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PRINTING FLUID CONTAINING A RED DYE AND CRYSTAL VIOLET LACTONE

Barrett K. Green, Dayton, Ohio, assignor to The National Cash Register Company, Dayton, Ohio, a corporation of Maryland

No Drawing. Continuation of abandoned application Serial No. 209,981, February 8, 1951. This application May 28, 1952, Serial No. 290,555

1 Claim. (Cl. 106—22)

This invention relates to a liquid printing fluid including a colored material and a color-forming reactant, for use on sensitized and unsensitized record material. The liquid has an intrinsic color which is color-stable upon exposure to light and air and is also color-stable on the sensitized and on the unsensitized record materials. The color-forming reactant is stable in its unreacted condition upon exposure to light and air and on the unsensitized record material but changes, without visually perceptible delay, to a distinctive color when applied to sensitized record material, said distinctive color being stable on exposure to light and air. The color-reactant preferably is substantially colorless so that marks made with the fluid on unsensitized record material are the color of the colored material alone whereas marks made with the fluid on sensitized record material are a distinctive blend of the colored material and of the color assumed by the color reactant on the sensitized record material. Although the preferred color reactants are normally colorless some may have a slight color in unreacted condition which changes to a more distinctive color when reaction occurs.

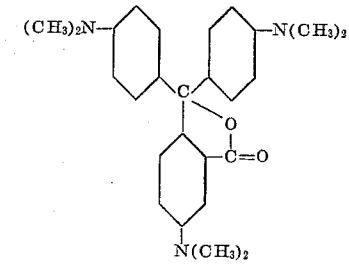
This is a continuation of my application Serial No. 209,981, filed February 8, 1951, which was, in turn, a continuation of my applications Serial No. 60,404, filed November 16, 1948, and Serial No. 60,642, filed November 18, 1948. All of these applications are now abandoned.

In general, it may be stated, the printing fluid includes a colored material which when applied to the record material makes a mark thereon by its own intrinsic color, and a color-reactant material which, without visually perceptible delay, assumes a distinctive color only when applied to sensitized record material by reason of a color-forming reaction occurring there. Thus, on sensitized record material the fluid produces two colors which are so chosen as to blend to make a resultant color distinctive from that made on unsensitized record material.

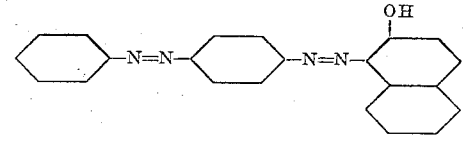
The preferred color-forming reaction employed is of the, so-called, adsorption type in which an inorganic material causes a color change in an organic material when in adsorption contact therewith, without the presence of an ionizing medium being required, although other color-forming reactions may be used instead. Of the preferred reactant materials employed, the organic material is an electron donor aromatic compound having a double bond system which is convertible to a more highly polarized conjugated form upon taking part in an electron acceptor-donor solid surface chemical reaction, giving it a distinctive color, and the inorganic material is one that is an acid relative to the organic material so

as to be an electron acceptor when in adsorption contact therewith. The printing fluid is applied to the record material by any kind of applicator, and the inorganic material is applied to the record material in fine particle form to furnish a large adsorption reactant surface.

The fluid is useful for making debit and credit records on paper coated in the sensitized zones with finely divided attapulgite, known also as Attapulgus clay. The attapulgite is most readily applied to the paper as a thin coating in a binder material. This attapulgite acts as an adsorbent for an adsorbate color-reactant material carried in the fluid and causes color change, without perceptible delay, in any such color-reactant adsorbed as a result of a transfer of it thereto at points of a printing impression. The preferred color reactant is crystal violet lactone, which is 3,3 bis(p-dimethylaminophenyl) 6-dimethylamino phthalide, having the structure



This compound may be made by a process disclosed in the United States Letters Patent Re. 23,024, which issued on the application of Clyde S. Adams. It is a solid, normally colorless or white in small particle form. In order to give it fluidity it may be dissolved in inert oily substances, such as chlorinated diphenyl with a chlorine content of about 48 percent. This crystal violet lactone carried by the fluid vehicle will be adsorbed on contact with the attapulgite producing a dark blue color, such contact being made wherever a printing impression is made with the printing fluid on a sensitized area. The preferred colored material is of a transparent red color which blends with the dark blue to produce a dark purplish-black mark on the sensitized record material. On unsensitized record material the red color of the colored material is unaffected. Such red colored material may be the red Sudan III dye, which is



and it may be dissolved in the same chlorinated diphenyl used for the crystal violet lactone.

Any colored material and fluid vehicle may be considered an equivalent as long as it will not cause a color reaction in the color-forming reactant and as long as its intrinsic color will blend with the color formed by the color reactant, on reaction, to produce a distinctive color, differing from that of the colored material and unreacted color-forming reactant alone.

The color-forming sensitizing reactant substances best suited for the record material of this invention are clay-like materials like the attapulgite mentioned, as they are white and inert to a large degree.

Therefore, it is an object of this invention to provide a printing fluid containing a colored material and a color-forming reactant, the latter intended to react with sensitized record material which causes a color without visually perceptible delay, which color blends with the intrinsic color of the colored material to form a new distinctive color different than that produced by the colored material and unreacted color-forming reactant alone on unsensitized record material.

It is further an object of the invention to provide such a printing fluid in which the color-forming reactant does not interfere with the intrinsic color of the colored material held in it.

It is a further object of the invention to provide such a printing fluid which makes marks the color of the colored material unless the impression is made onto especially sensitized zones of zonally sensitized record material whereupon a mark of another color is produced.

With the above objects in view, the essential elements of the invention are set forth in the claim, and a preferred form and other embodiments of it are hereinafter described.

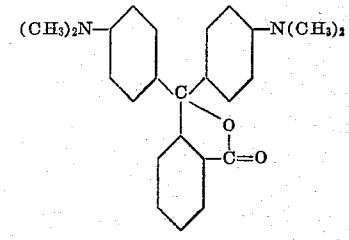
The sensitized paper is coated according to a process described in my application for United States Letters Patent, Serial No. 41,756, filed July 31, 1948, in conjunction with Robert W. Sandberg, which issued as United States Patent No. 2,548,366, on April 10, 1951. As disclosed in that application, the most satisfactory adsorbent material with which to sensitize the paper for the preferred type of color-reaction, that being the adsorption color reaction phenomena described among other places in my said application which issued as United States Letters Patent No. 2,548,366, is attapulgite. Other good color-reacant adsorbents, which are considered equivalents of attapulgite, and which may be substituted for it, are sodium aluminum zeolite material or such in which the base exchange cations are replaced by cations of nickel, copper, iron, zinc, mercury, barium, lead, cadmium or potassium; Halloysite; magnesium trisilicate; and kaolin. In making the sensitive coating with attapulgite, 20 percent, by weight, of paper coating starch in water is cooked at 200° Fahrenheit for 15 minutes and cooled to room temperature. Separately 1 part, by weight, of attapulgite is dispersed in three parts, by weight, of water. Four parts, by weight, of the attapulgite dispersion is mixed with one part, by weight, of the starch solution. The resultant mixture is applied to the sheet or to the zone or zones in the sheet which are to be sensitized, at room temperature, and dried. The coating should be about .0005 of an inch in thickness, but may be varied considerably in that characteristic. The sensitized zones are substantially white. Other coating binders may be used in place of the starch as long as the binders do not physically insulate the adsorbent particles. Attapulgite is preferred because of its needle-like particle formation which provides a brush-heap coating structure which prevents any complete physical masking of the adsorbent surfaces by the binder starch material. Casein and butadiene-styrene copolymer latex material may be used in place of starch as fully set out in the patent application last referred to. The adsorbent materials named as substitutes for attapulgite may be used in place of attapulgite in the same proportions.

The printing fluid, in addition to the colored material, contains, in the preferred form, the color reactant crystal violet lactone, of which mention was made, in a suitable fluid carrier. On contact with any of the attapulgite the crystal violet lactone, which is naturally a whitish solid material and colorless in a solvent such as chlorinated diphenyl, which is a suitable vehicle for it, turns to a dark blue color, without visually perceptible delay, blending with the colored material, but on the unsensitized portion of the record material it does not react and has no apparent color, and hence, the colored material contained in the printing fluid colors the impression with the

unmodified intrinsic color thereof. The dually charged printing fluid of the preferred form, is composed of three parts, by weight of Sudan III dye, 3 parts, by weight of crystal violet lactone and 94 parts, by weight, of chlorinated diphenyl of 48 percent chlorine content which acts as a fluid solvent.

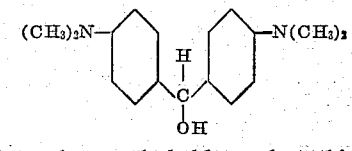
Among other adsorbate color reactants which, without visually perceptible delay will react on the sensitized paper to produce a color, and which may be used in place of crystal violet lactone and in the same amount are:

(1) Malachite green lactone which is 3,3 bis(p-dimethylaminophenyl) phthalide, having the structure



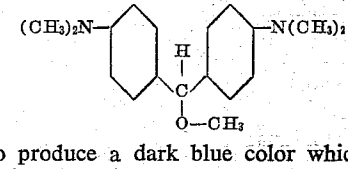
reacting to produce a green color and blending with red to produce a dark color;

(2) Michler's hydrol, which is 3,3 bis(p-dimethylaminophenyl) methanol, having the structure



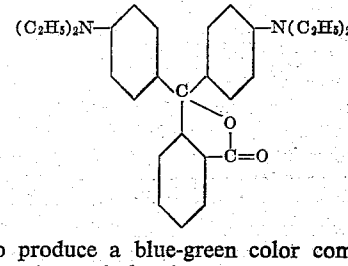
reacting to produce a dark blue color which combines with red to form a dark purple;

(3) Methyl ether of Michler's hydrol which is 3,3 bis-(p-dimethylaminophenyl) methoxy-methane, having the structure



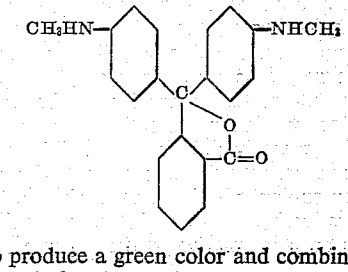
reacting to produce a dark blue color which combines with red to form a dark puple;

(4) The compound 3,3 bis(p-dimethylaminophenyl) phthalide, having the structure



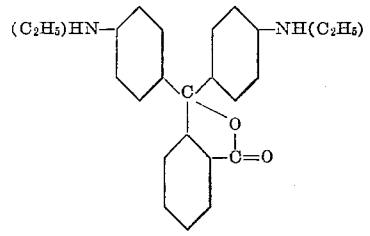
reacting to produce a blue-green color combining with the red to produce a dark color;

(5) The compound 3,3 bis(p-methylaminophenyl) phthalide, having the structure



reacting to produce a green color and combining with red to produce a dark color; and

(6) The compound 3,3 bis(p-ethylaminophenyl) phthalide, having the structure



reacting to produce a bright blue color and combining with red to produce a dark purple color; and many others.

Where the printing fluid is to be used in connection with an unabsorbent carrier, or one relatively unabsorbent, such as a paper ribbon or a paper manifold sheet, the active side may be coated with a dryable emulsion the internal phase of which is a fluid including an ink and a color-forming reactant, the internal phase remaining as minute fluid droplets in the dried continuous phase which forms a film rupturable on impact of a printing impression to release, locally, a number of the droplets which are transferred to the sheet to be printed, be it sensitized or unsensitized. An emulsion produced coating such as described, but having only the colorless color-forming reactant therein is described in my before-mentioned application for United States Letters Patent, Serial No. 41,756, filed on July 31, 1948, which issued as United States Patent No. 2,548,366.

Such a fluid carrier may be made in the following manner. The web, be it a ribbon of paper or a sheet of paper, is given a coating of emulsion prepared in the following manner: One part, by weight, of animal gelatin, having an iso-electric point of pH 8 and a jelly strength of 275 grams, as measured by the Bloom gelometer, is dissolved in 3 parts, by weight, of water heated to 150° Fahrenheit. Into four parts, by weight, of the gelatin solution there is dispersed, or emulsified, three parts, by weight, of a solution of 3 parts, by weight, of Sudan III dye and 3 parts, by weight, of crystal violet lactone, in 94 parts, by weight, of chlorinate diphenyl having a chlorine content of 48%. The latter solution is heated to the temperature of the gelatin solution before being added thereto. The emulsion is applied, at 150° Fahrenheit to the paper and air dried. The droplets in the dried film are 1 to 5 microns in diameter and spaced on the average a distance of ½ micron. A coating .001 of an inch thick is preferred. The droplets when transferred to unsensitized material are of a red color, but when transferred to material sensitized with attapulgite or similar color-forming reactants are of a dark purplish color.

All of the color reactions occur upon contact with the sensitized paper without visually perceptible delay.

The novel printing fluid, because it contains no pigmented material, may be used to impregnate porous type members such as are disclosed in United States Patent Re. 22,119 to Lohrey and in United States Patent No. 2,349,613 to Chollar.

I consider as other equivalents of the color-reactant crystal violet lactone, in addition to those specifically recited, any color-reactant compound that may be carried in a liquid vehicle, which compound is color-stable in light or air in the uncolored or unreacted form in which it is present in the unapplied printing fluid, which is color-stable on unsensitized record material in the presence of light or air, but which will turn to a colored form on contact with record material sensitized as specified, without visually perceptible delay, and remains color-stable in the colored form in the presence of light or air.

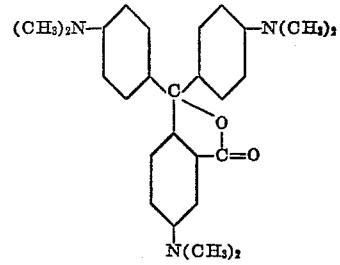
I do not consider as equivalents of crystal violet lactone, compounds of the vat dye class disclosed in the before-mentioned United States Patent No. 2,068,204, which issued on the application of Smith, because exposure of those vat dye compounds in the so-called leuco or "unoxidized" state to light and air results in their turning to the same colored oxidized form whether they are on unsensitized record material or on sensitized record material. Moreover, the compounds mentioned in the aforesaid Smith patent will not form color on any of the oxidizing materials disclosed in said Smith patent without visually perceptible delay even in the presence of strong sunlight, the oxidization to the colored form taking at least several hours.

I consider as equivalents of the color-reactant attapulgite, in addition to those compounds and minerals specifically recited, solid particulate chemical compounds and minerals which, without visually perceptible delay, cause a color change in the color reactant crystal violet lactone or its equivalents in the printing fluid, on contact therewith, which are substantially inert as to record material, and substantially white or colorless.

It will be appreciated that the examples of materials or particular embodiments of the invention, given, in no way limit the invention in its broader aspects, as the invention may be carried out with combinations of many kinds of base materials, inks, color-forming reactants and sensitizing materials.

What is claimed is:

A liquid printing fluid containing a red dye and 3,3 bis(p-dimethylaminophenyl) 6-dimethylamino phthalide, having the structure



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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,850,395 September 2, 1958

Barrett K. Green

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 48, for "bis(p-dimethylaminophenyl)" read -- bis(p-diethylaminophenyl) --; column 5, line 43, for "chlorinate" read -- chlorinated --.

Signed and sealed this 2nd day of December 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents