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COLORLESS PRINTING FLUID

David W. Steinhardt, Dayton, Ohio, assignor to The National Cash Register Company, Dayton, Ohio, a corporation of Maryland

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1 Claim. (Cl. 106—22)

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This invention relates to a printing fluid comprising a fluid vehicle containing two color-reactant compounds forming a substantially colorless solution which will produce a mark of one distinctive color hue on record material sensitized with a material which turns one of the fluid-held reactant compounds to its colored form on contact therewith, and which will produce a mark of another distinctive color hue on record material sensitized with another material which turns both of the fluid-held reactant compounds to their colored form on contact therewith. The two colors formed when both of the printing fluid-held color-reactants are turned to their colored form blend to produce a composite color distinctive from that color hue which is distinctive of the colored form of either reactant.

This fluid is adapted to be used either with different pieces of print-receiving or writing-receiving record material, each distinctively sensitized, or to a single piece of print-receiving or writing-receiving record material sensitized in one or more areas with one of the record material sensitizers and sensitized in one or more other areas with the other record material sensitizer.

The printing fluid is well adapted for use in preparing account forms requiring columns of debit and credit entries, and the columns can be individually sensitized with one or the other of the two record-material sensitizers, producing records of one color in one column and records of another color in the other column, using but the single printing fluid, the color produced being determined by the area to which the printing fluid is applied.

The printing fluid is adapted for use with any of the common printing fluid applicators such as printing type members, type ribbons, pens, or brushes. The printing fluid containing the two reactants can also be used in making record material having a transfer coating of wax or hydrophilic colloid films containing droplets or inclusions of printing fluid, such record material being substantially colorless insofar as the transfer film itself is concerned. Reference is made to United States Letters Patent No. 2,548,366, which issued on the application of Barrett K. Green and Robert W. Sandberg, for the type of transfer coating which is composed of a hydrophilic colloid film containing droplets of printing fluid. Reference is made to the application of Chester Davis and Ned Thacker, Serial No. 234,161, filed June 28, 1951, for record material having a transfer coating comprising a wax vehicle in which is incorporated a colorless oily printing fluid of the type

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described in this disclosure except that such fluid contained only one adsorption color reactant producing a single color hue.

As the invention is later described, it will be apparent that on unsensitized paper record material neither of the color-reactants assume the colored form, and that on paper sensitized with one of the record material sensitizers the fluid will make the color of the associated one of the color-reactants in the reacted form whereas on paper sensitized with the other color-reactant the printing fluid will make the composite color, that is to say—the color produced by blending the colors of both color-reactants in the colored form.

The colorless color-reactants deemed preferable are those aromatic organic compounds having a double bond structure which is converted to a more highly polarized conjugated form when adsorbed on acid-like inorganic solid material, such as attapulgite and calcium silicates, accompanied by the appearance of color.

Therefore, it is an object of this invention to provide a substantially colorless printing fluid which is adapted for use on sensitized record material of two kinds, the printing fluid making a mark of one distinctive hue on paper sensitized with one sensitizing material and making a mark of another distinctive hue on paper sensitized with another sensitizing material.

Another object of the invention is to provide a printing fluid in which the color-reactants assume their colored form by adsorption contact with fine particles of inorganic solid material with which the record material is sensitized, such inorganic material having acid-like properties and hence, acting as an electron-acceptor with respect to the printing fluid-held reactant with which it is associated, changing it from the colorless form to a colored form.

With these and incidental objects in view the invention includes certain novel features and combinations of ingredients, a preferred form or embodiment of which is hereinafter described.

The colors produced by the printing fluid of this disclosure are immediately produced and are stable to ordinary environmental conditions.

In the instance of each of the printing fluid-held color-forming reactants which will be disclosed the reaction is of the so-called adsorption type in which an inorganic material with which the paper is sensitized causes a color change in the fluid-held organic reactant when in adsorption contact therewith, without the presence of an ionizing medium being required. Of the color-reactant materials used in the print-

ing fluid are electron donor aromatic compounds 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 such reactant its distinctive color hue, and the inorganic paper sensitizing material is one that is an acid relative to the organic reactant with which it is associated, so as to be an electron acceptor when in adsorption contact therewith.

The two fluid-held color-reactants are chosen so that one requires a record material sensitizer of stronger acid characteristics than the other to cause it to change to the colored form. The record material sensitizers are chosen accordingly for their acid strength. Whereas the inorganic material with which one piece of record material or one area of record material is sensitized may act as an electron acceptor for both organic color-reactants held by the fluid, the inorganic material with which the other piece of record material or other area of the same sheet is sensitized, acts as an electron-acceptor only toward one of the organic reactants in the printing fluid. It is for this reason that the two different colors of printing can be obtained with the same printing fluid.

The preferred printing fluid has a non-evaporating vehicle consisting of chlorinated diphenyl having a chlorine content of about 48%. This vehicle acts as a solvent for the preferred organic color reactants which are dissolved therein in small quantities, as the color intensity produced by these organic reactants in the colored form is of high order. Amounts of the color reactants in the fluid may vary from 1% to 4%, by weight, of each, although 1% of each is sufficient to produce strong color. The color reactant preferred for color reaction on both types of sensitized record material is malachite green lactone which is 3,3 bis(p-dimethylaminophenyl) phthalide, which changes from its normal colorless form to a blue-green on adsorption contact with the inorganic material with which the papers are sensitized. This material normally is a colorless crystalline solid, but it may be dissolved in the specified fluid vehicle. The other organic reactant held by the fluid, and selected for its reaction only with a stronger acid-like inorganic compound may be N-p-nitrophenyl rhodamine B lactam, which is xanthene-9, o-benzoic acid, 3,6-bis-diethylamino-9-p-nitroanilinolactam. This compound, also normally a colorless crystalline solid, is dissolved in the fluid vehicle and produces on adsorption contact with the one record material sensitizing inorganic substance a red color, which combines with the blue-green color produced by the malachite-green lactone to form a purplish lavender color. Thus, it will be understood that the two colors produced by the printing fluid are distinctive in hue, one being in the blue-green region of the spectrum and the other being in the purple-lavender region of the spectrum. The preferred record material sensitizing ingredient for causing the appearance of color in both of the reactant compounds is attapulgus clay which may be applied to the paper by coating processes normal to the paper coating industry in which the clay is adhered to the paper by adhesives, such as paper-coating starch and synthetic latex materials.

The attapulgus clay may also be incorporated with paper pulp before it enters the paper-making machine and, thus the paper so made from it will be sensitized through and through, so both sides will produce color when the printing fluid is applied thereto. Other methods of coating the paper are by rolling the coating on one or both sides, or by spraying the material on at the wet end of the sheet on a paper mill. The inorganic record material sensitizing agent which causes the formation of color in only one of the organic color-reactants held by the fluid is calcium silicate material made by reaction between a water-soluble calcium salt and sodium silicate, such as described in my co-pending application for United States Letters Patent Serial No. 252,420, filed on the same day this application was filed. This will not cause the lactam compound specified to change to the colored form, but will cause the malachite-green lactone to change to the colored form.

The fluid vehicle may be an evaporable vehicle, if desired, aromatic solvents such as toluene being used in the same proportions, as the chlorinated diphenyl.

The preferred color-reactants are not to be deemed the only ones useful. For instance, 3,3 bis (p-ethylaminophenyl) phthalide, producing, a light blue color, may be used in place of malachite green lactone.

While the form of the invention herein described is admirably adapted to fulfill the objects primarily stated, it is to be understood that it is not intended to confine the invention to the one form or embodiment herein disclosed, for it is susceptible of embodiment in various other forms.

What is claimed is:

A substantially colorless printing fluid which will make marks of one color on record sheet sensitized with attapulgite and marks of another color on record material sensitized with calcium silicate, said fluid consisting of an oily chlorinated diphenyl in which have been dissolved xanthene-9, o-benzoic acid, 3,6-bis-diethylamino-9-p-nitroanilino-lactam and a compound selected from the group consisting of 3,3 bis(p-dimethylaminophenyl(phthalide and 3,3 bis(p-diethylaminophenyl) phthalide.

DAVID W. STEINHARDT.

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