

UNITED STATES PATENT OFFICE

2,505,481

PROCESS OF MAKING PRESSURE SENSITIVE
RECORD MATERIAL

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No Drawing. Original application November 8,
1947, Serial No. 784,939. Divided and this ap-
plication December 2, 1948, Serial No. 63,211

11 Claims. (Cl. 117—36)

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This invention relates to improvements in process of making a pressure-sensitive record material. This application is a division of the pending application of Barrett K. Green, Serial No. 784,939, filed November 8, 1947, for Process of making pressure-sensitive record material.

The principal object of this invention is to provide a process of making 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 process of making 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 process of making 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

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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 process of making 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 process of making 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 process of making 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 operation, 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 process of making a pressure-sensitive record material including the forming on a supporting member a film-like deposit of solid particles of a plurality of adsorption color-forming reactants disposed in contiguity with each other, 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 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 reaction employed is of the, so-called, adsorption type wherein an inorganic compound causes a color change in an organic compound coming into adsorption contact therewith.

Of the reactant materials employed the organic material is an electron donor aromatic

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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.

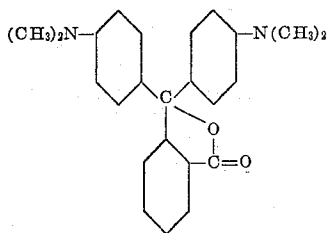
According to one embodiment of the invention, solid particles of a plurality of color-forming reactants are interspersed in a solid insulating medium, which insulates the particles from color-forming reaction contact with each other. The rupture of this solid insulating medium by the application of localized 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 another 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.

The insulating medium is a pressure-rupturable film derived from an organic film-forming hydrophilic colloid substance.

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 produces a material comprising 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

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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. According to this embodiment of the invention, the solid insulating medium may be casein or methyl cellulose, but other organic film-forming hydrophilic colloid materials such as gelatin, starch, polyvinyl alcohol or animal glue may be used instead. Attapulgit (Attapulgit 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.

Another embodiment of the invention for making the record material described above consists of the following method: 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, such as 0.3% by weight, of a suitable dispersing agent, such as sodium metaphosphate, was added to facilitate the dispersion of the particles of 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, dried thereon, and 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.

According to another embodiment of the invention, 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

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lose 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.

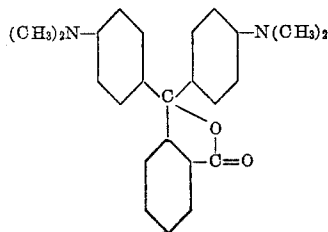
When these ingredients, in either embodiment, are applied to the paper as a coating thereon, such coating should weigh about .0023 pound per square foot of surface and should have a thickness of the order of from .0005 to .001 inch. The thickness of the coating varies, of course, with the treatment to 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 malachite green lactone is largely determined by the method of application of that ingredient. The particles of the reactant may be as large as ten microns in diameter and frequently are much smaller.

The pressure-sensitive record materials disclosed herein are not claimed in this application but are disclosed and claimed in the pending application of Barrett K. Green, Serial No. 784,938, filed November 8, 1947, for Pressure-sensitive record material, and in a division thereof, Serial No. 59,422 filed November 10, 1948.

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

What is claimed is:

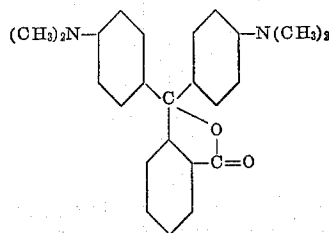
1. The process of making a pressure-sensitive record material including the forming on a supporting member a film-like deposit of solid particles of a plurality of adsorption color-forming reactants disposed in contiguity with each other and a solid insulating medium, derived from an organic film-forming hydrophilic colloid substance, insulating said reactant particles from color-forming reaction with each other, at least one of said reactants being an inorganic compound and at least another of said reactants being an organic compound adsorbable therewith, said reactants being 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, one of said color-forming reactants being the compound 3,3 bis(p-dimethylaminophenyl) phthalide, having the structure



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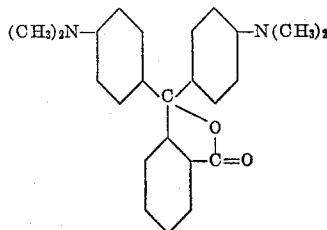
and the inorganic reactant being in fine particle form providing a large adsorbent surface area and which is an acid relative to the organic reactant so as to be an electron acceptor when in adsorption contact with said organic reactant.

2. The process of making a pressure-sensitive record material including the steps of coating a supporting member with a film of solid insulating material, derived from an organic film-forming hydrophilic colloid substance, having particles of a first color-forming solid reactant dispersed therein, and depositing on said film particles of a second color-forming solid reactant, one of said reactants being an inorganic compound and the other of said reactants being an organic compound adsorbable with it and said reactants being so selected as to form a distinctive color when brought into contact with each other, and said solid insulating material being such as to insulate the reactants from color-forming reaction contact with each other, the second color-forming reactant being the 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 second reactant so as to be an electron acceptor when in adsorption contact with said second reactant.

3. The process of making a pressure-sensitive record material including the step of forming on a supporting member a film of a solid insulating medium, derived from a film-forming hydrophilic colloid substance, having interspersed therein solid particles of a plurality of color-forming reactants, disposed in contiguity but insulated from color-forming reaction contact by such medium, at least one of the reactants being an inorganic compound and at least another of the reactants being an organic compound adsorbable with it, said reactants being so selected as to react in the absence of an ionizing medium to form a distinctive color when brought into contact with each other, one of the color-forming reactants being the 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 reactant so as to be an electron acceptor when in adsorption contact with said organic reactant.

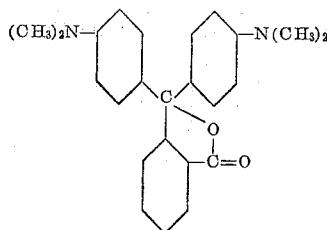
4. The process of claim 3 in which the inorganic color-forming reactants is kaolin.

5. The process of claim 4 in which the solid insulating medium is methyl cellulose.

6. The process of making a pressure-sensitive

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record material including the steps of forming a dispersion of solid particles of a first color-forming reactant in a solution of a solid insulating medium derived from an organic film-forming hydrophilic colloid substance, forming a dispersion of solid particles of a second color-forming reactant in a solution of said insulating medium, mixing said dispersions, coating a base web with the mixture of said dispersions, and evaporating the solvent therefrom, leaving on the base web a coating of solid insulating medium having said solid reactant particles interspersed therein, one of said reactants being an inorganic compound and the other of said reactants being an organic compound adsorbable with it and said reactants being so selected as to react in the absence of an ionizing medium to form a distinctive color when brought into adsorption contact with each other, the second color-forming reactant being the compound 3,3 bis(p-dimethylaminophenyl) phthalide, 20 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 reactant so as to be an electron acceptor when in adsorption contact with said organic reactant.

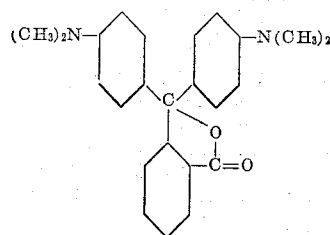
7. The process of claim 6 in which the inorganic color-forming reactant is kaolin.

8. The process of claim 7 in which the solid insulating medium is methyl cellulose.

9. The process of making a pressure-sensitive record material including the steps of forming a dispersion of solid particles of a first color-forming reactant in a solution of a solid insulating medium derived from an organic film-forming hydrophilic colloid substance, forming a dispersion of solid particles of a second color-forming

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reactant in a solution of said insulating medium, mixing said dispersions, coating a base web with the mixture of said dispersions and evaporating the solvent therefrom, leaving on the base web a coating of solid insulating medium having said solid reactant particles interspersed therein, one of said reactants being an inorganic compound and the other of said reactants being an organic compound adsorbable with it and said reactants being so selected as to react in the absence of an ionizing medium to form a distinctive color when brought into adsorption contact with each other, the dispersion of the solid particles of the second color-forming reactant being formed by precipitation thereof by the neutralization of an acidified solution of said reactant in the insulating medium, said particles being made of the compound 3,3 bis(p-dimethylaminophenyl) 6-dimethylamino phthalide, having the structure



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

35 10. The process of claim 9 in which the inorganic color-forming reactant is kaolin.

11. The process of claim 10 in which the solid insulating medium is methyl cellulose.

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REFERENCES CITED

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

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FOREIGN PATENTS

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