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2,550,470

PRESSURE SENSITIVE RECORD MATERIAL

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2 Claims. (Cl. 282—28)

1

This invention relates to pressure-sensitive record material, and more particularly pertains to such material having minute particles of two kinds of substances which are color reactive on contact, one of the substances being in liquid form and the other being in solid form, the particles of the two substances being arranged in proximity in profuse numbers but insulated from contact by material rupturable when pressure is applied, which pressure acts to bring the two kinds of substances together at the points of rupture to produce a distinctively colored localized mark.

This is a division of United States Patent application No. 38,547, filed July 13, 1948, by applicants herein.

The record material of this invention although adapted for response to stylus pressures, is particularly adapted for response to pressures applied to impact printing operations such as by the striking or pressing of type thereagainst and in that respect is an improvement over the record material of Barrett K. Green's United States Patent 2,505,470, for Pressure Sensitive Record Material, which was granted April 25, 1950.

The record material disclosed therein required the bringing together, by pressure, of two kinds of solid particles embedded in a rupturable solid insulating film. The low mobility of such solid particles rendered that record material more sensitive to pressures caused by drawing a stylus thereover than to pressures derived from the impact of type. This novel record material also is an improvement over that record material disclosed in United States Letter Patent No. 2,299,693, patented on October 20, 1942, on the application of Barrett K. Green. That patent discloses pressure-sensitive record material, especially adapted for impact work, such material including a rupturable insulating medium, in which are interspersed liquid droplets of two kinds which react on contact to form color. The liquid droplets included solid color-forming materials dissolved in an ionizing medium, glycerine, which reacted to produce color on contact by interchange of ions. Any liquid ionizing medium available for use in such system is hygroscopic making the record material unduly sensitive to moisture.

The present invention provides a record material with exceptional response to impact pressures and one having remarkable stability as no ionizing liquid is required. The liquid used to dissolve the active color ingredient in the liquid reactant substance is a non-ionizing inert oily

2

type of material which is non-hygroscopic and is used solely to dissolve the active ingredient and to obtain easier release and greater mobility of the droplets when the supporting film is ruptured. Because of the mobility of the released liquid droplets at points of rupture of the insulating medium, the new record material is highly sensitive both to drawing and to impact pressures yet it is resistant to destructive influences encountered in ordinary environment and normal handling operations. Thus, the new record material combines the best characteristics of known pressure responsive record materials by providing a novel liquid-solid reactant structure.

The principal object of the invention is to provide a pressure-sensitive record material on which a mark of distinctive color may be produced by the mere application of localized pressure, said material including color-forming substances of two kinds, one being solid and the other being liquid, the two substances normally being held insulated from reaction contact by a rupturable insulating medium until marking pressures rupture the insulating medium at points of pressure to bring about local contact of the two substances to produce a mark.

Another object of the invention is to provide a record material in which one of the color reactant substances is dissolved in a non-ionizing oily liquid which may be dispersed as droplets in a rupturable solid insulating film so as to be readily available and mobile locally to make contact with the other solid reactant material when released by rupture of the film.

Another object of the invention is to provide such a record material which is highly sensitive to impact pressures such as are met with in typewriter or letter press work and for this effect the two color reactants are arranged in separate overlying layers on a web so that marking pressures vertically applied to the said layers will cause penetration of the color reactant substances of one layer into that of the other layer.

Further objects and objects relating to details and economies of production, will definitely appear from the detailed description to follow. The objects of this invention have been attained by the several embodiments thereof described in detail in the following specification.. The invention is clearly defined and pointed out in the appended claims.

In the preferred form of this invention the liquid droplets of color reactant are dispersed in a film-forming substance which is applied as a

coating to a paper web and dried thereon leaving the liquid droplets entrapped therein. The solid color reactant particles, acting as adsorbents, are likewise dispersed in a film-forming substance which is applied as a second overlying coating. Both films are rupturable to force the reactant substances together.

Of the reactant materials employed, the liquid droplets contain an organic substance which is an electron donor aromatic compound having a double bond system which is converted to a more highly polarized conjugated form upon taking part in an electron donor-acceptor adsorption chemical reaction, giving it a distinctive color, and the solid particles are of an inorganic substance which is an acid relative to the organic substance so as to be an electron acceptor when in adsorption contact therewith. The solid material is in fine particle form in order to furnish a large reactant surface per unit area of the record material, which enhances the depth of color produced in the record material.

The film-forming substances are derived from hydrophilic colloid materials that form pressure-rupturable films.

The adsorbate substance may include one or more kinds of reactant such as crystal violet lactone, which is 3,3 bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, and tetrachloro malachite green lactone mixed together and dissolved in the oily liquid.

The web used as a support may be paper or other material suitable as a record base. For instance, either cardboard, glass, metal or wood may be used if desired. The total thickness of the pressure-sensitive film need be no greater than from .001 to .002 of an inch so it may be supported on very thin paper stock. By placing a number of such thin-coated paper sheets in superimposed relation in a typewriter a number of printed copies of typewritten material may be made without the use of a typewriter ink ribbon or carbon manifold paper as is now the common practice.

As it is difficult, if not impossible, to show the exact structure of this coating by use of a drawing none accompanies this specification.

In the following examples, there will be described embodiments of this invention by which the objects of the invention have been successfully attained.

Example 1.—The following embodiment of this invention constitutes the best mode of applying the principles thereof as contemplated up to the present time and may be considered the preferred embodiment. It comprises a base web of paper, or the like, on one surface of which two coatings are applied, the first or undercoating being an insulating film in which are entrapped a profuse number of liquid droplets in which a color reactant substance is dissolved. These droplets are, on the average, of the order of from 1 to 5 microns in diameter and are spaced apart, on the average, a distance of the order of ½ micron. The preferred thickness of this first coating, when dry, is of the order of .001 of an inch.

The first coating is made by dissolving one part by weight of animal gelatin, having an isoelectric point of pH 8 and a jelly strength of 275 grams as measured by the Bloom gelometer, with three parts by weight of water heated to 150° Fahrenheit.

Into four parts by weight of the gelatine solution there is dispersed, or emulsified, three parts by weight of a solution of crystal violet lactone in chlorinated diphenyl.

This solution of crystal violet lactone, which is 3,3 bis(p-dimethylaminophenyl) - 6 - dimethylamino phthalide, in chlorinated diphenyl is made by dissolving three parts by weight of the crystal violet lactone in ninety-seven parts by weight of chlorinated diphenyl which has a chlorine content averaging 48 per cent by weight. This chlorinated diphenyl solution is heated to the temperature of the gelatin solution before it is added thereto and emulsified.

The emulsion is applied while still hot, or if allowed to cool after reheating to 150° F., and is dried either under normal atmospheric conditions or by artificial means such as a hot air blast or on a heated drying drum such as is commonly used in paper coating machines. It is considered that drying under normal atmospheric environment gives a somewhat better water resistance to the dried film or coating in which the chlorinated diphenyl solution droplets are entrapped.

The dried undercoating is next treated to drive the droplets out of the top surface layer and into the interior of the film so as, in effect, to form an impermeable surface skin thereon. This is accomplished by wetting the surface with water at room temperature, that is from 70°–80° Fahrenheit, which water has had added thereto 1 per cent by weight of formaldehyde and 0.1 per cent by weight of a wetting agent such as dioctyl ester of sodium sulfosuccinate. The wetting should be allowed to persist for several minutes and thereafter the film is dried in a low humidity atmosphere. The surface wetting may be accomplished by floating the coated paper on the water, coated face down, or by carrying it on a partially submerged drum with the coated surface facing outwardly. The formaldehyde may be omitted, if desired.

The second, or overcoating, then is applied to the dried undercoating. In making the second coating 20 per cent, 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 finely divided zeolite material, preferably of an average particle size of less than 10 microns is dispersed in three parts by weight of water by use of a ball mill or equivalent.

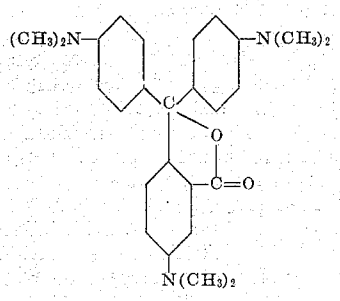
This zeolite material is selected from the group consisting of sodium aluminum silicate zeolite and such zeolite material in which the sodium base exchange cations have been replaced by cations of nickel, copper, iron, zinc, mercury, barium, lead, cadmium or potassium. Four parts, by weight, of the zeolite dispersion is mixed with one part, by weight, of the starch solution. The resultant mixture is applied, at room temperature, as an overcoating to the prepared paper having the gelatin coating dried thereon. This starch-zeolite overcoating is applied in any convenient manner, as by a paper coating machine. This overcoating when dry should have a thickness of the order of .0005 of an inch.

The thickness of the undercoating and the overcoating may be varied somewhat without interfering greatly with the sensitivity of the material, such variation range being of the order of 25 per cent in either direction.

This record material when finished has a substantially white appearance and produces a dark blue mark which sharply defines the area of pressure or impact.

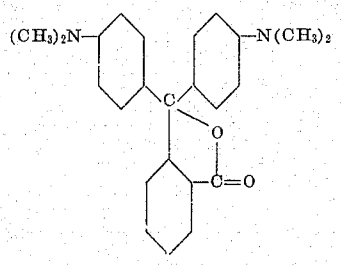
The impact of a marking instrument on the surface of this record material locally releases the oily droplets from the gelatin film and forces them into contact with the overlying zeolite particles. The porous aggregate structure of zeolite material prevents any substantial masking of the active surface areas of it by the starch binder, thus leaving the zeolite material available to adsorb the color reactant crystal violet lactone from the released oil. Therefore, in this coating system the zeolite solid particles are held in a non-masking or non-insulating binder whereas the oil-carried other reactant is protected as entrapped droplets in the gelatin insulating film.

The compound crystal violet lactone has the structure



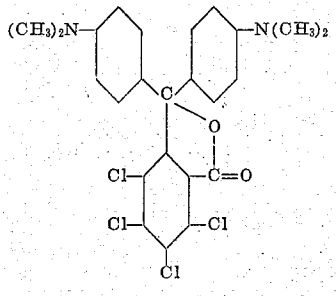
and the process of making it is described in United States Letters Patent No. 2,417,897, issued March 25, 1947, on the application of Clyde S. Adams filed June 16, 1945, which patent was reissued on August 17, 1948 under No. Re. 23,024.

Example 2.—Another embodiment of the invention is the use of malachite green lactone, that is to say 3,3 bis(p-dimethylaminophenyl) phthalide, having the structure



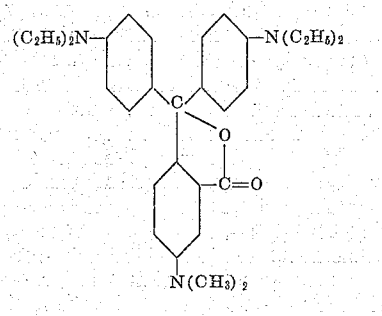
in place of the crystal violet lactone of Example 1 and in the same amount. This gives a substantially white record material producing a green mark when the pressure is applied. This green color is not as intense as the blue given by crystal violet lactone.

Example 3.—Another embodiment of the invention is the use of tetrachloro malachite green lactone, that is to say 3,3 bis(p-dimethylaminophenyl) 4,5,6,7 tetrachloro phthalide, having the structure



in the place of the crystal violet lactone of Example 1 and in the same amount. This gives a substantially white record material producing a green mark when pressure is applied.

Example 4.—Another embodiment of the invention is the use of 3,3 bis(p-diethylaminophenyl)-6-dimethylamino phthalide, having the structure



in place of the crystal violet lactone of Example 1 and in the same amount. This gives a substantially white record material producing a blue mark when pressure is applied.

In Examples 1 to 4, inclusive, there may be substituted for the starch a mixture of starch, casein, and a synthetic latex made of butadiene-styrene copolymer material. In such a binder when dried with the zeolite material therein, the amount of starch should be 7 per cent, the amount of casein should be 1 per cent, and the amount of latex should be 7 per cent all by weight with respect to the weight of the zeolite material. In making such a binder a starch solution is made as described in Example 1 and allowed to cool. Next one part of casein is dispersed in two parts of cold water, by weight, and allowed to swell for one-half hour, after which seven more parts of cold water and $\frac{1}{10}$ of a part of ammonium hydroxide of 25° Beaumé are added. This casein dispersion is heated on a water bath of 165° Fahrenheit for 15 minutes and then allowed to cool. The latex used contains 45 per cent of solids in water. The zeolite material to be used is dispersed in water as set out in Example 1 except the water contains 0.2% of sodium pyrophosphate. To 10 parts by weight of the dispersed adsorbent, eliminating the weight of the water, is added 3.5 parts by weight of the starch solution, 1.6 parts by weight of the latex, and 1 part by weight of the casein solution. This binder material is characterized by greater adhesion to the adjacent coating and by excellent properties as far as the access of the adsorbent material to the action of the liquid color reactant droplets is concerned.

The adsorbent material should be accessible to the liquid droplets containing the color reactant material to be adsorbed thereon and the action of the coating binder tends to mask the exterior surface available on such adsorbent particles. The porous structure of zeolites, contain interiorly active surfaces, not masked by the binder, which are left available for adsorbing the color reactant in the liquid droplets and, hence, this type of adsorbent is particularly suited for the novel structure which is the subject of this invention.

The methods and processes of making the pressure-sensitive record material as disclosed herein are disclosed and claimed in the co-pending application of Barrett K. Green and Robert W. Sandberg, Serial No. 38,548, filed July 13, 1948.

It is understood that the pressure-sensitive record material described herein is susceptible of considerable variations without departing from the spirit of the invention.

What is claimed is:

1. Pressure-sensitive record material including the combination of color-forming substances of two kinds, one kind being solid and the other kind being liquid, said liquid kind being held insulated from contact with the solid kind by being profusely dispersed in minute droplets in a solid rupturable film on the exterior of which is deposited a film bearing particles of the solid kind, the application of localized pressure to the record material rupturing the film at points of application and there bringing the color-forming substances together, whereby a distinctively colored mark is produced by mere application of localized pressure, the solid color-forming substance being selected from the group consisting of finely divided sodium aluminum silicate zeolite material and such material in which the sodium base exchange cations have been replaced by cations of nickel, copper, iron, zinc, mercury, barium, lead, cadmium and potassium, and said liquid color-forming substance being an organic electron donor aromatic compound having a double bond system which is converted to a more highly polarized conjugated form upon taking part in an electron donor-acceptor adsorption chemical reaction, giving it a distinctive color.

2. Pressure-sensitive record material including

the combination of a supporting web; a continuous rupturable solid insulating film applied thereto said film containing dispersed therethrough a profusion of minute liquid color-forming inclusions; and a coating on the outer surface of the insulating film, said coating containing a profuse number of solid color-forming particles which, when brought into contact with the liquid inclusions by application of localized pressure to the record material which ruptures the insulating film and coating, react with said liquid inclusions to form a distinctively colored mark at said points of localized pressure, the solid color-forming particles being selected from the group consisting of sodium aluminum silicate zeolite material and such material in which the sodium base exchange cations have been replaced by cations of nickel, copper, iron, zinc, mercury, barium, lead, cadmium and potassium, and said liquid color-forming substance being an organic electron donor aromatic compound having a double bond system which is converted to a more highly polarized conjugated form upon taking part in an electron donor-acceptor adsorption chemical reaction, giving it a distinctive color.

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No references cited.