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PRESSURE SENSITIVE RECORD MATERIAL

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No Drawing. Original application November 8, 1947, Serial No. 784,938. Divided and this application November 10, 1948, Serial No. 59,422

15 Claims. (Cl. 117—36)

1

This invention relates to improvements in pressure-sensitive record material. This application is a division of the pending application of Barrett K. Green, Serial No. 784,938, filed November 8, 1947, for Pressure-sensitive record material.

The principal object of this 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 and which is not subject to the disadvantages inherent in the pressure-sensitive record material disclosed in United States Letters Patent No. 2,299,693, patented October 20, 1942, on the application filed by Barrett K. Green on February 23, 1940. That patent discloses a pressure-sensitive record material including the combination of an insulating medium, a rupturable solid material such as gum dammar, having included therein interspersed droplets of a plurality of liquid reagents, which are chemically reactive to produce a distinctive color in the record material at the points of application of localized pressure thereto, such pressure rupturing the insulating medium to permit chemical reaction between the two liquid reagents. The two reagents disclosed in this patent are gallic acid and ferric ammonium sulphate, each dissolved in glycerine. These reagents are ionized by the glycerine, which constitutes an ionizing medium, and the chemical reaction proceeds by interchange of ions when the two solutions are allowed to mix, upon the rupture of the insulating medium. The reaction disclosed in that patent depends upon the presence of the reagents in an ionizing medium. However, any available ionizing medium is hygroscopic, with the result that the record material made in accordance with this patent is sensitive to an excess of moisture, and conditions of high humidity may cause the insulating medium to cease to be effective, with the result that the chemical reaction takes place without any application of localized pressure, and the record material is stained and discolored, so that it ceases to be useful.

As stated above, the principal object of the present invention is to provide a pressure-sensitive record material that is not subject to the defects and disadvantages of that disclosed in Patent No. 2,299,693, as indicated above.

Another object of the present invention is to provide a record material upon which a mark of

2

distinctive color may be produced, at the points of application of localized pressure thereto, by such mere application of localized pressure, and which will not become discolored or stained due to the effect of light, atmospheric conditions, or aging.

In short, it is the object of this invention to provide a pressure-sensitive record material in which the mark of distinctive color will be produced only at the points of application of localized pressure, and at no other points, and under no other conditions.

Another object of this invention is to provide a pressure-sensitive record material in which the mark of distinctive color is produced by the chemical reaction of color-forming reactants, in the absence of any liquid ionizing medium therefor.

A further object of this invention is to provide a pressure-sensitive record material in which a mark of distinctive color is produced by a reaction between solid particles of color-forming reactants.

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. This invention is clearly defined and pointed out in the appended claims.

In general, the present invention contemplates a pressure-sensitive record material comprising, in combination, a plurality of adsorption color-forming reactants, such reactants being so selected that they react, in the absence of a liquid ionizing medium for the reactants, to form a distinctive color when brought into adsorption contact with each other, and a solid insulating medium insulating said reactants from color-forming reaction contact with each other. Upon application of localized pressure to the record material, as by drawing a stylus across it, the insulating medium is ruptured at points of application of said localized pressure, and such rupture permits color-forming reaction contact between the reactants at such points, in the absence of any liquid ionizing medium for said reactants. The result is that a mark of distinctive color is produced by the mere application of localized pressure.

The 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 with it.

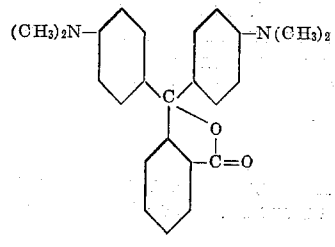
Of the reactant materials employed the organic material is an electron donor aromatic compound having a double bond system which is convertible to a more highly polarized conjugated form upon taking part in an electron acceptor-donor solid surface chemical reaction, giving it a distinctive color, and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

In this invention, both of the color-forming reactants, as well as the insulating medium, are in the solid state, and the color-forming reaction takes place upon mere contact of solid particles of the reactants. A pressure-sensitive record material may be provided in which the solid particles of a plurality of color-forming reactants are dispersed in a solid insulating medium, which insulates the particles from color-forming reaction contact with each other. The rupture of this solid insulating medium by the application of localized pressure permits the solid particles of color-forming reactants to react with each other, at the points of application of such pressure, to produce the mark of distinctive color. According to one form of this invention, solid particles of one of the color-forming reactants are carried by and dispersed in a solid insulating medium, to which a coating of solid particles of another color-forming reactant is applied. In this case, the application of localized pressure ruptures the solid insulating medium at the points of application of such pressure and brings about color-forming reaction contact between the solid particles of color-forming reactants at such points, thus producing the mark of distinctive color. Preferably, this pressure-sensitive record material includes a base web, such as a fibrous web of paper or the like, to which the coating of solid insulating medium and the color-forming reactants is applied.

Since it is difficult to show precisely the spatial relationship between the solid particles of color-forming reactants, the solid insulating medium, and the base web, it is preferred not to attempt to illustrate any embodiment of this invention by drawings.

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

This invention comprises a base web of paper or the like having applied thereto a coating including casein or methyl cellulose as the solid insulating medium and solid particles of two color-forming reactants; namely, kaolin and the compound 3,3 bis(p - dimethylaminophenyl) phthalide, also known as "malachite green lactone," having the structure.



This record material is normally white or light in color, and, upon application of localized pressure thereto, as by drawing a stylus thereover, a mark of dark blue-green color is produced at the points of application of such pressure. The solid insulating medium in this record material serves to insulate the solid particles of kaolin and "malachite green lactone" from color-forming reaction contact with each other, and this insulating medium is ruptured, at the points of application of localized pressure, to permit such color-forming reaction contact, resulting in the mark of distinctive color. This pressure-sensitive record material is not affected substantially by atmospheric moisture and remains stable over long periods of time.

Organic film-forming hydrophilic colloid substances such as gelatin, methyl cellulose, starch, polyvinyl alcohol, and animal glue are representative materials that may be substituted for casein as the solid insulating medium. Attapulgite (Attapulgus clay), pyrophyllite, talc, bentonite, halloysite, calcium sulphate, magnesium trisilicate, zinc sulphide, and calcium fluoride are inorganic materials any one of which may be substituted for the kaolin as one of the color-forming reactants. When any of these materials are substituted for the kaolin, the resulting record material will be white or light in color, and a dark blue-green mark will appear thereon as the result of the application of localized pressure. The coating should be from .0005 to .001 of an inch in thickness and the particle size of the color reactants should be of the order of 10 microns in diameter, or smaller.

The pressure-sensitive record material described above has been made, in one instance, by the following methods: A slurry of kaolin and water was prepared including fifty parts by weight of kaolin to fifty parts by weight of water, and a minor proportion of a suitable dispersing agent, such as sodium metaphosphate, was added to facilitate the dispersion of the particles of the kaolin through the slurry and to reduce its viscosity. A 20% by weight solution of casein in water was formed by, first, dispersing the casein in cold water by stirring for fifteen minutes at room temperature and, then, heating up to 60 degrees centigrade. Five parts of a 28% ammonium hydroxide solution were then added to the hot casein solution, which was stirred for about fifteen minutes and allowed to cool to room temperature. The kaolin slurry and the alkaline casein solution were then thoroughly mixed in the ratio by weight of kaolin to casein of 10 to 1, and blended, and it was found desirable to add a small percentage of tributyl phosphate in alcohol, or other anti-foaming agent, at this stage. This mixture of the kaolin slurry and the casein solution was then applied as a coating to the paper and dried thereon, and the record material was then calendered or treated in any desired way to give the proper surface finish. A solution in toluene of about 3% by weight of "malachite green lactone" was then applied to the coated side of the paper. The excess of this solution was removed and the treated paper dried to evaporate the toluene, after which it was ready for use.

The pressure-sensitive record material described above, having methyl cellulose as the solid insulating medium and kaolin and "malachite green lactone" as the color-forming reactants, was successfully made by the following method: A solution was prepared by dissolving about 5 parts by weight of methyl cellulose in

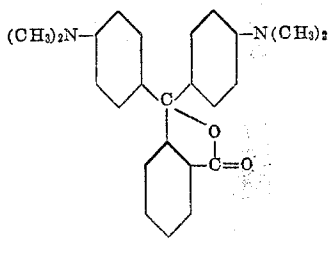
about 50 parts by weight of water, which solution was divided into two equal parts. To one portion of this methyl cellulose solution, the slurry of kaolin and water prepared as described above was added, in the ratio by weight of kaolin to methyl cellulose of 40 to 1, and thoroughly mixed. The other portion of the methyl cellulose solution was rendered alkaline by the addition of ammonium hydroxide solution, to an extent sufficient to precipitate the "malachite green lactone" from the acid solution thereof mixed with this portion. 6 grams of "malachite green lactone" were dissolved in 50 cc. of 3.7% hydrochloric acid solution, and this acid solution was mixed with the ammoniacal portion of the methyl cellulose solution, in such proportions that the ratio by weight of kaolin to "malachite green lactone" in the coating will be about 100 to 3, the mixture being neutral or slightly alkaline, so that the "malachite green lactone" is precipitated therein. The two portions of the methyl cellulose solution were then thoroughly mixed and applied as a coating to the paper, which coating was dried in the usual manner.

The methods and processes of making pressure-sensitive record material disclosed herein are not claimed in this application but are disclosed and claimed in the pending application of Barrett K. Green, Serial No. 784,939, filed November 8, 1947, for Process for making pressure-sensitive record material, and in the division thereof, Serial No. 63,211, filed December 2, 1948.

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

What is claimed is:

1. Pressure-sensitive record material including the combination of a supporting member, a plurality of adsorption color-forming reactants in the solid state, so selected as to react in the absence of a liquid ionizing medium for the reactants to form a distinctive color when brought into contact with each other, disposed in proximity to each other, at least one of the reactants being an inorganic compound and at least another of the reactants being an organic compound adsorbable one on the other, and a solid insulating medium, derived from an organic hydrophilic film-forming colloid material, insulating said reactants from color-forming reaction contact with each other, the application of localized pressure to the record material rupturing said insulating medium at the points of application of such pressure to permit color-forming reaction contact between the reactants at such points, whereby a mark of distinctive color is produced by mere application of localized pressure, one of said color-forming reactants being the organic compound 3,3 bis(p-dimethylaminophenyl) phthalide, having the structure

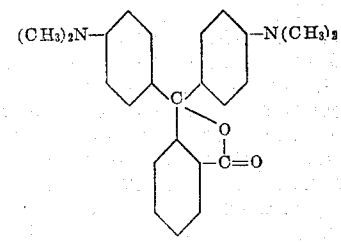


and the inorganic reactant being in fine particle form providing a large adsorbent surface area and which is an acid relative to the organic compound so as to be an electron acceptor when in adsorption contact with said organic compound.

2. The record material of claim 1 in which the inorganic color-forming reactant is kaolin.

3. The record material of claim 2 in which the solid insulating medium is casein.

4. Pressure-sensitive record material including the combination of a supporting member, solid particles of a plurality of adsorption color-forming reactants disposed in contiguity to each other, at least one of said reactants being an inorganic compound and at least another of said reactants being an organic compound one adsorbable on the other, and a solid insulating medium, derived from an organic hydrophilic film-forming colloid material, insulating said solid reactant particles from color-forming reaction contact with each other, said reactants being so selected as to react to form a distinctive color when particles of each are brought into contact, the application of localized pressure to the record material rupturing said insulating medium at the points of application of such pressure to permit color-forming reaction contact of the solid reactant particles at such points, whereby a mark of distinctive color is produced by mere application of localized pressure, one of said color-forming reactants being the organic 3,3 bis(p-dimethylaminophenyl) phthalide, having the structure



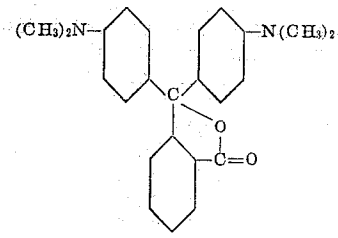
and the inorganic reactant being in fine particle form to provide a large adsorbent surface area and which is an acid relative to the inorganic compound so as to be an electron acceptor when in adsorption contact with said organic compound.

5. The record material of claim 4 in which the inorganic color-forming reactant is kaolin.

6. The record material of claim 5 in which the solid insulating medium is casein.

7. Pressure-sensitive record material including the combination of a supporting member, a solid insulating medium derived from an organic hydrophilic film-forming colloid material, solid particles of a first color-forming reactant dispersed therein and solid particles of a second color-forming reactant deposited thereon, said solid insulating medium insulating said solid reactant particles from color-forming reaction contact with each other, said reactants being so selected as to react, in the solid state, to form a distinctive color when brought into adsorption contact with each other, one of said color reactants being an inorganic compound and the other of said color reactants being an organic compound one adsorbable on the other, the application of localized pressure to the record material rupturing said insulating medium at the points of application of such pressure to permit color-forming reaction adsorption contact of the solid reactant particles at such points, whereby a mark of distinctive color is produced by mere application of localized pressure, and said second color-forming reactant being the organic compound 3,3 bis(p-

dimethylaminophenyl) phthalide, having the structure

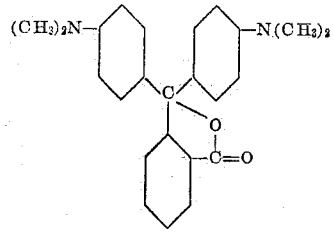


the first reactant being the inorganic compound in fine particle form to provide a large adsorbent surface area and which is an acid relative to the organic compound so as to be an electron acceptor when in adsorption contact with the organic compound.

8. The record material of claim 7 in which the first color-forming reactant is kaolin.

9. The record material of claim 8 in which the solid insulating medium is casein.

10. Pressure-sensitive record material including the combination of a support member, a solid insulating medium, derived from an organic hydrophilic film-forming colloid material, and solid particles of a plurality of adsorption color-forming reactants interspersed in said solid medium and insulated thereby from color-forming reaction contact with each other, at least one of said reactants being an inorganic compound and at least another of said reactants being an organic compound, one adsorbable on the other and said reactants having the property of reacting on adsorption contact to form a distinctive color when particles of each are brought into contact, the application of localized pressure to the record material rupturing said insulating medium at the points of application of pressure to permit color-forming reaction contact of the solid reactant particles at such points, whereby a mark of distinctive color is produced by mere application of localized pressure, one of said color-forming reactants being the organic compound 3,3 bis(p-dimethylaminophenyl) phthalide, having the structure

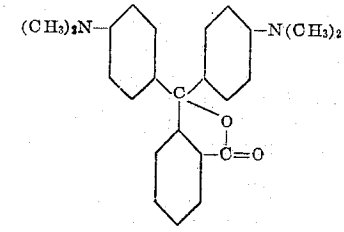


and the inorganic reactant being in fine particle form to provide a large adsorbent surface area and which is an acid relative to the organic compound so as to be an electron acceptor when in adsorption contact with the organic compound.

11. The record material of claim 10 in which the inorganic one of the color-forming reactants is kaolin.

12. The record material of claim 11 in which the solid insulating medium is methyl cellulose.

13. Pressure-sensitive record material including the combination of a base web and a coating thereon, said coating including a plurality of adsorption color-forming reactants in the solid state, so selected as to react in the absence of an ionizing medium to form a distinctive color when brought into contact with each other, and disposed in proximity to each other, at least one of said reactants being an inorganic compound and at least another of said reactants being an organic compound one adsorbable on the other, and a solid insulating medium, derived from an organic hydrophilic film-forming colloid material, insulating said reactants from color-forming adsorption reaction contact with each other, the application of localized pressure to the record material rupturing said insulating medium at the points of application of such pressure to permit color-forming reaction contact between the reactants at such points, whereby a mark of distinctive color is produced by mere application of localized pressure, one of said color-forming reactants being the organic compound 3,3 bis(p-dimethylaminophenyl) phthalide, having the structure



and the inorganic reactant being in fine particle form to provide a large adsorbent surface area and which is an acid relative to the organic compound so as to be an electron acceptor when in adsorption contact with the organic compound.

14. The record material of claim 13 in which the inorganic color-forming reactant is kaolin.

15. The record material of claim 14 in which the solid insulating medium is casein.

BARRETT K. GREEN.

REFERENCES CITED

The following references are of record in the file of this patent:

FOREIGN PATENTS

Number	Country	Date
550,332	Great Britain	Jan. 4, 1943