

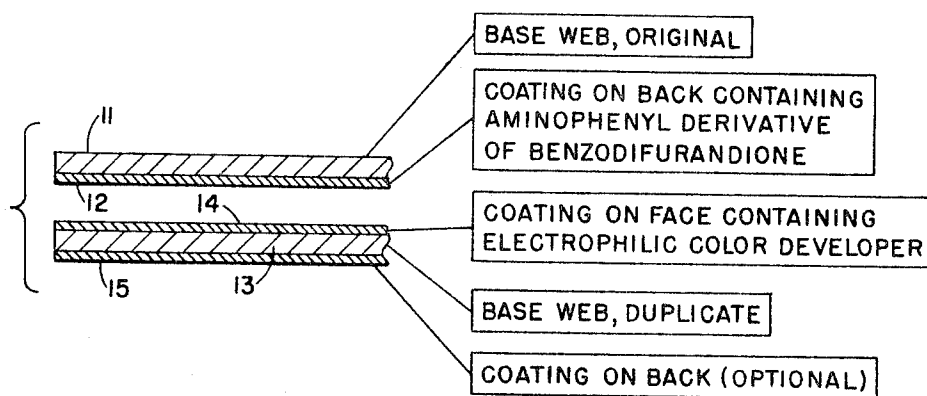
Aug. 23, 1966

E. J. GOSNELL ETAL

3,268,537

CHROMOGENOUS AMINOPHENYL DERIVATIVES OF BENZODIFURANDIONE

Filed Aug. 31, 1961



INVENTORS.
EARL J. GOSNELL
JOHN F. McCARTHY, JR.
BY
Harrie A. Mumma Jr.
ATTORNEY

1

3,268,537

CHROMOGENOUS AMINOPHENYL DERIVATIVES OF BENZODIFURANDIONE

Earl J. Gosnell, Irondequoit, N.Y., and John F. McCarthy, Jr., Brockton, Plymouth City, Mass., assignors to Burroughs Corporation, Detroit, Mich., a corporation of Michigan

Filed Aug. 31, 1961, Ser. No. 135,264

9 Claims. (Cl. 260-287)

This invention pertains to chromogenous compounds which are related generally to the amino-substituted triphenylmethanes and which have the form of colorless, that is, white, or lightly colored solids, and approach being colorless when in liquid solution, but which may be converted to dark-colored forms as solids or in solution upon contact with suitable color-developing substances. As applied to the printing and duplicating arts, marking in desired areas on base sheets may be accomplished by effecting localized contact, in areas where image elements are to be printed, between the chromogenous compound and the color-developing substance. Webs coated with films carrying individually the chromogenous compound and the color developer may be assembled in a manifolded set, so that localized pressure or impact will cause transfer of material from a coating on the web surface of one manifold unit to a coating on a contiguous web surface, where the desired localized contact is made to form the dark-colored materials in the image-marking areas.

Marking systems of these general types have been disclosed which utilize known chromogenous compounds. As examples of such chromogenous compounds there may be mentioned the leuco, or simple amino-substituted triphenylmethane, forms of malachite green, crystal violet, and ethyl violet; the corresponding amino-substituted triphenylmethyl carbinols; and the lactone forms, which are amino-substituted diphenylphthalides, corresponding to the above-mentioned leuco forms. These types of chromogenous compounds have their peculiar properties with respect to stability of the colorless or leuco forms against spontaneous color development, and with respect to their reactions with various color-developing agents having otherwise acceptable characteristics for use as coatings on paper webs. The color-developing response may be too easily triggered in some cases and too sluggish in others, with some substances even requiring heating to develop a good dark mark. Thus problems often arise from excessive background color in a coating containing the chromogenous compound after periods of storage or long exposure to light or heat, from slow or insufficient production of dark-colored materials upon contact with color-activating substances, and from limitations in the color hues and intensities of the dark-colored forms which can be developed from the chromogenous substances. To find the best answer to these problems for any given application it is advantageous to have available a choice of additional different chromogenous substances.

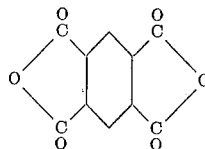
Accordingly it is an object of the present invention to provide new and improved, quite lightly colored substances having chromogenous properties, which advantageously may be incorporated in a transferable coating on a web surface to provide a novel manifold unit, and which are useful in carrying out improved methods of marking involving contact with a color-activating material to develop dark-colored materials in areas where marking is desired.

It is another object of the invention to provide novel colorless or lightly colored compounds, having molecular structures convertible to quinonoid resonant forms, which offer a new and improved variety of chromogenous char-

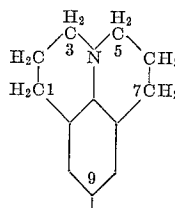
2

acteristics, and which develop, upon contact with color-activating materials, novel and much darker-colored substances having generally desirable and useful color intensities and hues.

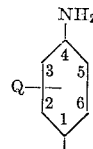
In accordance with the invention, there is provided a compound based on the structure of pyromellitic dianhydride



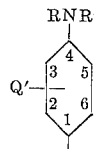
in which one of the two oxygen atoms attached to each heterocyclic ring is replaced by two aryl radicals, each individual one of the four such aryl radicals being selected from the group consisting of the 9-julolidyl radical



of a 4-aminophenyl radical

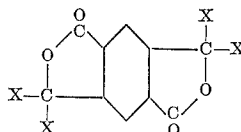


where the substituent Q is selected from the group of Q-substituents consisting of hydrogen, any single one of the methyl, fluoro, chloro, and bromo substituents in the 2-position, any single one of these substituents in the 5-position, and both of these single substituents individually in the 2- and 5-positions; and of an N-substituted 4-aminophenyl radical



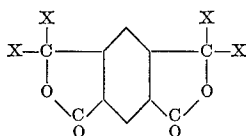
where the substituent Q' is selected from the above-listed group of Q-substituents, where the radical R is selected from the group of N-substituents consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical, and where the radical R' is selected from the group consisting of hydrogen and any one of the above-listed group of N-substituents.

In accordance with another feature of the invention, a new composition of matter comprises the dark-colored substance, having a quinonoid resonant form, developed by contact of a color-activating material with a colorless or lightly colored chromogenous compound selected from the group consisting of compounds having the structural formula



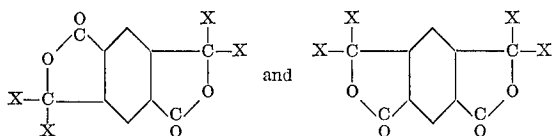
3

and or compounds having the structural formula



in which each individual one of the four radicals designated X is selected from the group of aryl radicals listed hereinabove; such chromogenous compound thus has two —CX₂—O—CO— heterocyclic ring components attached to the central benzene ring, and the aforementioned color-activating material is an electrophilic substance for opening, in the heterocyclic ring components, the bonds from the carbon atoms of the —CX₂— groups to the respective adjoining oxygen atoms to permit quinonoid resonance in the —CX₂ groups and convert the chromogenous compound to the dark-colored substance.

In a manifolding unit comprising a base web having on one side a coating made up of a film-forming material containing a colorless or lightly colored chromogenous compound transferable upon impact from the coating to a surface contiguous therewith, the improvement is provided, in accordance with the invention, in which the chromogenous compound is selected from the group consisting of components having the structural formulas



with the aryl radicals X, as defined hereinabove; the manifolding unit being adapted, upon such impact and transfer of the chromogenous compound to the contiguous surface, to produce a dark-colored material by the action of an electrophilic color-activating material, carried by the contiguous surface, in opening the bonds from the —CX₂— groups to the respective adjoining oxygen atoms, in the two —CX₂—O—CO— heterocyclic ring components attached to the central benzene ring in the chromogenous compound, to permit quinonoid resonance in the —CX₂ groups.

In accordance with a method feature of the invention, the method of marking by developing dark-colored materials from colorless or lightly colored chromogenous compounds comprises providing a chromogenous compound selected from the aforementioned group of compounds having the aryl radicals X, and bringing this chromogenous compound, having the two —CX₂—O—CO— heterocyclic ring components attached to the central benzene ring, into contact, in areas where marking is desired, with an electrophilic color-activating substance for opening the aforementioned bonds in the heterocyclic ring components to permit quinonoid resonance in the —CX₂ groups and produce a dark-colored form of the chromogenous compound by the action thereon in such areas of the electrophilic substance.

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, with or without additional similar manifolding units, in a manifoldd set. The manifolding units are 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.

A manifolding unit embodying the present invention is shown in the upper portion of the exploded view of the drawing. In such a manifolding unit, comprising a base web 11 having on one side, usually on the back surface, a

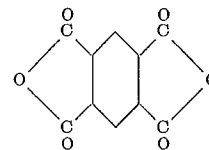
4

coating 12 made up of a film-forming material containing a colorless or lightly colored chromogenous compound transferable upon impact from the coating to a surface contiguous therewith such as the surface on the face of another base web 13, the present invention is embodied in an improvement in which the chromogenous compound is one of the novel substances provided by the invention.

For preparing these substances several procedures have been evolved. These procedures have indicated not only preferred methods of synthesis but also the structure of the substances prepared. Examples of these procedures follow.

Example 1

Quantities equal to 10.9 grams (0.05 mole) of pyromellitic dianhydride



30 grams (0.25 mole) of N,N-dimethylaniline, and 27 grams (0.2 mole) of freshly fused and ground zinc chloride were heated together in a round bottom flask equipped with a stirring apparatus for four hours at 120–125° C. Stirring was continued for the entire four hour reaction period. The crude condensation product from the above step was poured into 700 ml. of water containing 75 ml. of concentrated HCl and then made basic by the dropwise addition of 20% NaOH. The mixture then was steam-distilled to remove any unreacted dimethylaniline, and the remaining materials were cooled, filtered, and dried. The resulting tan solid material was extracted with two 300 ml. portions of boiling benzene, which then were mixed and evaporated almost to dryness to obtain the material in a more purified form. After cooling, cold ethanol was added and the solid material, having a greenish yellow color, was filtered and dried. This crystalline solid then was Soxhlet-extracted progressively with ethanol and benzene. Three fractions were obtained with melting points as indicated:

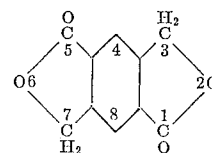
(I) Warm ethanol-soluble yellow-green crystals, M.P. 84–85° C.

(II) Warm benzene-soluble green solid, M.P. 255° C.

(III) Insoluble yellow solid, M.P. 360+° C.

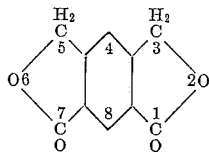
Fractions I and II were found to be essentially inactive when mixed intimately with a color-developing agent such as argosite clay. They did produce, however, a dark-colored material upon contact with an oxidizing agent such as chloranil or N,2,6-trichloro-p-benzoquinone imine, indicating the presence of the oxidizable leuco structure or the corresponding carbinol structure, viz., p-amino-substituted triphenylmethanol. Fraction III, however, produced immediately a deep blue-green color of considerable intensity on contact with the clay, but developed no color upon contact with the aforementioned oxidizing agents.

The development of dark-colored material upon contact with the clay, and the absence of color formation under oxidizing conditions, demonstrate that a poly(aminophenyl) derivative with the closed ring lactone structure was achieved in fraction III. Alternative synthesis procedures, described hereinbelow, elemental nitrogen analyses, and the high melting point have confirmed that the product indeed has a bifunctional lactone, or dilactone, structure. This structure may be either the 1H-3H-benzo (1,2-c:5-c')difuran-1,5(7H)-dione structure



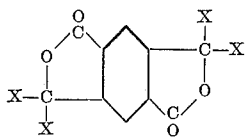
5

otherwise identified as the di-gamma-lactone of 2,5-bis(hydroxymethyl)terephthalic acid, or the 1H,3H-benzo(1,2-c; 4,5-c')difuran-1,5(7H)-dione structure

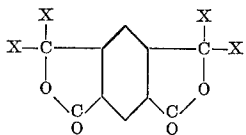


otherwise identified as the di-gamma-lactone of 4,6-bis(hydroxymethyl)isophthalic acid, in either of which each of the four hydrogen atoms in the 3,7-positions or in the 3,5-positions respectively is replaced by a p-dimethylaminophenyl radical.

Actually there usually is produced a mixture of these two isomeric structures, which will be discussed hereinbelow along with the separation of the two isomers when desired. Either of these isomers is seen to be a compound based on the structure of pyromellitic dianhydride in which one of the two oxygen atoms attached to each heterocyclic ring is replaced by two aryl radicals, in this example, by two p-dimethylaminophenyl radicals. Defined somewhat differently, each of these isomers is a substance selected from the group consisting of the compound having the structural formula

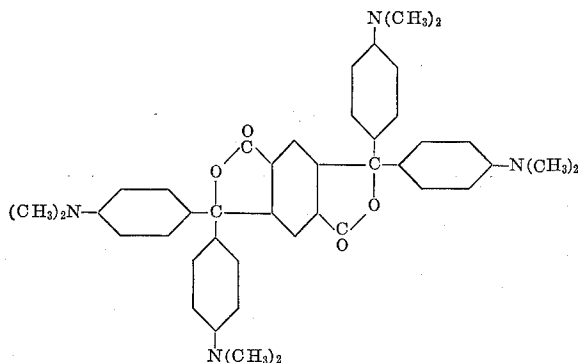


and of the isomeric compound having the structural formula



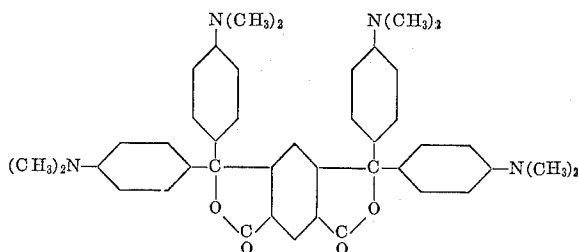
in which each of the four radicals designated X is the p-dimethylaminophenyl radical. The yield of fraction III, made up of these two isomers, was 3-4% of theoretical. It will be understood that the aryl radicals X will be correspondingly modified if unsubstituted aniline, or an H-monosubstituted aniline, or a different N,N-disubstituted aniline, were used in the synthesis described above. In any case, however, the dilactone product is an aminophenyl derivative of a benzodifurandione, and more specifically a 3,3,7,7-tetrakis(aminophenyl) or 3,3,5,5-tetrakis(aminophenyl) derivative respectively of one of the two benzodifurandione structures shown above.

The product of the synthesis described above thus may be represented as an isomeric mixture in roughly equal proportions of the compound having the structural formula

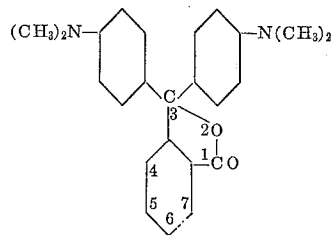


and of the compound having the structural formula

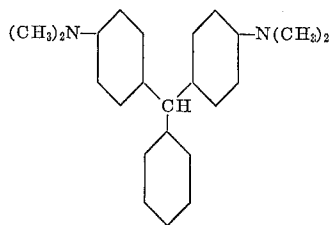
6



If either one of the two heterocyclic rings could be removed from the benzene nucleus of either of these two isomeric compounds, there would remain the compound 3,3-bis(p-dimethylaminophenyl)phthalide



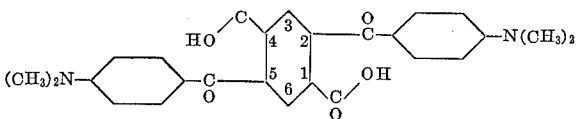
which is a lactone of the dye malachite green having the leuco form represented by the p-p'-diamino-triphenylmethane with the structure



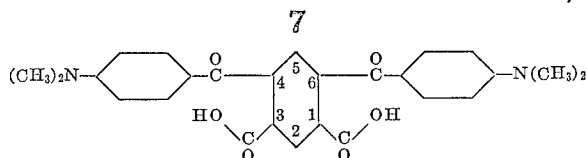
Example 2

Step 1.—Greatly increased yields of the dilactone product may be obtained through the synthesis of intermediate products using similar starting materials. A useful intermediate product is made by dissolving 100 grams (0.85 mole) of N,N-dimethylaniline in 400 grams of carbon disulfide and gradually adding while stirring 100 grams (0.75 mole) of anhydrous aluminum chloride. Stirring is continued to effect dissolution of the catalytic $AlCl_3$, at which time 37.3 grams (0.17 mole) of pyromellitic dianhydride are added in several portions, stirred another 30 minutes, and the preparation then allowed to stand several hours. The upper layer of the CS_2 solvent then is decanted, a sulfuric acid solution is prepared by adding 80 grams of concentrated H_2SO_4 to 1 liter of water, and this solution is added dropwise to the decanted CS_2 with stirring. The resulting aqueous suspension is diluted to 10 liters with water and allowed to stand 2 days, after which the solid reaction product is filtered, washed, and dried.

A yield of about 90% of theoretical is obtained of a high melting ($360+^{\circ}C.$) light greenish-yellow crystalline solid which does not develop appreciable darker color upon contact with chloranil or with argosite clay or attapulgite. A nitrogen analysis of 5.8% showed that the anhydride linkages in both of the heterocyclic rings had entered into the reaction to give the desired intermediate product, which, as is indicated by the products obtained in Step 2, is formed as an isomeric mixture of 2,5-bis(4'-dimethylaminobenzoyl)terephthalic acid



and 4,6-bis(4'-dimethylaminobenzoyl)isophthalic acid

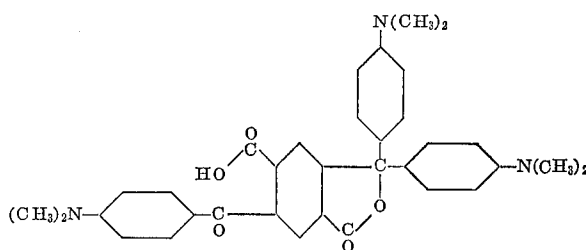


Again it will be understood that, instead of the dimethyl-aniline, other N,N-disubstituted anilines, or N-monosubstituted anilines, or aniline itself, may be used to form such intermediate products with corresponding changes in the amino groups. Such a dibenzoylbenzenedicarboxylic acid isomeric product will be referred to hereinbelow as the "intermediate mixture" used in the synthesis of the dilactone products of the invention.

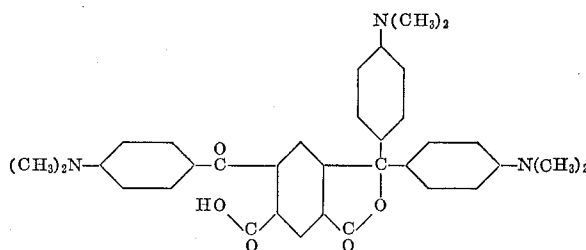
Step 2.—Twenty grams (0.044 mole) of the intermediate mixture of bis(dimethylamino)-substituted isomers obtained in Step 1, 11 grams (0.09 mole) of additional N,N-dimethylaniline, and 185 ml. of acetic anhydride are heated at reflux temperature for 24 hours. The reaction mixture is cooled and filtered to obtain a solid product and the filtrate. The solids are washed with cold acetic anhydride and dried to obtain 12.0 grams of a first preliminary fraction in the form of a yellow solid, melting point $360+^{\circ}\text{C}$. This solid is soluble to the extent of only about 2% in chlorinated biphenyl; it becomes a deep blue when this solvent is heated to aid solution, but the solution reverts to the yellowish color upon cooling.

The filtrate obtained as above is flooded with water, allowed to stand to facilitate precipitation of solids, filtered, washed, and dried. There are obtained 11.4 grams of a second preliminary fraction in the form of a light yellow-green solid, having a melting point which also is high but well below 300°C . This solid is soluble in chlorinated biphenyl in excess of 5%, and the solution does not change color upon warming.

Both the first and second preliminary fractions are stable in the presence of chloranil and also upon prolonged exposure to the atmosphere. A drop of a solution of either one in chlorinated biphenyl, placed on argosite clay, yields a deep blue-green color, indicating the presence of a molecular structure including the lactone of an amino-substituted triphenylmethane. Analyses for elemental nitrogen show a nitrogen content in each preliminary fraction approaching the theoretical 7.4%, confirming the formation of the monolactone isomers having the structural formulas



and

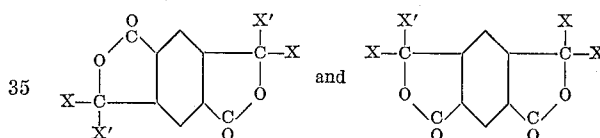


Based upon a theoretical 100% maximum yield of the two isomeric monolactones together, a total yield of 95.0% is obtained, made up of 48.8% of the first preliminary fraction and 46.2% of the second or acetic anhydride-soluble fraction. Yields from 26.1% to 48.8% of the first fraction and from 70.0% to 46.2% of the second fraction, with total yields from 87.9% to 96.1%, 75

have been obtained by varying the time for heating the reagents at reflux temperature between 4 and 34 hours.

Step 3.—Fourteen grams (0.025 mole) of an intimate mixture of the monolactone solids produced in Step 2, 9 grams (0.075 mole) of additional N,N-dimethylaniline, and another 50 ml. of acetic anhydride are heated at reflux temperature for 24 hours, cooled, filtered, and the filtrate set aside. The resulting solid material is washed with cold acetic anhydride and with ethanol, then dried to yield 8.5 grams of a first end fraction in the form of a yellow solid having a melting point of $360+^{\circ}\text{C}$. This acetic anhydride-insoluble fraction has essentially no solubility in most of the common organic solvents but is soluble to the extent of about 5% in chlorinated biphenyl. The filtrate now is poured over 1 kg. of crushed ice and allowed to stand, filtered, washed with water, and dried, yielding 3.5 grams of a second end fraction in the form of a light, somewhat greenish tan solid also having a melting point of $360+^{\circ}\text{C}$. This acetic anhydride-soluble second fraction also has very low solubility in the common solvents, but it is considerably more soluble in chlorinated biphenyl than the first end fraction.

Both the first and second end fractions are stable to the atmosphere and to chloranil. A solution of either one, or of both, in chlorinated biphenyl, brought into contact with argosite clay, forms an instantaneous dark blue-green color. Elemental nitrogen analyses of the separate solid end fractions both approached closely the theoretical 8.4% nitrogen content of the isomeric dilactones having the structural formulas



where the radicals designated X' represent the p-dimethylaminophenyl radicals present as substituents on the benzoyl groups in the intermediate mixture of isomers produced in Step 1, and the radicals designated X represent the additional p-dimethylaminophenyl radicals placed on the molecules, one in each monolactone isomer, by the use of more N,N-dimethylaniline in Step 2, and another in each dilactone isomer by the use of still more N,N-dimethylaniline in Step 3. Based on the total possible stoichiometric production of both of the dilactone isomers in Step 3, the first end fraction supplied 51.5% and the second end fraction supplied 21% of the theoretical total for a total recovery of almost three-fourths of the theoretical yield. It will appear that other N-substituted p-aminophenyl radicals may be obtained for each of the radicals designated X by using different N-substituted anilines in Step 2 and also in Step 3.

It is probable that Step 2 yielded the monolactone rather than the dilactone because water is formed in an amount equimolar with the N-substituted aniline which participates in the closing of the first lactone ring. This water reacts with some of the acetic anhydride to form twice the equimolar amount of acetic acid, which in turn reacts with any remaining N,N-dialkylaniline to form a quaternary salt. The dilactone can be formed in a single step by using a sufficient amount of the substituted aniline to make up this loss, as illustrated below.

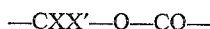
Example 3

Step 1.—The intermediate mixture of isomers is formed as in Step 1 of Example 2.

Step 2.—Twenty grams (0.044 mole) of the intermediate mixture, 25 grams (0.2 mole) of N,N-dimethylaniline, and 150 ml. of acetic anhydride are heated at reflux temperature for 24 hours, cooled, filtered, and the filtrate set aside. The solid product is washed with cold acetic anhydride and ethanol, then dried. This first fraction, insoluble in acetic anhydride, is a yellow solid

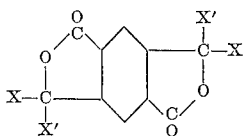
weighing 13.3 grams, melting point $360+^{\circ}$ C. The filtrate is poured over 1 kg. of crushed ice and allowed to stand, filtered, washed, and dried. This second fraction, soluble in acetic anhydride, is a greenish yellow solid weighing 10.3 grams, melting point $360+^{\circ}$ C. Elemental nitrogen analyses again closely approached the theoretical 8.4% for the dilactone, and the two fractions had the same color responses and other properties as did the two isomeric acetic anhydride-insoluble and soluble dilactone fractions obtained in Step 3 of Example 2. Example 3 differs in that the two fractions were formed directly from the intermediate mixture of isomers and in amounts equal to 46% and 35.5%, or over 80%, of the total theoretical maximum amount of the dilactone reaction product. Referring to the structural formulas shown above, having the radicals designated X and X', those designated X are the p-dimethylaminophenyl radicals which were derived in this instance from the N,N-dimethylaniline used in Step 2 of Example 3. Again, unsubstituted aniline, or another N-substituted aniline, may be used instead of N,N-dimethylaniline with corresponding changes in the radicals designated X.

It will be understood that alternatively the entire reaction product, after refluxing, may be cooled and the acetic anhydride then poured directly, along with the insoluble first fraction, over crushed ice to precipitate the acetic anhydride-soluble second fraction and recover a mixture of the two isomeric compounds in solid particulate form. Since the two isomers have very similar properties, they often may be used quite suitably when thus mixed together, and the trouble and expense of separating the two fractions then is avoided. The resulting mixture consists of the two isomeric compounds having individually the structural formulas shown above with the radicals X and X'. The two compounds are identical except for the relative directions of attachment of the two

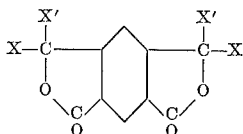


heterocyclic ring components in each compound to the central benzene ring, since the radicals designated X' in both isomeric compounds came from the same substituted aniline used in Step 1 of Example 3, and the radicals designated X in both of the compounds all came from the substituted aniline used in Step 2. Accordingly, both compounds are defined in the nature of the radicals X and X' in one of the two isomeric compounds is designated.

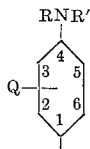
In any case, the novel substance of the present invention may be defined more broadly as being selected from the group consisting of compounds having the structural formula



and of compounds having the isomeric structural formula



in which each individual one of the four radicals designated X and X' is an N-substituted 4-aminophenyl radical



where the substituent Q is selected from the group consisting of hydrogen (corresponding to no substituent),

any single one of the methyl, fluoro, chloro, and bromo substituents in the 2-position, any single one of these substituents in the 5-position, and both of these single substituents individually in the 2- and 5-positions. In this same aminophenyl radical the substituent radical R is selected from the group of N-substituents consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical, while the substituent radical R' is selected from the group consisting of hydrogen (i.e., a secondary amine) and any one of the aforementioned group of N-substituents. As has been mentioned, in the usual synthesis the radicals designated X come from the same substituted aniline source and the radicals designated X' come from a common source. These similarities may be expressed by stating that the nuclear substituents Q and the N-substituted radicals R and R' are selected so that, in either isomeric compound or in a mixture of the two, the radicals designated X are identical and the radicals designated X' are identical.

Illustrations of representative syntheses which provide the radicals designated X and X' in the form of various such N-substituted 4-aminophenyl radicals now will be given.

Example 4

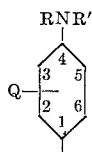
Again the intermediate mixture of isomers, formed as in Step 1 of Example 2, is used. Ten grams (0.022 mole) of the intermediate mixture, 16.3 grams (0.092 mole) of N,N-diisopropylaniline, and 75 ml. of acetic anhydride are heated at reflux temperature for the reaction period, then cooled, as in Step 2 of Example 3. The insoluble dilactone was removed by filtration, washed, and dried, yielding 6.6 grams of a yellow solid, melting point $350+^{\circ}$ C., corresponding to 38.4% of the total dilactone product theoretically possible from this synthesis. As with the dilactone products of the syntheses of Examples 2 and 3 using N,N-dimethylaniline, a solution of this acetic anhydride-insoluble yellow solid in chlorinated biphenyl, when brought into contact with argosite clay, produces instantaneously a dark blue-green colored form.

Pouring the filtrate obtained in Example 4 into cold water, however, did not effect the recovery of a solid, acetic anhydride-soluble isomer. In these cases it is not necessary to recover such a soluble fraction, since the insoluble fraction itself has desirable properties, including the ready formation of dark-colored materials upon suitable treatment, and a soluble isomer would be expected to have very similar properties. It is probable that the reactivity of an excess of the N,N-diisopropylaniline with the intermediate mixture is such as to produce much more of the fraction which is insoluble in acetic anhydride than of the acetic anhydride-soluble fraction, and the solubilities of the two isomers may be such that some of the soluble isomer is present, mixed with the less soluble isomer, in the solid fraction obtained from the original filtration. The acetic anhydride filtrate may be treated conventionally by evaporation or distillation to remove the solvent and any acetic acid present, and the resulting solids treated with other solvents to leach out unreacted aniline reagents or their quaternary salts, thus recovering a small yield of the isomeric dilactone which is more soluble in acetic anhydride. Alternatively, a smaller amount of the N,N-diisopropylaniline may be reacted with the intermediate mixture as in Step 2 of Example 2, the isomeric monolactones separated into two preliminary fractions as discussed in connection with that example, and the two fractions reacted separately with more N,N-diisopropylaniline, following with each fraction the procedures of Step 3 in Example 2, to obtain a somewhat larger yield of the dilactone isomer which is more soluble in acetic anhydride.

In general the reactivity of various N-substituted anilines with the intermediate mixture varies, giving total yields of the isomeric dilactones following the above procedures from well under 10% to over 90% of theoretical, and giving variations in the proportions of the two isomers produced. Two crystalline solid fractions

are not obtained in all cases by the procedures of Examples 2 and 3. One of the fractions, especially the fraction relatively soluble in acetic anhydride, may be obtained as a gummy mass. Standard procedures such as solvent or freeze crystallizations and selective solvent extractions may be utilized to obtain the purified crystalline solid isomer. Ordinarily, however, the more readily isolated fraction can be used successfully as a chromogenous substance or for other purposes, and recovery and purification of the other isomeric fraction need not be carried out unless needed to increase the yield. If any solid dilactone fraction is darker than a medium pastel shade, repeated purification treatments can be expected to yield a light-colored product approaching a creamy white, light tan, or light gray.

Referring to the structural formulas shown above, the radicals designated X' in the product of Example 4 again are the p-dimethylaminophenyl radicals already present as substituents in the intermediate mixture of isomers produced in Step 1 of Example 2. In the N-substituted 4-aminophenyl radical



for the radical X', Q then is hydrogen and R and R' are each methyl radicals. For the radical X, however, appearing in two positions in the isomer produced in major amount by the procedures of Example 4, Q is hydrogen but R and R' are each isopropyl radicals, X being the p-diisopropylaminophenyl radical.

Example 5

The same intermediate mixture is used again, so that X' remains the p-dimethylaminophenyl radical. In this example, however, the radicals designated X are p-N,N-diethylamino-o-tolyl radicals, where Q is the single methyl substituent in the 2-position, and R and R' are each ethyl radicals. Fifteen grams (0.033 mole) of the intermediate mixture of isomers, 27 grams (0.165 mole) of N,N-diethyl-m-toluidine and 90 ml. of acetic anhydride are heated at reflux temperature for 24 hours, cooled, filtered, and the filtrate set aside. The solid product is washed with cold acetic anhydride and ethanol, then dried to recover 5.4 grams of a bright yellow solid, M.P. 360°C . The filtrate is poured over 1 liter of crushed ice, allowed to stand, then filtered, washed, and dried to recover 15 grams of a light tan solid, M.P. 360°C , soluble in the acetic anhydride before dilution with water. The insoluble first fraction is soluble to the extent of several percent in chlorinated biphenyl and gives a green dark-colored form upon contact with an attapulugus clay fuller's earth product. The second isomeric fraction dissolves readily in the chlorinated biphenyl and gives a blue-green dark-colored form upon contact with the same clay. With certain other active clay materials, however, the second fraction gives a green color hardly distinguishable from the color of the colored product formed from the first fraction. The two fractions together yield 21.7% and 63% respectively of the total theoretical yield of isomeric dilactones.

Example 6

In the product obtained from this Example X' again is the p-dimethylaminophenyl radical, while X is another N-substituted 4-aminophenyl radical where the substituent Q is hydrogen (unsubstituted), R is the benzyl radical, and R' is the ethyl radical. Fifteen grams (0.033 mole) of the same intermediate mixture are reacted with 35 grams (0.165 mole) of N-ethyl-N-phenylbenzylamine in 90 ml. of acetic anhydride at reflux temperature for 24 hours, cooled, filtered, washed with cold acetic anhydride then with ethanol, and dried. This yields 4.8

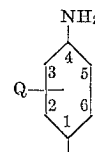
grams (17.5% of total theoretical yield) of a crystalline yellow solid, M.P. 360°C . A solution of up to several percent in chlorinated biphenyl gives a dark blue-green product upon contact with attapulugite. Dilution of the filtrate with ice water causes the formation of a rather dark green gum, and purification operations for producing another light-colored, crystalline chromogenous fraction are considered to be wasteful in view of the relative ease of recovery of the acetic anhydride-insoluble fraction. X is the p-N-benzyl-N-ethylaminophenyl group.

Example 7

To obtain another related product where X is the p-methylaminophenyl radical (Q being hydrogen, R the methyl radical, and R' hydrogen), 20 grams (0.044 mole) of the same intermediate mixture are reacted with 29 grams (0.27 mole) of N-methylaniline in 150 ml. of acetic anhydride following the procedures of Example 4. The insoluble fraction gives 4.6 grams (16.3% of total theoretical yield) of a yellow-tan solid, M.P. 360°C . The filtrate is treated with charcoal and poured over crushed ice. After standing, filtering, washing, and drying, 11.7 grams (41.5% of theoretical) of a gray solid are obtained, which can be heated to over 250°C . without melting or decomposition. The latter acetic anhydride-soluble fraction, as well as the insoluble fraction, is incompletely soluble in chlorinated biphenyl, but both solutions give relatively much darker forms, having a brown hue, upon contact with an attapulugus clay fuller's earth material and give dark orange-tan forms upon contact with other color-activating materials.

In modifications of Example 7, the N-methylaniline is replaced by N-ethylaniline, or N-isopropylaniline, or N-butaniline to give similar light-colored substances, having the radicals designated X in which Q and R' are hydrogen and R is the ethyl, or isopropyl, or butyl radical, giving dark-colored products having generally brown to olive hues. Using, as another modification, N-methyldiphenylamine instead of N-methylaniline, a light-colored dilactone substance is obtained having p-N-methylanilino-phenyl groups for the radicals designated X, in which Q is hydrogen, R is the phenyl radical, and R' is the methyl radical. This dilactone dissolved in chlorinated phenyl ether gives a dark green product with a color developer.

Likewise aniline itself may be used for reaction with the intermediate mixture to produce some of the benzodifurandione substance having, in addition to the two p-dimethylaminophenyl radicals, the two other radicals X in the form of the 4-aminophenyl radical. This dilactone product gives a darker-colored form having a reddish or purplish tan hue upon intimate contact with some color-activating materials. Instead of aniline, o-chloroaniline or m-toluidine can be used, for example. These are examples of such substances having 4-aminophenyl radicals



without N-substituents, where the substituent Q is selected from the group of nuclear Q-substituents consisting of hydrogen, as when aniline itself is used, any single one of the methyl, fluoro, chloro, and bromo substituents in the 2-position, as with the methyl substituent when m-toluidine is used, any single one of these substituents in the 5-position, as with the chloro substituent when o-chloroaniline is used, and both of these single substituents individually in the 2- and 5-positions.

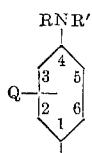
In a similar manner the procedure of Example 4 may be modified by using, instead of the diisopropylaniline, N,N-dibutaniline, giving a small yield of a yellow dilactone solid, insoluble in acetic anhydride, having the two radicals X in the form of p-dibutylaminophenyl radicals.

13

A solution of several percent in chlorinated biphenyl produces a bluish green dark-colored form upon contact with attapulgit and a dark green form upon contact with several other color-activating materials.

Also, the procedure of Example 6 may be followed using N-methyl-N-phenyl-benzylamine with similar results, giving a dilactone in which the radicals X are p-N-methylbenzylaminophenyl groups. In another modification of Example 6, N-phenyldibenzylamine was used to obtain a 23% yield of a light tan, acetic anhydride-insoluble dilactone compound; dissolved in small amounts in chlorinated biphenyl, this compound gives a dark form of bluish green to green hue upon contact with color-activating materials; here the radicals X are p-dibenzylaminophenyl groups. Thus in these modifications of Example 6 the N-substituent R again is the benzyl radical and R' is the methyl radical in the first modification and another benzyl radical in the latter.

Referring again to Example 4 using N,N-dimethylaniline and Example 5 using N,N-diethyl-m-toluidine, quite equivalent results can be obtained using instead diethylaniline with a beta-hydroxy-substituent, viz., 2-N-ethylanilinoethanol. A yellow-orange solid, insoluble in acetic anhydride, is obtained in 51% yield which is readily soluble in chlorinated biphenyl and gives a good, dark, bluish green color in contact with argosite clay. Thus in practice the beta-hydroxyethyl group functions very well as the equivalent of ethyl and methyl N-substituents in the p-N-alkylaminophenyl radicals. Accordingly, in Example 5, in which the substituted 4-aminophenyl radical



has for Q a 2-methyl substituent and for R and R' two ethyl radicals, both of the N-substituents instead may be beta-hydroxyethyl groups with generally equivalent results. Thus, instead of the N,N-diethyl-m-toluidine, there may be used 2,2'-(m-tolylimino)diethanol, giving an 18.5% yield of a bright yellow solid, insoluble in acetic anhydride, which dissolves readily in chlorinated biphenyl and also forms a dark substance of blue-green to green hue upon contact with various color-activating materials.

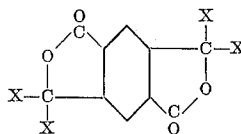
Example 5 also may be modified by providing a different nuclear substituent in place of the 2-methyl substituent Q; or by placing this substituent in the 5-position (which for a single substituent is the same as the 3-position) instead of in the 2-position. Thus, in place of the N,N-diethyl-m-toluidine reagent, N,N-diethyl-o-toluidine may be used to get a 5-methyl substituent with similar results. Halo substituents may replace the methyl nuclear substituent in Example 5 by using m-bromo-N,N-diethylaniline, or m-chloro-N,N-diethylaniline, or N,N-diethyl-m-fluoroaniline, giving with each reagent a 10-20% yield of a yellow solid, insoluble in acetic anhydride, which can be dissolved up to several percent in chlorinated biphenyl and form dark yellowish green materials on contact with argosite or attapulgit clay. Alternatively, the reagent 2,5-dichloro-N,N-diethylaniline may be used to obtain an 11% yield of an acetic anhydride-insoluble yellow dilactone which gives dark, blue to brown materials upon intimate contact with various color-activating materials. Other monoalkyl or dialkyl N-substituents having no more than four carbon atoms also may be used to get good results with these anilines having nuclear methyl or halo substituents.

Using the N-substituted 4-aminophenyl radicals, 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-

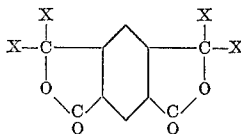
14

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, e.g., the 4-diethylamino-1-naphthyl radical, 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., gamma-hydroxy-propyl or delta-hydroxybutyl), sulfophenyl, tolyl, or one of the methylbenzyl radicals may be mentioned. Results equivalent to those with the N-substituted 4-aminophenyl radicals also may be expected with the p-piperidinophenyl group.

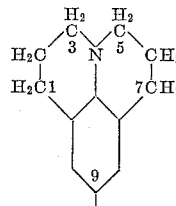
A light-colored substance embodying the invention may be selected from the group consisting of compounds having the structural formula



and of compounds having the structural formula



in which each individual one of the radicals designated X is selected from the group consisting of the 9-julolidyl radical



of a 4-aminophenyl radical as mentioned above with no N-substituents but with the nuclear Q-substituent, when present, and of an N-substituted 4-aminophenyl radical with the nuclear substituent Q', when present, selected from the same group of Q-substituents and with the amino substituents R and R' replacing one or both of the amino hydrogen atoms, as illustrated in the many examples and modifications given above. Examples of compounds containing the 9-julolidyl radical now will be given.

Example 8

The synthesis of julolidene itself, which is 2,3,6,7-tetrahydro-1H,5H-benzo(i,j)quinolizine, is discussed in E. C. Horning, "Organic Syntheses," Collective Volume 3, J. Wiley & Sons, Inc., New York, 1955, pages 504-505. A mixture having 66.5 grams (0.5 mole) of 1,2,3,4-tetrahydroquinoline and 400 grams of 1-bromo-3-chloropropane is heated at 155° C. for 20 hours, cooled, and a solution of 50 ml. of concentrated hydrochloric acid in 500 ml. of water is added. The dihalopropane is removed by steam distillation. The residue is cooled, made basic by addition of 40% NaOH solution, and extracted with two 300 ml. portions of ether. The ether solution is washed with water and dried over NaOH. The ether then is evaporated and the product fractionated to collect the portion boiling at 105-110° C. under 1 mm. pressure. Yields of 69-77 grams (80-87%) are obtained of a lemon-colored semi-solid, M.P. 40° C.

Fifteen grams (0.033 mole) of the intermediate mixture of isomers obtained as in Step 1 of Example 2, 28.6 grams of the julolidene obtained as above, and 90 ml. of acetic anhydride are heated at reflux temperature for 24 hours, cooled, and filtered. The solids filtered out are washed

with cold acetic anhydride and ethanol, then dried to give 11.6 grams (45% of total possible dilactone yield) of a light yellow-orange solid, M.P. $330 \pm ^\circ \text{C}$. The filtrate was poured over 1 liter of crushed ice, allowed to stand, filtered, washed, and dried to give 13.0 gram (50% yield) of a brownish solid, M.P. $300 \pm ^\circ \text{C}$. Referring to the structural formulas shown above, each heterocyclic ring has a carbon atom carrying two radicals designated X. In the isomeric dilactone fractions produced as just described, one of these two radicals X carried by each such carbon atom is the p-dimethylaminophenyl radical supplied in the compounds of the intermediate mixture, and the other radical X is the 9-julolidyl radical.

Each of the two fractions thus obtained is soluble to the extent of at least several percent in chlorinated biphenyl. The first, acetic anhydride - insoluble substance forms a dark blue material upon contact with one of the color-activating materials. The second, acetic anhydride-soluble substance forms a dark-colored material having a brown or almost black hue, and in some cases a dark blue-green color.

Example 9

Step 1.—Instead of the intermediate mixture of isomers used in Examples 2-8, there is made a different intermediate mixture of isomers each of which carries two 9-julolidyl radicals in place of the two p-dimethylaminophenyl groups shown above in the products of Step 1 in Example 2. To a solution of 35 grams (0.20 mole) of julolidine, produced as in Example 8, in 300 ml. of carbon disulfide, there are added gradually with constant stirring 28 grams (0.21 mole) of anhydrous aluminum chloride. Stirring is continued until solution of the AlCl_3 is essentially complete. Then 12.5 grams (0.057 mole) of pyromellitic dianhydride are added, stirred 30 minutes, and allowed to stand 1 hour. The upper CS_2 layer is then decanted and 400 ml. of 5% aqueous HCl is added while stirring. After stirring for about 3 hours, the aqueous suspension of the reaction product is filtered, washed, and dried. The mixture of 2,5 - disubstituted terephthalic acid and 4,6 - disubstituted isophthalic acid is obtained with 62.5% yield as a chartreuse solid which can be heated above 300°C . without melting or decomposing.

Step 2.—Ten grams (0.018 mole) of the intermediate isomeric mixture formed in Step 1, 15 additional grams (0.085 mole) of julolidine, and 70 ml. of acetic anhydride are refluxed for 24 hours, cooled, and filtered. After washing the recovered solids with cold acetic anhydride and ethanol and drying, 2.0 grams (12.6% of total theoretical yield) of a yellow-orange solid are obtained. The filtrate yields a rather dark gummy material when poured over ice, and purification of this material and separation from solvents of a dilactone product in crystalline form has not been carried out in view of the good results obtained with the acetic anhydride insoluble fraction. The latter, in 5% solution in phenyl ether, gives a dark-colored form having a brilliant green hue in contact with an absorbent color-activating clay. The light-colored dilactone product has the above-mentioned benzodifuran structure in which each of the four substituent radicals designated X is the 9-julolidyl radical.

It will be appreciated that a dilactone product similar to that obtained by the procedures of Example 8 also can be synthesized by forming the di-9-julolidoyl-substituted terephthalic and isophthalic acids in accordance with Step 1 of Example 9, and then reacting the isomeric intermediate mixture thus formed with an excess of N,N-dimethylaniline in the presence of acetic anhydride, as in Step 2 of Example 3. The same isomeric intermediate mixture alternatively may be reacted, for example, with N,N-diisopropylaniline, following the procedures of Example 4, to get a dilactone product having on each heterocyclic ring one 9-julolidyl radical X and one p-diisopropylaminophenyl radical X'. It follows that other radicals X' of the 4-aminophenyl or 4-alkylaminophenyl

type may be substituted by the use of appropriate aniline compounds for the formation of the dilactone product.

Referring again to the manifolding unit comprising the base web 11 having the back coating 12, it is possible to incorporate the generally light-colored chromogenous dilactone material, of the type described above, in the solid state in a back coating of waxy or thermoplastic film-forming material, which may be transferred from the base web upon impact to deposit some of the chromogenous material on a surface carrying a color-activating material. Production of the darker-colored form occurs best, however, if the chromogenous substance is dissolved in a solvent, 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 of a liquid vehicle carrying the colorless or lightly colored chromogenous compound. An oily solvent vehicle advantageously is used, such as chlorinated biphenyl, benzyl butyl phthalate, benzyl salicylate, phenyl ether or halogenated phenyl ethers, or mixtures of such vehicles. 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 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, these liquid cells being finely dispersed throughout the solid dried film of hydrophilic material which makes up the continuous phase in the coating 12. The dried coating 12 may be about 0.001 inch thick, and becomes insolubilized during the drying.

The manifolding units of the invention, carrying the novel chromogenous compounds, are adapted and arranged to produce a dark-colored material upon local impact and rupture of the coating 12 and contact of the chromogenous compound in the liquid vehicle with a contiguous surface carrying a color-activating material, which advantageously may be an inorganic electron acceptor material. Solid particles of the latter material conveniently are dispersed in water, mixed with an aqueous paper-coating starch solution in the proportions of roughly five parts by weight of the inorganic material to one part of starch on a dry basis, coated on the face of the base web 13 of paper or the like, and dried to form a dry, adherent coating 14, roughly 0.0005 inch thick, containing the color-activating material. Alternatively an aqueous latex of polybutadiene-styrene plastic material may replace some or all of the starch as the film-forming material. Thus the coated web 13, shown in the lower portion of the exploded view of the drawing, forms a second manifolding unit for use with the upper manifolding unit provided by the coated web 11.

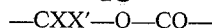
For use as a manifolded set, the first and second base webs 11 and 13 are maintained disposed together in face to face relationship, as suggested by the bracket at the left of the drawing, with the transfer coating 12 on the back of sheet 11, containing one of the chromogenous tetraaryl-substituted benzodifurandione substances of the type described hereinabove, held in contiguity with the adherent coating 14 on the face of the sheet 13, containing the inorganic electron acceptor material. For producing simultaneously an original and one copy sheet by use of a typewriter, for example, or by direct writing with pen or pencil, the web 11 advantageously serves as the original and the face-coated web 13 serves as the dupli-

cate. These manifolding units may be fastened together in a pad, or simply 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 pressure, on the face of the sheet 11 causes localized rupture of the back coating 12. This releases the vehicle, carrying the colorless or lightly colored chromogenous material, from those ones 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. Thus the chromogenous material in solution, upon such marking impact, is transferred to the surface having the coating 14. This coating, made as previously described, permits adequate adsorptive contact of the chromogenous material, so transferred in the image areas to be duplicated, with the many small particles of the inorganic electron acceptor material in those areas of the coating 14. Where this contact is effected, the dark-colored material is produced or developed locally by the action of the inorganic electron acceptor substance on the chromogenous compound, thus forming the duplicate image on the face of the duplicate sheet 13.

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 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 electron acceptor materials, 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 developer material on the almost colorless or white, or rather lightly colored, chromogenous material.

Numerous inorganic electron acceptor materials are available for incorporation as small solid particles in the face coating 14. These materials include certain clays, siliceous materials, and other inorganic materials such as attapulgite and argosite clay, silicates of magnesium, calcium, and aluminum such as magnesium trisilicate, which is a precipitated hydrated silicate having the approximate formula $Mg_2Si_2O_8 \cdot 5H_2O$, calcined diatomaceous silica, activated silica, sodium aluminum zeolite material and related silicate zeolite materials in which sodium is replaced by the cations of potassium or other metals having similar functions, attapulgite with similar cation replacements, pyrophyllite, bentonite, halloysite, magnesium montmorillonite, calcium sulfate, zinc sulfate, barium sulfate, basic aluminum sulfate (aluminum hydrate), and calcium fluoride.

In more general terms, the manifolding unit including the coating 12 is adapted to produce a dark-colored material upon local transfer of the chromogenous compound to the contiguous surface of the web 13 and contact of that compound with an electrophilic color-activating material, carried by that contiguous surface in a coating generally similar to the above-described face coating 14 on the web 13. Referring to the structural formulas shown hereinabove for the benzodifurandione chromogenous compounds, each compound has two heterocyclic lactone ring components $-CX_2-O-CO-$ or



attached to the central benzene ring, where X and X' represent the aryl substituents exemplified by the p-amino-phenyl and 9-julolidyl radicals. An electrophilic material such as a source of protons, preferably a weakly acid proton source, or an aprotic acid (a Lewis acid), serves upon contact as a color-activating or developing material for opening the bonds from the $-CX_2-$ or $-CXX'-$ groups to the adjoining oxygen atoms to permit quinonoid resonance in the $-CX_2$ or $-CXX'$ groups, each of which is attached to the central benzene ring so that the carbon atom carrying the two aryl radicals in these groups resembles the methane carbon of a triphenylmethane compound. The cleavage of the gamma-lactone rings in the chromogenous compound thus is understood to convert the compound locally at the point of contact to a quinonoid resonant form having the desired intense dark color.

It will be appreciated that the choice of a color-activating material for use with a particular chromogenous substance in a specific system may require the exercise of the good judgment of one experienced in the art, and in some instances a little experimentation, to arrive at a reasonably effective combination of materials. The same dilactone chromogenous substance can produce dark-colored forms having noticeably different color responses or hues when brought into contact with different electrophilic materials, and the color intensity of the colored forms produced in a given system or arrangement can show gross variations when different color-activating materials are used. Similar dilactone substances prepared by different methods may show minor variations in color response, probably due to production or separation of the isomers in different proportions. While the dilactone chromogenous substances produce dark-colored forms of useful intensities after being brought into ordinary contact with many electrophilic color-activating materials, the use of certain color-activating materials may require the application of heat or pressure to cause reasonably good color development. This might be accomplished, for example, by the momentary use of strong infrared lamps or pressure rolls.

It will appear from the above that marking or printing may be accomplished, without the use of conventional inks containing dyes and pigments, by using instead of such inks an oily ink vehicle in which the chromogenous compound is dissolved. For letterpress printing the resulting oily vehicle is applied to the type, which then is impressed on a web surface having a coating such as the aforementioned face coating 14 containing an electrophilic color-activating substance. Alternatively sheets having such a face coating may be used in a typewriter provided with a ribbon impregnated with an oily ribbon-inking vehicle containing the chromogenous substance in solution. A ribbon so impregnated will not soil the fingers or clothing while being installed on or removed from the typewriter.

Such arrangements involve embodiments of the method, in accordance with the invention, of marking by developing dark-colored materials from colorless or lightly colored chromogenous compounds or from mixtures of isomeric dilactone compounds. This method accordingly comprises providing a chromogenous substance selected from the group of benzodifurandione derivatives described hereinabove, and bringing this chromogenous substance, which preferably is dissolved in an oily vehicle, into contact, in areas where marking is desired, with the electrophilic color-activating substance, which may be a weak acid such as citric acid powder or tartaric acid. As described above, this contact opens the bonds, in the heterocyclic ring components, from the carbon atoms carrying the aryl groups designated X to the respective adjoining oxygen atoms and produces a dark-colored form in the areas of contact by the action of the electrophilic substance on the chromogenous substance. In another embodiment of this method, the solid colorless or lightly

19

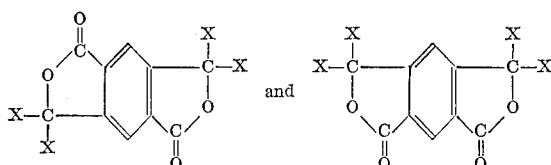
colored chromogenous compound is incorporated in a surface coating and brought into contact with an electrophilic substance by applying such substance, in the form of liquid droplets of acetic acid, to the surface coating where dark-colored marks are desired. The method, of course, may be carried out also by the use of the manifolded set shown in the drawing. To complete an illustration of such a method embodying the invention, the back coating 12 on the web 11 advantageously contains cells of an oily liquid in which is dissolved a chromogenous compound or mixture in the form of the dilactone substance having the 9-julolidyl or p-alkylaminophenyl substituents. Thus there is provided a chromogenous compound or mixture of isomeric compounds which, under marking, printing, or writing impact or pressure applied to the face of the web 11, is forced from the cells in the coating 12 and brought into contact, in localized areas on the face coating 14 carried by the duplicate web 13, with an inorganic electron acceptor substance in the coating 14 to develop a dark-colored material, in the areas of the marks to be duplicated, by the action of such substance on the chromogenous compound.

Accordingly, it appears that the present invention provides a group of novel substances offering a new and desirable choice of chromogenous characteristics useful, by way of example as illustrated hereinabove, in marking and duplicating systems.

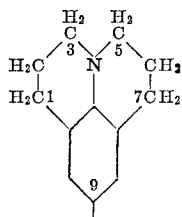
While there have been described what at present are considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention. It is aimed, therefore, in the appended claims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

What is claimed is:

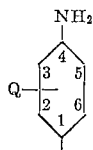
1. A mixture of two isomeric compounds, insoluble in hydrochloric acid and sodium hydroxide and individually of the formulas



and being identical except for the relative directions of attachment of the two $-CX_2-O-CO-$ side ring components in each compound to the central benzene ring, in which each individual X in one of said two isomeric compounds is selected from the group consisting of 9-julolidyl



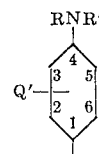
of 4-aminophenyl



where the substituent Q is selected from the group of Q-substituents consisting of hydrogen, any single one of the methyl, fluoro, chloro, and bromo substituents in the 2-position, any single one of said substituents in the 5-position, and both of said single substituents individually in

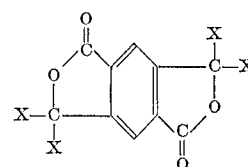
20

the 2- and 5-positions; and of N-substituted 4-amino-phenyl

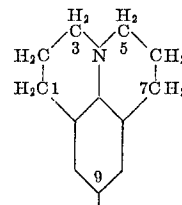


where the substituent Q' is selected from said group of Q-substituents, where the R is elected from the group of N-substituents consisting of alkyl of one to four carbon atoms, benzyl, and phenyl, and where the R' is selected from the group consisting of hydrogen and any one of said group of N-substituents.

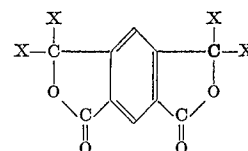
2. A compound insoluble in aqueous solutions selected from the group consisting of dilute hydrochloric acid and dilute sodium hydroxide and of the formula



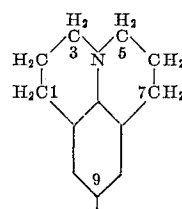
in which each X is



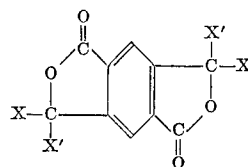
3. A compound insoluble in aqueous solutions selected from the group consisting of dilute hydrochloric acid and dilute sodium hydroxide and of the formula



in which each X is

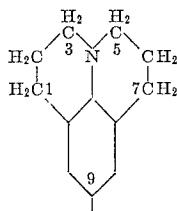


4. A compound insoluble in aqueous solutions selected from the group consisting of dilute hydrochloric acid and dilute sodium hydroxide and of the formula



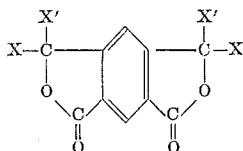
21

in which each X is

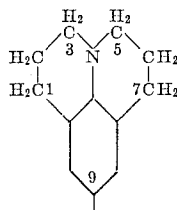


and each X' is p-dimethylaminophenyl.

5. A compound insoluble in aqueous solutions selected from the group consisting of dilute hydrochloric acid and dilute sodium hydroxide and of the formula

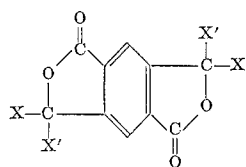


in which each X is



and each X' is p-dimethylaminophenyl.

6. A compound insoluble in aqueous solutions selected from the group consisting of dilute hydrochloric acid and dilute sodium hydroxide and of the formula

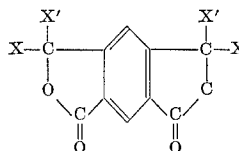


in which each X is p-diisopropylaminophenyl and each X' is p-dimethylaminophenyl.

7. A compound insoluble in aqueous solutions selected

22

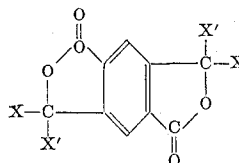
from the group consisting of dilute hydrochloric acid and dilute sodium hydroxide and of the formula



5

10 in which each X is p-diisopropylaminophenyl and each X' is p-dimethylaminophenyl.

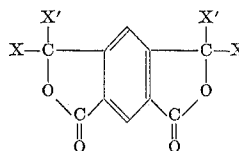
8. A compound insoluble in aqueous solutions selected from the group consisting of dilute hydrochloric acid and dilute sodium hydroxide and of the formula



20

in which each X is p-N-benzyl-N-ethylaminophenyl and each X' is p-dimethylaminophenyl.

9. A compound insoluble in aqueous solutions selected from the group consisting of dilute hydrochloric acid and dilute sodium hydroxide and of the formula



30

in which each X is p-N-benzyl-N-ethylaminophenyl and each X' is p-dimethylaminophenyl.

35

References Cited by the Examiner

UNITED STATES PATENTS

2,449,088	9/1948	Smith	260—396
2,554,543	5/1951	Steiger	260—396
2,870,040	1/1959	Gill	117—36.2
2,935,938	5/1960	O'Sullivan	101—149.4
2,940,983	6/1960	Sartori	260—346.2
3,012,042	12/1961	Hoi	260—346.2

45

OTHER REFERENCES

Bishop: Anal. Chim. Acta., vol. 22, pages 117—119 (1960).

50

ALEX MAZEL, *Primary Examiner*.

MURRAY KATZ, NICHOLAS S. RIZZO, *Examiners*.

D. M. KERR, D. G. DAUS, *Assistant Examiners*.