dark-colored compound of the two materials are formed where the reagents are brought together on the duplicate surface. In the absence of the second reagent, no amount of handling can cause smudging. Shortcomings such as unwanted color formation on the treated surfaces during storage or casual handling, or insufficient speed of formation, contrast, and stability of the colored marks, or the necessity of maintaining adequate moistness or other reaction environment at the marking surface, have kept such systems using many types of color reagents from extensive use.

Marking systems of this general type have been proposed which utilize as color-producing or chromogenous compounds the leuco, or simple amino-substituted triphenylmethane, substances such as leuco-malachite green, crystal violet, and ethyl violet, or the corresponding para-amino-substituted triphenylmethyl carbinols. From the standpoints of stability of both the chromogenous compounds and the color-activating materials used therewith, and of control in developing the colored forms, it has been found advantageous in some marking or image-duplicating systems to utilize the lactone forms, which are p-amino-substituted diphenylphthalides, corresponding to the above-mentioned leuco forms, or the lactones or colorless bases of the rhodamine dyes.

It is known that lactone materials of these types, dissolved in an oily liquid, may be brought into contact with particles of an inorganic material such as attapulgite, halloysite, magnesium trisilicate, calcium silicate, or basic aluminum silicate to produce dark-colored products. Weak acids such as acetic acid and tartaric acid also have been suggested for use with the lactone color-forming compounds to develop dark-colored products, but in practice the clay-like materials or other inorganic solids such as those mentioned above have been used for this purpose. In addition to acetic and tartaric acids, diluted stronger acids also have been suggested generally for this purpose, but without naming any specific acids, strengths, or dilutions, and there is no indication that any specific inorganic acids or any other carboxylic acids have been found to be desirable or particularly suitable. The weaker inorganic acids, such as boric acid, also appear to have little if any efficacy in producing dark-colored products from the chromogenous lactone compounds. Thus it is neither necessary nor especially probable that a material having the chemical constitution and dissociation properties recognized as characteristic of acids will be desirable or particularly suitable for such a purpose. Even when using the inorganic color-developing materials mentioned above, the solid colored products lose much or all of their color in the presence of various polar solvents and their vapors, notably water; they tend to deteriorate with age and are noticeably unstable to irradiation as from sunlight or fluorescent lamps.

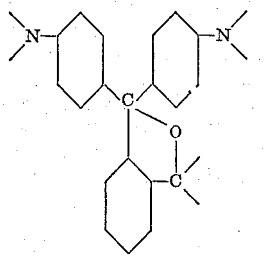
It is an object of the present invention, therefore, to provide novel and improved web coatings, methods of marking and duplicating or otherwise developing dark-colored materials, and such materials themselves, which avoid one or more of the disadvantages of the prior art.

It is another object of this invention to provide new coating arrangements and associated color-developing systems for use with lactone and related chromogenous compounds, so as to provide novel, spirit-soluble and oil-soluble, dark-colored materials or marks having generally improved characteristics such as color intensity, speed of color development, insensitivity to moisture, and resistance to radiation, oxidizing agents, and other environmental influences which tend to cause deterioration of the colored product.

It is a further object of this invention to provide a manifolded set arrangement, utilizing a novel combination of colorless or lightly colored smudge-proof materials, for producing one or more copies by transfer of color-generating substances from the back surface of each sheet in the set to the face of the next lower sheet to form marks or characters of improved high contrast and durability on the lower sheet or sheets immediately upon writing or printing on the top sheet.

It is still another object of this invention to provide new and improved methods of developing dark-colored materials from chromogenous compounds, useful in particular for producing marks on a substrate, and for making duplicate images by new and improved modifications of the spirit-duplicating process.

In accordance with the invention, an article of manufacture is provided in the form of a web carrying a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol, methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which the two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol, such phenolic compound being evenly distributed in amounts of from 0.2 to 8 grams per 1,000 square inches of web surface, and the web being adapted for the production of dark-colored material by contact of the phenolic compound carried by the web with a colorless or lightly colored chromogenous compound which includes as its major functional arrangement the molecular structure



In a modification the web has on one side an adherent coating which comprises a film-forming material containing the phenolic compound as a finely dispersed phase but accessible to other materials coming into contact with portions of the coating, the web being adapted for developing dark-colored material at a portion of the coating by the action of the phenolic compound on such chromogenous compounds when the latter come into contact with that portion of the coating. In some arrangements the web carries the specified phenolic compound transferable upon local impact from the web to a surface contiguous therewith, whereon contact may be made of the portions so transferred with such a chromogenous compound to develop the dark-colored material.

In accordance with a feature of the invention, a manifolded set comprises a first base web having on one side a transfer coating containing the above-identified chromogenous compound, which is transferable upon impact from the coating to a surface contiguous therewith, and a second base web carrying on at least one active surface one of the aforementioned phenolic compounds, the first and second webs being maintained disposed together in face to face relationship with the transfer coating in contiguity with the active surface, whereby, upon such impact in localized areas, a dark-colored material is produced locally by the action of the phenolic compound carried on the active surface in opening the bond from the central methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in the chromogenous compound transferred to the active surface. In accordance with a more specific feature of the invention, the transfer coating is made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a liquid vehicle carrying the chromogenous compound. In a related but broader aspect of the invention, either one of the two constituents—the chromogenous compound and the phenolic compound—is selected and dissolved in the liquid vehicle present as the numerous cells in the transfer coating on the first base web, while the other of these constituents is bonded to the second web in an adherent coating thereon but accessible to the first-selected constituent when it comes into contact wih portions of the adherent coating.

In accordance with a method feature of the invention, the method of developing dark-colored materials from chromogenous compounds comprises bringing the aforementioned chromogenous compound into reaction contact with the phenolic compound. In the method of marking on a substrate, the chromogenous compound is brought into contact, in areas on the substrate where marking is desired, with the phenolic compound to produce marks in such areas of a dark-colored material formed by the action of the phenolic compound on the chromogenous compound. The invention also encompasses the new composition of matter comprising the dark-colored substance obtained by intimate contact of the phenolic compound with the colorless or lightly colored chromogenous compound.

In a method of duplicating, in accordance with the invention, two colorless or lightly colored substances are provided, these substances being the aforementioned chromogenous compound and the phenolic compound, and the method then comprises forming, on the surface of a master sheet, deposits of a preselected one of these two substances in areas representing an image to be duplicated but with mirror-reversed image elements. Thereafter a solution of the remaining one of the two substances in a solvent liquid is applied to the surface of a duplicate sheet, and this duplicate sheet surface, wetted with the solvent liquid containing that remaining one of the two substances, is pressed against the master sheet surface to effect transfer by the solvent liquid of portions of the image-representing deposits of the preselected one of the two substances from the master sheet surface to the duplicate sheet surface in areas thereon representing the image, whereby a duplicate image is formed on the duplicate sheet surface of dark-colored material produced by the action of the phenolic compound on the chromogenous compound. In a modification of the method of duplicating, in accordance with the invention, the remaining one of the two substances is carried at all times on the surface of the duplicate sheet, and a liquid which is a solvent for the preselected one of the two substances is applied to that surface, which then is pressed, thus wetted, against the master sheet surface to cause portions of the preselected one of the two substances deposited thereon to dissolve in the liquid and to be transferred into contact with the remaining one of the two substances, carried on the duplicate sheet surface, in the areas thereon representing the image, whereby the resulting dark-colored material forms a duplicate image on the duplicate sheet surface.

For a better understanding of the present invention, together with other and further objects thereof, reference is had to the following description taken in connection with the accompanying drawing, and its scope will be pointed out in the appended claims.

The single figure of the drawing shows in exploded view two manifolding units, suitable for use together in face to face contiguity in a manifolded set with or without additional similar manifolding units. These units are shown as coated webs, illustrated in cross section with the thicknesses of the base webs and of the coatings on the web surfaces greatly exaggerated for convenience of illustration.

The manifolded set illustrated comprises a base web **11** having on one side a transfer coating **12**, containing as a coating constituent a substance which interacts with a second substance to generate a colored material, and which is transferable upon impact from the coating **12** to a surface contiguous therewith. The coating **12** may be simply the solid substance to be transferred, bonded to the web **11** by a solid adhesive or binder of a waxy or resinous material which may be dislodged under pressure from the web surface, but preferably a liquid vehicle is provided, dispersed throughout a solid film, which carries the substance to be transferred, as will be discussed in greater detail hereinbelow. Thus the first base web **11** preferably has the coating **12** made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a solvent liquid vehicle. Another base web **13** also is provided, having an adherent coating **14** on one side, being the side nearer the web **11** and its coating **12**. During use, as will be discussed, the two webs are maintained disposed together in face to face relationship. The adherent coating **14** carries the aforementioned second substance such that the two individual coating constituents, although each is colorless or only lightly colored, together form upon intimate contact with each other a dark-colored product. One of these coating constituents is a colorless or lightly colored chromogenous compound of a type identified hereinbelow. The other coating constituent is a phenolic substance which may be classified as a biphenol and which also will be identified more particularly hereinbelow. For convenience of reference the term "biphenol" is used here, although it will appear that related phenolic compounds, likewise containing two benzene rings carrying phenolic hydroxyl groups, also are intended, including principally methylenediphenols, alkylidenediphenols, terphenyldiol, thiodiphenol, and sulfonyldiphenol.

Accordingly, in one embodiment of the invention, a manifolded set is arranged with the phenolic substance in the transfer coating **12**. The web **11** then carries, transferable therefrom upon local impact to a surface contiguous therewith, the selected phenolic substance, so that the web is adapted, upon such impact and transfer of portions of the substance locally to the contiguous surface of the web **13**, for contact thereon of the portions so transferred with the chromogenous compound to develop a dark-colored material by the action of the substance so transferred on the chromogenous compound. However, one advantage of these phenolic substances, as color developers for the class of chromogenous compounds involved, is the ready solubility of most of the phenolic substances in many vehicles, including nonvolatile liquids having physical properties well suited for use as vehicles in color-producing and marking systems; color-developing substances such as the clay-like inorganic substances recommended by prior art practice lack such solubility. Thus the transfer coating **12** may be made up of a film-forming material such as casein, gelatin, a cellulose derivative, or polyvinyl alcohol, applied as a hydrophilic aqueous composition containing an oily liquid vehicle emulsified therein, so that the dried film is rupturable upon impact and contains as a finely dispersed phase numerous microscopic droplets or cells of the liquid vehicle carrying the phenolic substance dissolved therein. The vehicle may be any one of numerous suitable nonvolatile solvent vehicles, such as castor oil, sperm oil, a chlorinated phenyl ether, or benzyl butyl phthalate. In this embodiment the other color-reactive material, or chromogenous compound, is bonded to the web **13** in the adherent coating **14** by a cementitious material.

A few phenolic substances, especially in impure or admixed forms, are in the liquid state at fairly low temperatures, and can be emulsified in a film-forming composition with the use of little solvent material to form a liquid dispersed phase. In another aspect, a web with a transfer coating containing a phenolic substance may take the form of a fabric ribbon impregnated with ribbon-inking oils which carry the substance to be transferred. Such a ribbon may be used in a typewriter for applying the transferable substance to the surface of a sheet carrying the other color-reactive or chromogenous material. Dark-colored marks or characters then are formed on the sheet by impact of the types through the ribbon, even though the ribbon and the sheet surface are white in color prior to use. On the other hand, some systems for developing dark-colored marks are operative with a transfer ribbon or sheet containing the solid transferable material in a simple frangible transfer medium of, for example, solid or plasticized wax.

In a different arrangement in accordance with the invention, the first base web **11** in the manifolded set has a transfer coating **12** on the back containing the specified chromogenous compound, which is most cases may be viewed as a compound related to, or a derivative of, triphenylmethane but having a heterocyclic ring including the methane carbon atom, more specifically a 1,1-bis(p-aminophenyl)phthalan compound or a 3,3-bis(p-aminophenyl)phthalide compound, usually with substituents. The second base web **13** in this embodiment of the invention then carries the phenolic substance, preferably evenly distributed in amounts of from 0.2 to 8 grams per 1,000 square inches of web surface. When it is of a suitable material, the web or its surface regions on one side may be impregnated by dissolving the phenolic substance in a volatile solvent, applying the solution to the web, and drying. The phenolic substance accordingly is carried on at least one active surface of the web. Preferably the web carries on only one active face an adherent coating containing the phenolic substance as the color developer. Some of the phenolic substances may be made to adhere as a coating to most paper or film web materials without the use of an adhesive or film-forming substance. Usually, however, it is desirable to include an inert binder in this coating. The coating nevertheless readily may contain enough phenolic substance to make up much more than half of its weight, and in any case the web should have on one side and adherent coating comprising the phenolic substance bonded to the web in an amount equal to at least ten percent of the weight of the coating. For this purpose the adherent coating conveniently comprises a film-forming material containing the phenolic compound as a separate, finely dispersed phase but accessible to other materials coming into contact with portions of the coating, so that the coated web is adapted for developing dark-colored material at a portion of the coating when a colorless or lightly colored chromogenous compound of the type described herein comes into contact with that portion of the coating. Whether the phenolic substance is carried on a web in a transfer coating or in an adherent coating, the web is adapted for the production of dark-colored material by contact of the phenolic substance supplied by or on the web with the chromogenous compound.

The use in large proportions of an impervious adhesive material which would coat or cover most of the phenolic substance in an adherent coating would render the coating practically ineffective by preventing contact of much of the developer substance with any chromogenous compound brought onto the surface of the coating. Assuming that the coating is sufficiently pervious so that the developer material therein is accessible, one means for bringing the chromogenous compound into contact with portions of the coating to develop colored material is to incorporate in or on the same coating numerous very small capsules containing the chromogenous compound dissolved in a solvent liquid. With this arrangement local impact or pressure on the coating causes the capsules to break locally, bringing about contact of the two materials within the single coating to develop the dark-colored marks. Desirable marking sensitivities and color-free unmarked surfaces are more easily obtained, however, when the coated web carrying the developer material is used as a manifolding unit in a manifolded set, as illustrated for example in the drawing. Of course, the developer substance in the coating **14** would be accessible to chromogeneous material coming into contact with the coating if substantial portions of the developer substance are exposed at the top of the coating, even though the adhesive which joins the lower portions of the developer substance to the face of the web **13** is itself impervious. If the chromogenous compound is carried by a liquid vehicle which permits the chromogenous compound to penetrate to the developer substance in the coating **14**, it obviously would not be necessary that the developer substance in the coating be accessible to all materials which might reach the coating.

For applying the phenolic substance to the web **13** as an adherent coating **14**, in which the phenolic substance is accessible to chromogenous materials coming into contact with the coated face of the web, many film-forming or cementing materials are available for use as bonding agents. Various agents have different tendencies to coat the phenolic substance and so partially obstruct access thereto of the chromogenous material, but the proportion of phenolic substance to cementing material on a dry basis ordinarily can be made high enough to insure entirely sufficient access while permitting adequate bonding. If the coating procedure involves dispersion of the phenolic substance in a liquid-dispersed or dissolved film-forming composition, there may be a tendency when certain materials are used for the phenolic substance to dissolve in the coating composition, but, upon evaporation of the liquid medium during drying, any such dissolved phenolic substance usually crystallizes out as solid portions which are accessible to the chromogenous material while being bonded to the web.

A preferred binder material for the phenolic substance is a film former which can be applied to the web surface as a latex. A synthetic latex conveniently may be used, and ordinarily the phenolic substance, and conventional dispersing and foam-inhibiting agents when desired, are readily compatible with such a latex. A polybutadiene-styrene latex advantageously may be used, such as one having in the water vehicle 48% by weight of resin solids formed from monomers with a 2:1 butadiene:styrene ratio. An example of this coating composition follows, as applied for instance to a paper or film web such as a 12 pound sulfite bond paper, then dried:

Coating Composition Ingredients	Parts by Weight, Wet	Parts by Weight, Dry
Phenolic compound	35	35
Polybutadiene-styrene latex	14.6	7
Neutral white pigment	4	4
Dispersing agent	3.2	0.8
Antifoaming agent	0.2	0.2
Water, to adjust viscosity	43	---------
Totals	100	47

Other polybutadiene styrene latices having larger or smaller butadiene-styrene ratios with suitable dispersing agents may be used in this formulation, and other film-forming latices also may be substituted for the polybutadiene-styrene latex, usually with a lower proportion of phenolic compound to latex solids. Neutral or inert pigments serve to make the adherent coating whiter and more opaque and frequently are desirable in amounts of roughly a tenth of the coating weight on a dry basis. Titanium dioxide pigment has been used, for which zinc oxide, zinc sulfide, or zirconium dioxide, as other examples, may be substituted. These pigments, at least in such quantities, have no noticeable effect on the color-developing activity of the adherent coating; in fact, if the phenolic substance were to be omitted from the coating, leaving only such an inert pigment, the coating would have no color-developing utility. For the dispersing agent there was used in the compoistion given above a solution of the sodium salt of naphthalene-sulfonic acid condensed with formaldehyde; a number of dispersing agents of this and related types are available to the art. When an antifoaming agent is indicated, small amounts of conventional materials such as the silicones, fatty acid esters, petroleum distillates, and the higher aliphatic alcohols may be used in the latex composiiton.

A coating composition such as the one just described may be applied so as to obtain useful dried coatings in a very broad range of thicknesses and weights. A coating roughly 0.0002 inch thick of this dried composition, having a coating weight of about 4 grams per 1,000 square inches and a weight of the phenolic compound of about 3 grams per 1,000 square inches, usually gives excellent results. While a range of about 1.5 to 4 grams of the phenolic compound per 1,000 square inches of web surface is preferred, coatings giving useful results ordinarily may have amounts of from 0.2 to 8 grams per 1,000 square inches. Smaller amounts in extremely thin coatings ordinarily would not provide adequate color-developing action, while larger amounts in relatively thick coatings ordinarily would not be justified by any improvement in color-developing activity. The dry coating of the example given above has a high ratio of five times as much phenolic compound as resin binder by weight, but entirely useful coatings can be obtained when the inert bonding materials weigh several times as much as the phenolic substance in the coating. Thus it appears that amounts of the phenolic substance in the coating equal to well over 10% of the dry coating weight and within the aforementioned weight limits per unit web area may be obtained readily.

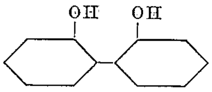
Reference now will be made to the chemical structure of the various phenolic substances included or utilized in the several embodiments of the present invention. As mentioned above, these phenolic substances may be classified broadly as biphenols, including for present purposes methylenediphenols and certain other related compounds. More specifically, the phenolic compound involved in the embodiments of the present invention is selected from the group consisting of:

(a) biphenol,
(b) bicresol,
(c) dibenzylbiphenol,
(d) diethylbiphenol,
(e) dipropylbiphenol,
(f) diallylbiphenol,
(g) dihalobiphenol,
(h) biphenyltetrol,
(i) terphenyldiol,
(j) methylenediphenol,
(k) alkylidenediphenol,
(l) cycloalkylidenediphenol,
(m) methylenediresorcinol,
(n) methylenebis(alkylphenol),
(o) methylenebis(benzylphenol),
(p) methylenebis(phenylphenol),
(q) methylenebis(halophenol),
(r) methylenebis(trihalophenol),
(s) methylenebis(tetrahalophenol),
(t) substituted methylenediphenol in which each phenol has only two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which these two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group,
(u) thiodiphenol, and
(v) sulfonyldiphenol.

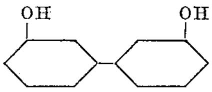
There are mentioned hereinbelow examples of all of the phenolic compounds identified in the above tabulation. These examples illustrate the variety of compounds available, including those which differ from each other primarily by the positions of the phenolic hydroxyl groups and of other substitutents on the benzene rings. These variations of substituents and their positions often affect to some degree the speed or ease of production, and the brilliance or even the hue, of the dark-colored marks obtained when contact is effected with a given chromogenous compound.

The first type of phenolic compound to be considered will be the biphenols themselves, shown below under a heading having the same designating letter used in the above tabulation.

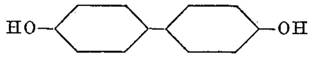
(a) *Biphenol*



o, o′-biphenol



m, m′-biphenol

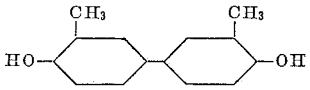


p, p′-biphenol

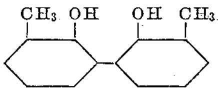
All of the six biphenol isomers are useful as color-developing materials, but only the more commonly available symmetrical biphenols are shown. The o,o′-biphenol has very good color-developing capability with the chromogenous compounds, while the other two are moderately active. When a p-aminophenyl-substituted phthalide color-forming composition is dissolved in benzyl butyl phthalate, for example, and applied to a surface carrying the p,p′-biphenol, it is helpful to heat the surface mildly to hasten the formation of a dark-colored material giving intensely colored marks. Other solvent liquids suitable as carriers for one of the color reagents, usually for the chromogenous compound, are suggested herein. In the case of the phthalide compound used with the biphenol color developer just mentioned, and also with many of the other color-developing materials and chromogenous compounds mentioned below, significant variations in the speed of reaction and color intensity of the dark products formed often may be obtained by choosing different solvent or carrier liquids.

Among the biphenols having on each benzene ring a methyl, ethyl, propyl, allyl, benzyl, or halo substituent may be mentioned the following, symmetrical compounds likewise being illustrated:

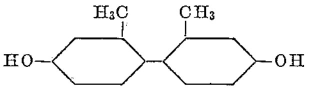
(b) *Bicresol*



4,4′-bi-o-cresol

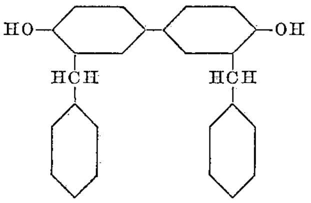


6,6′-bi-o-cresol



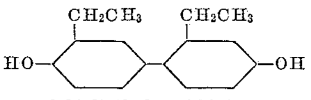
4,4′-bi-m-cresol

(c) *Dibenzylbiphenol*

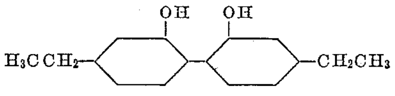


α,α′-diphenyl-4,4′-bi-o-cresol

(d) *Diethylbiphenol*

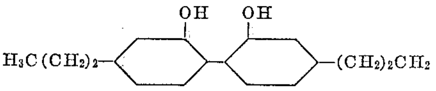


2,2′-diethyl-p,p′-biphenol

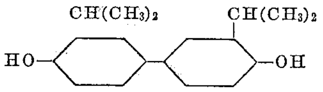


5,5′-diethyl-o,o′-biphenol

(e) *Dipropylbiphenol*

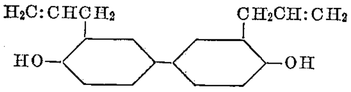


5,5′-dipropyl-o,o′-biphenol



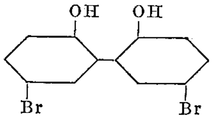
2,2′-diisopropyl-p,p′-biphenol

(f) *Diallylbiphenol*



2,2′-diallyl-p,p′-biphenol

(g) *Dihalobiphenol*

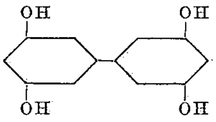


4,4′-dibromo-o,o′-biphenol

The bicresols, or dimethylbiphenols, provide moderate to good color-developing properties. As regards the dibenzylbiphenol, the positions of the phenolic hydroxyl groups and the benzyl radicals may be varied, of course, to obtain other useful compounds, corresponding for example to the bicresols shown above with various positions of the substituents. It will be appreciated, also that the allyl radicals in a diallylbiphenol compound may be replaced by other groups, such as the 1-methylallyl, 2-methylallyl, and 2-chloroallyl groups, to obtain generally equivalent properties. While a dibromobiphenol is shown as illustrating the dihalobiphenols, it will appear that other halo radicals such as the chloro radical may replace the bromo radical, and that, again, the positions of the substituents on the biphenyl structure may be varied, as with the bicresols.

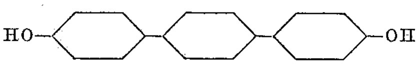
The biphenol may have more than one phenolic hydroxyl radical on each benzene ring. Moreover, if the two phenolic rings are separated in the molecular structure, a phenylene group may be interposed between them. Such compounds are illustrated by the following:

(h) *Biphenyltetrol*



3,3′,5,5′-biphenyltetrol

(i) *Terphenyldiol*

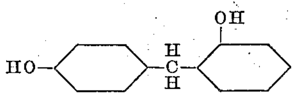


p-terphenyl-4,4″-diol

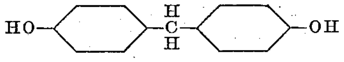
These two compounds, especially the 3,3′,5,5′-biphenyltetrol, exhibit good color-developing activity.

In addition to the compounds of the biphenol type, it has been found that many compounds containing the two phenolic groups linked by a methylene radical provide high color-developing potential. A substituted methylene radical in the form of an alkylidene radical may replace the methylene radical; in this usage the term alkylidene may be taken to exclude methylene but to include ethylidene, propylidene, etc. Alternatively, the compound may include a substituted methylene radical in the form of a cycloalkylidene radical. Illustrative of such compounds are the following:

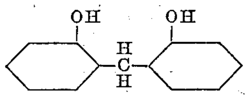
(j) *Methylenediphenol*



2,4′-methylenediphenol

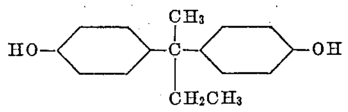


4,4′-methylenediphenol

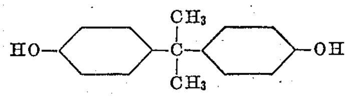


2,2′-methylenediphenol

(k) *Alkylidenediphenol*

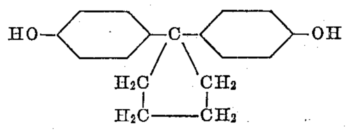


4,4′-sec-butylidenediphenol

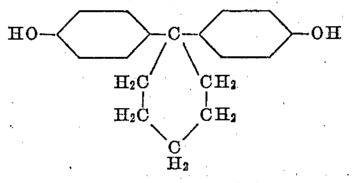


4,4′-isopropylidenediphenol

(l) *Cycloalkylidenediphenol*

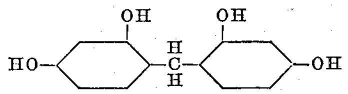


4,4′-cyclopentylidenediphenol



4,4′-cyclohexylidenediphenol

(m) *Methylenediresorcinol*

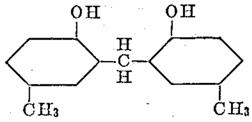


4,4′-methylenediresorcinol

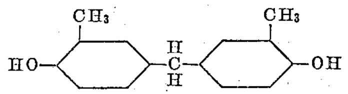
Among these compounds special reference may be made to the sec-butylidenediphenol compounds, particularly 4,4′-sec-butylidenediphenol, which has been found to be particularly advantageous for use as a color-developing substance.

Particularly good results also have been obtained with a number of substituted methylenediphenols in which each phenyl ring carries an alkyl, benzyl, phenyl, or halo substituent in addition to the phenolic hydroxyl group. These compounds are exemplified by the following:

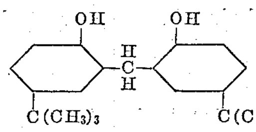
(n) *Methylenebis(alkylphenol)*



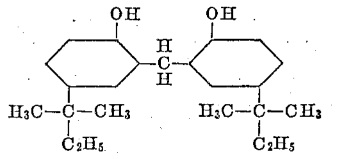
2,2′-methylenedi-p-cresol



4,4′-methylendi-o-cresol

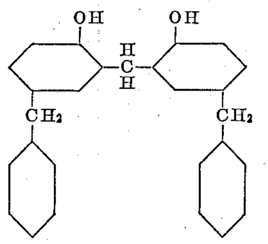


2,2′-methylenebis(4-tert-butylphenol)



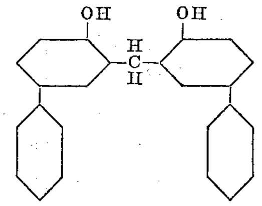
2,2′-methylenebis(4-tert-pentylphenol)

(o) *Methylenebis(benzylphenol)*



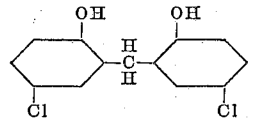
2,2′-methylenebis(α-phenyl-p-cresol)

(p) *Methylenebis(phenylphenol)*

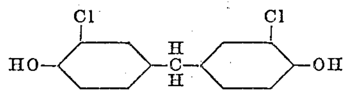


2,2′-methylenebis(4-phenylphenol)

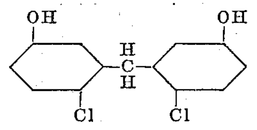
(q) *Methylenebis(halophenol)*



2,2′-methylenbis(4-chlorophenol)



4,4′-methylenebis(2-chlorophenol)



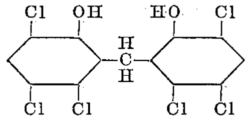
3,3′-methylenebis(4-chlorophenol)

Preferred among the compounds just shown are those with the structure of a substituted 2,2′-methylenediphenol having a substituent, in each of the two para or 4,4′-positions, selected from the group consisting of the methyl and other alkyl, benzyl, phenyl, and halo radicals. Notable among these compounds are 2,2′-methylenebis(4-phenylphenol) and 2,2′-methylenebis(4-chlorophenol). As to the methylenebis(halophenols) illustrated, a bromo or another halo radical may be substituted for the chloro radical.

Some of these compounds are found in commercially available resinous products, which thus may be used as color-developing materials to the extent that they contain a methylenediphenol compound of the type described herein.

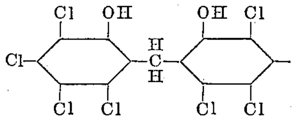
Certain methylenediphenol compounds having two or more substituents on each phenyl ring in addition to the hydroxyl group also are useful in the arrangements and methods of the invention, as illustrated by the following:

(r) *Methylenebis(trihalophenol)*



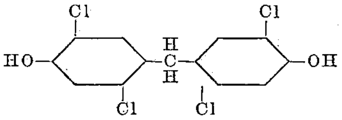
2,2′-methylenebis(3,4,6-trichlorophenol)

(s) *Methylenebis(tetrahalophenol)*

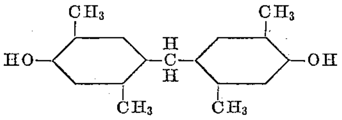


2,2′-methylenebis(3,4,5,6-tetrachlorophenol)

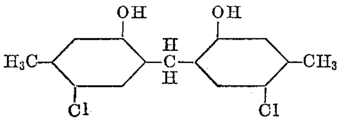
(t) *Methylenebis(disubstituted-phenol)*



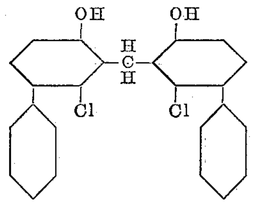
4,4′-methylenebis(2,5-dichlorophenol)



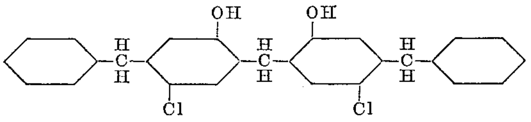
4,4′-methylenedi-2,5-xylenol



6,6′-methylenebis(4-chloro-m-cresol)



2,2′-methylenebis(3-chloro-4-phenylphenol)

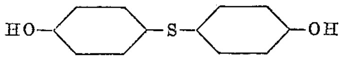


6,6′-methylenebis(4-chloro-α-phenyl-m-cresol)

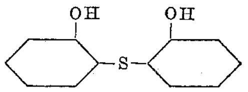
Certain methylenebis(disubstituted-phenol) compounds have been found to have relatively low activity as color developers. While weak color responses have been noted with some of these compounds, their use in general is not recommended. Accordingly it is preferred to use such substituted methylenediphenols, in which each phenol has only two substituents, wherein these two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group. The aforementioned two substituents may be selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals, as illustrated above. The compounds given above are illustrative only; other methylenedixylenols, for example, may be used.

Good results also have been obtained with thiodiphenol and sulfonyldiphenol, as illustrated by the following examples:

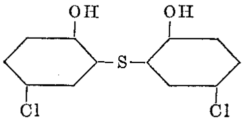
(u) *Thiodiphenol*



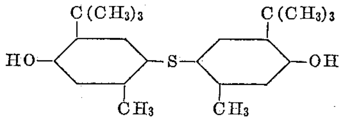
4,4′-thiodiphenol



2,2′-thiodiphenol

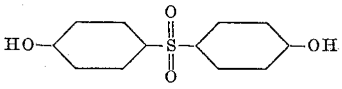


2,2′-thiobis(4-chlorophenol)

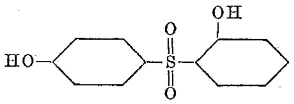


4,4′-thiobis(6-tert-butyl-m-cresol)

(v) *Sulfonyldiphenol*



4,4′-sulfonyldiphenol



2,4′-sulfonyldiphenol

Among the compounds just mentioned, the thiodiphenols, and particularly the compound 4,4′-thiodiphenol, have high color-developing activity. Chloro-substituted and alkyl-substituted thiodiphenols, such as those also shown above, give generally equivalent results.

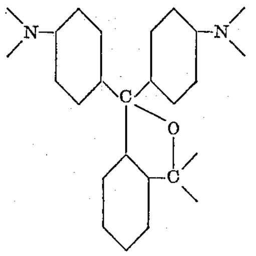
For the most part the phenolic color-developing compounds of the types disclosed above do not exhibit substantial solubility in water. If use in a particular system should make water solubility desirable, the sodium, ammonium, or potassium derivatives of many of the phenolic compounds disclosed above may be utilized. These derivatives, which may be designated phenoxides or phenates, in general have substantial water solubility while retaining in large measure the color-developing properties of the corresponding phenolic compounds, and thus have been found to be essentially equivalent thereto in the systems of the present invention.

Ordinarily, however, the insolubility of the phenolic compounds themselves in water is found to be advantageous. They are considered to be superior for most of the intended puposes to other phenolic color-developing substances in further respects as well, such as their high stability against oxidation, low volatility, good pigment characteristics for use in coatings, and lower tendency to cause odor or physiological sensitivity.

Manifolded set arrangements which include webs carrying the phenolic compounds discussed hereinabove, especially the face-coated webs carrying the phenolic color-developing substance adherent thereto, now will be described in greater detail, and particular reference then will be made to the variety of chromogenous materials suitable for inclusion in the arrangements and methods utilizing the phenolic color-activating substances.

The web or sheet **13** described hereinabove, having on one side an adherent coating **14** carrying a phenolic substance as described hereinabove, conveniently is included, in an embodiment of the present invention, as the lower or second base web or sheet in a manifolded set which also comprises the upper or first base web or sheet **11**. In this arrangement the first base web **11** has on one side the transfer coating **12** made up of a film-forming material containing a colorless or lightly colored chromogenous compound which is transferable upon impact from that coating to a surface contiguous therewith.

This chromogenous compound includes as its major functional arrangement the molecular structure



having a p-amino-substituted triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom. It will be understood that substituents may be present on the benzene rings in this compound provided that the illustrated structure remains the effective major functional arrangement in the compound.

The first and second webs **11** and **13** are maintained disposed together in face to face relationship, as suggested by the bracket at the left of the drawing, with their respective transfer and adherent coatings **12** and **14** in contiguity with each other, whereby, upon impact in localized areas, a dark-colored material is produced locally by the action of the many small particles of the phenolic substance, carried by the adherent coating **14**, in opening the bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in the small masses of the chromogenous compound which are transferred locally to the contiguous adherent coating from the transfer coating **12** as a result of the impact. For producing simultaneously an original and one copy sheet by use of a typewriter, for example, or by direct writing with pen, pencil, or stylus, the web **11** advantageously serves as the original and the face-coated web **13** serves as the duplicate. These two coated manifolding units **11** and **13** and other pairs like them may be fastened together in successive sets in a pad, or they may simply be laid one over the other on a writing surface, or held together on the platen of a typewriter. Typing or writing impact, or other printing or marking pressure, on the face of the sheet **11** causes localized rupture of the back coating **12**, releasing and transferring some of the chromogenous compound from that coating locally to the contiguous surface of the adherent face coating **14**. Of course, it is possible to cause a similar transfer by impact applied to the back of the web **13**.

It is possible to incorporate the generally light-colored chromogenous material, of the type described above and in the solid state, into a back coating **12** of waxy or thermoplastic film-forming material, which may be transferred from the base web **11** upon impact to deposit some of the solid chromogenous material on a surface, such as that of the coating **14**, carrying a color-activating material. Production of the darker-colored form occurs best, however, if the chromogenous substance is dispersed or preferably dissolved in a liquid, permitting intimate contact of the molecules of the chromogenous substance with the color-developing material. It is possible to provide some of this solvent on the surface carrying the color-developing material. Preferably, however, the film-forming material of the back coating **12**, which is rupturable upon impact or other localized pressure, contains as a finely dispersed phase numerous cells, or microscopic droplets, of a liquid vehicle carrying the colorless or lightly colored chromogenous compound. The cell walls may be simply boundary regions within the continuous film or may consist of a third encapsulating material. A low vapor pressure, lipophilic (oil-loving), nonpolar or mildly polar liquid solvent vehicle advantageous is used, such such as benzyl butyl phthalate, benzyl salicylate, phenyl ether or halogenated phenyl ethers, chlorinated biphenyl, partially hydrogenated terphenyls, lauryl bromide, butyl oleate, or other such vehicles or mixtures thereof, in which the chromogenous compound is dissolved.

A solution of from about 1% to 10% by weight of the chromogenous compound in such a solvent vehicle may be prepared, for example, and then emulsified in a conventional aqueous film-forming material such as polyvinyl alcohol in colloidal solution, or such as a colloidal aqueous solution of casein, gelatin, or the like. The resulting emulsion of the lipophilic solvent in the hydrophilic film former is coated on the back surface of the base web **11**, which may be a strip or sheet made of paper or other fibrous material or of a plastic film base, and then is dried to form the coating **12** containing numerous liquid cells of the water-insoluble solvent vehicle carrying, dissolved therein, the chromogenous substance. Use of a suitable emulsion results in such liquid cells being finely dispersed throughout the solid film, formed by drying the hydrophilic film former, which makes up the continuous phase in the coating **12**. The dried coating **12** may be about 0.001 inch thick. The ratio of the solvent vehicle containing the chromogenous compound to the dried film-forming materials in the coating advantageously may be in the approximate range of 1:1 to 1.5:1.

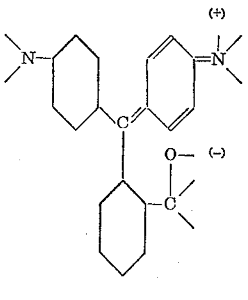
Marking pressure or impact then releases the chromogenous material from those of the tiny cells in the coating **12** which occupy the areas immediately beneath the areas of impact on the original printing or writing surface. The above-disclosed phenolic substance in the contiguous coating **14** is adherent to the web **13** but is accessible to materials applied to the surface of this coating, so that adequate contact occurs of the chromogenous compound, transferred from the coating **12**, with the phenolic substance, and the dark-colored form of the chromogenous compound thus is produced to provide dark marks in the duplicate image areas on the coating **14**.

It will be understood that, if desired, a coating **15** may be formed on the back surface of the duplicate web **13** in just the same manner as the back coating **12** is formed on the original web **11**. With this optional back coating **15** on the web **13**, one or more additional duplicate coated webs, identical with the coated web **13**, may be manifolded beneath the web **13**, permitting simultaneous production of triplicate and quadruplicate copies. In fact, most of the phenolic substances utilized in accordance with the present invention, when applied in face coatings such as the coating **14** described above, themselves provide good original printing or writing surfaces, so that a sheet such as the sheet **13**, when provided with the back coating **15** as well as the face coating **14**, may serve either as an original sheet or as a duplicate sheet in a manifolded set or stack. Thus identical paper sheets, each having white or light-colored face and back coatings acceptable as ordinary paper surfaces to most users, may be manifolded in sets of two or more, or several sheets may be manifolded in which the face coating may be omitted from the top sheet only and the back coating may be omitted from the bottom sheet only. No smudging or soiling of the paper sheets or of the users' hands occurs in ordinary usage, and dark-colored material is formed only in the duplicate image areas by the aforementioned action of the phenolic developer material on the almost colorless or white, or rather lightly colored, chromogenous material.

More generally described, the manifolded set comprises a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous droplet-like cells of the solvent liquid vehicle, and a second base web having on one side an adherent coating, in a manifolding arrangement which maintains these first and second webs disposed together in face to face relationship with the respective transfer and adherent coatings in contiguity with each other. Two coating constituents are provided, one in the form of the chromogenous compound which includes the major functional arrangement with the molecular structure shown above, and another coating constituent in the form of a color-activating phenolic substance. One of the coating constituents is dissolved in the solvent liquid vehicle present in the numerous cells in the transfer coating on the first base web, and the other of the coating constituents is bonded to the second web in the adherent coating thereon but is accessible to other materials coming into contact with portions of that adherent coating.

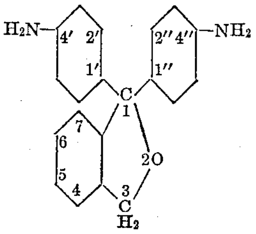
An advantage of the color-activating phenolic substances utilized in accordance with the present invention is that, if desired, each of them can be dissolved readily in certain organic liquids recognized as solvents therefor. Thus the phenolic substance may be dissolved in the liquid cells in the transfer coating on the first web, and the chromogenous compound may be bonded to the contiguous surface of the second web. Of course, if the phenolic substance is a liquid at ordinary ambient temperatures, it may be emusified directly in the aqueous film-forming solution used in forming the transfer coating, so that the phenolic substance serves in a sense as its own liquid solvent. However, it usually is preferred to adopt the reverse system, described more particularly hereinabove, and dissolve the chromogenous compound in the liquid dispersed in minute cells in the back coating **12** on the web **11**, while bonding the color-activating substance to the web **13** in the adherent face coating **14**.

In either case, upon local impact and rupture of the transfer coating, the release of the liquid vehicle containing one coating constituent from some of the liquid cells onto the contiguous adherent coating carrying the other coating constituent effects contact between the two coating constituents to produce a dark-colored material by the action of the phenolic substance on the chromogenous compound. The mechanism of this action need not be demonstrated in showing the operation of the arrangements and methods of the present invention. Nevertheless, it commonly is theorized, in the study of colored substances having an aminotriphenylmethane structure, that absorption or reflection of light selectively in various portions of the visible spectrum is associated with the presence of the quinonoid structure in one of the p-aminophenyl groups as may be represented in the structural formula

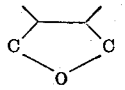


having a double bond from the methane carbon atom to a quinonoid-modified aminophenyl group, and that this quinonoid structure shifts through resonance from one to another of the aminophenyl groups. This structural formula will be recognized as being related to the molecular structure of the major functional arrangement in the chromogenous compound described hereinabove. Presumably contact of the color-activating material with the chromogenous compound results in loss of an electron from the latter, promoting the quinonoid structure having a double bond from a aminophenyl group to the methane carbon atom, with opening of the bond from the methane carbon atom to the heterocyclic oxygen atom in thet chromogenous compound. The precise or complete structure of the dark-colored material, produced by the action of a phenolic color-activating material on these chromogenous compounds, is not known, and the hypothetical formula for the quinonoid form, given above, is not intended to be a complete structural representation. Whatever the exact mechanism may be, it seems reasonable in view of the present state of the art to assume that the color-activating substance acts by effectively opening a bond from the methane carbon atom with establishment of the double bond arrangement associated with an adjacent quinonoid group, permitting quinonoid resonance in the chromogenous compound.

Reference now will be made again to the chromogenous compound, before it is acted upon by the color-activating substance, having the major functional arrangement involving the molecular structure, shown hereinabove, with a p-amino-substituted triphenylmethane group and a heterocyclic ring; the methane carbon atom of the triphenylmethane group has a bond to the hetero oxygen atom, which in turn is bonded to a carbon atom affixed to one of the phenyl groups in the ortho position. This molecular structure is included with the minimum of substituents in the compound 1,1-bis(p-aminophenyl) phthalan. The latter compound is represented by the structural formula



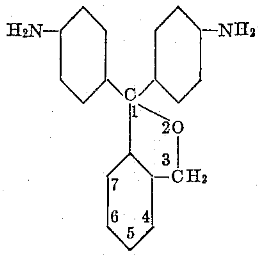
The colorless or lightly colored chromogenous compound preferably is selected from the group consisting of the last-mentioned compound, the 2',2''-epoxy, 3-oxo, and 2',2''-epoxy-3-oxo derivatives thereof, bifunctional derivatives of each of these compounds having a second heterocyclic ring



fused to the 5,6 side of the benzene nucleus and similarly carrying extracyclic substituents the same as those carried by the carbon atoms designated 1 and 3, the 5-amino derivatives of the 1,1-bis(p-aminophenyl)phthalan and of the above-mentioned epoxy and oxo derivatives thereof, and N-substituted derivatives of each of the compounds here listed in which each individual substituent for an amino hydrogen atom is selected from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical.

Each of these compounds can be seen to include as its major functional arrangement the molecular structure set forth hereinabove, with hydrogen atoms or appropriate substituents on the amino nitrogen atoms and on the available heterocyclic carbon atom, and with or without other substituents, such as the epoxy linkage and the third p-amino radical, or such as the bifunctional arrangement involving a second bis(p-amino-phenyl)methyl group and a second heterocyclic ring fused with the 5,6 side of the benzene nucleus. The N-substituted derivatives of the several compounds listed above by far the most important members of this group of chromogenous compounds. Examples of the chromogenous substances having particular utility in connection with the present invention will be given now.

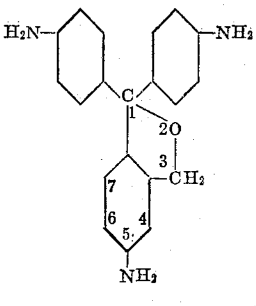
Turning first to the 1,1-bis(p-aminophenyl)-phthalan itself, its structural formula may be redrawn as follows:



It may be used, preferably dissolved in a lipophilic solvent, to develop a violet color when brought into contact with a phenolic color, activating or developer substance.

However, it is preferred to provide related chromogenous compounds in which at least one of the two hydrogen atoms in each amino radical is replaced by a substituent tending to increase the color intensity or modify the hue of the dark-colored material which may be formed from the chromogenous compound. Thus the corresponding N-monosubstituted compound 1,1-bis(p-ethylaminophenyl)phthalan develops a greenish blue color of greater intensity, while the N-disubstituted compound 1,1-bis(p-dimethylaminophenyl)phthalan forms a still more intensely colored quinonoid form with a green, or somewhat bluish green, hue. The compound 1,1-bis(p-diethylaminophenyl)-phthalan produces an intense, green dark-colored form in contact with the phenolic developer substances, and similar dark-colored forms may be obtained, for example, from similar compounds having diisopropylaminophenyl and dibutylaminophenyl groups. These compounds illustrate the selection of one or more of the individual N-substituents, that is, substituents for the amino hydrogen atoms, from the alkyl radicals of not more than four carbon atoms. In general, more intense and more stable colors may be obtained when there are substituents replacing most or all of the amino hydrogen atoms. Moreover, instead of these N-alkyl-substituted compounds, the benzyl-substituted compounds 1,1-bis(p-benzylaminophenyl)phthalan and 1,1-bis(p-dibenzylaminophenyl)phthalan may be used to obtain dark greenish blue quinonoid forms. As an example of an alternative derivative, having N-phenyl substituents, there may be mentioned 1,1-bis-(p-N-methylanilinophenyl)phthalan, having methyl and phenyl radicals on each nitrogen atom, which gives a somewhat yellowish green colored form.

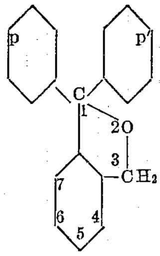
The 5-amino derivative of 1,1-bis(p-aminophenyl)-phthalan having the structural formula



may be brought into contact with an active phenolic developer material to produce a violet-red or bluish red dark-colored form of fair intensity. A deeper, bluish violet-colored substance may be produced from 5-amino-1,1-bis(p-methylaminophenyl)-phthalan.

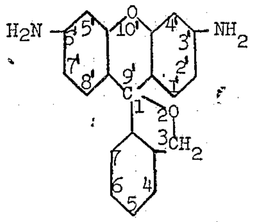
Among the more preferred 5-amino derivatives of 1,1-bis(p-aminophenyl)phthalan, however, may be mentioned 5-dimethylamino-1,1-bis(p-dimethylaminophenyl) phthalan, forming a bluish violet quinonoid substance. Another N-substituted modification of the 5-amino derivative is, for example, 5-anilino-1,1-bis(p-anilinophenyl)phthalan, which has three N-monophenyl-substituted amino groups and gives greenish blue to blue dark-colored quinonoid materials.

It will appear that N-substituted 1,1-bis(p-aminophenyl)phthalan and 6-amino-1,1-bis(p-aminophenyl)phthalan compounds are particularly desirable for use in systems in which white or light-colored chromogenous compounds are converted to dark-colored forms. Thus, for such use there may be provided advantageously a colorless or lightly colored chromogenous compound having a modified 1,1-diphenylphthalan structural formula



which includes the three points, designated thereon the p,p′,5-positions, each para to the position of a bond to the methane carbon atom occupying the 1-position, and which is modified by the inclusion of an amino radical in at least the first-mentioned two of the three p,p′,5-positions. Each such amino radical furthermore has at least one substitutent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical. When the first-mentioned two p,p′-positions carry such amino radicals, the compound is a 1,1-bis(p-aminophenyl)phthalan with one or two substituents for the hydrogen atoms in each amino radical. When all three p,p′,5-positions carry such amino radicals, the compound is, of course, an N-substituted 5-amino-1,1-bis(p-aminophenyl)phthalan.

Turning now to the 2′,2″-epoxy derivatives of 1,1-bis(p-aminophenyl)phthalan, this derivative without further substituents is 3′,6′-diaminospiro(phthalan-1,9′-xanthene) having the structural formula



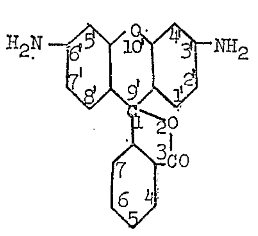
This compound develops a generally red or bluish red color upon contact with various phenolic developers. However, a colorless or lightly colored chromogenous compound is preferred in the form of a substituted 3′,6′-diaminospiro(phthalan-1,9′-xanthene)compound, having the structural formula shown just above, in which each of the amino radicals also has at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical. Accordingly, a more intense bluish red is obtained from the corresponding N-mono-alkyl-substituted chromogenous compound 3′,6′-bis(ethylamino)spiro(phthalan-1,9′-xanthene), while a still more intensely colored quinonoid form having a red or somewhat bluish red color may be obtained from the N-dialkyl-substituted compound 3′,6′-bis(dimethylamino)spiro(phthalan-1,9′-xanthene). The 5-amino-2′,2″-epoxy derivatives of 1,1-bis(p-aminophenyl)-phthalan may be exemplified by the N-substituted compound 3′,5,6′-tris(dimethylamino)spiro(phthalan-1,9′-xanthene), which develops a very intense reddish violet color.

The compounds given in the above examples, having the 5-membered heterocyclic ring containing the hetero oxygen atom, may be referred to as cyclic ethers. Compounds of this type, and webs carrying transfer coatings containing such compounds, are disclosed and claimed in the concurrently filed application for Letters Patent of the United States Ser. No. 135,307, entitled Chromogenous Amino Derivatives of Diphenylphthalan and Marking Method Using Same, filed in the names of John R. Johnson and Earl J. Gosnell and assigned to the same assignee as the present invention.

Such cyclic ether compounds without the epoxy bridge may be prepared by reduction of the corresponding lactones of p-amino-substituted triphenylmethanes, namely 3,3 - bis(p - aminophenyl)phthalide, 6 - amino - 3,3 - bis-(p-aminophenyl)phthalide, and the N-substituted derivatives thereof. Procedures for making these lactones are discussed in U.S. Patents Nos. 2,417,897, 2,474,084, and 2,597,965 to Adams and No. 2,742,283 to Crounse.

The synthesis of the cyclic ethers from such lactones may be achieved with the use of anhydrous aluminum lithium hydride; for example, about 10 grams of the $AlLiH_4$ may be refluxed with about 0.025 mole of the appropriate lactone in 350 ml. of ethyl ether for several hours. After adding water, the ether layer is decanted and dehydrated, and the ether is evaporated to obtain the solid product, usually having a white or light pastel color. If the solid chromogenous material which has been synthesized is darker than a medium pastel shade, repeated purification treatments using standard procedures, such as solvent or freeze crystallizations and selective solvent extractions, as with ether, can be expected to yield a light-colored product approaching a colorless, that is, white, solid. Such chromogenous substances can be incorporated readily on paper in transfer coatings which appear substantially white or which have a creamy color quite acceptable as an ordinary paper surface.

Synthesis of the cyclic ether compounds with the epoxy bridge, namely the 2′,2″-epoxy and 5-amino-2′,2″-epoxy derivatives of 1,1-bis(p-aminophenyl)phthalan with N-substituents as desired, also may use a lactone as a starting material. Lactones with the epoxy bridge may be formed by reaction, in the presence of $ZnCl_2$, of phthalic anhydride or 4-aminophthalic anhydride and m-aminophenol, with appropriate substituents for the amino hydrogen atoms in both of these reagents. The aminophenol conveniently may be melted and the other materials dispersed in the melt. The mixture is maintained in molten condition during the reaction period, at the conclusion of which the melt contains in major amount 3′,6′-diaminofluoran having the structural formula

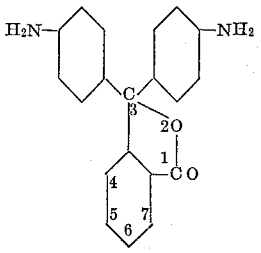


with corresponding substituents. Thus, if 4-aminophthalic anhydride is used, the lactone compound has a 5-amino group. Similarly, the aforementioned substituents for the hydrogen atoms in the amino groups of both reagents appear as N-substituents in this fluoran product, known in the art as a rhodamine lactone or colorless base. The lactone conveniently may be separated from the crude reaction mixture by digestion in dilute aqueous ammonium hydroxide to dissolve other materials and convert the lactone to solid particles of the corresponding carbinol or color base, which are filtered off, washed, and dried. Refluxing the carbinol in benzene under dehydrating conditions effects recovery of the colorless or lightly colored lactone product shown above in the structural formula for diaminofluoran.

Alternatively the lactone product may be obtained from the commercial rhodamine dye, such as Rhodamine B. The dye, incidentally, may be obtained conventionally by extracting the carbinol or color base, produced as above, with benzene and further extracting the resulting benzene solution with dilute hydrochloric acid, whereupon crystals of the purified dye separate from the aqueous acid solution on cooling. When starting with the dye, the carbinol is regenerated by treatment of an aqueous solution of the dye with sodium hydroxide, extracting, filtering, and drying, followed by the above-mentioned refluxing in benzene under dehydrating conditions to close the lactone ring and form the fluoran product.

Refluxing the substituted 3′,6′-diaminofluoran, or rhodamine lactone, material thus obtained in anhydrous ether containing aluminum lithium hydride effects reduction to the desired corresponding cyclic ether compound with the epoxy bridge. This substituted 3′,6′-diaminospiro(phthalan-1,9′-xanthene) compound may be termed a rhodamine cyclic ether. Such a reduction procedure is analogous to the reduction of the 3,3-bis(p-aminophenyl) phthalides to their corresponding cyclic ethers utilizing aluminum lithium hydride, as described above. While the rhodamine lactones themselves are chromogenous compounds useful in the production of colored forms in accordance with the present invention, as will be mentioned hereinbelow, the corresponding rhodamine cyclic ethers exhibit considerably greater stability against premature conversion to colored forms and are considered preferable for use in accordance with the present invention.

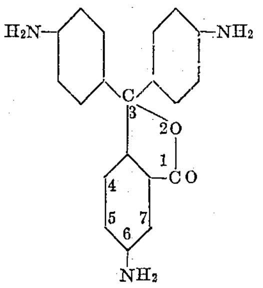
Turning next to the 3-oxo derivative of 1,1-bis(p-aminophenyl)phthalan, this compound is a lactone having the structural formula



Since more conventional nomenclature treats this compound as a phthalide derivative, namely, 3,3-bis(p-aminophenyl)phthalide, the usual numbering of the ring components for phthalide will be used, as shown above. With N-substitutents as desired, this is the same phthalide substance already mentioned in connection with the synthesis of the cyclic ethers. The unsubstituted 3,3-bis(p-aminophenyl)phthalide develops a violet color upon intimate contact with a recommended phenolic color-activating substance. A more intense, greenish blue color can be obtained using 3,3-bis(p-methylaminophenyl)phthalide. However, formation of darker quinonoid compounds can be expected from N-tetraalkyl-substituted compounds. Thus a considerably more intense green or somewhat bluish green color is developed using 3,3-bis(p-dimethylaminophenyl)phthalide, which conveniently may be referred to as the lactone of leuco-malachite green, and an excellent dark, intense, bluish green quinonoid form also is produced from 3,3-bis(p-diethylaminophenyl)phthalide. Similarly, a blue-green color is obtained with 3,3-bis(p-dipropylaminophenyl)phthalide. Also quite satisfactory, although not N-alkyl-substituted, is 3,3-bis(p-dibenzylaminophenyl)phthalide, giving a greenish blue colored form.

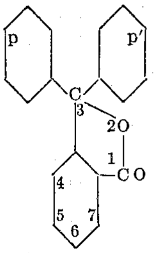
The 5-amino-3-oxo derivatives of 1,1-bis(p-aminophenyl)phthalan, also a lactone, is better named 6-amino-

3,3-bis(p-aminophenyl)phthalide, having the structural formula



Preparation of this triamino-substituted 3,3-diphenylphthalide also is mentioned above. A violet-red or bluish red color may be developed from this compound, as shown without amino substituents. Bluish-violet colors generally are obtained in the quinonoid forms of such compounds which have two or preferably three N-alkyl substituents, such as 6-amino-3,3-bis(p-methylaminophenyl) phthalide and 6-ethylamino-3,3-bis(p-ethylaminophenyl) phthalide. However, for the property of rapid production of intense, dark, bluish violet quinonoid forms it is preferred to use N-hexaalkyl-substituted compounds. These are exemplified by 6-dimethylamino-3,3-bis(p-dimethylaminophenyl)phthalide, also identified as crystal violet lactone, and by 6-diethylamino-3,3-bis(p-diethylaminophenyl)phthalide and the same compound with three dipropylamino groups in place of the diethylamino groups. Considered particularly desirable for the production of bluish violet colored forms is 3,3-bis(p-diethylaminophenyl)-6-dimethylaminophthalide, for which there may be substituted the compound 3,3-bis(p-diisopropylaminophenyl) - 6 - dimethylaminophthalide. Similar properties also are obtained with n-butyl groups, as in 6-dibutylamino - 3,3-bis(p-dibutylaminophenyl)phthalide. Again, benzyl and phenyl substituents may be used in place of alkyl substituents. Thus, a different color for the quinonoid form may be obtained from 6-N-benzyl-N-methylamino-3,3-bis(p-N-benzyl-N - methylaminophenyl)phthalide having a red-violet quinonoid form, and the compound 3,3-bis(p-anilinophenyl)-6-dimethylaminophthalide has a blue dark-colored form.

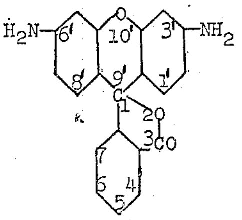
It will appear from the foregoing that the N-substituted 3,3-bis(p-aminophenyl)phthalide and 6-amino-3,3-bis(p-aminophenyl)phthalide compounds are preferred for their good chromogenous properties. Such colorless or lightly colored compounds may be defined as chromogenous compounds having a modified 3,3-diphenylphthalide structural formula



which includes the three points, designated on the above formula as the p,p′-6-positions, each para to the position of a bond to the methane carbon atom occupying the 3-position in this formula, and which is modified by the inclusion of an amino substituent in each of at least the first-mentioned two of the three p,p′-6-positions. When those two p,p′-positions have that substituent, the compound is a 3,3-bis(p-aminophenyl)phthalide, and when all three p,p′,6-positions have that substituent, the chromogeneous compound is in the form of a 6-amino-3,3-bis(p-aminophenyl)phthalide. Again, each of the amino radicals in these compounds should have at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical.

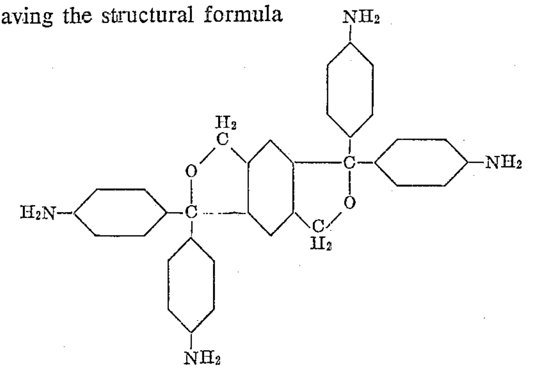
The examples mentioned above indicate that the alkyl groups in these compounds advantageously are methyl, ethyl, n-propyl, and isopropyl groups. A particular preference is noted for the hexaalkyl-triamino-substituted 3,3-diphenylphthalide chromogeneous compounds, in the form of 6-dialkylamino-3,3-bis(p-dialkylaminophenyl) phthalide compounds in which each individual alkyl radical of the three dialkylamino groups has not more than three carbon atoms.

The 2′,2″-epoxy-3-oxo derivative of 1,1-bis(p-aminophenyl)phthalan is 3′,6′-diaminofluoran having the structural formula

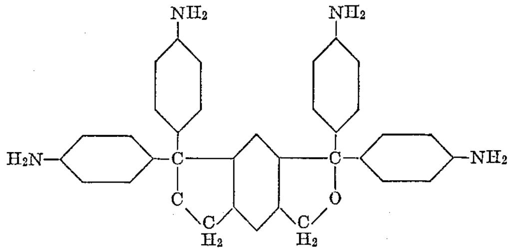


which can be used to develop a reddish color with a tinge of blue or violet. The N-substituted derivatives or rhodamine lactones are preferred, and their synthesis by known procedures is summarized hereinabove. Better color intensity of the quinonoid form is obtained from 3′,6′-bis(ethylamino)fluoran and still deeper color from 3′-diethylamino-6′-ethylaminofluoran, which is the lactone of Rhodamine 4G, while a preferred chromatogenous amino-substituted fluoran is 3′,6′-bis(diethylamino)fluoran, the lactone of Rhodamine B; these chromogenous compounds have bluish red quinonoid dark-colored forms. The compound 3′,6′-dianilinofluoran also is useful and forms a violet dark-colored substance. Compounds which may be viewed as 5-amino-2′,2″-epoxy-3-oxo derivatives of 1,1-bis(p-aminophenyl)phthalan, in other words 3′,5,6′-triaminofluoran, with N-substituents, also may be obtained, as by the synthesis mentioned above using the reagents 4-aminophthalic anhydride and m-aminophenol with corresponding N-substituents; an example is the chromogenous compound 3′,5,6′-tris(dimethylamino)fluoran, which can form a very intensely colored reddish violet substance. The lactone ring structure present in these aminofluoran compounds has a tendency to open with consequent premature formation of a colored material, and it has been reported that this tendency is fostered in the presence of highly polar solvents such as alcohol, acetone, and water. Accordingly, when these chromogenous compounds are used, they should be protected against contact with such materials or vapors prior to formation of the desired permanent dark-colored forms by contact with the color-activating material on the face-coated sheet in accordance with the invention; or corresponding rhodamine cyclic ethers may be used.

Coming now to the bifunctional derivatives of 1,1-bis(p-aminhphenyl)phthalan having a second heterocyclic ring fused to the 5,6 side of the benzene nucleus, these derivatives will be seen to be based on the compounds having the structural formula



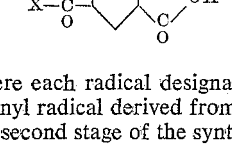
and the isomeric structural formula



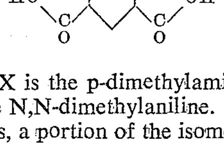
These isomeric compounds may be named respectively 1,1,5,5-tetrakis(p-aminophenyl)-7-hydro - 1H,3H - benzo-(1,2-c:4,5-c′)difuran and 1,1,7,7 - tetrakis(p-aminophenyl)-5-hydro-1H,3H-benzo(1,2-c:4,5-c′)difuran. Each of these two compounds has two heterocyclic furan rings fused to the central benzene nucleus, and each of these furan rings includes one carbon atom carrying two unsubstituted hydrogen atoms, as may be seen at the bottom of the last structural formula shown above.

The last mentioned carbon atoms may be oxo-substituted; that is, the two hydrogen atoms carried by each carbon atom may be replaced by an oxygen atom. Each furan ring thus assumes a gamma-lactone structure, instead of the cyclic ether structure, giving a bifunctional lactone, or dilactone, compound. The respective dilactone compounds may be named 3,3,7,7-tetrakis(p-aminophenyl) - 1H,3H - benzo(1,2-c:4,5-c′)difuran - 1,5(7H)-dione and 3,3,5,5-tetrakis(p-aminophenyl)-1H,3H-benzo-(1,2-c:4,5-c′)difuran-1,7(5H)-dione.

Dilactone compounds of the last-mentioned type are disclosed and claimed in the concurrently filed application for Letters Patent of the United States Serial No. 135,264, entitled Chromogeneous Aminophenyl Derivatives of Benzodifurandione and Marking Method Using Same, filed in the names of Earl J. Gosnell and John F. McCarthy, Jr., and assigned to the same assignee as the present invention. A representative N-substituted dilactone compound may be synthesized by dissolving one mole of N,N-dimethylaniline in about four times its weight of carbon disulfide and stirring in about 0.9 mole of anhydrous aluminum chloride as a catalyst. After dissolution of the $AlCl_3$, 0.2 mole of pyromellitic dianhydride is added, stirred, and allowed to stand. The upper layer of the CS_2 is decanted and 1250 ml. of 8% sulfuric acid added to it slowly. After dilution with about 10 liters of water and standing, the first stage of the synthesis gives an approximately 90% yield of a solid intermediate product which is a mixture of two isomeric compounds having the structural formulas

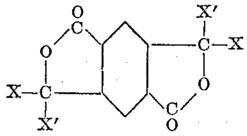


and

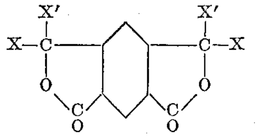


where each radical designated X is the p-dimethylaminophenyl radical derived from the N,N-dimethylaniline. In the second stage of the synthesis, a portion of the isomeric intermediate mixture then is heated at reflux temperature for 24 hours, with a further amount of N,N-dimethylaniline equal to about 4.5 to 5 times the equimolar weight, in a volume of liquid acetic anhydride weighing about 7 to 8 times as much as the weight of the N-substituted aniline. Cooling and filtering gives a solid acetic anhydride-insoluble product of light yellow color, and pouring the filtrate over crushed ice and filtering gives a solid acetic anhydride-soluble product of light greenish yellow color, both in good yields. A mixture of these two solid products may be obtained by flushing with ice water before filtering out the acetic anhydride-insoluble fraction.

These two light-colored products are the chromogenous substances selected from the group consisting of the isomeric compounds having the structural formulas



and

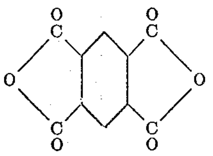


where X is as above and the radical designated X′ also is the p-dimethylaminophenyl radical, derived in this instance from the dimethylaniline used in the reaction with the intermediate mixture. It will be appreciated that aniline itself, or other N-substituted anilines, may be used in forming the intermediate mixture with corresponding variations in the p-aminophenyl radical X, while aniline, or still another N-substituted aniline, may be used as the reagent with the intermediate isomers to get the dilactone product with other corresponding variations in the p-aminophenyl radical X′. Yields of the acetic anhydride-insoluble and -soluble fractions vary, and standard purification procedures such as solvent or freeze crystallizations and selective solvent extractions can be utilized where necessary to recover crystalline products having substantially colorless creamy or light pastel shades. The dilactones generally can be heated well above 300° C. without melting or decomposition.

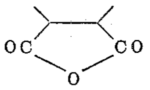
The synthesis of a specific chromogenous dilactone compound, or isomeric mixture of such compounds, having the structure represented by the formulas given above where all of the radicals designated both X and X′ are p-dimethylaminophenyl groups, is mentioned hereinabove by way of example. The two isomeric fractions have very low solubilities in most of the common organic solvents. However, they dissolve up to a few percent or more in some of the solvent vehicles such as the simple or chlorinated phenyl ethers and chlorinated polyphenyls, and the solution of either one or both of the abovementioned fractions gives instantaneously a dark blue-green colored form when brought into contact with one of the phenolic substances listed hereinabove.

Indicating the variety of dilactone chromogenous compounds which can be utilized in accordance with the present invention, the use of unsubstituted aniline in the synthesis described above gives the tetrakis(p-aminophenyl)-benzodifurandione or dilactone substance without N-substituents, X and X′ both being p-aminophenyl radicals, and contact with developers yields a reddish or purplish tan colored form. It is much preferred, however, to use substituted anilines, particularly N,N-disubstituted anilines. Thus the N,N-dimethylaniline advantageously is used in many cases to make the intermediate product having the p-dimethylaminophenyl group for the radical X. However, appropriate variations in the substituted aniline reacted with the intermediate product in the second stage of the synthesis described above yield dilactone products in which the radical X′ consists of different N-substituted p-aminophenyl groups, preferably other N-dialkyl-substituted groups with alkyl radicals of not over three carbon atoms. X′ accordingly may be the p-diisopropylaminophenyl radical, while X remains the p-dimethylaminophenyl radical. This dilactone substance also gives a dark blue-green quinonoid form on contact with a phenolic developer material. Blue-green forms also are obtained from the dilactone in which X′ is the p-N-benzyl-N-ethylaminophenyl group, while the dilactone in which X′ is the p-dibenzylaminophenyl group gives a bluish green to green dark-colored form. Corresponding and sometimes superior results can be obtained with halo or methyl substituents on the phenyl ring in the p-aminophenyl radical. Thus, when m-chloro-N,N-diethylaniline is used in the second stage of the synthesis, the resulting dilactone product has o-chloro-p-diethylaminophenyl groups for the X′ radicals, X still remaining the p-dimethylaminophenyl group. This substance gives a green dark-colored form. When X′ is the p-diethylamino-o-tolyl group, the quinonoid form has a strong dark green color. Thus certain compounds, with halo and methyl substituents in the ortho, and meta, positions of the p-aminophenyl groups, are equivalent to the compounds without such substituents.

A preferred dilactone substance of the type just described, having dialkylaminophenyl groups, will be seen to include a colorless or lightly colored chromogenous compound based on the structure of pyromellitic dianhydride



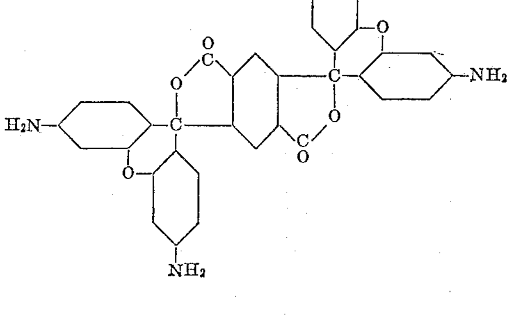
including, fused to opposite sides of the benzene nucleus, two heterocyclic rings



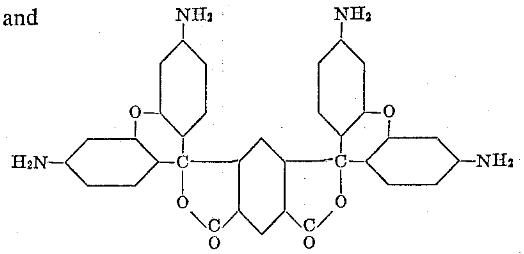
each containing a hetero oxygen atom in the ring, and to each of which two other oxygen atoms are attached. One of these two oxygen atoms attached to each heterocyclic ring thereof is replaced by two p-dialkylaminophenyl groups, in which each individual one of the four alkyl radicals has not more than three carbon atoms.

Instead of a dilactone substance, there may be used the corresponding bifunctional cyclic ethers, which are the usually N-substituted derivatives of the 1,1,5,5-tetrakis(p-aminophenyl - 7 - hydro-1H,3H-benzo(1,2-c:4,5-c′) difuran and of its isomer, shown above. To produce the bifunctional cyclic ethers, or dicyclic ethers, appropriate dilactones, such as those just mentioned, may be added to ethyl ether which is maintained at reflux temperature and which contains aluminum lithium hydride, and the bifunctional cyclic ether recovered by filtration and solvent evaporation. These products after purification have chromogenous characteristics similar to those of the corresponding dilactone materials, having the same N-substituted p-aminophenyl groups represented by the radicals X and X′ in the structural formulas shown above.

In addition to such bifunctional cyclic ethers, and the bifunctional lactones, or dilactones, already described, the corresponding bifunctional derivatives of 1,1-bis(p-aminophenyl)phthalan having the epoxy bridges also may be used. In this category the diepoxy-substituted dilactones have the isomeric structural formulas

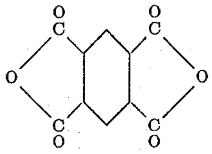


and

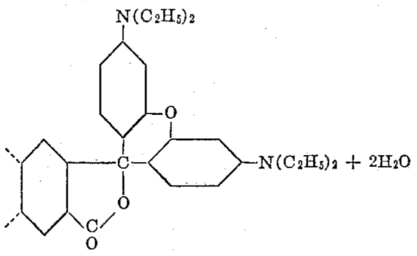


and the amino hydrogen atoms again preferably are replaced by alkyl, benzyl, or phenyl radicals. Thus all of the amino groups may be dialkylamino groups in which each alkyl radical has no more than three carbon atoms, e.g., dimethylamino groups or diethylamino groups.

As an example, the isomeric substance having diethylamino groups may be obtained by heating one mole of m-diethylaminophenyl and roughly one mole of anhydrous zinc chloride with 0.2 mole of pyromellitic dianhydride

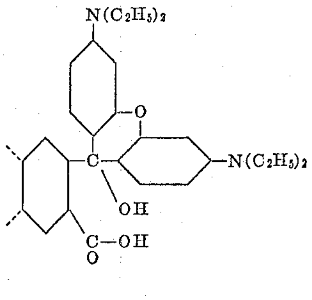


for several hours at 160° C. while stirring the melt, to form in the melt a moderate yield of a bifunctional compound including the structure



It will be seen that the portion of the molecular structure illustrated here is the lactone of Rhodamine B, that is 3′,6′-bis(diethylamino)fluoran. It will be understood further that the pyromellitic dianhydride acquires a similar spiro-linked xanthene structure, not illustrated here, on the other side of the benzene nucleus, where another one of the dianhydride carbonyl oxygen atoms is replaced with two more aminophenyl radicals. Thus a third molecule of water is split off, formed from this oxygen atom and the hydrogen atoms in the 6-positions on two additional 3-diethylaminophenyl molecules. A second xanthene epoxy bridge also is formed by removal of a fourth water molecule from the two adjacent phenolic hydroxyl groups in these two additional aminophenol molecules.

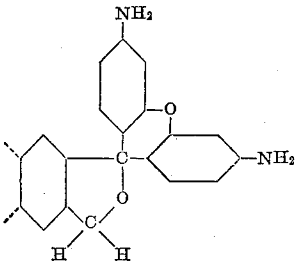
To recover this product from the reaction mixture, a procedure related to that indicated hereinabove in connection with production of the familiar rhodamine lactones then may be followed. Thus the melt, containing the reaction product formed from the pyromellitic dianhydride and the 3-diethylaminophenol, may be cooled, finely powdered, and digested with dilute aqueous ammonium hydroxide, leaving undissolved the bifunctional carbinol



This substance is separated by filtering it out of the ammonium hydroxide solution, washing with fresh dilute ammonium hydroxide, and drying. Reclosure of the two lactone rings is accomplished by refluxing the carbinol with benzene, which conveniently is done with a standard condenser and Stark and Dean tube apparatus to remove the water split off from the carbinol hydroxyl groups and the adjacent carboxyl hydrogen atoms. The resulting benzene solution is then filtered and evaporated under vacuum to recover the bifunctional rhodamine lactone substance, whose structure is illustrated by the isomeric formulas shown above, all the amino hydrogen atoms being replaced by ethyl radicals in this example.

This product is more or less colorless, having a creamy to light pink color. By using other N-substituted m- or 3-aminophenols, a variety of other chromogenous rhodamine dilactone compounds, having different N-substituents and also only lightly colored, may be prepared, as will be understood from a consideration of the various N-substituted dilactone compounds discussed hereinabove, which are the corresponding bifunctional lactones without the epoxy bridges. The colored forms of these rhodamine dilactone substances resemble in hue the colored forms of the corresponding rhodamine lactones, giving generally bluish red colors. However, the rhodamine dilactone substances share with the monofunctional rhodamine lactone compounds a tendency toward premature opening of the lactone rings, which may cause coloration of the chromogenous material before marking contact has been effected with the desired color-activating material. Of course, the rhodamine dilactone substance may be protected from premature contact with atmospheric or other environments which permit premature coloring.

However, it may be preferable to convert the rhodamine dilactones to the corresponding bifunctional cyclic ether substances, which have considerably more stability against adventitious color formation as when exposed to a humid atmosphere. Such bifunctional cyclic ether substances include the structure



with suitable N-substituents. Each monofunctional molecular arrangement in this category of bifunctional substances will be seen to include the structure of 3′,6′-diaminospiro(phthalan-1,9′-xanthene), as illustrated here. These bifunctional cyclic ether substances likewise may have either, or a mixture of both, of the isomeric forms corresponding to the two isomeric structural formulas given above for the rhodamine dilactone substances. Any two isomeric compounds of this structure give very similar colored forms, which also are similar in hue to the colored forms produced from the corresponding rhodamine dilactone and rhodamine lactone substances, although with some N-substituents minor differences in hue may be observed, even between isomeric pairs, depending on the color-activating substance used.

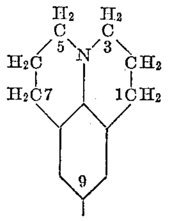
All of the bifunctional substances in the categories of bifunctional lactones, cyclic ethers, rhodamine lactones, and rhodamine cyclic ethers have high melting points and generally can be heated above 300° C. in a neutral atmosphere without melting or decomposing. Several nonpolar or mildly polar solvents may have to be tried in order to find one which will dissolve several percent or more of these bifunctional chromogenous substances.

The bifunctional rhodamine cyclic ethers, having the functional arrangement illustrated above, are obtained by reduction of the corresponding chromogenous rhodamine dilactone substances, using either of the isomeric forms thereof or a mixture of such forms. The rhodamine dilactone is stirred slowly into a semidissolved mixture of aluminum lithium hydride in anhydrous ethyl ether. The resulting mixture is refluxed to permit reaction, cooled, and water is added dropwise. The ether layer is decanted, dried with a solid desiccant such as anhydrous sodium sulfate, and the ether evaporated to obtain the chromogenous, substantially colorless or light pink, solid rhodamine dicyclic ether substance.

The chromogenous bifunctional compounds comprising the dicyclic ethers reduced from dilactone substances, the rhodamine dilactone substances with the epoxy bridges, and the bifunctional rhodamine dicyclic ethers prepared therefrom as just described, are disclosed and claimed in a concurrently filed application for Letters Patent of the United States Ser. No. 135,359, entitled Chromogenous Tetrakis(Aminophenyl) Derivatives of Benzodifuran and Marking Method Using Same, filed in the name of Earl J. Gosnell and assigned to the assignee of the present invention.

All of the monofunctional and bifunctional chromogenous compounds described hereinabove have a bis(p-aminophenyl)-methyl group, or a 3,6-diamino-9-xanthenyl group, with an additional linkage from the methyl carbon atom in the former, or from the carbon atom designated 9 in the latter, to the hetero oxygen atom. Some of the monofunctional compounds have a third amino radical, on the benzene nucleus one side of which is in the heterocyclic ring. In the preferred chromogenous compounds these amino radicals have substituents, for which the methyl and ethyl N-substituents are chosen frequently. Propyl and butyl substituents for one or both of the amino hydrogen atoms provide quite similar properties, so that alkyl radicals of not more than four carbon atoms are suitable. Examples of N-benzyl and N-phenyl groups also appear hereinabove.

Equivalent results also may be obtained, for example, with certain saturated monoalkyl radicals having five carbon atoms or with the mono-n-hexyl radical as N-substituents, and N-substituted cycloalkyl groups such as the cyclopropyl and cyclohexyl groups may be present, but these N-substituents are not preferred. As further examples, the N-phenyl-substituted compounds may be modified by including naphthyl radicals instead of phenyl radicals as N-substituents, or certain small additional substituents may be included on the N-substituted radicals mentioned above, and generally equivalent properties still will be obtained; in this connection such N-substituted groups as the chloromethyl, hydroxyalkyl (e.g., beta-hydroxyethyl, gamma-hydroxypropyl, or delta-hydroxybutyl), sulfophenyl, tolyl, or one of the methylbenzyl radicals may be mentioned. Equivalent to the aminophenyl groups themselves in some chromogenous compounds are amino-1-naphthyl groups; thus 4-diethylamino-1-naphthyl groups may replace p-diethylaminophenyl groups. Instead of N-substituted amino groups, equivalent results also may be expected with piperidino groups, or an entire N-substituted p-aminophenyl group may be replaced by the 9-julolidyl radical



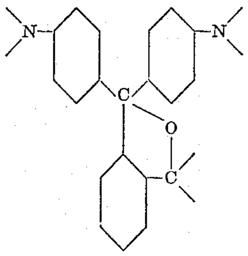
It will be appreciated likewise that substantially equivalent properties also are obtainable in the chromogenous compounds when one small substituent or several small substituents, notably one or more methyl, chloro, bromo, fluoro, or nitro radicals, is or are substituted for one or more of the available hydrogen atoms on the phenyl rings in the aminophenyl radicals or on the benzene nucleus one side of which is in the heterocyclic ring.

It should be noted that the choice of one of the phenolic materials disclosed herein as the color-activating material to be used with a particular chromogenous substance, or the choice of the chromogenous substance to be used together with a particular phenolic material, may require the exercise of the good judgment of one experienced in the art, and in some instances a little experimentation, to arrive at an effective or reasonably satisfactory combination of materials for a specific system. Certain combinations of such phenolic substances and chromogenous substances naturally give the best results in terms of rapid development of very dark and intense colored forms upon ordinary contact of the two substances. The same chromogenous substance can produce dark-colored forms having noticeably different color responses or hues when brought into contact with different ones of the phenolic materials useful as color-activating substances, and the color intensity of the colored forms produced in a given system or arrangement can show gross variations when different phenolic materials are used. The colors given hereinabove for the dark-colored or quinonoid forms of certain chromogenous substances are examples of the colors ordinarily obtained when quite active color-developing phenolic compounds are used. While the phenolic materials useful in accordance with the present invention produce dark-colored forms of useful intensities after being brought into ordinary contact with many chromogenous materials, the use of some of the phenolic substances identified hereinabove which exhibit somewhat lower reactivity as color developers than the best of these color-activating substances, or the use of a less reactive chromogenous compound, may require the application of heat, or utilization of other means of obtaining more intimate contact of the materials, to cause reasonably good color development. This might be accomplished, for example, by concentrated infrared irradiation or by conductive contact with a hot surface. For each combination of chromogenous and color-activating materials which is to be used, it has been found highly desirable to try a number of solvent liquids for the chromogenous compound, or for the color-developer when it is to be dissolved, to obtain the concentration and other environmental conditions which favor the efficient formation of a dark-colored material with desirable color intensity and hue.

As already discussed, the chemical structure of the dark-colored forms produced from these chromogenous compounds by the action of the phenolic substances has not been established, and accurate analytical methods for providing dependable and incontrovertible evidence of their chemical structure apparently are not available. It is presumed, however, that the phenol or some substantial residue thereof remains bonded or associated with the colored form to which the chromogenous compound is converted, since the color materials differ, in improved resistance to moisture and in other characteristics, from the colored materials produced with inorganic color-developing materials and with the acids proposed for that purpose. Accordingly there is provided a new composition of matter, comprising the dark-colored substance obtained by intimate contact of the selected phenolic substance with one of the colorless or lightly colored chromogenous compounds. These new compositions formed by the action of the phenolic substances on the chromogenous compounds may be classified as novel dyestuffs which in most cases are spirit-soluble and oil-soluble.

When these dark-colored materials are formed, the method is being carried out, embodying an aspect of the present invention, in which dark-colored materials are developed from chromogenous compounds by bringing

a colorless or lightly colored chromogenous compound, which includes as its major functional arrangement the molecular structure



into reaction contact with a substance selected from the group of phenolic substances listed above. It will appear from the above that marking or printing may be accomplished, without the use of conventional links containing dark pigments or colored dyes, by using instead of such inks an oily ink vehicle in which the chromogenous compound is dissolved. For letterpress printing, by way of example, the resulting, substantially colorless oily vehicle is applied to the type, which then is impressed on a web surface having a coating containing the phenolic substance to develop dark characters on the web. Alternately, sheets having such a face coating may be used in a typewriter, which is supplied with a ribbon impregnated with an oily ribbon-inking vehicle containing one of the chromogenous substances in solution. Neither the ribbon so impregnated nor the face-coated sheets will soil the fingers or clothing.

Such arrangements illustrate the method of the invention involving, more specifically, the marking on a substrate by developing dark-colored materials from chromogenous compounds, in which one of the chromogenous compounds specified above is provided, preferably dissolved in an oily vehicle, and is brought into contact, in areas on the substrate where marking is desired, with the phenolic compound to produce marks in such areas of the dark-colored product formed from the two compounds. In the illustrations just given, the phenolic color-developing material had been applied to the web, sheet, or other substrate, prior to bringing the chromogenous material into contact with the surface of the web, so that the web carries the phenolic material evenly distributed in amounts preferably of from 0.2 to 8 grams per 1,000 square inches of web surface. It will be understood that the chromogenous material may be brought into contact with the phenolic developer in many other ways, some being suggested hereinabove, whether or not the chromogenous material itself actually is transported to effect the contact. The phenolic compound may be carried to the chromogenous compound, or both compounds may be brought into a new location to effect mutual contact there. To give another illustration, the chromogenous material may be cemented in solid form on a paper web, using for example a starch binder, and the necessary contact then may be effected through the application of small quantities of the phenolic compound, dissolved in a solvent or at a temperature at which the phenolic compound in either pure or impure condition is in the liquid state, to the surface coating in the form of liquid droplets applied where dark-colored marks are desired. Both the phenolic compound in such liquid form and the chromogenous compound dissolved in a solvent alternatively may be applied sequentially to a surface to form marks thereon, or the two liquids may be contained in individual rupturable capsules on the same surface. Of course, the marking method may be carried out by the use of the manifolded sets described hereinabove. Any of the 1,1-bis(p-aminophenyl)phthalan derivatives may be used as the chromogenous compound, the oxo-substituted 3,3-bis(p-aminophenyl)phthalides and 6-amino-3,3-bis(p-aminophenyl)phthalides having N-substituents often being preferred; although an N-substituted 1,1-bis-

(p-aminophenyl)phthalan or 5-amino-1,1-bis(p-aminophenyl)phthalan, or an N-substituted 3′,6′-diaminospiro-(phthalan-1,9′-xanthene), or one of the dilactone substances with p-dialkylaminophenyl groups, also usually is particularly suitable for the purpose. Some of the most active of the phenolic substances, preferred for use in the marking method of the invention, and for forming the novel dark-colored compositions of the invention by that or other methods, have been pointed out more particularly hereinabove.

Use of the phenolic color-developing substances provided in accordance with the present invention in modified spirit-duplicating systems is attractive. Two colorless or lightly colored substances are provided in such duplicating methods embodying the invention, one of these two substances being a chromogenous compound as specified herein, and the other of the two substances being one of the phenolic substances. Deposits are formed, on the surface of a master sheet, of a preselected one of these two substances in areas representing an image to be duplicated but with mirror-reversed image elements. These deposits should contain the preselected chromogenous or phenolic material in a binder which is insoluble in the duplicating fluid or spirit to be used, the fluid thus being a solvent for the aforesaid preselected material which is to be transferred but not for its binder.

There is more than one way to use the spirit transfer principle to obtain many duplicate copies from this master sheet. In one variation of this duplicating method, a solution of the remaining one of the two substances in a solvent liquid is applied to the surface of each duplicate sheet in sequence. The duplicate sheet surface, wetted with the solvent liquid containing the remaining one of the two substances, is pressed against the master sheet surface to effect transfer by the solvent liquid of portions of the deposits of the preselected one of the two substances from the master sheet surface to the duplicate sheet surface onto the areas of the latter which represent the image. By this procedure a duplicate image is formed, on the duplicate sheet surface, of dark-colored material produced by the action of the phenolic substance on the chromogenous compound.

This method may be carried out by forming a reversed image of deposits of the phenolic substance on the master sheet, and then wetting the duplicate sheets with a solvent liquid containing the chromogenous compound. However, it is preferred to use the chromogenous material for making the image-representing deposits on the master sheet. The reverse image conveniently can be formed using transfer sheets or ribbons carrying the chromogenous compound. Transfer ribbons accordingly may be impregnated with the chromogenous material dispersed in a paraffin oil; or transfer coatings consisting of the chromogenous material, dispersed in a binder of wax or of a paraffin oil may be formed on a web surface to provide transfer sheets. Such a transfer sheet, for example, is placed in a typewriter beneath the master sheet with the transfer coating facing the master sheet. Typing or writing with a stylus then causes a reverse image to be formed of the chromogenous material transferred to the lower master sheet surface, opposite the surface impressed with the types or the stylus. The successive duplicate sheets then are wetted with a solvent liquid in which the phenolic developer substance is dissolved, whereby a duplicate image is formed, on the duplicate sheet surface, of dark-colored material produced by the action of the phenolic substance in the solvent liquid on the portions of the chromogenous compound transferred by the solvent liquid from the master sheet surface to the duplicate sheet surface. The solvent liquid may be, for example, acetone, toluene, benzene, 2-butanone (methyl ethyl ketone), or methyl or ethyl alcohol. The solvent liquid and the binder used for the deposits on the master sheet are chosen so that the binder is not dissolved during successive transfers of portions of the chromogenous material from the master sheet to the duplicate sheets.

In another variation, a predetermined one of the two colorless or lightly colored substances again is used to form the deposits representing the reversed image on the master sheet surface. The procedure is varied, however, by arranging the remaining one of the two substances to be carried on at least one surface of the duplicate sheets, usually as a thin coating of the solid substance in a small amount of an adhesive binder. Then a liquid, such as one of the volatile liquids just mentioned, which is a solvent for the preselected one of the two substances is applied to that surface of the duplicate sheet. The duplicate sheet surface, thus wetted with the solvent liquid, is pressed against the master sheet surface to cause portions of the preselected one of the two substances deposited thereon to dissolve in the liquid and to be transferred into contact with the remaining one of the two substances, carried on the duplicate sheet surface, in the areas representing the image. By this procedure a duplicate image again is formed, on the duplicate sheet surface, of dark-colored material produced by interaction of the two chromogenous and phenolic substances.

In the duplicating method just described, the preselected substance may be the chromogenous compound, in which case the remaining substance, which is the phenolic substance, is carried on each duplicate sheet. Under certain circumstances, however, it may prove to be more feasible to pick the phenolic compound instead as the preselected substance. In preparing the master sheet, the phenolic compound then is transferred in a binder to the master sheet surface in the configuration of the reversed image, and the chromogenous compound is carried on the active surface of each duplicate sheet. Solvent spirits for the phenolic compound are used, such as one of the solvents mentioned above which does not readily affect the binder used in the phenolic deposits. When the active surface of each duplicate sheet is wetted with this solvent liquid and pressed against the master sheet surface, portions of the image-representing deposits of the phenolic substance thereon dissolve in the liquid and are transferred into contact with the chromogenous compound carried on the duplicate sheet surface, causing the dark-colored material to form in the areas on the duplicate sheet surface representing the image to be duplicated.

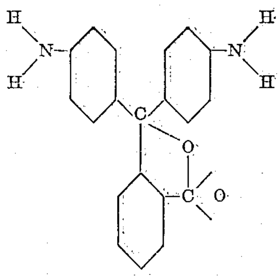
It appears from the discussion hereinabove that highly useful dark-colored marking materials or dyes are produced, when utilizing the arrangements and methods of the invention, by the action of the phenolic substances disclosed hereinabove on suitable chromogenous compounds, the latter being exemplified by the bis(p-aminophenyl)phthalan cyclic ether compounds, by the triphenylmethane lactones, and by the rhodamine lactone or colorless base compounds and by their cyclic ethers. As compared with the dark forms produced from the lactones by the action of inorganic developer materials, or by the action of weak acids such as acetic acid and tartaric acid, these new dark colors generally are more permanent in nature, have increased resistance to fading under ultraviolet radiation and to loss of color in the presence of moisture, and have improved color intensity.

While there have been described what at present are considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention. It is aimed, therefore, in the appended claims to cover all such changes and modifications which fall within the true spirit and scope of the invention.

What is claimed is:

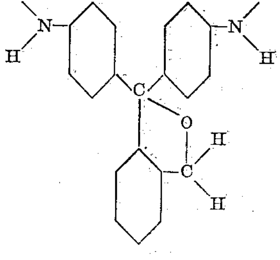
1. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells

of a solvent liquid vehicle; a second base web having on one side an adherent coating, said first and second webs being maintained disposed together in face to face relationship with said respective transfer and adherent coatings in contiguity with each other; one coating constituent in the form of a colorless or lightly colored chromogenous compound which includes as its major functional arrangement the molecular structure



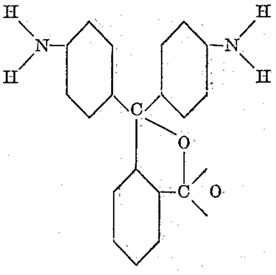
having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; and another coating constituent in the form of a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylene-bis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenyl), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; one of said coating constituents being dissolved in said solvent liquid vehicle present as said numerous cells in the transfer coating on said first base web, and the other of said coating constituents being bonded to said second web in said adherent coating thereon but being accessible to other materials coming into contact with portions of the adherent coating; whereby, upon local impact and rupture of said transfer coating, releasing said liquid vehicle containing said one coating constituent from some of said cells onto said contiguous adherent coating, contact is effected between said two coating constituents to produce a dark-colored material by the action of said phenolic compound in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in said chromogenous compound.

2. A manifolded set, comprising: a first base web having on one side a transfer coating containing a colorless or lightly colored chromogenous compound which is transferable upon impact from said coating to a surface contiguous therewith and which includes as its major functional arrangement the molecular structure



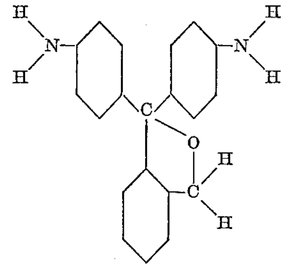
having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; and a second base web carrying on at least one active surface a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby, upon said impact in localized areas, a dark-colored material is produced locally by the action of said phenolic compound carried on said active surface in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in said chromogenous compound transferred to said active surface.

3. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a liquid vehicle carrying a colorless or lightly colored chromogenous compound, said chromogenous compound including as its major function arrangement the molecular structure



having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; and a second base web carrying on at least one active surface a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby, upon local impact and rupture of said transfer coating, releasing said liquid vehicle from some of said cells onto said active surface, a dark-colored material is produced locally by the action of said phenolic compound carried on said active surface in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in the chromogenous compound carried by said liquid vehicle.

4. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a solvent liquid, carrying dissolved therein a colorless or lightly colored chromogenous compound, said chromogenous compound including as its major functional arrangement the molecular structure

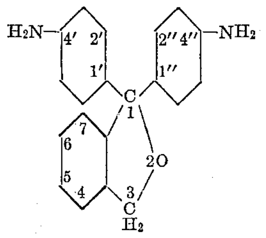


having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; and a second base web carrying on at least one active surface a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substitutents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby upon local impact and rupture of said transfer coating, releasing said solvent liquid containing said chromogenous compound from some of said cells onto said active surface, a dark-colored material is produced locally by the action of said phenolic compound carried on said active surface in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in said chromogenous compound.

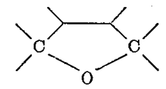
5. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a solvent liquid carrying dissolved therein a colorless or lightly colored chromogenous compound in the form of a 6-dialkylamino-3,3-bis(p-dialkylaminophenyl)phthalide compound in which each individual alkyl radical of said dialkylamino groups has not more than three carbon atoms; and a second base web carrying on at least one active surface a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, sulfonyldiphenol; said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby,

upon local impact and rupture of said transfer coating, releasing said solvent liquid containing said chromogenous compound from some of said cells onto said active surface carrying said phenolic compound, a dark-colored material is produced locally by the action of said phenolic compound on said chromogenous compound.

6. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a liquid vehicle, carrying a colorless or lightly colored chromogenous compound selected from the group consisting of 1,1-bis(p-aminophenyl)phthalan having the structural formula



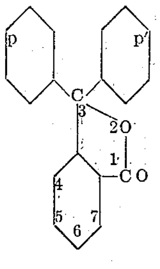
the 2′,2″-epoxy, 3-oxo, and 2′,2″-epoxy-3-oxo derivatives thereof, bifunctional derivatives of each of said compounds having a second heterocyclic ring



fused to the 5,6 side of the benzene nucleus and similarly carrying extracyclic substituents the same as those carried by the carbon atoms designated 1 and 3, the 5-amino derivatives of said 1,1-bis(p-aminophenyl)phthalan and of said epoxy and oxo derivatives thereof, and N-substituted derivatives of each of said compounds in which each individual substituent for an amino hydrogen atom is selected from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and a second base web carrying on at least one active surface a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenbis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby upon local impact and rupture of said transfer coating, releasing said liquid vehicle from some of said cells onto said active surface carrying said phenolic compound, a dark-colored material is produced locally by the action of said phenolic compound on the chromogenous compound carried by said liquid vehicle.

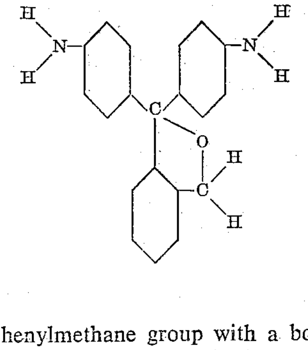
7. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a liquid vehicle, carrying a colorless or lightly colored

chromogenous compound having a modified 3,3-diphenylphthalide structural formula

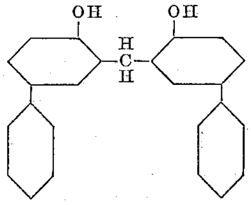


which includes the three points, designated thereon the p,p',6-positions, each para to the position of a bond to the methane carbon atom occupying the 3-position, and which is modified by the inclusion of an amino radical in each of at least the first-mentioned two of said three p,p',6-positions, each such amino radical having at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and a second base web carrying on at least one active surface a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby, upon local impact and rupture of said transfer coating, releasing said liquid vehicle from some of said cells onto said active surface carrying said phenolic compound, a dark-colored material is produced locally by the action of said phenolic compound on the chromogenous compound carried by said liquid vehicle.

8. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a liquid vehicle carrying a colorless or lightly colored chromogenous compound, said chromogenous compound including as its major functional arrangement the molecular structure

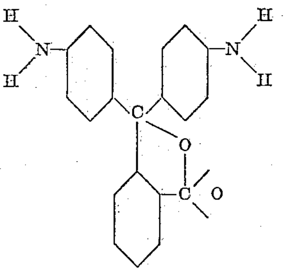


having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; and a second base web carrying on at least one active surface the compound 2,2'-methylenebis(4-phenylphenol) having the structural formula

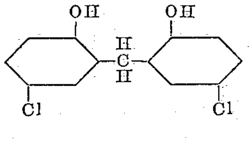


said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby, upon local impact and rupture of said transfer coating, releasing said liquid vehicle from some of said cells onto said active surface, a dark-colored material is produced locally by the action of said 2,2'-methylenebis(4-phenylphenol) carried on said active surface in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in the chromogenous compound carried by said liquid vehicle.

9. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a liquid vehicle carrying a colorless or lightly colored chromogenous compound, said chromogenous compound including as its major functional arrangement the molecular structure



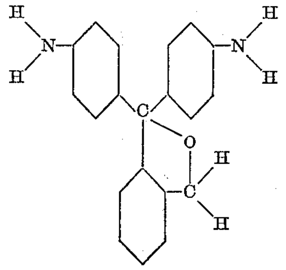
having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; and a second base web carrying on at least one active surface the compound 2,2'-methylenebis(4-chlorophenol) having the structural formula



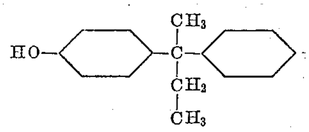
said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby, upon local impact and rupture of said transfer coating, releasing said liquid vehicle from some of said cells onto said active surface, a dark-colored material is produced locally by the action of said 2,2'-methylenebis(4-chlorophenol) carried on said active surface in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in the chromogenous compound carried by said liquid vehicle.

10. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a liquid vehicle carrying a colorless or lightly colored chromogenous compound, said chromogenous compound

including as its major functional arrangement the molecular structure

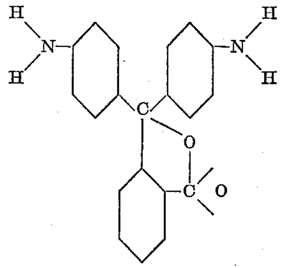


having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; and a second base web carrying on at least one active surface the compound 4,4′-sec-butylidenediphenol having the structural formula

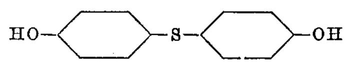


said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby, upon local impact and rupture of said transfer coating, releasing said liquid vehicle from some of said cells onto said active surface, a dark-colored material is produced locally by the action of said 4,4′-sec-butylidenediphenol carried on said active surface in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in the chromogenous compound carried by said liquid vehicle.

11. A manifolded set, comprising: a first base web having on one side a transfer coating made up of a film-forming material which is rupturable upon impact and which contains as a finely dispersed phase numerous cells of a liquid vehicle carrying a colorless or lightly colored chromogenous compound, said chromogenous compound including as its major functional arrangement the molecular structure

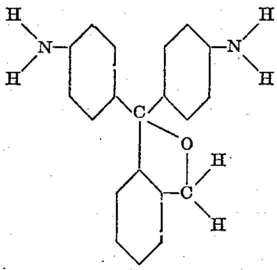


having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; and a second base web carrying on at least one active surface the compound 4,4′-thiodiphenol having the structural formula



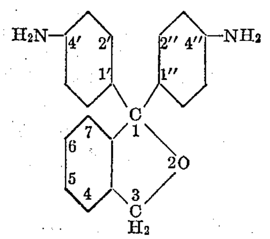
said first and second webs being maintained disposed together in face to face relationship with said transfer coating in contiguity with said active surface, whereby, upon local impact and rupture of said transfer coating, releasing said liquid vehicle from some of said cells onto said active surface, a dark-colored material is produced locally by the action of said 4,4′-thiodiphenol carried on said active surface in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in the chromogenous compound carried by said liquid vehicle.

12. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound which includes as its major functional arrangement the molecular structure

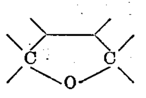


having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol, to produce marks in said areas of a dark-colored material formed by the action of said phenolic compound in opening said bond from the methane carbon atoms to the heterocyclic oxygen atom to permit quinonoid resonance in the chromogenous compound.

13. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound selected from the group consisting of 1,1-bis(p-aminophenyl)phthalan having the structural formula

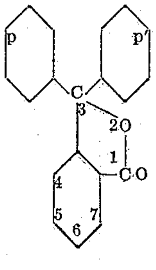


the 2′,2″-epoxy, 3-oxo, and 2′,2″-epoxy-3-oxo derivatives thereof, bifunctional derivatives of each of said compounds having a second heterocyclic ring



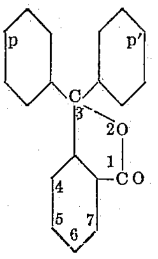
fused to the 5,6 side of the benzene nucleus and similarly carry extracyclic substituents the same as those carried by the carbon atoms designated 1 and 3, the 5-amino derivatives of said 1,1-bis(p-aminophenyl)phthalan and of said epoxy and oxo derivatives thereof, and N-substituted derivatives of each of said compounds in which each individual substituent for an amino hydrogen atom is selected from the group consisting of alkyl radicals of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, sulfonyldiphenol, to produce marks in said areas of a dark-colored material formed by the action of said phenolic compound on said chromogenous compound.

14. The method of marking on a substrate by developing dark-colored material from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound having a modified 3,3-diphenylphthalide structural formula



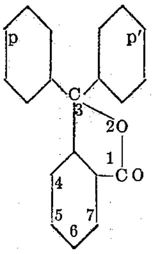
which includes the three points, designated thereon the p,p',6-positions, each para to the position of a bond to the methane carbon atom occupying the 3-position, and which is modified by the inclusion of an amino radical in each of at least the first-mentioned two of said three p,p',6-positions, each such amino radical having at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas of said substrate where marking is desired, with a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol, to produce marks in said areas of a dark-colored material formed by the action of said phenolic compound on said chromogenous compound.

15. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound having a modified 3,3-diphenylthalide structural formula

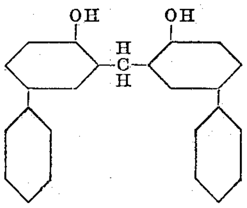


which includes the three points, designated thereon the p,p',6-positions, each para to the position of a bond to the methane carbon atom occupying the 3-position, and which is modified by the inclusion of an amino radical in each of at least the first-mentioned two of said three p,p',6-positions, each such amino radical having at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with a substituted 2,2'-methylenediphenol compound having a substituent in each of the two 4,4'-positions selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals, to produce marks in said areas of a dark-colored material formed by the action of said substituted 2,2'-methylenediphenol compound on said chromogenous compound.

16. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound having a modified 3,3-diphenylphthalide structural formula

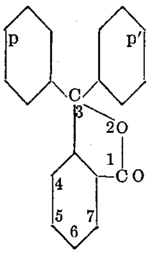


which includes the three points, designated thereon the p,p',6-positions, each para to the position of a bond to the methane carbon atom occupying the 3-position, and which is modified by the inclusion of an amino radical in each of at least the first-mentioned two of said three p,p',6-positions, each such amino radical having at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with the compound 2,2'-methylenebis(4-phenylphenol) having the structural formula

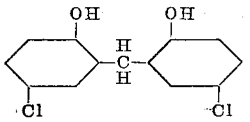


to produce marks in said areas of a dark-colored material formed by the action of said 2,2'-methylenebis(4-phenylphenol) on said chromogenous compound.

17. The method marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound having a modified 3,3-diphenylphthalide structural formula

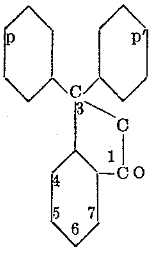


which includes the three points, designated thereon the p,p',6-positions, each para to the position of a bond to the methane carbon atom occupying the 3-position, and which is modified by the inclusion of an amino radical in each of at least the first-mentioned two of said three p,p',6-positions, each such amino radical having at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with the compound 2,2'-methylenebis(4-chlorophenol) having the structural formula



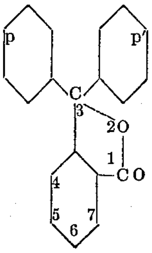
to produce marks in said areas of a dark-colored material formed by the action of said 2,2'-methylenebis(4-chlorophenol) on said chromogenous compound.

18. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound having a modified 3,3-diphenylphthalide structural formula

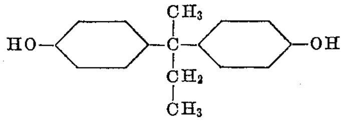


which includes the three points, designated thereon the p,p',6-positions, each para to the position of a bond to the methane carbon atom occupying the 3-position, and which is modified by the inclusion of an amino radical in each of at least the first-mentioned two of said three p,p',6-positions, each such amino radical having at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with a sec-butylidenediphenol to produce marks in said areas of a dark-colored material formed by the action of said sec-butylidenediphenol on said chromogenous compound.

19. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound having a modified 3,3-diphenylphthalide structural formula

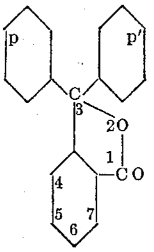


which includes the three points, designated thereon the p,p',6-positions, each para to the position of a bond to the methane carbon atom occupying the 3-position, and which is modified by the inclusion of an amino radical in each of at least the first-mentioned two of said three p,p',6-positions, each such amino radical having at least one substitutent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with the compound 4,4'-sec-butylidenediphenol having the structural formula



to produce marks in said areas of a dark-colored material formed by the action of said 4,4'-sec-butylidenediphenol on said chromogenous compound.

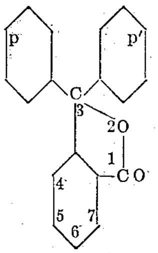
20. The method of marking on a stubstrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound having a modified 3,3-diphenylphthalide structural formula



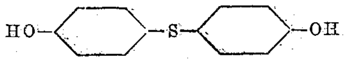
which includes the three points, designated thereon the p,p',6-positions, each para to the position of a bond to the methane carbon atom occupying the 3-position, and which is modified by the inclusion of an amino radical in each of at least the first-mentioned two of said three p,p',6-positions, each such amino radical having at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with a thiodiphenol to produce marks in said areas of a dark-colored material formed by the action of said thiodiphenol on said chromogenous compound.

21. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly

colored chromogeneous compound having a modified 3,3-diphenylphthalide structural formula



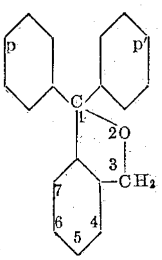
which includes the three points, designated thereon the p,p′,6- positions, each para to the position of a bond to the methane carbon atom occupying the 3-position, and which is modified by the inclusion of an amino radical in each of at least the first mentioned two of said three p,p′,6-positions, each such amino radical having at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogeneous compound into contact, in areas on said substrate where marking is desired, with the compound 4,4′-thiodiphenol having the structural formula



to produce marks in said areas of a dark-colored material formed by the action of said 4,4′-thiodiphenol on said chromogenous compound.

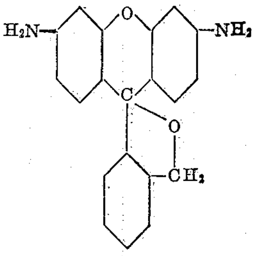
22. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorles or lightly colored chromogenous compound in the form of a 6-dialkylamino-3,3 - bis(p-dialkylaminophenyl)phthalide compound in which each individual alkyl radical of said dialkylamino groups has not more than three carbon atoms; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol, to produce marks in said areas of a dark-colored material formed by the action of said substituted phenol on said chromogenous compound.

23. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound having a modified 1,1-diphenylphthalan structural formula



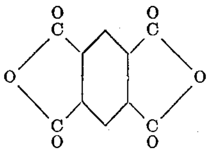
which includes the three points, designated thereon the p,p′,5-positions, each para to the position of a bond to the methane carbon atom occupying the 1-position, and which is modified by the inclusion of an amino radical in at least the first-mentioned two of said three p,p′,5-positions, each such amino radical having at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetraholophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol, to produce marks in said areas of a dark-colored material formed by the action of said phenolic compound on said chromogenous compound.

24. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound in the form of a substituted 3′,6′-diaminospiro(phthalan - 1,9′ - xanthene) compound having the structural formula



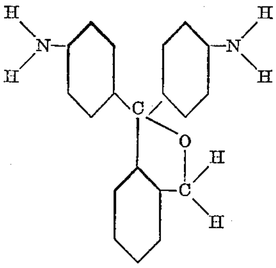
in which each of the amino radicals has at least one substituent selected individually from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylene diresorcinol, methylenebis (alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetraholophenol) substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relaltive to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol, to produce marks in said areas of a dark-colored material formed by the action of said phenolic compound on said chromogenous compound.

25. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: providing a colorless or lightly colored chromogenous compound based on the structure of pyromellitic dianhydride



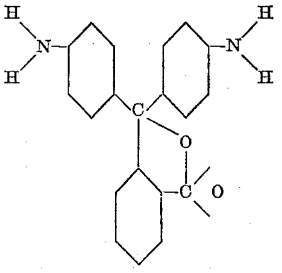
one of the two oxygen atoms attached to each heterocyclic ring thereof being replaced by two p-dialkylaminophenyl groups, in which each individual one of the four alkyl radicals has not more than three carbon atoms; and bringing said chromogenous compound into contact, in areas on said substrate where marking is desired, with a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetraholophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol, to produce marks in said areas of a dark-colored material formed by the action of said phenolic compound on said chromogenous compound.

26. The method of marking on a substrate by developing dark-colored materials from chromogenous compounds, comprising: bringing a colorless or lightly colored chromogenous compound which includes as its major functional arrangement the molecular structure



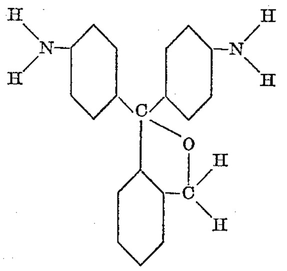
into contact, in areas where marking is desired, with the surface of a web carrying, evenly distributed in amounts of from 0.2 to 8 grams per 1,000 square inches of web surface, a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol, whereby marks are produced in said areas of a dark-colored material formed by the action of said phenolic compound on said chromogenous compound.

27. The method of duplicating, comprising: providing two colorless or lightly colored substances, one of these two substances being a chromogenous compound which includes as its major functional arrangement the molecular structure



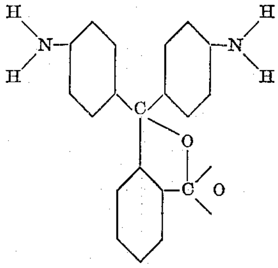
having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom, and the other of said two substances being a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; forming on the surface of a master sheet deposits of a preselected one of said two substances in areas representing an image to be duplicated but with mirror-reversed image elements; applying a solution of the remaining one of said two substances in a solvent liquid to the surface of a duplicate sheet; and pressing said duplicate sheet surface, wetted with the solvent liquid containing said remaining one of the two substances, against said master sheet surface to effect transfer by the solvent liquid of portions of said deposits of said preselected one of the two substances from the master sheet surface to the duplicate sheet surface in areas thereon representing said image, whereby a duplicate image is formed on said duplicate sheet surface of dark-colored material produced by the action of said phenolic compound in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in said chromogenous compound.

28. The method of duplicating, comprising: forming on the surface of a master sheet, in areas representing an image to be duplicated but with mirror-reversed image elements, deposits of a colorless or lightly colored chromogenous compound which includes as its major functional arrangement the molecular structure



having a triphenylmethane group with a bond from the methane carbon atom to the heterocyclic oxygen atom; applying to the surface of a duplicate sheet a solvent liquid which carries dissolved therein a phenolic compound selected from the group consisting of biphenol, bicresol, dibenzylbiphenol, diethylbiphenol, dipropylbiphenol, diallylbiphenol, dihalobiphenol, biphenyltetrol, terphenyldiol, methylenediphenol, alkylidenediphenol, cycloalkylidenediphenol, methylenediresorcinol, methylenebis(alkylphenol), methylenebis(benzylphenol), methylenebis(phenylphenol), methylenebis(halophenol), methylenebis(trihalophenol), methylenebis(tetrahalophenol), substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; and pressing said duplicate sheet surface, wetted with the solvent liquid, against said master sheet surface to effect transfer by the solvent liquid of portions of said deposits from the master sheet surface to the duplicate sheet surface in areas thereon representing said image, whereby a duplicate image is formed on said duplicate sheet surface of dark-colored material produced by the action of said phenolic compound in said solvent liquid in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in the portions of said chromogenous compound transferred to the duplicate sheet surface.

29. The method of duplicating, comprising: providing two colorless or lightly colored substances, one of these two substances being a chromogenous compound which includes as its major functional arrangement the molecular structure



having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom, and the other of said two substances being a phenolic compound selected from the group consisting of

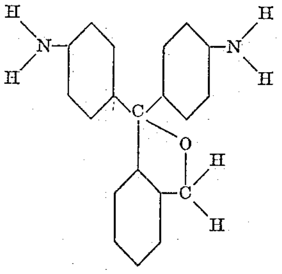
biphenol,
bicresol,
dibenzyldiphenol,
diethylbiphenol,
dipropylbiphenol,
diallylbiphenol,
dihalobiphenol,
biphenyltetrol,
terphenyldiol,
methylenediphenol,
alkylidenediphenol,
cycloalkylidenediphenol,
methylenediresorcinol,
methylenebis(alkylphenol),
methylenebis(benzylphenol),
methylenebis(phenylphenol),
methylenebis(halophenol),
methylenebis(trihalophenol),
methylenebis(tetrahalophenol),

substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; forming on the surface of a master sheet deposits of a preselected one of said two substances in areas representing an image to be duplicated but with mirror-reversed image elements; applying to a surface of a duplicate sheet, which carries on at least said surface the remaining one of said two substances, a liquid which is a solvent for said preselected one of the two substances; and pressing said duplicate sheet surface, wetted with the solvent liquid, against said master sheet surface to cause portions of said preselected one of the two substances deposited thereon to dissolve in said liquid and to be transferred into contact with said remaining one of the two substances, carried on the duplicate sheet surface, in the areas thereon representing said image, whereby a duplicate image is formed on said duplicate sheet surface of dark-colored material produced by the action of said phenolic compound in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in said chromogenous compound.

30. The method of duplicating, comprising: forming on the surface of a master sheet, in areas representing an image to be duplicated but with mirror-reversed image elements, deposits of a phenolic compound selected from the group consisting of

biphenol,
bicresol,
dibenzylbiphenol,
diethylbiphenol,
dipropylbiphenol,
diallylbiphenol,
dihalobiphenol,
biphenyltetrol,
terphenyldiol,
methylenediphenol,
alkylidenediphenol,
cycloalkylidenediphenol,
methylenediresorcinol,
methylenebis(alkylphenol),
methylenebis(benzylphenol),
methylenebis(phenylphenol),
methylenebis(halophenol),
methylenebis(trihalophenol),
methylenebis(tetrahalophenol),

substituted methylenediphenol in which each phenol has two substituents selected from the group consisting of the alkyl, benzyl, phenyl, and halo radicals but in which said two substituents and the linkage to the methylene group do not occupy all of the 2,4,6-positions relative to the phenolic hydroxyl group, thiodiphenol, and sulfonyldiphenol; providing a duplicate sheet carrying on at least one active surface a colorless or lightly colored compound which includes as its major functional arrangement the molecular structure



having a triphenylmethane group with a bond from the methane carbon atom thereof to the heterocyclic oxygen atom; applying to said active surface of the duplicate sheet a liquid which is a solvent for said phenolic compound; and pressing said duplicate sheet surface, wetted with the solvent liquid, against said master sheet surface to cause portions of said deposits of the phenolic compound thereon to dissolve in said liquid and to be transferred into contact with said chromogenous substance, carried on the duplicate sheet surface, in the areas thereon representing said image, whereby a duplicate image is formed on said duplicate sheet surface of dark-colored material produced by the action of said transferred portions of the phenolic compound in opening said bond from the methane carbon atom to the heterocyclic oxygen atom to permit quinonoid resonance in said chromogenous compound carried by said duplicate sheet.

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