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3,775,424

FURO[3,4-b]PYRIDINE-7(5H)-ONES

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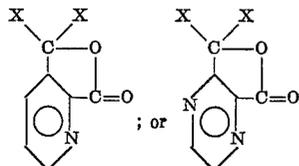
Int. Cl. C07d 5/34

U.S. Cl. 260—295 B

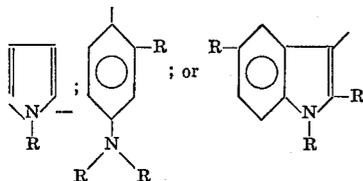
2 Claims

ABSTRACT OF THE DISCLOSURE

A novel chromogenic compound of normally colorless form is disclosed, having the structural formula:



wherein each X is



wherein each R is hydrogen, an alkyl radical having 1 to 4 carbon atoms, an alkoxy radical having 1 to 4 carbon atoms or a phenyl radical. These colorless, but colorable dyes are employed in pressure-sensitive record material and mark-forming manifold systems.

This invention relates to chromogenic compounds. These colorless, but colorable dyes are employed in pressure-sensitive record material and in mark-forming manifold systems. In another aspect, this invention relates to a method of marking on a substrate by developing dark-colored materials from these colorless chromogenic compounds.

Pressure sensitive recording sheets employing various phthalides, pyromellitides and the like are known in the art. For example, see U.S. Pats. 3,540,909 through 3,540,914.

The pyridine and pyrazine compounds of this invention now have been found. These compounds have an extraordinary amount of fade resistance and a high degree of tinctorial power. Also, these colorless, but colorable reactants are synthesized in a single step process.

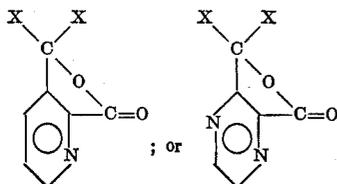
Accordingly, an object of this invention is to provide chromogenic compounds.

Another object of this invention is to provide pressure-sensitive record material and mark-forming manifold systems employing these chromogenic compounds.

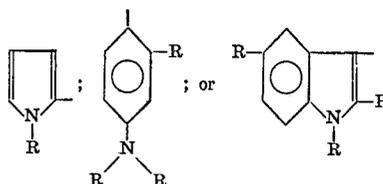
Still another object of this invention is to provide a method of marking on a substrate by developing dark-colored materials from these chromogenic compounds.

Other objects, aspects and advantages of this invention will be apparent to one skilled in the art from the following disclosure and appended claims.

The pyridine and pyrazine compounds of this invention are represented by the formula:

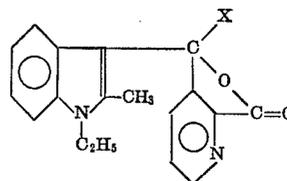


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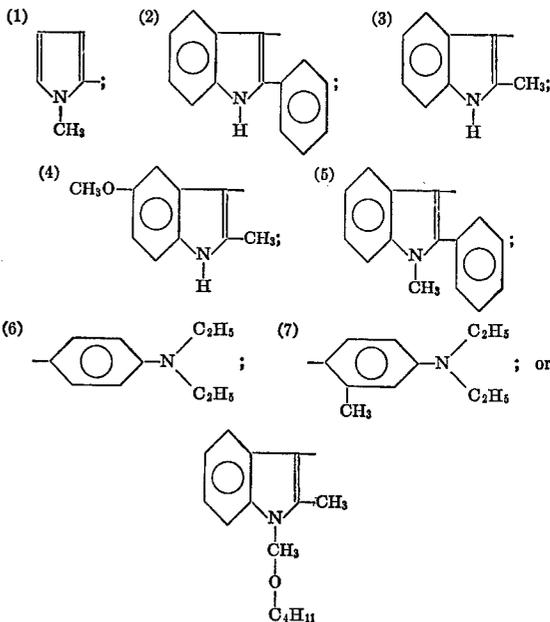


wherein each R is hydrogen, an alkyl radical having 1 to 4 carbon atoms, an alkoxy radical having 1 to 4 carbon atoms or phenyl radical.

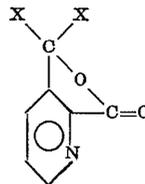
Specific examples of these compounds are represented by the following formula:



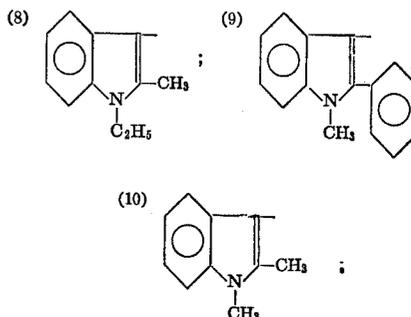
wherein X is one of the following:



Other examples of these compounds are represented by the formula:



wherein both X's are:



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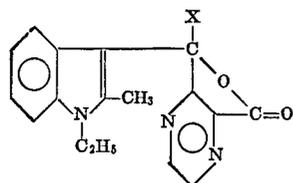
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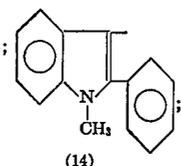
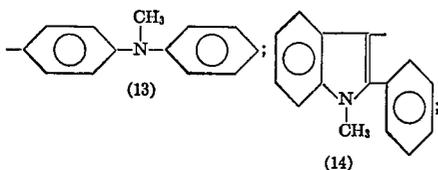
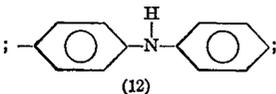
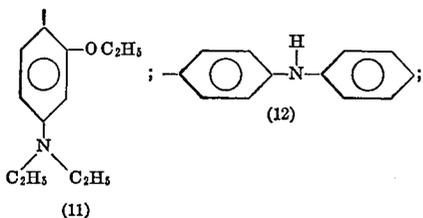
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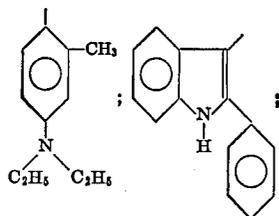
Still other examples of these compounds are represented by the formula:



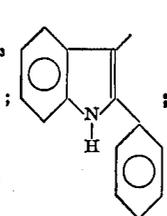
wherein X is one of the following:



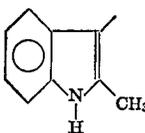
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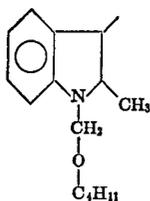
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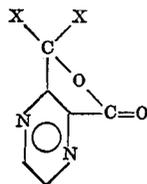
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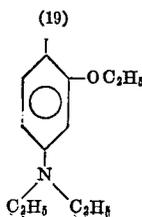
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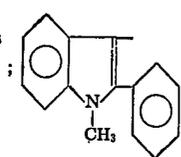
Additional examples of these compounds are represented by the formula:



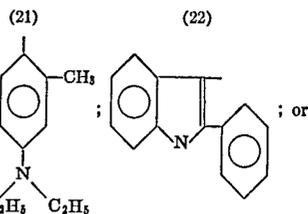
wherein both X's are:



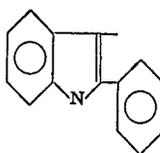
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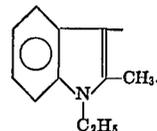
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Pressure-sensitive mark-forming systems provide a marking system of disposing on and/or within sheet support material the unreacted mark-forming components (at least one of which is a polymeric material) and a liquid solvent in which each of the mark-forming components is soluble, said liquid solvent being present in such form that it is maintained isolated by a pressure-rupturable barrier from at least one of the mark-forming components until the application of pressure causes a breach or rupture of the barrier in the area delineated by the pressure pattern. The mark-forming components thereby are brought into reactive contact, producing a distinctive mark.

The method of marking of this invention, i.e., by developing a dark-colored material from the substantially colorless or slightly colored chromogenic compounds comprises providing a chromogenic compound selected from among the above-mentioned compounds and bringing such chromogenic compound into reactive contact in areas where marking is desired with an acidic color-activating substance to produce a dark-colored resonant form of the chromogenic compound by the action thereon in said areas of the said acidic substance.

The acidic materials employed in this invention can be any compound within the definition of a Lewis acid, i.e., an electron acceptor. Preferably, acidic organic polymers such as phenolic polymers are employed as the acidic material. The chromogenic compounds exhibit the advantage of improved color stability when reacted with such phenolic polymers. The solution formation of the solid particles of polymeric material in the same solvent with the substantially colorless chromogenic compounds allows penetration of the color into the support sheet, if porous, e.g., paper, so that the colored form of the chromogenic compound sinks into the body of the sheet and is not merely on the surface of the sheet. This feature protects against erasure of recorded data by attrition of the surface of the record sheet.

It is noted that the polymeric mark-forming components should have a common solubility with the chromogenic compound in at least one liquid solvent when the acid-reacting material is a phenolic or other organic acidic polymer. It is also noted that in a single system several chromogenic compounds can be used with the same or different polymeric materials. Several polymeric materials can be reactively contacted with a single chromogenic compound or with a mixture of chromogenic compounds.

As mentioned above, the solvent is maintained in physical isolation in minute droplets until such time as it is released by application of pressure. This is accomplished by several known techniques, but preferably isolation is maintained by individual encapsulation of the solvent droplets in a microcapsule according to the procedures described, for example, in U.S. Pat. No. 2,712,507, issued to Barrett K. Green on July 5, 1955; 2,730,457, issued to Barrett K. Green and Lowell Schleicher on Jan. 10, 1956; 2,800,457, issued to Barrett K. Green and Lowell Schleicher on July 23, 1957; and 2,800,458, issued to Barrett K. Green on July 23, 1957, reissued as Reissue Pat. No. 24,899 on Nov. 29, 1960.

The microscopic capsules, when disposed within or upon a supporting web as a multiplicity in contiguous juxtaposition, are rupturable by pressure, such as normal marking pressures utilized, for example, in writing or typing operations.

The material or materials chosen as the wall material of the microcapsule, in addition to being pressure rupturable, must be inert with respect to the contents of the capsule and the other mark-forming components so that the wall material remains intact under normal storage conditions until such time as it is released by the application of marking pressure. Examples of such wall materials are gelatin, gum arabic and many others thoroughly described in the aforementioned patents.

For use in record material, the capsule size should not exceed 50 microns in diameter. Preferably, the capsules should be smaller than 15 microns in diameter.

The acidic polymeric material useful in this invention include phenol polymers, phenol acetylene polymers, maleic acid-rosin resins, partially or wholly hydrolyzed styrene-maleic anhydride copolymers and ethylene-maleic anhydride copolymers, carboxy polymethylene and wholly or partially hydrolyzed vinyl methyl ether maleic anhydride copolymer and mixtures thereof.

Among the phenolic polymers found useful are alkyl-phenol-acetylene resins, which are soluble in common organic solvents and possess permanent fusibility in the absence of being treated by cross-linking materials. A specific group of useful phenolic polymers are members of the type commonly referred to as "novolac," (as sold by Union Carbide Corp., New York, N.Y.) which are characterized by solubility in common organic solvents and which are, in the absence of cross-linking agents, permanently fusible. Generally, the phenolic polymer material found useful in practicing this invention is characterized by the presence of free hydroxyl groups and the absence of groups such as methylol, which tend to promote infusibility or cross-linking of the polymer, and by their solubility in organic solvents and relative insolubility in aqueous media. Again, obviously, mixtures of these phenol-aldehyde polymers can be employed.

Resoles, if they are still soluble, are used, though subject to change in properties upon aging.

A laboratory method useful in the selection of suitable phenolic resins is the determination of the infrared absorption pattern. It has been found that phenolic resins showing an absorption in the 3200-3500 cm^{-1} region (which is indicative of the free hydroxyl groups) and not having an absorption in the 1600-1700 cm^{-1} region are suitable. The latter absorption region is indicative of the desensitization of the hydroxyl groups and, consequently, makes such groups unavailable for reaction with the chromogenic materials.

The preparation of the phenolic formaldehyde polymeric materials for practicing this invention is described in "Industrial and Engineering Chemistry," vol. 43, pp. 134 to 141, January 1951, and a particular polymer thereof is described in Example 1 of U.S. Pat. No. 2,052,293, issued to Herbert Hönel on Aug. 25, 1936, and the preparation of the phenol-acetylene polymers is described in "Industrial and Engineering Chemistry," vol. 41, pp. 73 to 77, January 1949.

The preparation of the maleic anhydride copolymer is described in the literature, such as, for example, one of the maleic anhydride vinyl copolymers, as disclosed in the publication, "Vinyl and Related Polymers," by Calvin E. Schildknecht, second printing, published April 1959, by John Wiley & Sons, Incorporated, See pp. 65 to 68 (styrene-maleic anhydride copolymer), 628 to 630 (vinyl methyl ether-maleic anhydride copolymer, and 530 to 531 (ethylene-maleic anhydride copolymer).

When the acidic material is one of the aforementioned organic polymers, the liquid solvent chosen must be capable of dissolving the mark-forming components. The

solvent can be volatile or non-volatile, and a single or multiple component solvent may be used which is wholly or partially volatile. Examples of volatile solvents useful in the aforesaid basic chromogen-acidic polymer are toluene, petroleum, distillate, perchloroethylene, and xylene. Examples of non-volatile solvents are high-boiling point petroleum fractions and chlorinated biphenyls.

Generally, the solvent chosen should be capable of dissolving at least 0.3%, on a weight basis, of the chromogenic compound and about a 3-5%, on a weight basis, of the polymeric material to form an efficient reaction. However, in the preferred system, the solvent should be capable of dissolving an excess of the polymeric material, so as to provide every opportunity for utilization of the chromogenic compound and, thus, to assure the maximum coloration at a reaction site.

A further criterion of the solvent is that it must not interfere with the mark-forming reaction. In some instances, the presence of the solvent can interfere with the mark-forming reaction or diminish the intensity of the mark, in which case the solvent chosen should be sufficiently vaporizable to assure its removal from the reaction site after having, through solution, brought the mark-forming components into intimate admixture, so that the mark-forming contact proceeds.

Since the mark-forming reaction requires an intimate mixture of the components to be brought about through solution of said components, one or more of the mark-forming components can be dissolved in the isolated solvent droplets, the only requirement being that at least one of the components essential to the mark-forming reaction be maintained isolated until reactively contacted with the other.

In the usual case, the mark-forming components are so chosen as to produce a mark upon application of pressure at room temperature (20 to 25 degrees centigrade). However, the present invention includes a system in which the solvent component is not liquid at temperatures around room temperature but is liquid and in condition for forming solutions only at elevated temperatures.

The support member on which the components of the system are disposed may comprise a single or dual sheet assembly. In the case where all components are disposed on a single sheet, the record material is referred to as a "self-contained" system. Where there must be a migration of the solvent, with or without mark-forming component, from one sheet to another, the record material is referred to as a "transfer" system. (Such a system can also be referred to as a "two-fold" system, in that at least two sheets are required and each sheet includes a component, or components, essential to the mark-forming reaction.) Where a copious amount of the colored reaction product in liquid form is produced on a surface of one sheet, it can produce a mark by transfer to a second sheet as a colored mark.

In the preferred case, where microcapsules are employed, they can be present in the support material either disposed therethroughout or as a coating thereon, or both. The capsules can be applied to the sheet material while still dispersed in the liquid vehicle in which they were manufactured, or, if desired, separated and the separated capsules thereafter dispersed in a solution of the polymeric component (for instance, 30 grams of water and 53 grams of a 1% aqueous solution of polyvinyl methyl ether maleic anhydride) to form a coating composition in which, because of the inertness of the solution and the capsules, both retain their identity and physical integrity. When this composition is disposed as a film on the support material and dried, the capsules are held therein subject to rupture to release the liquid contained. This latter technique, relying on the incompatibility of the microcapsule and the dispersing medium of the film-forming mark-forming component, allows for a method of preparing a sensitive record coating with the capsules inter-

spersed directly in a dry film of the polymeric material as it is laid down from the solution. A further alternative is to disperse in a liquid medium one or more mark-forming components, insoluble therein, and disperse in said medium the insoluble microcapsules, with the result that all components of the mark-forming system can be disposed on or within the support sheet in the one operation. Obviously, the several components can be applied individually.

The respective amounts of the several components vary, depending primarily upon the nature of the materials and the architecture of the record material unit. Suitable lower amounts include, in the case of the chromogenic material, about .005 to .075 pound per ream (a ream in this application meaning five hundred (500) sheets of 25" x 38" paper, totaling 3,300 square feet); in the case of the solvent, about 1 to 3 pounds per ream; and in the case of the polymer, about ½ pound per ream. In all instances, the upper limit is primarily a matter of economic consideration.

In the instance where the mark-forming components are interspersed throughout a single support sheet material (so-called self-contained unit), the following technique or procedure has been found useful:

The slurry of capsules can be applied to a "wet" web of paper as it exists on the screen of a Fourdrinier paper machine, so as to sink into the paper web a distance depending on the freeness of the pulp and the water content of the web at the point of application.

The capsules can be placed directly in the paper or in a support sheet. Not only capsule structures, but films which hold a multitude of droplets for local release in an area subject to pressure may be utilized. (See U.S. Pat. No. 2,299,694, which issued Oct. 20, 1942, to B. K. Green.)

With respect to the acidic organic polymeric component, a solution thereof in an evaporable solvent is introduced into twice as much water and agitated while the evaporable solvent is blown off by an air blast. This leaves an aqueous colloidal dispersion slurry of the polymeric material, which can be applied to the paper so as to leave a surface residue, or the slurry can be applied to paper at the size-press station of a paper-making machine by roller. In another method of making a polymer-sensitized sheet, the water-insoluble polymer is ground to the desired particle size in a ball mill with water, preferably with a dispersing agent, such as a small quantity of sodium silicate. If a binder material of hydrophilic properties is ground with the phenolic material, the binder itself may act as a dispersant. If desired, an amount of binder material of up to 40%, by weight of the employed amount of the polymeric material can be added to the ball-milled slurry of materials, such binder materials being of the paper coating binder class, including gum arabic, casein, hydroxyethylcellulose, and latex (such as styrene-butadiene copolymer). If desired, oil adsorbents in the form of fuller's earths may be added to the polymeric material particles to assist in retaining, in situ, the liquid droplets to be transferred to it in data-representing configuration, for the purpose of preventing "bleeding" of the print.

Another way of applying the chromogenic or polymeric material individually to a single sheet of paper is by immersing a sheet of paper in a 1% to 10% solution of the material in an evaporable solvent. Obviously, this must be done alone for each reactant, because if the other reactant material were present, it would result in a premature coloration over the sheet area. A dried sheet with one component then can be coated with a solution of the other component, the solvent of which is a non-solvent to the already supplied component.

The polymeric material can be dissolved in ink composition vehicles to form a printing "ink" of colorless character and, thus, can be used to spot-print a proposed record sheet unit sensitized for recording in a reaction-

produced color in those areas by application of a solution of the chromogenic material.

In the case of phenolic polymer, a printing ink can be made of up to 75% weight, of the phenolic polymeric material in a petroleum solvent to a viscosity suitable for printing purposes. The relative amounts of components to be used are the most convenient and economical amounts consistent with the proper visibility of the recorded data. The resolution of the recorded data is, among other things, dependent on particle size, distribution and amount of particles, liquid solvent migration, chemical reaction efficiency, and other factors, all of which are things that can be worked out empirically by one familiar with the art, and which do not determine the principle of the invention, which, in part, involves means for enabling the bringing into solution, by marking pressure, of two normally solid components in a common liquid solvent component held isolated as liquid droplets, preferably in marking-pressure rupturable capsules having film walls, or else held isolated in a continuous marking-pressure-rupturable film as a discontinuous phase.

In the base-acid color system of this invention the acidic mark-forming component(s) reacts with the basic chromogenic material(s) to effect distinctive color formation or color change. In a multi-sheet system in which an acid organic polymer is employed, it is desirable to include other materials to supplement the reactants. For example, kaolin can be added to improve the transfer of the liquid and/or the dissolved materials between the sheets. In addition, other materials such as bentonite, attapulgite, talc, feldspar, halloysite, magnesium trisilicate, silica gel, propylite, zinc sulfide, calcium sulfate, calcium citrate, calcium phosphate, calcium fluoride, barium sulfate and tannic acid can be included.

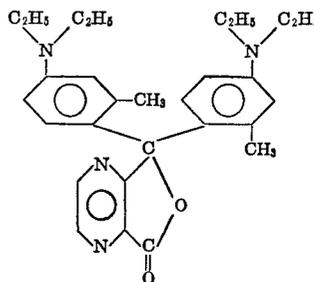
Various methods known to the prior art and disclosed in the aforementioned application Ser. No. 392,404 to Miller et al. and U.S. patent application Ser. No. 420,193 to Phillips et al. can be employed in coating compositions of the mark-forming materials into their supporting sheets. An example of the compositions which can be coated onto the surface of an underlying sheet of a two-sheet system to react with the capsule coating on the underside of any overlying sheet is as follows:

Coating composition:	Percent by weight
Phenolic polymer mixture	17
Paper coating kaolin (white)	57
Calcium carbonate	12
Styrene butadiene latex	4
Ethylated starch	8
Gum arabic	2
	—
	100

The advantages of this invention are further illustrated by the following examples. The reactants and the proportions and other specific conditions are represented as being typical and should not be construed to limit the invention unduly.

EXAMPLE I

Preparation of 7,7-bis-(3-methyl-diethylaminophen-4-yl)-5,7-dihydro[3,4-b]pyrazine-5-one

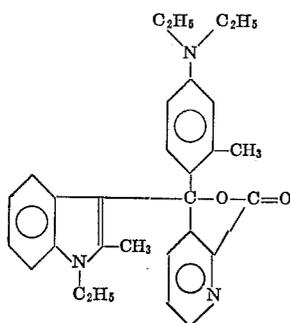


16.8 g. (10 mmols) of 2,3-pyrazine dicarboxylic acid was dissolved in 100 ml. of hot acetic anhydride. When all was dissolved, 40.75 g. of N,N-diethyl-m-toluidine was added and the reaction mixture refluxed 10 minutes¹ and poured into ice and neutralized with ammonia. The aqueous was extracted with benzene and the benzene washed with water. The benzene was dried (Na₂SO₄) and evaporated to a small volume and chromatographed on alumina, eluting with benzene, then benzene:ether and then ether and then ethyl acetate. The concentrates were dissolved in benzene and pet ether added and seeds were added. After standing overnight, filtering and drying, 2.3 g. of nicely crystalline material was obtained. Added petroleum ether to the mother liquor and a 3.75 g. more material obtained. Total weight obtained 6.05 g. (13%). The material has a nondescript M.P. but can be characterized by its T.L.C. characteristics which are on silica gel very bright green aging to a brownish-black. Its color (benzene soln.) on resin sheets are bright green and on Silton a dark green.

In this and the following example, resin, unless otherwise stated, is 80 parts by weight para-tertiary butylphenol and 20 parts by weight para-chlorophenol and clay, unless otherwise stated, is Silton.

EXAMPLE II

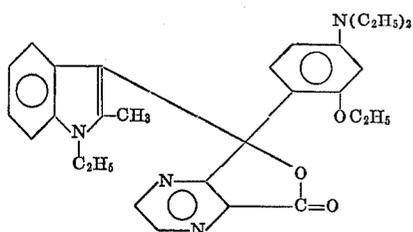
Preparation of 7-(1-ethyl-2-methylindol-3-yl)-7-(3-methyl-dimethylaminophen-4-yl) - 5,7 - dihydrofuro[3,4-b]pyridin-7-one



A mixture of (1-ethyl-2-methylindol-3-yl)-(2-carboxypyridin-3-yl) ketone 1.0 g., (3.3 mmols) and 1.58 g., (9.7 mmols) and 5 ml. of acetic anhydride were refluxed 1 hour. The reaction mixture was poured into ice and ammonia. The aqueous mixture was extracted with benzene and the benzene layer washed with water twice and dried (Na₂SO₄). Chromatography of the concentrated benzene gave a material which melted at 143-5° C. This material when applied to paper coated with resin or clay gave a blue color.

EXAMPLE III

Preparation of 7-(1-ethyl-2-methylindol-3-yl)-7-(3-ethoxydiethylaminophen-4-yl) - 5,7 - dihydrofuro[3,4-b]pyrazin-5-one

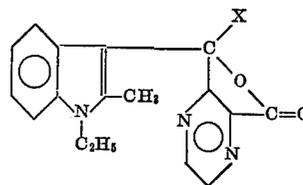


A mixture of 4.65 g. (15 mmols) of (1-ethyl-2-methylindol-3-yl)-2-carboxypyrazine-5-yl ketone, 2.9 g. (15 mmols) of m-ethoxydiethylaminobenzene and 21 ml. of

¹ A longer reflux period did not result in a higher yield.

acetic anhydride were heated at 120-130° C. for 15 minutes. The mixture was poured into ice and ammonia and extracted with 500 ml. of benzene and dried (Na₂SO₄). The solvent was evaporated and the residual oil triturated with petroleum ether. An amorphous solid was obtained, 4.0 g. (55%) which had a single spot on thin layer chromatography. A benzene solution of this material when contacted to a sheet coated with clay or resin gave a blue color.

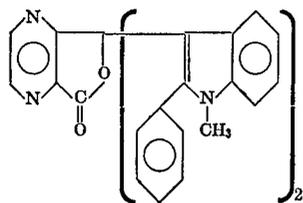
A few mgs. of the above keto-acid was allowed to react with a substituted indole or aniline in mg. quantities in the presence of a few drops of acetic anhydride. After adding water and ammonia the mixture was extracted with benzene applied to paper coated with resin or clay. The resultant colors are tabulated below.



Where X is—	Color	
	Resin	Silton
30	Blue.....	Purple.
35	Green.....	Green-blue.
40	Blue.....	Blue.
45	Purple.....	Purple.
50	Green.....	Blue.
55	Purple.....	Purple.
60	Red.....	Red.
65	Red.....	Red.
70	Red.....	Red.
75		

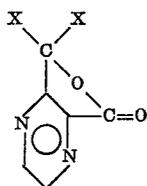
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EXAMPLE IV

Preparation of 7,7-bis-(1-methyl-2-phenylindol-3-yl)-
5,7-dihydrofuro[3,4-b]pyrazin-5-one



Several milligrams each of 2,3-pyrazine dicarboxylic acid and 1-methyl-2-phenyl indole and 3 drops of acetic anhydride were heated for 1 minute at reflux. The mixture was cooled, treated with dilute ammonia and extracted with benzene. The benzene solution when contacted with resin or clay CF sheets have a purple color.

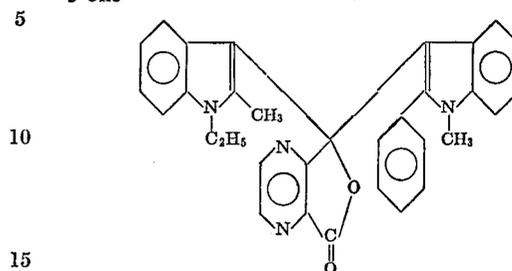
In a similar manner other substituted anilines and indoles were allowed to react with 2,3-pyrazine dicarboxylic acid and worked up as above. The colors when applied to paper coated with resin or clay are tabulated below.



Where X is—	Color	
	Resin	Silton
	Green.....	Green.
	Purple.....	Purple;
	Green.....	Green.
	Purple.....	Purple.
do.....	Do.

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EXAMPLE V

Preparation of 7-(1-ethyl-2-methylindol-3-yl)-7-(1-methyl-2-phenylindol-3-yl) - 5,7-dihydrofuro[3,4-b]pyrazin-5-one



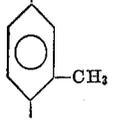
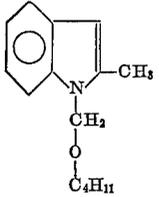
A mixture of 3.0 g. (14.2 mmols) of 1-ethyl-2-methyl indol-3-yl)-(2-carboxy-pyrazin-5-yl) ketone 4.3 g. (14.2 mmols) of 1-methyl-2-phenylindole and 15 ml. of acetic anhydride was refluxed 5 minutes and poured into ice and ammonia and extracted twice with benzene. The benzene was washed with water and dried. Evaporation afforded 4.7 g. of material (68%), M.P. 240-1° C. A benzene solution of this material when applied to paper coated with resin or clay sheets, turned it purple.

The above keto-acid was allowed to react with an indole, pyrrole or substituted aniline by heating a few mgs. of each with a few drops of acetic anhydride, diluting with water, ammonia and extracting the reaction mixture with benzene. The benzene layer was washed with water and applied to paper coated with resin or clay. The colors are tabulated below:

Where X is—	Color	
	Resin	Silton
		Red.
		Purple.
		Do.
		Red.
		Purple;
		Blue;

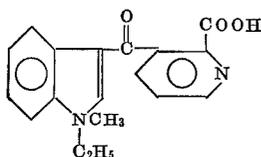
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TABLE—Continued

Where X is—	Color
$N(C_2H_5)_2$	Blue.
	
	Purple.

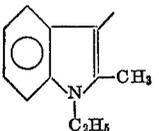
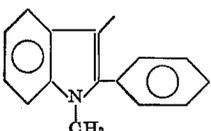
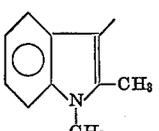
EXAMPLE VI

Preparation of (1-ethyl-2-methylindol-3-yl)-(2-carboxypyridin-3-yl) ketone



A mixture of 2,3-pyridinedicarboxylic anhydride 14.9 g. (100 mmols) and 1-ethyl-2-methylindole 15.9 g. (100 mmols) were heated on a steam bath for 72 hours. The reaction mixture was extracted with dilute ammonia and filtered. The filtrate was washed with benzene and filtered again. The pH of the filtrate was then adjusted to 4.4 and the resultant precipitate filtered, washed with water and recrystallized from alcohol. This afforded 12.5 g. (36%) of air dried material. Repeated recrystallization of a sample of this material from alcohol gave a constant M.P. of 186–8° C. (first melting at 105–7° C. and resolidifying). This sample was dried for analysis. Calculated for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 69.83; H, 5.24; N, 8.83.

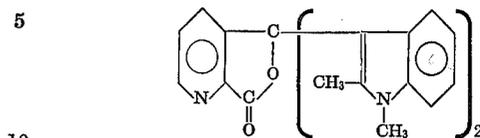
A few mgs. of the above anhydride were allowed to react with a few mgs. of an indole in the presence of a few drops of acetic anhydride for one minute. The mixture was diluted with water and ammonia added. The reaction mixture was then extracted with benzene and the benzene washed with water. The colors obtained when this solution was applied to paper coated with resin or clay are tabulated below.

	Color
	Red-purple.
	Purple.
	Red-purple.

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EXAMPLE VII

Preparation of 7,7-bis-(1,2-dimethylindol-3-yl)-5,7-dihydrofuro[3,4-b]pyridin-7-one

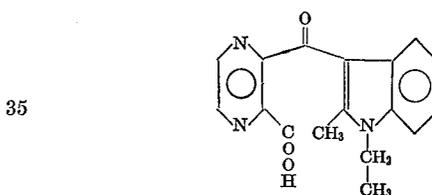


A mixture of 2,3-pyridinedicarboxylic anhydride 1.5 g. (10 mmols), 1,2-dimethylindole, 3.64 g. (25 mmols) and 10 ml. of acetic anhydride were refluxed for one half hour and poured into ice and 5% sodium bicarbonate solution. The aqueous layer (pH 8) was extracted with benzene and the benzene layer washed with water and dried (sodium sulfate). On evaporation of the benzene and washing of the residue with petroleum ether there was obtained 1.9 g. (22%) of crystalline material. T.L.C. of this material revealed two spots which indicated that an isomeric mixture was obtained. A solution of this material when contacted with either paper coated with resin or clay gave a bright purple color.

On recrystallization and chromatography a single isomer (faster moving on T.L.C.) was obtained M.P. 257.5–8° C.

EXAMPLE VIII

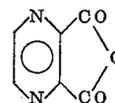
Preparation of (1-ethyl-2-methylindol-3-yl) (2-carboxypyrazin-3-yl) ketone



A mixture of 6.3 g. (50 mmols) of 2,3-pyrazine dicarboxylic anhydride and 7.85 g. (50 mmols) of 1-ethyl-2-methylindole were heated overnight on the steam bath. The molten mixture was cooled, extracted with dilute ammonia and brought to a pH of 4, filtered and recrystallized from alcohol. This afforded 3.15 g. (20%) of material M.P. 189.5–9° C.

EXAMPLE IX

Preparation of pyrazine-2,3-dicarboxylic anhydride



A mixture of 15.0 g. of pyrazine dicarboxylic acid and 45 ml. of acetic anhydride were heated on a steam bath 16 hours and allowed to cool. The resultant voluminous precipitate was filtered, washed with acetic acid and vacuum dried at 80° C. A yield of 12.0 g. (91.5%) was obtained M.P. 203° C. This material was used without further purification.

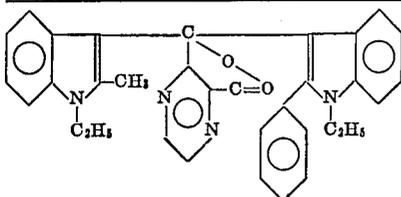
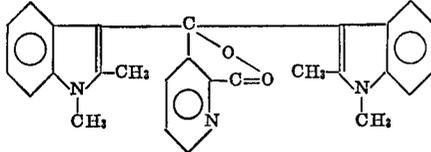
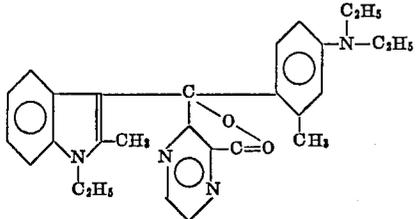
EXAMPLE X

Prints were made on sensitized sheets with 3 compounds. The following table consists of the reflective intensities obtained on a variety of prints. R is defined as:

$$R = \frac{\text{Reflectance of print}}{\text{Reflectance of background}}$$

A value of 1.000 would indicate no color. Therefore, the more reflectance the higher the R value and the more absorbance of light, i.e., the more intense the color the lower the R value. If R increases with time, the print fades. Compounds which exhibit good fade resistance will demonstrate small increases in R with the passage of time.

TABLE

	Fresh print		Print, 4 hours old		Print, 8 weeks old	
	R	K/S	R	K/S	R	K/S
	0.275	0.956	0.215	1.433	0.225	1.335
Paraphenylphenol.....	0.242	1.187	0.238	1.220	0.222	1.363
Silton.....	0.110	3.600	0.118	3.297	0.150	2.408
Attapulgitte.....	0.173	1.977	0.160	2.205	0.202	1.576
	0.202	1.576	0.180	1.868	0.210	1.486
Paraphenylphenol.....	0.178	1.898	0.178	1.898	0.198	1.624
Silton.....	0.078	5.450	0.083	5.066	0.170	2.026
Attapulgitte.....	0.118	3.297	0.178	1.898	0.170	2.026
	0.210	1.486	0.190	1.727	(2)	(2)
Paraphenylphenol.....	0.190	1.727	0.178	1.898	(2)	(2)
Silton.....	0.138	2.692	0.205	1.542	(2)	(2)
Attapulgitte.....	0.215	1.433	0.343	0.630	(2)	(2)

¹ 80 parts by weight para-tertiary-butylphenol and 20 parts by weight para-chlorophenol.

² Not carried out.

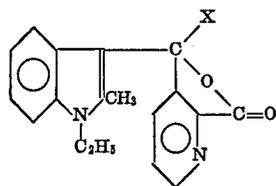
These reflective values demonstrate the extraordinary fade resistance of the pyridine and pyrazine compounds of this invention. In some cases, there was little, if any, increase in R with time, thereby demonstrating little or no fade. In fact, the reflective values decrease with time indicating they become more intense with aging.

The reflectance values were converted to Kubelka-Munk functions (K/S) as shown in the table. The calculations and use of these functions are described by Dr. G. Kortun et al. in *Angewandte Chemie, International edition*, 2, pp. 333-341 (1963). These functions are a reliable measure of the quantity of color present per unit area of print tested. While reflectance values (R) provide a measure of color intensity, Kubelka-Munk functions (K/S) provide a measure of quantity of color present. The Kubelka-Munk rules (K/S) in the table demonstrate the high degree of tinctorial power of the compounds of this invention.

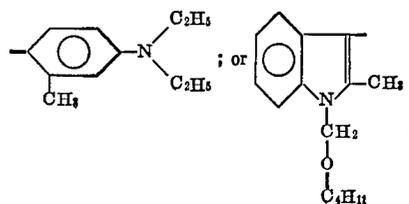
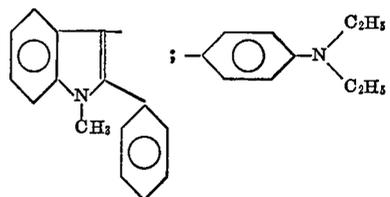
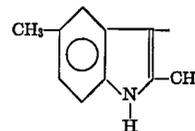
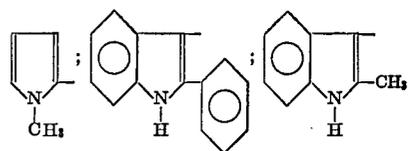
Although this invention has been described in considerable detail, it must be understood that such detail is for the purpose of illustration only and that many variations and modifications can be made by one skilled in the art without departing from the scope and spirit thereof.

What is claimed is:

1. What chromogenic compound represented by the formula:



wherein X is one of the following:

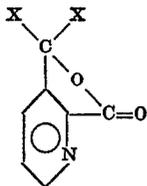


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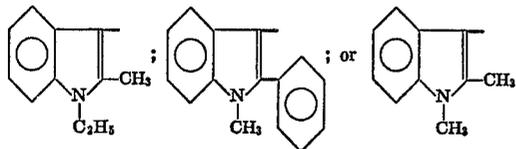
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2. A chromogenic compound represented by the formula:



wherein both X's are:



15

18

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HENRY R. JILES, Primary Examiner

10 G. T. TODD, Assistant Examiner

U.S. Cl. X.R.

260—250 R; 117—36.2