FIG. 1

PRESSURE APPLICATOR—FOR INSTANCE, A PENCIL

MARK MADE BY WRITING INSTRUMENT MARKING MATERIAL

MARK MADE BY REACTION OF COLORLESS REACTANTS RELEASED FROM RUPTURED CAPSULES 22 ONTO ACIDIC COMPONENTS 24. THE CAPSULE-HELD REACTANTS COLLECTIVELY APPEARING BLACK IN COLORED STATE.

FIG. 2

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BY
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HIS ATTORNEYS
COLORLESS INK TO GIVE BLACK PRINT
Paul S. Phillips, Jr., Dayton, Ohio, assignor to The National Cash Register Company, Dayton, Ohio, a corporation of Maryland
Continuation-in-part of application Ser. No. 688,596, Dec. 6, 1967. This application Mar. 13, 1969, Ser. No. 807,130
U.S. Cl. 106—21

ABSTRACT OF THE DISCLOSURE
A colorless marking liquid comprising a vehicle in which is dissolved a compound of several colorless reactants each exhibiting its own distinctive color on reaction with an eligible acidic record material sensitizing substance, the ink yielding an apparent substantial black on record material sensitized with an eligible acidic material for each reactant and otherwise yielding an apparent color where at least one but not all of the necessary eligible acidic substances to produce black are absent.

This is a continuation-in-part of copending application for United States Letters Patent Ser. No. 688,596, filed Dec. 6, 1967, now abandoned, in the name of the present inventor.

This invention relates to a multicomponent normally colorless ink which is reactive to produce distinctive, substantially black, marks on appropriately sensitized record material by absorbing some or substantially all of the visible spectrum. The colorless reactants are at least two in number, each alone exhibiting a color on reaction with record material sensitized with eligible acidic material for it. Some acidic materials will develop all the component colorless reactants, and some will develop less than all of the component colorless reactants. In applying the ink to a sensitized record material, the yield of a colored mark indicates the lack of one of the necessary eligible acid materials, and the yield of a substantially black-appearing mark means that the necessary acidic materials to react all the colorless reactants are present. Some all-purpose acidic materials develop all the color reactants in the novel ink, and some do not. The yielding of a colored mark serves to indicate the sensitization of a sheet in a negative manner that an all-purpose acidic material is not present. This negative response of a sheet is useful in two ways; to wit, (a) to identify an ink-receiving sheet as to its sensitization potential, and (b) to yield colored marks where so sensitized, whereas, on fully sensitized sheets, the ink yields black marks. The ink comprises a liquid oil solvent of a viscosity to act as an ink vehicle, and colorless dye materials of several kinds dissolved therein in the amount of several percent, as required, so that, when color is developed from them by contact with acid-sensitized record material, a collective result of the mixture appears black to the eye or to electromagnetic sensitive devices such as photoconductors.

In a preferred practice of the invention, the ink is encapsulated in microscopic capsules which are coated on base sheet record material, in close contact, said sheet yielding the ink under pressure of writing against a sensitized under sheet, in a pattern of droplets corresponding to the written matter, in accordance with the disclosure of such a capsule-bearing sheet in U.S. Pat. No. 2,712,507, which issued July 5, 1955, on the application of Barrett K. Green.

BRIEF DESCRIPTION OF THE DRAWING
The drawing is a diagrammatic representation of a two-sheet unit manifold 19 of record material. FIG. 1 is a perspective view in which the bottom surface 21 of the overlying foil sheet 20 is supplied on the surface or near it with a multiplicity of minute pressure-rupturable microcapsules 22, each containing a droplet of the novel ink of this invention. Each droplet of a base sheet or at least two chemically basic chromogenic components. A chemically acidic component, such as an acid clay or a colorless phenolic polymeric material 24 of acid characteristics, lies within the lower foil sheet 23 or upon the upper surface of the lower foil sheet. In the preferred embodiment, a very dark-colored mark 25 is made by the use of a stylus such as a pencil 26, a type character, or other pressure-writing means applied to the twosheet unit manifold. The mark 27 is a pencil mark, whereas the mark 25 is produced by color reaction between released droplet-held material and acidic component.

The encapsulated droplets are released by the rupture of capsules in writing operations. The liquid novel ink composing the liquid droplets is transferred in the pattern of the data configuration to the top of the underlying sheet. The top of the underlying sheet is coated or impregnated with a least one material which is an acid reactant with respect to the basic chromogenic material of the ink and produces color with any such component that is reactive therewith. Representative acidic coating materials are, on one hand, oil-insoluble minerals or inorganic particulate solid material, represented by kaolin, attapulgite, silica gel, zeolites, and the like, and, on the other hand, organic polymeric acidic materials, such as nonreacting phenolic resins of oil-soluble characteristics. Eligible polymeric materials will be disclosed later in the specification.

One of the chief features of this invention is the provision of an ink having numerous components which will collectively make an apparent black color or by molecular mixture of distinctive colors, through their combined absorption of incident white light components, whether the acidic material be polymeric, mineral, or nonmineral inorganic in content, or a combination of such acidic materials.

Another object of the invention is to provide a transfer sheet having a colorless ink in encapsulated droplets arrayed thereon, wherein each of the droplets will develop a black color on eligible-acidic-material-sensitized record material.

DETAILED DESCRIPTION
The formation of a print upon application of colorless basic chromogenic material to an acidic substrate by use of a chemically basic colorless ink has heretofore been unattainable to achieve physiological and spectral black. This invention solves the problem of obtaining a black print upon the reactive combination of a basic, chemically basic, novel ink composition with an acidic receiving surface.

An object of this invention is to obtain a black print on a sensitized substrate from the rupture of a microcapsule containing a novel ink by acid-base reaction. A further object of this invention is the provision of a print from such an encapsulated ink, said print having enhanced readability by optical recognition equipment. A still further object of this invention is the provision of a multiple-component ink for differentiating between various types of chemically-sensitized receiving sheets. The record member consists of a member either of fibrous construction, such as paper, or of continuous structure, such as films of organic polymeric material, carrying the color reactant in an
exposed state with respect to applied ink. The acid reactant, when of particulate nature, is arranged in intimate juxtaposition to form an apparently unbroken surface. The reactive surface of each particle individually is available for contact with applied ink. If the phenolic polymer acidic material is used, it may be applied to the record material as a solution coating with insoluble acidic particles dispersed therein, if desired. While the surface member is adapted to receive any kind of ink, whether colored or colorless, its special utility is its use with the novel oily ink, which is normally colorless and carries colorless chromogenic reactants in liquid solution. All of the eligible substrates are substantially insoluble in water, however, at least one kind of eligible particle may be soluble in the oily ink, and at least one other kind of eligible particle may be insoluble in the oily ink. The kind of chromogenic reactant materials of the novel ink of this invention generally undergo an acid-base reaction with their paired kind of acid reactant where applied to a record member to produce a distinctively colored mark; however, at least one of the kinds of chromogenic reactant material cited as useful herein—namely, benzoyl leuco methylene blue—undergoes hydrolysis followed by an oxidation-reduction reaction when and where applied to its paired kind of material on said member to produce its distinctive color. As the several chromogenic reactant materials are dispersed homogeneously in the common solvent to the same areas, the collective color will be a blend of the individual hues in the colored state. While, in its simplest form, the invention can be carried out by the use of the provided colorless inks in combination with acidic reactants, typified by powdered acid-reacting oil-soluble phenolic polymers and acid materials alone or in combination, for which examples will be given, disparate kinds of reactants may be used for diverse properties, reactant or not, which may be desired in the record member. These diverse properties may be physical or chemical.

Color-reacting recording systems are so called because the reactant chromogenic material content of the ink used in such systems is substantially colorless and assumes a color when applied to a specially-sensitized recording surface, either coloring at once or finally yielding color on prolonged contact with the associated acidic material. The sheet, even though sensitized, can be printed on at one time or in one area with conventional color printing inks and at another time in another area on the sheet with the novel colorless ink. As distinguished from pigment inks, the chromogenic material in the novel colorless ink of this invention is a combination of colorless dyes that, through chemical reaction, a visually collective distinctive color when undergoing reaction with the acidic reactants on the sheet.

For most recording purposes, it is essential from a commercial standpoint that a distinctive color mark appear on the application of the colorless ink to the recording surface, to produce a visible representation of whatever is meant to be recorded; that the color be of distinctive hue and also of high intensity; and that the mark remain colored for a long period of time consistent with the objective of permanent recording. Colored dyes have well-known infirmities as regards permanence, such infirmities relating to light-fading, thermal fading, and molecular rearrangements and disintegrations of various kinds, in which part or all of the visually perceptible color is lost. It is an object of the invention to overcome, as far as possible, by the provision of special ink components that act in a comprehensive manner, the losses of color in whole or in part in the color-reactant marks which losses are occasioned by passage of time, by exposure to environment, or by intentional chemical or physical attrition or obliteration.

Eligible polymeric materials of sufficient activity in an acid sense and suitable for use in this invention because they are oil-soluble are disclosed in a continuation application for U.S. Letters Patent, Ser. No. 744,601, filed July 17, 1968, based on application for United States Letters Patent Ser. No. 392,404, filed Aug. 27, 1964, by Robert E. Miller and Paul S. Phillips, Jr., the latter being the applicant herein, the invention claimed in said applications being directed not to a sheet of record material sensitized both with oil-insoluble acid of polymers and with polymeric material adapted to color applied ink, as is one case in the instant invention, but to a pressure-sensitive system of oil-soluble acid polymeric material, colorless color reactant, and capsule- or film-isolated solvent liquid droplets situated either together on one sheet or in a couplet of sheets, all of the reactant components being oil-soluble. In this present invention, both oil-soluble and oil-insoluble nonchromogenic solid acid reactant materials are used. Moreover, the main object of the present invention is to make a black-appearing color.

Among the oil-soluble organic polymeric materials suitable for use in combination with appropriate ink solvents to be used therewith, acid-reaction phenol-aldehyde and phenol-acetylene polymers, maleic acid-resin derivatives, maleic acid-resin partially or wholly hydrolyzed styrene-maleic anhydride copolymers and ethylene-maleic anhydride copolymers, carboxy polyethylene (Carbopel 934), and wholly or partially hydrolyzed vinyl methyl ether-maleic anhydride copolymers are specified as typical of the reactive acid polymeric materials.

Among the phenol-aldehyde polymers found useful are members of the type commonly referred to as novolaks, which are characterized by solubility in common organic solvents and which are, in the absence of cross-linking agents, permanently fusible. Another group of useful phenol polymeric materials are alklyphenol-acetylene resins, likewise soluble in common organic solvents and possessing permanent fusibility in the absence of being treated by cross-linking materials. Generally, the phenolic polymer materials useful in practicing this invention are characterized by the presence of free hydroxyl groups and by 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.

A laboratory method useful in the selection of suitable phenolic resins is a determination of the infrared radiation absorption pattern of a candidate material. It has been found that phenolic resins show 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 material to be specified.

The preparation of the phenolic-formaldehyde polymeric materials suitable for practicing this invention is described in "Industrial and Engineering Chemistry," volume 43, pages 134 to 141, January 1951; a particular polymer thereof is described in Example I of United States Pat. No. 2,052,093, which issued on Aug. 25, 1936, on the application of Herbert Hönel; and the preparation of the phenol-acetylene polymers is described in "Industrial and Engineering Chemistry," volume 41, pages 73 to 77, January 1949.

The preparation of the maleic anhydride copolymers 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 pages 65 to 68 (stylene-maleic anhydride copolymer), pages 628 to 630 (vinyl methyl ether-maleic anhydride copolymer), and pages 530 and 531 (ethylene-maleic anhydride copolymer).

The liquid solvent portion of the ink used must be
capable of dissolving the mark-forming chromogenic components. The solvent may be volatile or nonvolatile, and a single or multiple component solvent which is wholly or partly volatile may be used. Examples of volatile solvents useful with the basic chromogen and acidic polymeric mark-forming components specified are toluene, petroleum distillate, perchoroethylene, and xylene. Examples of nonvolatile solvents are high-boiling-point petroleum fractions and chlorinated diphenyls.

Generally, the solvent forming the ink vehicle to a large extent should be chosen so as to be capable of dissolving at least 1% of the basic chromogenic material, preferably in excess of 2%, and a larger amount of polymeric material—up to, say, 15% or more—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 maximum reaction utilization of the chromogenic material and thus to assure the maximum coloration at a reaction site.

A further criterion of the selected solvent is that it must not interfere with the mark-forming reaction. In some cases, the presence of the solvent may 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 leaving the reaction site after having, through solution, brought the mark-forming components into intimate admixture, so that the mark-forming reaction proceeds.

In the base-acid color system, as stated above, the polymeric mark-forming component(s) chosen must be acidic relative to the basic chromogenic compound and reactive with the chromogenic material to effect the distinctive color formation or color change.

Kaolin is generally known and used in the papermaking industry as "china clay" and is outstandingly preferable as a particulate oil-insoluble and water-insoluble mineral material of acid characteristics necessary to color benzoyl leuco methylene blue, one of the chromogenic components, where that component is necessary. A white kaolin is used, and, because of its whiteness, its plate-like particle form, which gives it unparalleled coating properties in aqueous slurries, its universal abundance in supply, its historical general usage in the papermaking and paper-converting industries, and its low cost, it is an ideal material. Other types of particulate and substantially colorless water- and oil-insoluble materials of the necessary acid properties are deemed equivalents of kaolin, some being bentonites.

Attapulgite can be used in this invention as an efficient colorless mineral reactive material to color those colorless chromogenic compounds of the novel ink of this invention that react on contact in an electron-donor-acceptor reaction, and, by reason of its high oil absorbency, is doubly useful as an absorbent reactive coating on paper to form color with such chromogenic compounds dissolved in oil as may be applied to it.

From the foregoing choice of materials, a number of different specific compositions on a dry basis may be made, and these may then be used as desired, as being made into an aqueous slurry to be coated on a finished paper sheet, to be applied to a wet sheet of paper in the formative state in any desired manner, or made a part of the paper furnish from which a paper sheet is made, or on the other hand applied as a dispersion coating to a continuous film-like web such as synthetic organic polymeric material made into record sheets, bands, or strips, or to any record support material surface, all coming within certain limits merely set as practical and not set for any chemical or physical reason. In general, so as to be economical, the materials should be used in just sufficient quantities to make use effective for the purpose in view, and this relates to criteria of the factors of intensity, definition, color and a great many other factors with regard to the characteristics of the base web material, the characteristics of the ink to be applied, and the environment of use, all of which come within the paper manufacturers' and printers' skill and general knowledge and are not deemed to be of inventive concept. Generally, but not as a limitation in any sense, an aqueous dispersion of the particular materials could well be from 40% to 75% water, by weight, and the remainder from 60% down to 25% of the particulate reactants divided generally on a basis of five parts, by weight, of the oil-insoluble component to one part, by weight, of the oil-soluble component, as a guide, but not as a limitation. Amounts of papercoating adhesive binders are added as is necessary to cause the particles to adhere to the base web to which they are applied, but, of course, adhesives that have a tendency to mask the particles physically or to chemically deactivate the particles should not be used, nor should any material be used as an adhesive in great excess of actual requirements, all of such factors tending to decrease the efficient use of the associated active particles because of a limitation of the exposed surface area. Binders of particular use herein may be chosen from among papercoating latexes such as styrene-butadiene and acrylic latexes. Here again, the paper makers' and printers' skill and judgement should govern.

Where the particles of kaolin and acid polymeric material are slightly delayed in responsiveness because of their physical situation or condition in the support sheet, an amount of silica gel up to equal the amount of acid polymeric material may be used for its beneficial effect in the characteristics stated, but such use is not necessary to the practice of the invention in its simplest form. Silica gel is insoluble in oil but is absorbent therefore, may be finely ground, is colorless, disperses readily in water, and may be treated to increase its porosity and effectiveness as an acid.

The particle size of the reactants preferably should be from one to three microns in largest dimension, although considerable latitude at the expense of efficiency and economy is tolerable. For instance, if the grinding of materials to the most effective size is too expensive, their larger particle sizes are tolerable as long as sufficient color reaction per unit area of the record material is provided.

One of the chief considerations in selecting a preferred embodiment of the invention must be concerned with the manufacture of the record sheet, and, as of now, the best way to sensitize a sheet is to apply an aqueous slurry of the novel composition to a finished web of paper as it passes a coating station in a papermaking machine. Such a coating composition contains binder material and may contain defoamers and dispersing agents common to papercoating practices, but their specification in no way is to mean a limitation of the practice of the invention in regard to either choice or necessity.

**COATING COMPOSITIONS**

**Example I:**

<table>
<thead>
<tr>
<th>Solids, parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Papercoating kaolin (white)</td>
</tr>
<tr>
<td>Oil-soluble acid-reactant organic polymeric material</td>
</tr>
<tr>
<td>Binder as required, in up to sufficient water to make a solids content of 25% to 60%</td>
</tr>
</tbody>
</table>

**Example II:**

<table>
<thead>
<tr>
<th>Solids, parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Papercoating kaolin (white)</td>
</tr>
<tr>
<td>Attapulgite</td>
</tr>
<tr>
<td>Oil-soluble acid-reactant organic polymeric material</td>
</tr>
<tr>
<td>Binder as required, in up to sufficient water to make a solids content of 25% to 60%</td>
</tr>
</tbody>
</table>
Example III:

(a) Clay—one or more selected from the group consisting of kaoline, attapulgite, and bentonite, used singly or in combination —— 100
(b) Polymeric material—acid-reacting phenolic resin —— 33 to 100
(c) Binder —— 20 to 112.5
(d) Water to yield a total solids content of 4% to 31%.

It will be apparent that the ratio of the solids content of acid mineral to polymeric material content of the compositions may vary greatly, as from 10 to 1 in Example I to 1 to 1 in Example III. The examples pertain especially to the coatings for paper. In filling paper furnish with these reactant materials, only such quantitative amounts should be used that will insure reaction with the ink and integrity of the paper web, such being determined empirically by the paper maker.

For coating nonfibrous web material, the application should be less wet, as there ordinarily will be no drying of the coating by absorption.

The term “acid” used herein in any sense includes Lewis acids in general and is not restricted in any sense to any specialized definition.

In any of the systems, the end purpose is to produce visually-sensitive marks or electrooptically-sensitive marks. Specific examples of chromogenic material useful in making the novel ink of this invention comprise:

CHROMOGENIC BASIC REACTANTS

(I) Crystal violet lactone, which is named 3,3-bis(4-dimethylaminophenyl)-6-dimethylaminophthalide yielding a blue color at once on acid-reactant material but tending to fade easily in light when reacted on a surface-active solid acid type of reactant. This is disclosed in U.S. Pat. Re. 23,024, issued Aug. 17, 1948, on the application of Clyde S. Adams.

(II) One of the group consisting of

(a) 4,4'-bis(dimethylamino) benzophenone, which is Michler’s Ketone, and
(b) the diethylaminol analog of Michler’s Ketone, which is named 4,4'-bis(diethylamino) benzophenone,

which are commercially available and react with the acid materials eligible for use in this invention to give a yellow color.

(III) One of the group consisting of

(a) 3,3-bis(1,2-dimethylindol-3-yl) phthalide, which is prepared according to the method disclosed in U.S. Pat. application Ser. No. 612,369, filed Jan. 30, 1967, in the name of Chao-Han Lin;
(b) 3 - (1-ethyl, 2-methylindol-3-yl) - 3 -(2-methylindol-3-yl) phthalide, the preparation of which is disclosed in U.S. pat. application Ser. No. 612,558, filed Jan. 30, 1967, in the name of Chao-Han Lin;
(c) 2 - chloro - 6 - diethylamino - 3-methyl-spiro [9H-xanthene-9,1'-phthalide], the preparation of which is given below;
(d) 9 - diethylaminospiro [1,2 - H - benzo(a)xanthene-12,1'-phthalide], the preparation of which is given below,

all of which yield color in the red region of the spectrum.

(IV) 3,7 - bis(dimethylamino) - 10 - benzoxy phenothiazine, which is benzoyl leuco methylene blue, commercially obtainable, which yields a blue color on several hours’ contact with kaolin.

(V) One of the group consisting of

(a) N-phenylauramine, which is named 4,4'-bis(dimethylamino) benzophenone phenylimine, and
(b) the diethylaminol analog of N-phenylauramine, which is named 4,4'-bis(diethylamino) benzophenone phenylimine,

which yield an orange color and are made, for instance, by reacting in toluene or xylene the raw materials aniline and the appropriate bis(p-dialkylaminophenyl)methylamine.

EXAMPLES OF A TWO-COMPONENT INK

A specific example of a novel two-component ink comprises 2% each of Basic Reactants I and Va or Vb, dissolved in a two-to-one mixture of chlorinated biphenyl and saturated hydrocarbon, by weight. Such a two-component ink is the preferred embodiment of this invention. Because auramine is used in the preparation of Reactant Va, and because of reports of the possible carcinogenicity of auramine (named bis(dimethylaminophenyl) methylenimine) and the lack of such carcinogenicity of its diethylamino analog, Reactant Vb is preferred for use herein. This preferred ink, a combination of Reactants I and Vb in the solvent vehicle specified above, yields instant black on oil-soluble, acid-reacting phenolic polymeric material either alone or in combination with kaolin.

EXAMPLES OF A THREE-COMPONENT INK

Example A

Another specific example of a novel ink, this one comprising three color-generating components, consists of:

Component: Parts by weight
Basic Reactant I ———— 1.2
Basic Reactant IIIb ———— 1.2
Basic Reactant IVb ———— 4.8
2:1 mixture of chlorinated biphenyl and saturated hydrocarbon ———— 112.8

Example B

A different ink analogous to Example A includes:

Component: Parts by weight
Basic Reactant I ———— 1.2
Basic Reactant IIIc ———— 1.2
Basic Reactant IIb ———— 4.8
2:1 parts, by weight, of chlorinated biphenyl and saturated hydrocarbon ———— 112.8

Example C

A third example of an ink analogous to that of Example A comprises:

Component: Parts by weight
Basic Reactant I ———— 1.5
Basic Reactant IIb ———— 6.0
Basic Reactant IIIb ———— 1.0
Basic Reactant IV ———— 1.25
2:1 mixture of chlorinated biphenyl and saturated hydrocarbon ———— 90.25

Note that the application of the ink of this example to one of the previously given sheets coated with acidic co-reactant materials will give an apparent instant black color due to the reaction of Basic Reactants I, IIb, and IIIb with acidic material. The slow-developing blue color furnished by the reaction of Basic Reactant IV will later fortify the black print by supplementing the blue color instantly developed by Basic Reactant I, which tends to fade slowly in sunlight, particularly when developed against acidic mineral particles in the absence of oil-soluble acid-reacting phenolic polymeric material.
EXAMPLE OF THE ENCAPSULATION OF THE NOVEL INK

A novel ink comprising 1.5% of Basic Reactant I, 1.0%, by weight, of Basic Reactant III, and 4%, by weight, of Basic Reactant II, was collectively dissolved in chlorinated biphenyl of 48% chlorine content. 95 milliliters of the foregoing ink was emulsified into 68.0 grams of an 11%, by weight, solution of pigskin gelatin in water and an additional quantity of water having a weight of 37.3 grams. The foregoing emulsion, which had a pH of 9.0 at a temperature of 55 degrees centigrade, was stirred for ten minutes before being added to a solution containing 45.5 grams of an 11%, by weight, solution of gum arabic in water, 6.0 grams of a 5% solution of polyvinylmethyl maleic anhydride copolymer in water, and an additional quantity of 326.0 grams of water, to form a coacervable mixture. To the coacervable mixture, which had a pH of 9.0 or above, was added 6.75 milliliters of a 14%, by weight, aqueous solution of acetic acid in drop-sized increments with continuous agitation until a pH of approximately 6.0 was reached. Droplets of the internal phase of ink so produced had deposited thereon a liquid capillary wall consisting of a complex of gelatin, gum arabic, and polyvinylmethyl maleic anhydride copolymer, in a dense state, said deposit of material around the oil droplets having been caused by coacervate forces. When the deposition of polymeric material was completed, the capsules thus formed were solidified by being chilled to a temperature of 10 degrees centigrade while being continuously agitated. When the capsules were thus chilled, and when their walls were thus solidified, there was added 3.75 milliliters of a 25%, by weight, aqueous solution of glutaraldehyde. The effect of the glutaraldehyde upon the walls of polymer materials was to harden and insolubilize them. After one hour, 2.5 milliliters of a 20% aqueous solution of sodium carbonate was added to buffer the mixture, and, after an additional hour, an additional quantity of 7.0 milliliters of a 5%, by weight, aqueous solution of polyvinylmethyl maleic anhydride copolymer was added to prevent agglomeration of the capsules. The pH was then slowly adjusted to 10.2 by the dropwise addition of sodium hydroxide. The capsules could then be treated as solids dispersed in a residual aqueous medium, or they could be dried and treated as minute solid units. The drying may be accomplished in any manner desired to remove the water, including: centrifugation, filtration, centrifugation, or subjecting to heat or cold drying environments. It is desirable to eliminate from the capsules any left-over materials used in the formation thereof, such as may be effected by filtering and washing processes common in the art. Thus, a dispersion of finished capsules may be filtered repeatedly and washed with water.

The cleaned capsules can be redispersed in any liquid in which it is desired to use them.

PREPARATION OF BASIC REACTANT IInd

18.2 grams of 3-diethylaminophenol, 14.8 grams of phthalic anhydride, and 150 milliliters of toluene were heated to boiling and filtered. The filtrate thus obtained was refluxed for three hours and then stirred, whereupon precipitation occurred. The reaction mixture was again filtered, and the precipitate was washed with hot toluene. 2.1 grams of ketocacid prepared, 1.4 grams of 4-chloro-metacresol, and 40 milliliters of an aqueous 80% solution of sulfuric acid were stirred at a temperature of 95 degrees centigrade and then maintained at that temperature for three hours. The reaction mixture was then poured into 200 milliliters of water, made alkaline by the addition of ammonium hydroxide, and stirred for thirty minutes. A precipitate of 2-chloro-6-diethylaminio-3-methyl-spiro (9-H-xanthene-9,1'-phthalide) was stirred with 2 N ammonium hydroxide for three hours, washed with water, and dried. The product had a weight of 2.7 grams. When coated on a sheet of paper and contacted with clay, the product turned orange; when contacted with a mixture of kaolin and phenolic resin, the product appeared vermilion.

PREPARATION OF BASIC REACTANT III

18.2 grams of 3-diethylaminophenol, 14.8 grams of phthalic anhydride, and 150 milliliters of toluene were heated to boiling and thereafter filtered. A filtrate thus obtained was refluxed for three hours and then stirred, whereupon precipitation occurred. The reaction mixture was refiltered, and the precipitate obtained was washed with hot toluene.

2.1 grams of the precipitate, 1.4 grams of β-naphthol, and 40 milliliters of an aqueous 80% solution of sulfuric acid were heated to 105 degrees centigrade and were allowed to cool and to stand for sixteen hours. The reaction mixture thereafter was poured into 400 milliliters of water and treated with ammonium hydroxide until a pH of about 4.0 was indicated. A precipitate was formed, separated from supernatant liquid, washed with water, and suspended in 300 milliliters of benzene. The suspension was shaken with 200 milliliters of 5 N ammonium hydroxide repeatedly.

The compound 9-diethylaminospiro 1,2-H-benzo[α] xanthene-1,1′-phthalide) was further purified by conventional means.

SELECTIVE USE OF DISCLOSED COMPONENTS

Generally speaking, those chromogenic compounds which are used collectively together in the ink of this invention may be commonly identified by their reaction color.

These chromogenic compounds will be listed by their before-given identifying Roman numeral groups in conjunction with eligible acid material together with the apparent yielded reactant color if used alone on each reactant (acid) separately. Benzoyl leuco mephenine blue (of Reactant Group IV) is used to produce late-appearing blue where permanent blue is needed to reinforce the temporary blue.

COLORLESS COLOR REACTANTS

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
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<tr>
<td>Kioiiln</td>
<td>None</td>
<td>Yellow</td>
<td>Red</td>
<td>Blue</td>
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</table>

It will be understood that "black" is developed by the collective appearance of blue, yellow, and red colors or the equivalent appearance of blue and orange colors. The effect on the eye or other sensing means is a mixture of light-absorbing colors which does not depend on the physiology of the eye, as is the case with the black system, where the pointillistic effect of small closely-spaced dots of the three colors is used, as disclosed in copending United States patent application Ser. No. 665,228, filed Aug. 25, 1967, in the name of Paul S. Phillips, Jr., inventor.

From the chart, a number of potentially black inks may be assembled for use with particular acid sensitizing material to produce a desired ink.

What is claimed is:

1. A marking liquid composition comprising an organic solution of...
(a) one part by weight of a member of the group consisting of crystal violet lactone and benzoyl leuco methylene blue and
(b) about one part by weight of a 4,4'-bis(di-lower-alkylamino) benzophenone phenylimine.
2. The marking liquid composition of claim 1 wherein crystal violet lactone is used.
3. The liquid ink composition of claim 1 wherein 4,4'-bis(diethylamino)benzophenone phenylimine is used.
4. A marking liquid composition comprising an organic oil solution of
(a) one part by weight of a member of the group consisting of crystal violet lactone and benzoyl leuco methylene blue;
(b) about one part by weight of a member of the group consisting of
(1) 3,3-bis(dimethylindol-3-yl) phthalide,
(2) 3 - (1-ethyl-2-methylindol-3-yl)-3-(2-methylindol-3-yl) phthalide,
(3) 2-chloro-6-diethylamino-3-methyl-spiro[9-H-xanthene-9,1'-phthalide], and
(4) 9-diethylaminospiro[1,2 - H - benzoz(a)-xanthene-12,1'-phthalide]; and
(c) about four parts by weight of a 4,4'-bis(di-lower-alkylamino) benzophenone.
5. The marking liquid composition of claim 4 wherein crystal violet lactone is used.
6. The marking liquid composition of claim 4 the 4,4'-bis(di-lower-alkylamino) benzophenone is 4,4'-bis(diethylamino) benzophenone.

References Cited
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PHILIP E. ANDERSON, Primary Examiner
J. B. EVANS, Assistant Examiner
U.S. Cl. X.R.
106—22, 23, 32; 260—37; 117—1.7, 362; 106—14.5
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Inventor(s) PAUL S. PHILLIPS, JR.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 14, "comyonsents" should be --components--; line 20, "use invention" should be --use in this invention--; line 21, "acid-reaction" should be --acid-reacting--. Column 5, line 33, "effective" should be --effect--. Column 7, line 15, "to the coatings" should be --to coatings--. Column 8, line 7, "Reactants" should be --Reactants--. Column 9, line 32, "where" should be --were--. Column 10, line 34, "9-diethylaminospiro 1,2" should be --9-diethylaminospiro[1,2 --; line 35, "xanthene-1,1'" should be --xanthene-12,1' --. Claim 6, line 1, after "claim 4" and before "the", insert --wherein--.

SIGNED AND
SEAL

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents

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