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# UNITED STATES PATENT OFFICE

2,505,483

## 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 application December 2, 1948, Serial No. 63,213

2 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

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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 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 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.

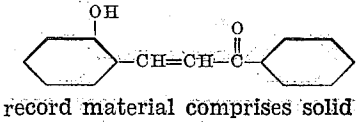
According to one embodiment of the invention, solid particles of one of the color-forming reactants are carried by and dispersed in a solid insulating medium, to which a coating of solid particles of another color-forming reactant is applied. In this case, the application of localized pressure ruptures 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.

The preferred embodiment of this invention produces a pressure-sensitive record material including a base web of paper having applied thereto a coating including casein as the solid insulating medium and two color-forming reactants; namely, kaolin and the compound o-hydroxybenzalacetophenone, having the structure




This record material comprises solid particles of kaolin and o-hydroxybenzalacetophenone insulated from color-forming reaction contact with each other by casein as the solid insulating medium. The record material is normally light yellow in color, and application of localized pressure thereto ruptures the insulating medium at the points of application of such pressure, permitting color-forming reaction contact between the particles at such points and producing a reddish-yellow mark.

According to this embodiment of the invention, this record material was made by first coating the paper with a solution of casein rendered alkaline by the addition of sodium carbonate, and having dispersed therein particles of kaolin. The ratio of kaolin to casein was about ten to one. When this coating had been dried on the paper and the paper suitably calendered or treated to give it the desired surface finish, a 3% by weight solution of the organic color-forming reactant dissolved in methyl ethyl ketone was applied to the coated side of the paper, the excess of solution was removed, and the treated paper was dried to remove the solvent, after which the record material was ready for use.



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 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 organic color reactant, o-hydroxybenzalacetophenone is largely determined by the method of application of that ingredient. The particles of these reactants may be as large as ten microns in diameter and frequently are much smaller.

Other 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. 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.

A method constituting one embodiment of this invention that has been used successfully to make the pressure-sensitive record material 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 0.075% 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 a solution of equal parts 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

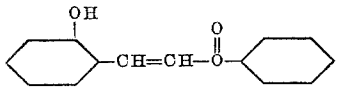
proper surface finish. A solution in toluene of about 3% by weight of o-hydroxybenzalacetophenone was then applied to the coated side of the paper, the excess of this solution was removed in any suitable way, as by passing under a doctor blade, and then the treated paper was dried to evaporate the toluene, and was ready for use.

The 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. 59,424, 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:

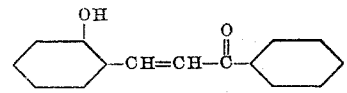
1. The process of making a pressure-sensitive record material including the forming on a supporting member a film-like deposit of solid particles of a plurality of adsorption color-forming reactants disposed in contiguity with each other and a solid insulating medium, derived from an organic film-forming 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 adsorption contact with each other, and one of the color-forming reactants being the compound o-hydroxybenzalacetophenone, 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.

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 therewith, and said reactants being so selected as to form a distinctive color when brought into adsorption 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 o-hydroxybenzalacetophenone, 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.

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 |