

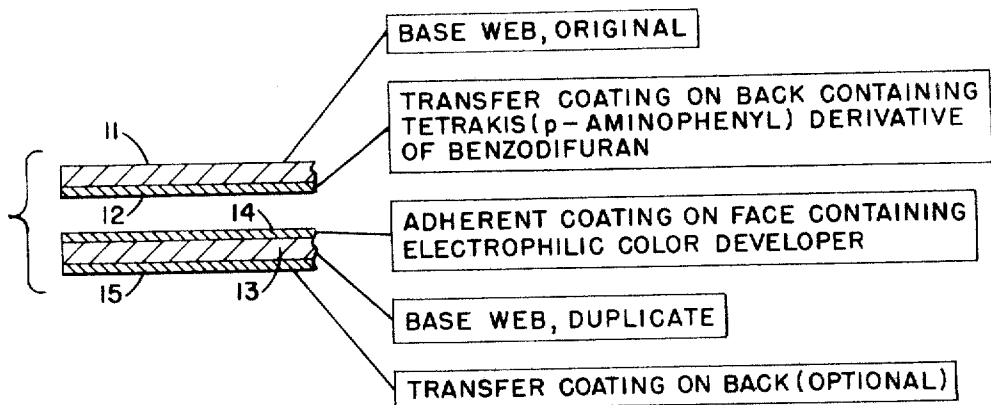
Aug. 15, 1967

E. J. GOSNELL

3,336,337

CHROMOGENOUS TETRAKIS(AMINOPHENYL) DERIVATIVES OF BENZODIFURAN

Filed Aug. 31, 1961



INVENTOR.
EARL J. GOSNELL

BY

Harrie d. Munn
ATTORNEY

1

3,336,337

CHROMOGENOUS TETRAKIS(AMINOPHENYL) DERIVATIVES OF BENZODIFURAN

Earl J. Gosnell, Irondequoit, N.Y., assignor to Burroughs Corporation, Detroit, Mich., a corporation of Michigan
Filed Aug. 31, 1961, Ser. No. 135,359
7 Claims. (Cl. 260—343.4)

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 manifolding 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.

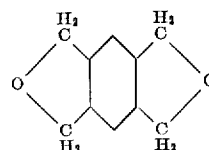
Accordingly it is an object of the present invention to provide new and improved, quite lightly colored substances having chromogenous properties, which advantageously may be incorporated in a transferable coating on a web surface to provide a novel manifolding unit, and which are useful in carrying 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 characteristics, and which develop, upon contact with color-activating materials, novel and much darker-colored sub-

2

stances having generally desirable and useful color intensities and hues.

In accordance with the invention, there is provided a substance selected from the group consisting of (A) a tetraaryl-substituted compound based on the structural formula



in which, in each heterocyclic ring, the two hydrogen atoms attached to one of the carbon atoms in the ring are replaced by a pair of p-aminophenyl aryl radicals having bonds to that carbon atom; (B) a diepoxy-substituted compound, having the structure of a tetraaryl-substituted compound A, in which the two p-aminophenyl radicals in each of the pairs of such radicals are linked by an epoxy bridge between respective positions in those radicals ortho to the positions of the aforementioned bonds; (C) a dioxo-substituted compound, having the structure of a compound B, in which, in each of the first-mentioned heterocyclic rings, the remaining carbon atom with two hydrogen atoms is oxo-substituted; and (D) N-substituted derivatives of each of such compounds A, B, and C in which each individual N-substituent is selected from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical.

In accordance with a feature of the invention, a new composition of matter comprises the dark-colored substance developed by contact of a colorless or lightly colored chromogenous compound selected from the group identified above, such compound having two heterocyclic rings each containing a carbon atom bonded to a hetero oxygen atom wherein that carbon atom is the methane carbon atom of a bis(p-aminophenyl)methane group, with an electrophilic color-activating substance for opening the bonds from such methane carbon atoms to the respective hetero oxygen atoms to permit quinonoid resonance in the bis-(p-aminophenyl)methane 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 the compounds identified as A, B, C, and D hereinabove, this 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 on the contiguous surface in opening the bond in each of the heterocyclic rings from the carbon atoms carrying the pair of p-aminophenyl aryl radicals to the adjoining hetero oxygen atoms, permitting quinonoid resonance in the groups comprising the pairs of aryl radicals and the carbon atoms carrying them.

In a related feature of the invention, a 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 minute droplets, or cells, of a liquid carrying, dissolved therein, a colorless or lightly colored chromogenous compound selected from the

3

aforementioned group, and further comprises a second base web having on one side an adherent coating containing an electrophilic color-activating material, these first and second base webs being maintained disposed together in face to face relationship with their respective transfer and adherent coatings in contiguity with each other, whereby, upon local rupture of the transfer coating and release of the liquid vehicle, contact is effected of the chromogenous compound in the vehicle with the electrophilic color-activating material in the adherent coating, causing the bond in each of the heterocyclic rings from the carbon atom carrying the pair of p-aminophenyl aryl radicals to the adjoining hetero oxygen atom to open and convert the chromogenous compound locally to a dark-colored material.

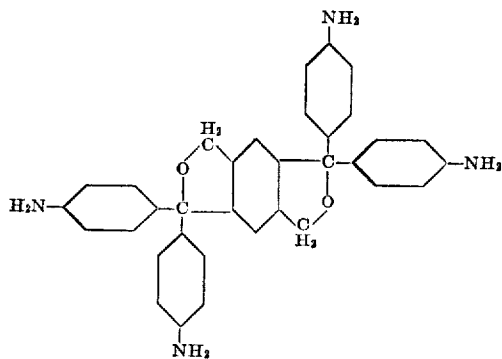
In accordance with a method feature of the invention, the method of marking by developing dark-colored materials from colorless or lightly colored chromogenous compounds comprises providing a chromogenous compound selected from the aforementioned group of compounds each of which includes in each heterocyclic ring a carbon atom, carrying a pair of aryl radicals, having a bond to an adjoining hetero oxygen atom, and bringing the chromogenous compound into contact, in areas where marking is desired, with an electrophilic color-activating substance for opening that bond in each heterocyclic ring to permit quinonoid resonance 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 manifolded 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.

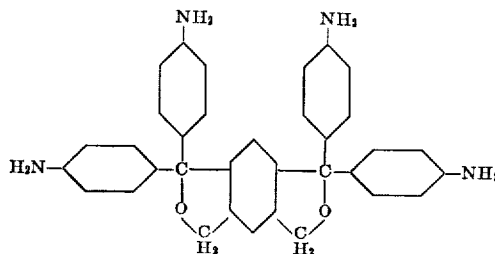
A manifolding unit embodying the present invention is shown in the upper portion of the exploded view of the drawing. In such a manifolding unit, comprising a base web 11 having on one side, usually on the back surface, a coating 12 made up of a film-forming material containing a colorless or lightly 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.

The chromogenous compounds involved in the aforementioned embodiments of the present invention may be considered to be based on compounds having the structural formula



4

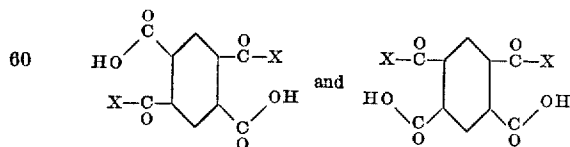
and the isomeric structural formula



As will appear from the specific names for these isomeric compounds, they (and also their derivatives having epoxy bridges, and other derivatives having additionally, oxo substituents forming lactone rings) may be viewed as tetrakis(p-aminophenyl) derivatives of benzodifuran. 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.

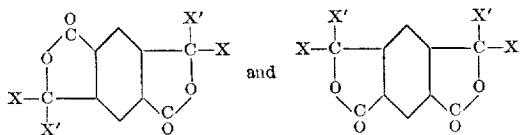
Dilactone compounds of the last-mentioned type are disclosed and claimed in the concurrently filed application for Letters Patent of the United States Ser. No. 135,264, now matured to U.S. 3,268,537, entitled "Chromogenous Aminophenyl Derivatives of Benzodifurandione and Marking Method Using Same," filed 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 and approximately 90% yield of a solid intermediate product which is a mixture of two isomeric compounds having the structural formulas



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



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 fraction 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.

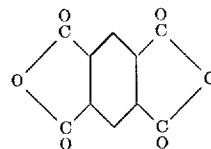
The synthesis of a specific chromogenous dilactone compound, or isomeric mixture of such compounds, having the structure represented by the formulas given above where all of the radicals designated both X and X' are p-dimethylaminophenyl groups, is mentioned hereinabove by way of example. The two isomeric 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 above-mentioned fractions gives a dark blue-green colored form when brought into contact with an electrophilic developer substance. The aforementioned application of Earl J. Gosnell and John F. McCarthy, Jr., is referred to for further details regarding the synthesis and properties of numerous dilactone compounds.

A variety of such dilactone compounds, themselves useful as chromogenous compounds as well as in making the benzodifuran derivatives of interest in accordance with the present invention, may be synthesized. Thus, 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, as pointed out 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. As pointed out particularly in the aforementioned Gosnell and McCarthy application, this dilactone substance also gives a dark blue-green quinonoid form on contact with a developer material. Alternatively the compound

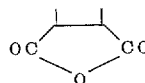
may include butylamino groups. Blue-green forms also may be obtained from the dilactone in which X' is the p-N-benzyl-N-ethylaminophenyl group, while the dilactone in which X' is the p-dibenzylaminophenyl group gives a bluish green to green dark-colored form. X' may be the

p-N-methylanilinophenyl group with N-phenyl and N-methyl substituents, from which a dark green form may be developed. As mentioned hereinbelow, there may be halo or methyl substituents on the phenyl ring in the p-aminophenyl radical. Thus, when m-chloro-N,N-diethyl-aniline 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 dihy-



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



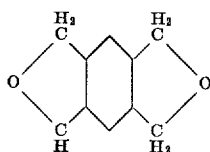
each containing a hetero oxygen atom in the ring, and to each of which two other oxygen atoms are attached. One of these two oxygen atoms attached to each heterocyclic ring thereof is replaced by two p-dialkylaminophenyl groups, in which each individual one of the four alkyl radicals has not more than 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. The present invention is directed particularly to these products and to certain epoxy-substituted compounds related thereto.

As an example of preparation of the bifunctional cyclic ethers of the present invention, either isomer, or a mixture of the two isomers, of the dilactone substance having the isomeric formulas given above, in which all four of the radicals designated X and X' are p-dimethylaminophenyl radicals, may be used as the starting material. Sixteen grams of the AlLiH_4 are mixed into 550 ml. of ethyl ether, previously rendered anhydrous by drying over metallic sodium, and the mixture is refluxed with stirring for 1 hour to effect partial solution of the hydride. For 15 minutes thereafter 13.3 grams (0.02 mole) of the dilactone substance are added a portion at a time, followed by 2 more hours of refluxing to allow the reaction to pro-

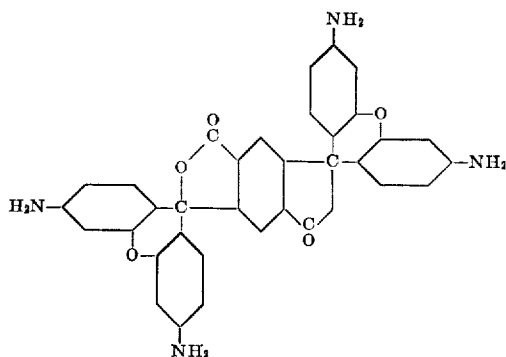
7

ceed. After cooling, about 25 ml. of water are added slowly with stirring so that unwanted reagent may be separated in granular form. The bifunctional cyclic ether which is recovered thereafter is a tetraaryl-substituted compound based on the structural formula

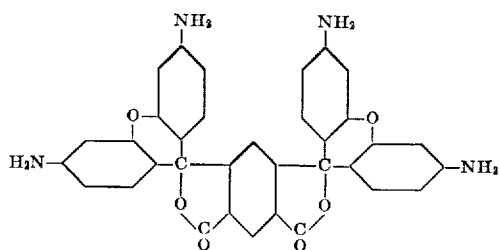


in which, in each heterocyclic ring, the two hydrogen atoms attached to one of the carbon atoms are replaced by a pair of N-substituted p-aminophenyl aryl radicals, specifically p-dimethylaminophenyl radicals. A blue-green colored form may be produced by effecting contact with a developer substance such as attapulgite or magnesium trisilicate. It will be appreciated from the discussion of the dilactone starting substances that N-substituted derivatives of the bifunctional cyclic ether compound are useful in which each individual N-substituent is selected from the group consisting of an alkyl radical of not more than four carbon atoms, the benzyl radical, and the phenyl radical.

In the structural formula just given, both p-aminophenyl aryl radicals in the pair attached to one of the carbon atoms in each heterocyclic ring have bonds to such respective carbon atoms. The present invention also is embodied by a diepoxy-substituted compound, having the structure of the tetraaryl-substituted—that is, tetra-kis-(p-aminophenyl)-substituted—compound as in the structural formula just given, but, in which the two p-aminophenyl radicals, in each of such pairs of aryl radicals are linked by an epoxy bridge between respective positions in the radicals ortho to the carbon atom in the heterocyclic ring. These compounds may be called rhodamine dicyclic ethers. Another embodiment is a dioxo-substituted compound, having the structure of the diepoxy-substituted compound just described, but in which, in each of the heterocyclic rings, the remaining carbon atom carrying two hydrogen atoms is oxo-substituted. The diepoxy-substituted compound (and its N-substituted derivatives or rhodamine cyclic ethers) conveniently are obtained by reduction of the corresponding compound having both diepoxy and dioxo substituents, which may be called a rhodamine dilactone. The latter compound may be represented by the isomeric structural formulas



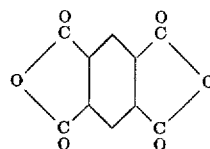
and



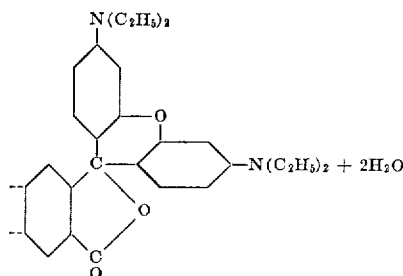
8

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, or 164 grams, of m-diethylaminophenol and roughly one mole—smaller amounts of about 0.7 mole, or about 100 grams, usually suffice—of anhydrous zinc chloride with 0.2 mole, or 43.6 grams, of pyromellitic dianhydride

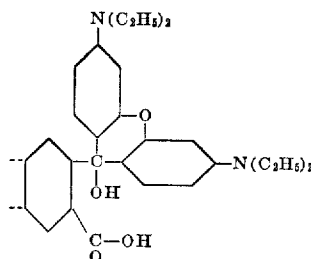


for 4 to 5 hours at 160° C. while stirring the melt continuously. There is formed in the melt a moderate yield of a bifunctional compound including the structure



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 each molecule of pyromellitic dianhydride likewise 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-diethylaminophenol 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. Two isomers may be formed in this way, and both usually are in some amount, depending on which of the two carbonyl oxygen atoms is replaced, as just described, on the other side of the benzene nucleus of a given pyromellitic dianhydride molecule.

To recover this product from the reaction mixture, however, the melt conveniently is cooled, finely powdered, and digested with dilute aqueous ammonium hydroxide, obtained from 40 grams of 28% NH_4OH in 0.8 liter of additional water, for several hours at room temperature, leaving undissolved the isomeric bifunctional carbinols

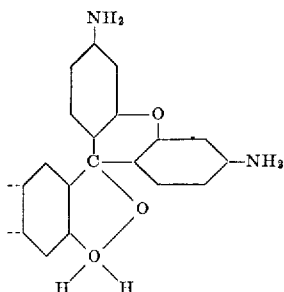


This substance is separated by filtering it out of the ammonium hydroxide solution, washing with fresh dilute ammonium hydroxide, and drying. Reclosure of the two lactone rings in each molecule is accomplished by refluxing the carbinol with benzene, which conveniently is done with a standard condenser and Stark and Dean tube ap-

paratus 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 substances used.

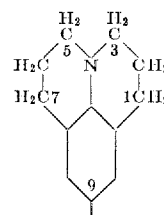
All of the bifunctional substances in the categories of bifunctional lactones, cyclic ethers, rhodamine lactones, and rhodamine cyclic ethers have high melting points and generally can be heated above 300° C. in a neutral atmosphere without melting or decomposing. Several nonpolar or mildly polar solvents 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. Ten grams of

the rhodamine dilactone, synthesized and recovered as described above, are stirred slowly into a semidissolved mixture of 12 grams of aluminum lithium hydride in 0.4 liter of anhydrous ethyl ether. The resulting mixture is refluxed for two hours, 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. Upon intimate contact with a developer substance such as attapulgit or magnesium trisilicate, this product is converted to an intense, bluish red, colored form.

In the preferred chromogenous compounds of the present invention the amino nitrogen atoms carry substituents, for which the methyl and ethyl N-substituents are chosen frequently. Propyl and isopropyl N-substituents also function similarly, and chromogenous compounds with p-di-alkylaminophenyl groups in which each individual alkyl radical has not over three carbon atoms are recommended. In these bifunctional compounds all four of the aminophenyl groups preferably are di-substituted as here recommended. Also, and more generally, butyl substituents in place of 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 one the benzene nucleus one side of which is in the heterocyclic ring. Typical examples of such substituents in the aminophenyl radicals are discussed in the aforementioned Gosnell and McCarthy application, where it is disclosed in general, for the aminophenyl radicals in which the amino substituent is taken to be in the 4-position, that the phenyl ring may carry at least one substituent defined as being selected

from the group consisting of 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 (or 3-position), and both of these single substituents individually in the 2- and 5-positions. Conversion of dilactone compounds having such substituents to the corresponding bifunctional cyclic ether compounds, for example, produces useful chromogenous substances equivalent in nature and function to the compounds without such substituents.

Referring again to the manifolding unit comprising the base web 11 having the back coating 12, it is possible to incorporate one of the generally light-colored chromogenous compounds, as identified 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 substances 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 by weight or from about 0.5% to 5%, or even 10% is solubility permits, 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 manifold 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

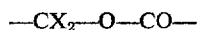
left of the drawing, with the transfer coating 12 on the back of sheet 11, containing one of the chromogenous tetraaryl-substituted benzodifuran substances of the type described hereinabove, held in contiguity with the adherent coating 14 on the face of the sheet 13, containing the inorganic electron 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 duplicate. 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 absorptive 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 impact and 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 substituted benzodifuran chromogenous compounds, each compound has two heterocyclic ring components —CX₂—O—CH₂— or



fused to the central benzene ring, where X₂ represents the pair of aryl radicals, more specifically the bis(p-aminophenyl) or spiro-linked xanthenyl substituent, having bonds to one of the carbon atoms in the ring, such carbon atom in turn having a bond to the adjoining hetero oxygen atom as shown in the ring components just illustrated. 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 bond in each of the heterocyclic rings from the carbon atom carrying the pair of aryl radicals X₂ to the adjoining hetero oxygen atom, permitting quinonoid resonance in the groups comprising these pairs of p-aminophenyl aryl radicals and the carbon atom carrying each pair. The latter carbon atoms resemble the methane carbon atoms of the p-amino-substituted diphenylmethane and triphenylmethane dye compounds. The cleavage of the heterocyclic rings in the chromogenous compound is understood to convert the compound locally at the point of contact to a quinonoid resonant form having the desired intense dark color, although the precise structure of the dark-colored forms apparently cannot be established incontrovertibly by reasonably usable methods and is not a part of the present invention.

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 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 bifunctional chromogenous substances may show minor variations in color response, probably due to production or separation of isomers in different proportions. While the chromogenous substances of the present invention 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 utilization of other means of obtaining more intimate or effective 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. It has been found highly desirable, furthermore, to try a number of solvent liquids for a given chromogenous compound, when it is to be brought into contact with a given color-activating substance, to obtain the concentration and other environmental conditions which favor the efficient formation of a dark-colored material with desirable color intensity and hue.

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 a chromogenous compound of the invention 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.

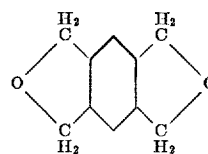
Such arrangements involve embodiments of the method, in accordance with the invention, of marking by developing dark-colored materials from colorless or lightly colored chromogenous compounds. This method accordingly comprises providing a chromogenous substance selected from the group of benzodifuran based tetrakis(p-aminophenyl) 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 bond in each of the heterocyclic rings from the carbon atom carrying the pair of aryl radicals to the adjoining hetero oxygen atom and produced 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 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 minute droplets or cells (which may or may not be encapsulated in thin shells of a substance differing from that of the continuous phase of the coating) of an oily liquid in which is dissolved one of the chromogenous compounds. Thus a chromogenous compound is provided which, under marking, printing, or writing impact or pressure applied directly or indirectly 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 chromogenous compound selected from the group consisting of (A) a tetraaryl-substituted compound based on the structural formula

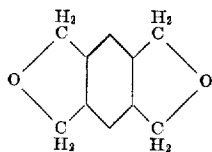


in which, in each heterocyclic ring, the two hydrogen atoms

15

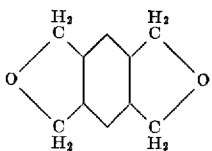
attached to one of the carbon atoms are replaced by a pair of aryl radicals having bonds to said carbon atoms, said aryl radicals being selected from the group consisting of (i) the p-aminophenyl radical, (ii) p-aminophenyl radicals having on the phenyl ring a substituent selected from the group consisting of methyl, chloro, bromo, fluoro and nitro radicals, (iii) the amino-1-naphthyl radical, and (iv) the 9-julolidyl radical; (B) a diepoxy-substituted compound, having the structure of a tetraaryl-substituted compound A, in which the two p-aminophenyl radicals in each of said pairs are linked by an epoxy bridge between respective positions in said radicals ortho to the positions of said bonds; (C) a dioxo-substituted compound, having the structure of a compound B, in which, in each of said first-mentioned heterocyclic rings, the remaining carbon atom with two hydrogen atoms is oxo-substituted; and (D) N-substituted and N, N-disubstituted derivatives of compounds A, B, and C in which each individual N-substituent is a radical selected from the group consisting of (i) an alkyl radical selected from the group consisting of methyl, ethyl, propyl, and butyl radicals, (ii) benzyl, (iii) methylbenzyl, (iv) phenyl, (v) naphthyl, (vi) chloromethyl, (vii) beta-hydroxyethyl, (viii) gamma-hydroxypropyl, (ix) delta-hydroxybutyl, (x) sulfophenyl, and (xi) tolyl.

2. A tetraaryl-substituted compound based on the structural formula



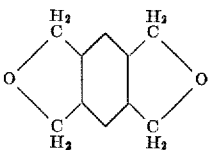
in which, in each heterocyclic ring, the two hydrogen atoms attached to one of the carbon atoms are replaced by a pair of p-aminophenyl radicals having at least one N-substituent selected individually from the group consisting of (i) an alkyl radical selected from the group consisting of methyl, ethyl, propyl, and butyl radicals, (ii) benzyl, (iii) methylbenzyl, (iv) phenyl, (v) naphthyl, (vi) chloromethyl, (vii) beta-hydroxyethyl, (viii) gamma-hydroxypropyl, (ix) delta-hydroxybutyl, (x) sulfophenyl, and (xi) tolyl.

3. A tetraaryl-substituted compound based on the structural formula



in which, in each heterocyclic ring, the two hydrogen atoms attached to one of the carbon atoms are replaced by a pair of p-dialkylaminophenyl groups in which said alkyl radicals are selected from the group consisting of methyl, ethyl, propyl and butyl radicals.

4. A compound based on the structural formula

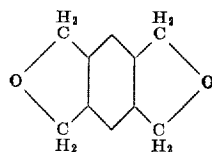


in which, in each heterocyclic ring, the two hydrogen atoms attached to one of the carbon atoms are replaced by a pair of p-aminophenyl radicals having bonds to said carbon atom, the two p-aminophenyl radicals in each of said pairs being linked by an epoxy bridge between respective positions in said radicals ortho to the positions of said bonds, and each of said four p-aminophenyl radicals having at least one N-substituent selected individually from the group consisting of (i) an alkyl radical selected from the group consisting of methyl, ethyl, propyl, and butyl radicals, (ii) benzyl, (iii) methylbenzyl, (iv) phenyl,

16

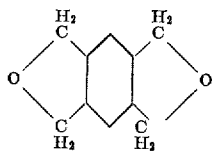
(v) naphthyl, (vi) chloromethyl, (vii) beta-hydroxyethyl, (viii) gamma-hydroxypropyl, (ix) delta-hydroxybutyl, (x) sulfophenyl, and (xi) tolyl.

5. A compound based on the structural formula



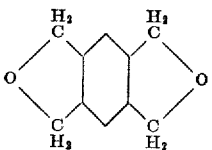
in which, in each heterocyclic ring, the two hydrogen atoms attached to one of the carbon atoms are replaced by a pair of p-dialkylaminophenyl groups in which said alkyl radicals are selected from the group consisting of methyl, ethyl, propyl and butyl radicals; the two p-dialkylaminophenyl groups in each of said pairs being linked by an epoxy bridge between respective positions in the phenyl rings of said groups ortho to the positions of said bonds.

6. A compound based on the structural formula



in which, in each heterocyclic ring, the two hydrogen atoms attached to one of the carbon atoms are replaced by a pair of p-aminophenyl radicals having bonds to said carbon atom, the two p-aminophenyl radicals in each of said pairs being linked by an epoxy bridge between respective positions in said radicals ortho to the positions of said bonds, the remaining carbon atom with two hydrogen atoms in each of said heterocyclic rings being oxo-substituted, and each of said four p-aminophenyl radicals having at least one N-substituent selected individually from the group consisting of (i) an alkyl radical selected from the group consisting of methyl, ethyl, propyl, and butyl radicals, (ii) benzyl, (iii) methylbenzyl, (iv) phenyl, (v) naphthyl, (vi) chloromethyl, (vii) beta-hydroxyethyl, (viii) gamma-hydroxypropyl, (ix) delta-hydroxybutyl, (x) sulfophenyl, and (xi) tolyl.

7. A compound based on the structural formula



in which, in each heterocyclic ring, the two hydrogen atoms attached to one of the carbon atoms are replaced by a pair of p-dialkylaminophenyl groups in which said alkyl radicals are selected from the group consisting of methyl, ethyl, propyl and butyl radicals; the two p-dialkylaminophenyl groups in each of said pairs being linked by an epoxy bridge between respective positions in the phenyl rings of said groups ortho to the positions of said bonds, and the remaining carbon atom with two hydrogen atoms in each of said heterocyclic rings being oxo-substituted.

References Cited

UNITED STATES PATENTS

65	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
70	3,012,042	12/1961	Hoi	260—346.2

WALTER A. MODANCE, *Primary Examiner*.

M. KATZ, *Examiner*.

75 J. A. PATTEN, *Assistant Examiner*.