Patented Apr. 25, 1950 2,505,477

UNITED STATES PATENT OFFICE

2,505,477

PRESSURE SENSITIVE RECORD MATERIAL

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

No Drawing. Original application November 8, 1947, Serial No. 784,938. Divided and this application November 10, 1948, Serial No. 59,427

20 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 hydroscopic, 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 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

2

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 inoizing 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 the 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 compound causes a color change in an organic compound when in adsorption contact therewith.

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

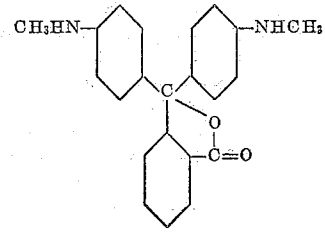
material which enhances the depth of color per unit area of the record material.

In the preferred form of 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.

One embodiment of this invention consists of the pressure-sensitive record material comprising a web of paper having applied thereto a coating including casein as the solid insulating medium and solid particles of two color-forming reactants; namely, kaolin and the compound 3,3 bis-(p-methylaminophenyl phthalide, having the structural formula

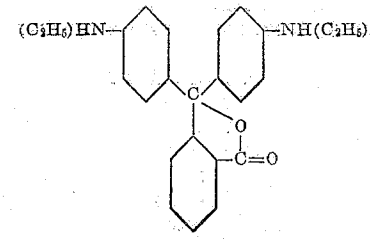


This record material is normally white, but the application of localized pressure thereto ruptures the insulating medium, casein, at the points of application of such pressure, permitting color-forming reaction contact between the solid particles of kaolin and the solid particles of the compound 3,3 bis(p-methylaminophenyl) phthalide, resulting in the production of a bright blue mark.

The record material just described has been successfully made by coating a web of paper with a casein solution having solid particles of kaolin dispersed therein, the ratio of kaolin to casein being about ten to one. The paper so coated was dried, and the coated side of the paper was treated with a 3% solution in toluene of the compound 3,3 bis(p-methylaminophenyl) phthalide. The excess of solution was removed, and the treated paper was dried to evaporate the solvent.

The compound 3,3 bis(p-methylaminophenyl) phthalide, referred to above, is described and claimed in the pending application of Clyde S. Adams, Serial No. 588,077, filed April 12, 1945, now Patent No. 2,474,084, for Secondary amines of 3,3 bis(p-aminophenyl) phthalide.

Another embodiment of this invention is a pressure-sensitive record material consisting of a web of paper having applied thereto a coating consisting of casein as the solid insulating medium and solid particles of two color-forming reactants; namely, kaolin and the compound 3,3 bis-(p-ethylaminophenyl) phthalide, having the structural formula



This record material is normally white, but the application of localized pressure thereto ruptures the solid insulating medium at the points of application of such pressure, thus permitting color-forming reaction contact between the solid particles of kaolin and 3,3 bis (p-ethylaminophenyl) phthalide, resulting in a bright blue mark.

The record material described above was successfully made by coating a web of paper with a casein solution having solid particles of kaolin interspersed therein, the ratio of kaolin to casein being about ten to one. The coating so applied having been dried, the coated side of the paper was treated with a 3% by weight solution in toluene of the compound 3,3 bis(p-ethylaminophenyl) phthalide. The excess of this solution was removed and the treated paper dried to evaporate the solvent.

The compound 3,3 bis(p-ethylaminophenyl) phthalide, referred to above, is described and claimed in the pending application of Clyde S. Adams, Serial No. 588,077, filed April 12, 1945, for Secondary amines of 3,3 bis(p-aminophenyl) phthalide.

When these ingredients are applied to the paper as a coating thereon, such coating should weigh about .0023 pound per square foot of surface and may have a thickness of the order of from .0005 to .001 inch. The thickness of the coating varies, of course, with the treatment to which the record material is subjected in finishing. The solid particles of kaolin in this record material may be of about the order of ten microns in diameter, although considerable variation in particle size is possible without any ill effects. Particle size of the phthalide compounds is largely determined by the method of application of those ingredients. The particles of these reactants may be as large as ten microns in diameter and frequently are much smaller.

Organic film-forming hydrophilic colloid materials 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. Any of the following inorganic materials may be substituted for kaolin as one of the color-forming reactants:

attapulgite (Attapulgus clay), pyrophyllite, talc, bentonite, halloysite, calcium sulphate, calcium citrate, magnesium trisilicate, zinc sulphide, zirconium dioxide, calcium phosphate, barium sulphate, and calcium fluoride. When any of these materials are substituted for kaolin in this combination, the resulting record material will be white or bluish white in color, and a bright blue mark will appear thereon as the result of the application of localized pressure.

One method that has been used successfully to make the pressure-sensitive record materials described above is as follows: A slurry of kaolin and water was prepared including fifty parts by weight of kaolin to fifty parts by weight of water, and a small amount of a suitable dispersing agent, such as sodium metaphosphate, for instance, in the proportion of 0.75% by weight was added to facilitate the dispersion of the particles of kaolin throughout the slurry. The addition of this dispersing agent reduces the viscosity of the slurry considerably, thus facilitating its mixing and application and also preventing the settling of the solid particles of kaolin. 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 by weight of a 28% ammonium hydroxide solution—that is, one having a specific gravity of 25.9° Bé., at

$$\frac{20°}{4}\ \text{C.}$$

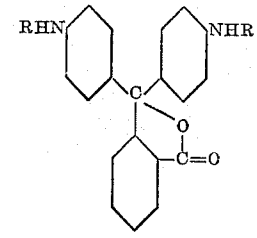
were then added to the hot casein solution, which was stirred for about fifteen minutes and allowed to cool to room temperature. The kaolin slurry and the alkaline casein solution were then thoroughly mixed and blended in the ratio of ten parts by weight of kaolin to one part of casein, and, at this stage, a small percentage—for instance, about 0.05% by weight—of tributyl phosphate in alcohol, or other anti-foaming agent, was added. This mixture of the kaolin slurry and the casein solution was then applied as a coating to the paper, and the coated paper was dried and calendered or treated in any desired way to give the proper surface finish. A solution in toluene of about 3% by weight of the phthalide compound was then applied to the coated side of the paper, the excess of this solution was removed in any suitable way, as by passing under a doctor blade, and then the treated paper was dried to evaporate the toluene and was ready for use.

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 the division thereof, Serial No. 63,216, 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, at least one of the reactants being an inorganic compound and at least one other reactant being an organic compound, disposed in proximity to each other, and a solid insulating medium, derived from a film-forming hydrophilic colloid substance, 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 an organic compound of the structure

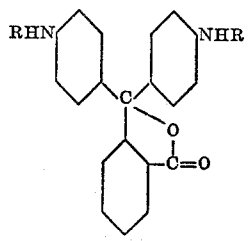


wherein R is selected from the group consisting of CH_3 and C_2H_5, and the inorganic reactant being in fine particle form to provide a large adsorbent surface area and which is an acid relative to the organic compound so as to be an electron acceptor when in adsorption contact with the organic compound, the organic compound and the inorganic material being adsorbable one upon the other.

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, and a solid insulating medium, derived from an organic film-forming hydrophilic colloid material, insulating said solid reactant particles from color-forming reaction contact with each other, at least one said reactants being an inorganic material and at least another one of said reactants being an organic material one adsorbable on the other, said reactants being so selected as to react to form a distinctive color when particles of each are brought into adsorption 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 an inorganic compound of the structure



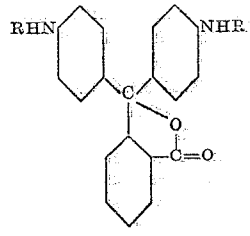
wherein R is selected from the group consisting of CH_3 and C_2H_5, and the inorganic material being in fine particle form to provide a large adsorbent surface area and being an acid relative to the organic compound so as to be an electron ac-

ceptor when in adsorption contact with the 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 colloid substance, 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, one of said reactants being an inorganic compound and the other reactant being an organic compound one adsorbable on the 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, 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, the second of said color-forming reactants being an organic compound of the structure



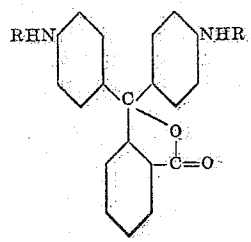
wherein R is selected from the group consisting of CH_3 and C_2H_5, and the second reactant is inorganic material in fine particle form providing a large adsorbent surface area and which is an acid relative to the organic compound so as to be an electron acceptor when in adsorption contact with the organic compound.

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

9. The record material of claim 7 in which the solid insulating medium is casein.

10. 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, at least one of the reactants being an inorganic compound and at least another of the reactants being

an organic compound one adsorbable upon the other, and disposed in proximity to each other, and a solid insulating medium, derived from an organic film-forming hydrophilic colloid substance, 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 an organic compound of the structure



wherein R is selected from the group consisting of CH_3 and C_2H_5 and the inorganic material is in fine particle form to provide a large adsorbent surface area and is an acid relative to the organic compound so as to be an electron donor when in adsorption contact with the organic compound.

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

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

13. The record material of claim 1 in which R is CH_3.

14. The record material of claim 4 in which R is CH_3.

15. The record material of claim 7 in which R is CH_3.

16. The record material of claim 10 in which R is CH_3.

17. The record material of claim 1 in which R is C_2H_5.

18. The record material of claim 4 in which R is C_2H_5.

19. The record material of claim 7 in which R is C_2H_5.

20. The record material of claim 10 in which R is C_2H_5.

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