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PROCESS OF MAKING PRESSURE SENSITIVE RECORD MATERIAL

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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 produced, at the point of application of localized

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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.

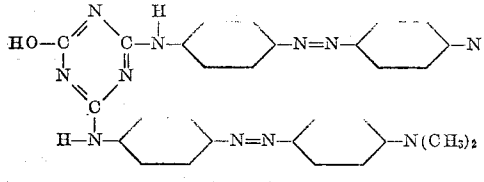
According to one embodiment of the invention, solid particles of one of the color-forming reactants are carried by and dispersed in a solid insulating medium, to which a coating of solid particles of another color-forming reactant is applied. In this case, the application of localized pressure ruptures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

An embodiment of this invention produces a material that comprises 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 2,4-bis [p-(p-dimethylaminophenylazo) anilino] 6-hydroxy sym. triazine, having the structure



The pressure-sensitive record material made using these ingredients is normally yellow in color, and the application of localized pressure thereto, as by drawing a stylus across the material, ruptures the solid insulating medium and permits the solid particles of kaolin and the organic color-forming reactant to come into color-forming reaction contact with each other, producing a dark blue mark at the points of application of such localized pressure. This record material is not affected by atmospheric moisture and is relatively stable for a long period of time. Other organic film-forming hydrophilic colloid substances such as gelatin, starch, methyl cellulose, or polyvinyl alcohol may be substituted for casein as the solid insulating medium in the record material constituting this embodiment of the

invention. Attapulgite may be substituted in this embodiment for the kaolin as the inorganic material, using gelatin or polyvinyl alcohol as the solid insulating medium.

One embodiment of the invention for making a pressure-sensitive record material, using the ingredients above referred to, consists of the following method: A slurry of kaolin and water was prepared including 50 parts by weight of kaolin to 50 parts by weight of water and a minor proportion of a suitable dispersing agent, such as sodium metaphosphate. A 20% by weight solution of casein in water was made, to which 5 parts by weight of a 28% ammonium hydroxide solution were added. The kaolin slurry and this alkaline casein solution were thoroughly mixed, in the ratio by weight of kaolin to casein of 10 to 1, and blended, and the mixture was applied to the paper as a coating, which was dried thereon, after which the coated paper was calendered or treated in any desired way to give the proper surface finish. A solution in toluene of about 0.5% by weight of the organic color-forming reactant above referred to was then applied to the coated side of the paper. The excess of this solution was removed, and the treated paper was dried to evaporate the toluene, after which it was ready for use.

The casein constitutes the solid insulating medium, insulating one of the color-forming reactants—that is, kaolin—from color-forming reaction contact with the other color-forming reactant—that is, the triazine compound. Upon the application of localized pressure to the coated paper, as by drawing a stylus thereover, a dark blue mark is produced at the points of application of such localized pressure. Such application of pressure ruptures the solid insulating medium at the points of application of pressure, permitting color-forming reaction contact between the solid particles of kaolin and the solid particles of the triazine compound.

When the coating ingredients are applied to the paper, 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 triazine compound 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.

This record material has also been made using gelatin as the solid insulating medium and attapulgite as the inorganic color-forming reactant. In this case, a slurry of attapulgite and water was made, which was thoroughly mixed with a 20% by weight solution of gelatin. The proportions of attapulgite and gelatin used should be such that, in the finished coating, the weight of the gelatin will be about 20% of the weight of the attapulgite. The mixture of the attapulgite slurry and the gelatin solution was applied to the paper as a coating, which was dried thereon. Thereafter, a solution in toluene of about 0.5% by weight of the organic color-forming reactant was 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

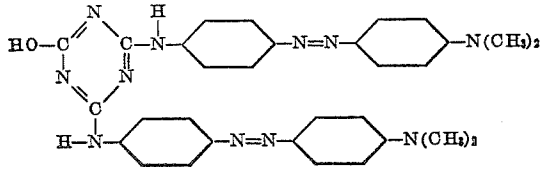
it was ready for use. The same procedure was successfully used with a solution of polyvinyl alcohol substituted for the gelatin solution. The proportions of polyvinyl alcohol and of attapulgite used were such that the finished coating had attapulgite and polyvinyl alcohol therein in the ratio by weight of 10 to 1.

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 of it Serial No. 59,423, 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.

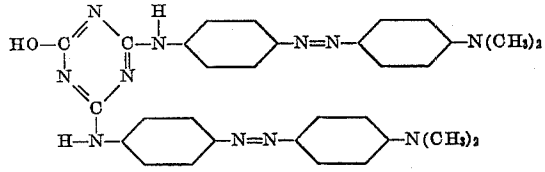
What is claimed is:

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 the reactants being an organic compound adsorbable therewith, and 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, one of the color-forming reactants being the compound 2,4-bis[p - (p - dimethylaminophenylazo)anilino] 6 hydroxy sym. triazine, 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, said second color-forming reactant being the compound 2,4 bis [p - (p - dimethylaminophenylazo) anilino] 6-hydroxy sym. triazine, 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