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ELECTROGRAPHIC RECORDING MIXTURE CONTAINING A MORPHOLINYL DIPHENYL METHANE AND 2 TRIPHENYL METHANE

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ABSTRACT OF THE DISCLOSURE

Publication of electrosensitive recording media containing as the color forming agent a substantially colorless organic chromogen substance which develops color by reaction with an electron acceptor material in the absence of an oxidizing medium. The organic chromogenic substance is a leucoauramine which when incorporated in a recording paper base, together with an inorganic salt and/or other conventional components if desired, and subjected to an electric current, produces colored indicia at the positive electrode. The organic chromogenic substances employed provide rapid and deep colorations which are relatively permanent.

This invention relates to novel electrosensitive recording media, and to processes for preparing them.

It has long been known to produce colored indicia by the application of electrical energy to sensitized recording material. It is well known also, to utilize various mechanisms to assist in the development of color in preselected areas. Such mechanisms include

(1) Transference of ions from the electrode to the sensitized material.
(2) Creation of an oxidation or reduction milieu at the point of contact of the electrode and sensitized material.
(3) Alteration of the pH at the point of contact of the electrode and the sensitized material.

Considerable effort has been expended in development of more sensitive systems but the demand for greater rapidity of color-formation and permanency of the indicia has resulted in defects which militate against the unqualified success of the available systems.

The ultimate system should possess most, and desirably all, of the following basic characteristics:

(1) The system should produce clear marks rapidly when activated by a relatively weak electric current.
(2) The marks should be of high definition and devoid of fringes or feathering.
(3) The marks should be stable over extended periods of time.
(4) The color of the marks should be not only attractive, but also in sharp contrast with the background color.
(5) The sensitized material should be stable on exposure to the normal atmosphere and to light.
(6) The material should be manufactured with reasonable ease and should not contain any hazardous chemicals.
(7) The sensitized material should not deteriorate on normal handling, and not require any elaborate or complicated processing, either prior or subsequent to use.

To date, the intensive research in this art has resulted in the evaluation of a number of systems, none of which has been completely satisfactory, being deficient in one or more of the above mentioned characteristics. Chromogenic substances such as leuco-bases, diphenyl methane compounds, etc., have been employed in electrographic applications and in general require oxidation-reduction conditions to produce the color. In particular chromogenic substances, including diazotizable amines, diazoamino compounds, diazonium salts, oxidized triphenylmethanes, diaminotriarylmethanes and the like, have been suggested, but none of these classes of chromogenic compounds have been entirely satisfactory due either to slowness, incompleteness of color development, poor stability of the developed color or similar reasons. Accordingly, such chromogenic substances as are presently employed in the electrographic art are of limited utility.

It is therefore an object of this invention to provide novel electrosensitive recording media having the desired characteristics above mentioned.

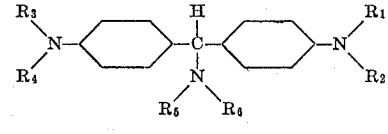
More particularly, it is an object of this invention to provide an electrosensitive recording composition which develops color in the absence of an oxidizing medium and produces highly legible images which are rapidly produced.

Other objects and features will be apparent from the following description of the invention.

As is well known, application of suitable voltages and currents through a sensitized material in an electrographic process causes migration of ions and results at the anode, in an electron rich, i.e. an acidic condition. We have discovered that colorless or substantially colorless organic chromogenic substances which develop color by reaction with an electron acceptor material in the absence of an oxidizing medium, such as leucoauramines, diarylmethane carbinols, triarylmethane carbinols, diarylmethane carbinol ethers, triarylmethane carbinol ethers, triarylmethane carbinol lactones, etc., are highly effective when present in relatively minor quantities in the sensitized compositions and that the electron-donating chromogen in the presence of acid is converted from the colorless compound to a colored derivative at the point of contact of the electrode, thereby yielding highly legible permanent marks.

Of the chromogens named above as suitable for use in the instant compositions, we have found that the leucoauramines are especially effective. Such novel compositions which may be impregnated in or coated on a suitable substrate, such as a fibrous web, e.g., paper, cotton, silk, wool, nylon and the like, films, metal sheets, glass and the like, contain essentially an electron-donating chromogen such as a leucoauramine and an alkaline buffering substance to maintain the pH of the sensitized composition above about 7. Preferably, a salt, such as potassium chloride, to provide an electrically conductive medium, is present also. Humectants, such as glycerol, sorbitol and the like, to insure the presence of moisture may also be present.

The preferred leucoauramines used in the present invention are generally known compounds and conform to the following general formula:



wherein R_1, R_2 and R_3 and R_4 are the same or different lower alkyl groups, or substituted lower alkyl groups, e.g., methyl, ethyl, butyl, β-chloroethyl and the like. R_5 and R_6 are the same or different, and may be hydrogen, alkyl, aryl, aralkyl, acyl, aryl sulfonyl or alkyl sulfonyl and R_5 and R_6 together with the nitrogen atom may form a 4, 5 or 6 membered heterocyclic ring.

Representative compounds of this class are exemplified by the following:

Leucoauramine
N-phenyl leucoauramine
N-amyl leucoauramine
N,N-diethyl leucoauramine
N-bis-(p-dimethylaminophenyl)methyl diethylamine and similar aliphatic amino derivatives of bis(p-dialkylaminophenyl)methane disclosed in U.S. Pat. 2,983,756.
Phenylsulfonamide-bis(p-dimethylaminophenyl)-methane and similar N-bis(p-dialkylaminophenyl)-methyl sulfonamides disclosed in U.S. Pat. 2,948,753.
Bis(p-dimethylaminophenyl)benzotriazyl methane and similar heterocyclic nitrogen derivatives of bis(p-dialkylaminophenyl)methane disclosed in U.S. Pat. 2,981,738.
Bis(p-diethylaminophenyl)morpholinyl methane and similar N-bis(p-dialkylaminophenyl)methyl derivatives of nitrogen containing saturated heterocyclic compounds disclosed in U.S. Pat. 2,981,733.

In addition, quaternary derivatives of these leucoauramines can be used as the chromagen such as N-[bis(p-dimethylaminophenyl)methyl] - N,N'-dimethylpiperazinium methyl sulfate. The compound and related quaternary leucoauramines are disclosed and claimed in copending U.S. application Ser. No. 463,942, filed June 14, 1965 now Pat. No. 3,467,658.

Other classes of organic chromogenic compounds which develop color by reaction with an electron acceptor in the absence of an oxidizing medium are exemplified by the following typical compounds:

2-omega-substituted vinylene derivatives of 3,3-disubstituted-3H-indoles disclosed and claimed in copending application Ser. No. 285,563, filed June 5, 1963, now Pat. No. 3,346,571.
2-(arylimino-polymethylidyne)-3,3-disubstituted indolines disclosed and claimed in copending U.S. application Ser. No. 444,807, filed Apr. 1, 1965.
Diarylmethane carbinols such as Michler's Hydrol.
Diarylmethane carbinol ethers such as the ether of Michler's Hydrol.
Triarylmethane carbinols such as tris(p-dimethylaminophenyl)methanol.
Triarylmethane carbinol ethers such as tris(p-diethylaminophenyl)methoxy methane.
Triarylmethane carbinol lactones such as Crystal Violet Lactone.

Mixtures of these and equivalent chromogenic substances are contemplated for use in the novel compositions of our invention.

As is well known, these chromogenic compounds are colorless, or substantially so, in an alkaline medium. However, when placed in an acidic medium, that is in a medium the pH of which is below 7, they rapidly change from the colorless to an intense shade. Although the rapidity of the change, as well as the permanence of the developed color will vary somewhat among the individual members of this class, it is generally true to state, that as a class, the leucoauramines, especially those bearing a substituent or substituents on the amino group attached to the methyl group joining the two phenyl nuclei, develop color rapidly and said color is of satisfactory

permanence compared to chromogenic compounds known in this art.

The chromogenic compounds of the type disclosed above and especially leucoauramines are soluble in various organic solvents, e.g., lower alkanols such as ethanol, isopropanol and aromatic hydrocarbons, such as benzene and toluene. It is convenient to apply the leuco compound to the substrate or supporting material, such as paper or cloth, by immersing the substrate in a solution of the chromogen, which preferably also contains an alkaline reacting compound, such as triethanolamine, to maintain the sensitized medium alkaline prior to development. The sensitized medium may then be freed of excess solution, e.g., by passing it through squeeze rollers and then dried, e.g. in air or a suitable drier. The dried impregnated material may then be impregnated, e.g. by dipping, spraying or other convenient procedure, with an aqueous solution of an electrolyte, e.g. potassium chloride, and the impregnated material again dried, e.g., in air of controlled relative humidity. Humectants, e.g. glycerol, diethylene glycol, sorbitol and the like, binders, such as starch and polyvinyl acetate, pigments such as zinc oxide, titanium dioxide and the like, may be added to the substrate in either of the above impregnating solutions.

In many instances the permanence of the developed color can be improved by utilizing a mixture of chromogens, one component of which is characterized by the extremely rapid rate at which it develops the full intensity of its colored form and the other component of which is characterized by being relatively slow to develop its full intensity of color on the passage of the electric current. By the use of such a mixture of slow and fast developing chromogens, indicia are produced which are fast forming and long lasting. Such mixtures are of advantage in applications wherein rapid printing is desired. The leucoauramines disclosed above are highly sensitive and thus particularly suited to use as the fast forming color component, whereas the N-aryl-leucomethylene blues and triphenylmethane lactones, being relatively slow to attain maximum color density, are suitable for use as the "slow" color forming chromogenic component.

It is not considered that the proportions in which the chromogen is present in the sensitized composition is of particular importance. In general, relatively small amounts of the chromogen in a solvent, for example as little as .25 to 2 parts by weight in a suitable solvent such as alkanol is effective to impregnate the substrate.

The imaging producing mechanism by which the colored indicia are produced in or on the sensitized media of the present invention are well known in this art. Many patents and periodical articles are readily available which describe in detail the construction and operation of suitable electrographic indicia producing systems. Accordingly a detailed description of this ancillary facet of our invention will not be given here. In general any system capable of producing localized areas of acidic nature is suitable. Either high voltage and low amperage or low voltages and high amperages are satisfactory. Satisfactory imaging have been obtained at voltages as low as 1.5 volts, at close to one ampere, as well as up to several thousand volts and currents of the order of several microamperes.

The development of dense images, under normal conditions, is accomplished in exceedingly short time. For example when using a conventional stylus print-out device, equipped with tungsten styli of the order of several mils in diameter, an electrical input of 500 volts at 100 milliamperes, an image is obtained on appliaction of pulse times of 50 microseconds or less.

The development of the colored indicia is due solely to the alteration of the pH in the area of application of the electrical current and is not dependent upon any chemical reaction involving the electrodes. Thus, chemically inert materials such as platinum, carbon and the like, can be used as electrodes.

The sensitized composition preferably contains an electrolyte, which is generally a water soluble inorganic salt. Typical suitable electrolytes include the following:

Aluminum chloride	Calcium acetate
Aluminum nitrate	Calcium carbonate
Aluminum potassium sulfate	Calcium nitrate
Aluminum sulfate	Calcium nitrite
Ammonium chlorate	Calcium chloride
Ammonium chloride	Cadmium chloride
Ammonium carbonate	Cadmium sulfide
Ammonium borofluoride	Cadmium sulfate
Ammonium paramolybdate	Cobalt chloride
Ammonium sulfate	Copper sulfate
Barium chlorate	Chromium fluoride
Barium chloride	Ferrous sulfate
Barium nitrate	Lead acetate
Barium nitrite	Silver nitrate
Magnesium bromide	Sodium acetate
Magnesium chloride	Sodium bromate
Magnesium sulfate	Sodium bromide
Mercuric chloride	Sodium carbonate
Phosphotungstic acid	Sodium chromate
Phosphomolybic acid	Sodium dichromate
Potassium dihydrogen orthophosphate	Sodium fluoride
	Sodium borofluoride
Potassium sulfate	Sodium hypochlorite
Potassium acetate	Sodium iodide
Potassium bromide	Sodium molybdate
Potassium chloride	Sodium nitrate
Potassium carbonate	Sodium chloride
Potassium dichromate	Sodium nitrite
Potassium borofluoride	Sodium acid orthophosphate
Potassium ferrocyanide	
Potassium iodide	Sodium sulfate
Potassium permanganate	Sodium sulfite
Strontium chloride	Sodium bisulfite
Zinc bromide	Sodium chlorate
Zinc chloride	Sodium orthophosphate
Zinc nitrate	Sodium thiosulfate
Barium sulfate	

Mixtures of these and equivalent salts are contemplated also for use in this invention.

As indicated above the salt may be omitted completely as an additive, since we have found that the normal hydrolysis of water is sufficient to enable the passage of electric current. This is so when paper is used as the substrate, since we believe that a small amount of salt or salts carried over from the processing of the paper pulp suffices to provide an electrically conductive medium.

Generally, the color produced is independent of the electrolyte used. Of course, some salts are colored themselves, such as potassium permanganate, sodium dichromate and the like. However, the alteration of the shade, in those instances, is due to the colored salt, per se. Salts containing an oxidizing anion may assist in the formation of colorations from chromogens which develop color in oxidizing environments, and such salts will be helpful when such chromogens are used in admixture with the leucoauramines. Salts containing cations which form insoluble hydroxides, such as aluminum, calcium, magnesium and the like, may contribute to the stability of the colored indicia, since the insoluble hydroxides which probably are formed at the negative electrode during the passage of the current stabilize the cation and thereby prevent recombination with the colored form of the leucoauramine and image fading by reversion to the colorless form. Such immobilization of the hydroxyl ions also may assist in maintaining an acid condition in the area of the positive electrode.

The amount of electrolyte used is not critical, and the concentration may be varied from as little as 0.05% by weight to as much as 35% or more by weight of the sensitized composition. Preferably an amount of electrolyte within the range of about 1.0 to about 7.0% is used.

The passage of electric current through the sensitized material requires the presence of water, which acts as a source of hydrogen ions at the negative electrode. The amount of water is not critical and can be varied over a broad range, from amounts as little as about 10% to as much as about 50% or more. The power requirements apparently vary inversely with the moisture content. Preferably an amount of moisture from about 20 to about 40% by weight of the sensitized material used should be present. As indicated above, stability of the moisture content can be enhanced by the use of humectants.

When paper stock is used as the substrate, the pH and the thickness of the paper stock are of importance.

In general the stock should be selected so as to provide a neutral to basic substrate, preferably from pH of 7.0 to about 7.5. Such a condition insures against the premature development of color on impregnation of the paper with solutions of chromogens containing inadequate amounts of alkaline agents. Since most papers are produced by procedures which result in an acid pH, care in selection of the paper is of importance.

The thickness of the base stock is of importance also. In general the thinner the base stock, the higher the current density produced at the electrodes and hence deeper the color produced for given power and time factors. The thickness of the stock also exerts an influence on the stabililty of the image produced, probably due to the decreased ease of migration of the hydroxyl ions back to the anode area after imaging as the thickness increases.

The following examples will illustrate the present invention. Parts are by weight and temperatures are given in degrees centigrade.

EXAMPLE 1

A solution of 0.8 part of bis(p-dimethylaminophenyl)-morpholinylmethane and about 1.65 parts of triethanolamine in about 79 parts of ethyl alcohol was prepared and used to impregnate a sheet of unwashed Whatman No. 5 filter paper. The impregnated paper was dried in air having 60% RH (relative humidity) for 5 minutes. The paper was next immersed in a solution of 1 part of potassium chloride in 20 parts of water and again dried in 60% RH air.

A metal addressing plate, containing a raised image of the information to be printed is attached to the positive terminal of a 90 volt Eveready NO 490 battery. The sensitized paper, prepared above, is placed on top of the addressing plate and superimposed with a piece of aluminum foil, which is connected to the negative terminal of the battery. Care is taken to ensure that the foil does not overlap the edges of the paper and short out the circuit to the anode. A rubber roller is passed over the back of the aluminum foil and the filter paper is removed from the package. A deep blue image of the information on the addressing plate is produced on the paper on that side in contact with the raised image.

EXAMPLE 2

A mixture of 0.8 part bis(p-dimethylaminophenyl)-morpholinylmethane, 0.4 part 4,4',4'' - tris(dimethylamino) - 2 - methyltriphenylmethane, 0.5 part 4-chloro-4',4'' - bis(diethylamino) - triphenylmethane and about 1.65 parts of triethanolamine was dissolved in about 63 parts of isopropyl alcohol. This solution was mixed with a solution of 1 part of potassium chloride in 20 parts of distilled water.

The resulting solution can be applied to various porous substrate, such as paper, cotton cloth and the like, to provide electrosensitive compositions. For example a piece of cotton cloth was immersed in the above prepared solution and the wetted cloth was blotted to remove excess solution and then dried in air until the cloth con-

tained about 35 to 40% moisture. The thus treated cloth was used in place of the sensitized filter paper as described in Example 1 above. When in place of the metal addressing plate used in Example 1, a zinc or copper letter press plate such as is used in photoengraving processes was used, more complicated designs were developed on the sensitized cotton cloth.

EXAMPLE 3

To about 8 parts of ethanol, about 1 part of triethanolamine, 0.25 part of bis(p-dimethylaminophenyl) morpholinylmethane, 10 parts of zinc oxide, 5 parts of polyvinylacetate emulsion (55% solids) and 5 parts of 10% aqueous potassium chloride were added. The mixture was agitated well and then applied as a coating to aluminum foil laminated to a sheet of ordinary paper. Such foil laminated papers are well known and have been widely used as packaging material especially for cigarette packages.

The coating was applied at a controlled thickness using conventional coating techniques, such as dip-coating, reverse roll application, air-knife, trailing blade, wire-wound rod, curtain-coating and the like.

The coated laminated foil was dried in a controlled humidity oven to about 35% moisture content and thereafter indicia were developed thereon by the procedure described in Example 1 above.

The chromogen used in the above formulation which produced stable greenish blue markings, was replaced with a like amount of 2,4'-N-2''-cyanoethyl-N-methyl-aminostyryl-3,3-dimethyl-3H-indole (which is disclosed and claimed in U.S. Pat. No. 3,346,571) the markings developed on the sensitized paper were deep red in color.

From the above description and examples, it will be evident that the leucoauramine and other types of chromogens of this invention are valuable and effective color formers for use in electrographic marking procedures.

This invention has been described and illustrated with reference to specific embodiments thereof. While the examples include our preferred procedures, it should be noted that these procedures are purely illustrative and that many variations thereof are possible. Thus the zinc oxide which is used in the coating formulation to provide an absorption surface for the chromogen-salt combination may be replaced in whole or in part by other pigments such as titanium dioxide, magnesium oxide and the like. The polyvinylacetate emulsion which functions as a binder may be replaced by other water soluble binding media such as carboxy methyl cellulose, polyvinyl alcohol and the like. Further, other conductive undercoatings than the aluminum foil can be used, e.g., super conductive carbon black suspensions, such as those commercially available under the trade names of "Aquadag" or "Laqdag" may be applied to the paper to furnish a return electrode for the marking system.

Other variations in the details of the illustrative examples will be obvious to those skilled in this art. Such variations which do not depart from the scope or spirit of our invention are to be included therein.

We claim:

1. An electrographic recording composition which comprises a supporting material and a sensitized material, said sensitized material consisting essentially of (1) a mixture of substantially colorless chromagen electron donors consisting of (a) bis(p-dimethylaminophenyl) morpholinyl methane, (b) 4,4',4''-tris(dimethylamino)-2-methyltriphenyl methane and (c) 4-chloro-4',4''-bis(diethylamino)triphenyl methane, wherein said component (a) develops color at a rapid rate and said components (b) and (c) develop color at a slower rate relative thereto, (2) potassium chloride and (3) triethanolamine in an amount sufficient to maintain the pH of said sensitized material above 7.

2. A composition as claimed in claim **1** wherein said supporting material is paper.

References Cited

UNITED STATES PATENTS

2,306,471	12/1942	Solomon	204—2
2,513,238	6/1950	Greig	204—2
2,981,733	8/1961	Kranz	260—247.5
3,096,711	7/1963	Ritzerfeld	101—149.4
3,145,156	8/1964	Oster.	

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