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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 October 4, 1949, Serial No. 119,576

13 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 application of Barrett K. Green, Serial No. 784,939, filed November 8, 1947, for Process of Making Pressure Sensitive Record Material, which issued as U. S. Patent 2,505,471 on April 25, 1950.

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 that Patent 2,299,693 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.

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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 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 interspersed 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 adsorption contact with each other, and a solid insulating medium insulating said reactants from color-forming reaction contact with each other. Upon application of local-

ized 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 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 reactant 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.

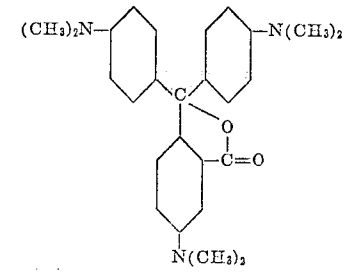
According to this invention, solid particles of a plurality of color-forming reactants are interspersed at random in a solid insulating medium, which insulates the particles from color-forming reaction contact with each other. The rupture of this solid insulating medium by the application of localized 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, claimed in the application of which this is a division, 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, such 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.

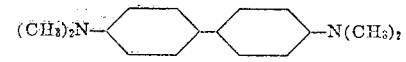
The insulating medium is a pressure-rupturable film derived from an organic film-forming hydrophilic colloid substance.

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 following embodiment of this invention constitutes the best mode of applying the principle thereof contemplated up to the present time, and may be considered the preferred embodiment. It consists of a process for making a pressure-sensitive record material that comprises a base web, of paper or the like, to which is applied a coating including casein and solid particles of three color-forming reactants; namely, kaolin, the compound 3,3 bis (p-dimethylaminophenyl)-6 dimethylamino phthalide, referred to as "crystal violet lactone" and having the structure



and the compound tetramethylbenzidine, having the structure



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 reactants—that is, crystal violet lactone and tetramethylbenzidine. This record material is normally white or bluish white in color, and, upon the application of localized pressure thereto, 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 crystal violet lactone and tetramethylbenzidine, thus causing the color change at such points that produces the mark.

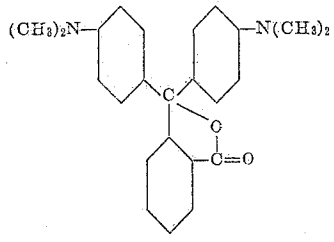
The compound 3,3 bis (p-dimethylaminophenyl)-6 dimethylamino phthalide—that is, "crystal violet lactone"—and the process of making it are disclosed in United States Letters Patent No. 2,417,897, issued March 25, 1947, on the application of Clyde S. Adams filed June 16, 1945, although the compound is incorrectly named in said patent as "3,3 bis (4-dimethylaminophenyl)-6 dimethylaminophenyl phthalide." Reissue Patent Re. 23,024 correctly names the compound.

It is not considered that the proportions, in which these several ingredients are present in the record material, are of particular importance, but good results have been obtained with a pressure-sensitive record material having such ingredients present in the following proportions by weight in the coating on the base web:

	Percent
Casein	8.85
Kaolin	88.50
Crystal violet lactone	2.25
Tetramethylbenzidine	.40

When these ingredients are applied to the paper as a coating thereon, such coating weighs 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

In another embodiment of this invention the compound 3,3 bis (p-dimethylaminophenyl) phthalide, also known as "malachite green lactone," having the structure



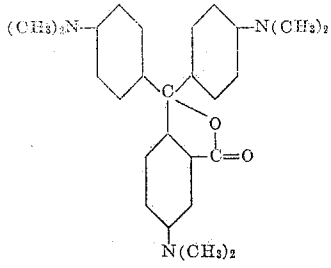
is used in place of the crystal violet lactone.

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.

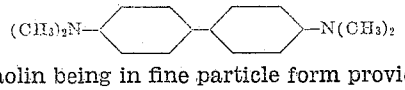
It is understood that the process of making a pressure-sensitive record material described herein is susceptible of considerable variation without departing from the spirit of the invention.

What is claimed is:

1. The process of making a pressure-sensitive record material including the step of forming on a supporting member a film of a solid insulating medium, derived from an organic hydrophilic colloid substance, having interspersed therethrough at random solid particles of a plurality of adsorption color-forming reactants, disposed in contiguity, but insulated from color-forming reaction contact by such medium, at least one of said reactants being kaolin and at least another of said reactants being a mixture of the compound 3,3 bis(p-dimethylaminophenyl)-6-dimethylamino phthalide, having the structure



and the compound tetramethylbenzidine, having the structure



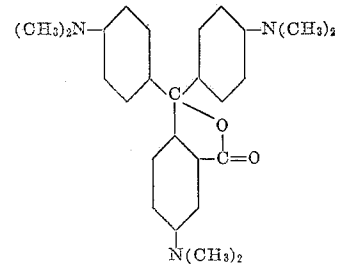
the kaolin being in fine particle form providing a large adsorbent surface area.

2. The process of claim 1, in which the solid insulating medium is casein.

3. The process of making a pressure-sensitive record material including the step of forming on a supporting member a film of casein having interspersed therethrough at random solid particles of a plurality of adsorption color-forming reactants, disposed in contiguity, but insulated from color-forming reaction contact by such casein film, 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 an ionizing medium to form a distinctive color when brought into adsorption contact with each other, the organic one of said reactants being solid particles of an electron-donor aromatic organic compound

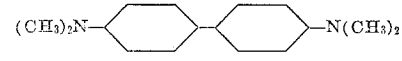
having a double bond system which is convertible to a more highly polarized conjugated form upon taking part in an electron acceptor-donor solid surface chemical reaction, giving it a distinctive color, and the inorganic reactant being in fine particle form providing a large adsorbent surface area and which is an acid relative to the first reactant so as to be an electron acceptor when in adsorption contact with said first reactant.

4. The process of making a pressure-sensitive record material including the step of forming on a supporting member a film of solid insulating medium, derived from an organic hydrophilic colloid substance, having interspersed therethrough at random solid particles of a plurality of adsorption color-forming reactants, disposed in contiguity but insulated from color-forming reaction contact by such medium, at least one of said reactants being an inorganic compound and another of said reactants being the aromatic compound 3,3 bis(p-dimethylaminophenyl)-6-dimethylamino phthalide, having the structure



said inorganic compound being in fine particle form providing a large adsorbent surface area and which is an acid absorbent for said aromatic compound and acting as an electron acceptor when in adsorption contact therewith, whereby a distinctive color is formed in said aromatic compound on such adsorption contact.

5. The process of claim 4 in which the 3,3 bis(p-dimethylaminophenyl) - 6 dimethylamino phthalide is mixed with the compound tetramethylbenzidine, having the structure



6. 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 casein, forming a dispersion of solid particles of a second color-forming reactant in a solution of said casein, 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 casein having said solid reactant particles interspersed therethrough at random, 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 react in the absence of an ionizing medium to form a distinctive color when brought into adsorption contact with each other, the organic reactant being an electron donor aromatic organic 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 reactant being in fine particle form, providing a large adsorbent surface area and which is an acid relative to the organic re-

size of the crystal violet lactone and the tetramethylbenzidine 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.

Gelatin, methyl cellulose, starch, polyvinyl alcohol, and animal glue are representative organic hydrophilic colloid 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 the kaolin in this combination, the resulting record material will be white or bluish white in color, and a dark blue mark will appear thereon as the result of the application of localized pressure.

If the tetramethylbenzidine be omitted and the pressure-sensitive record material be made using kaolin and crystal violet lactone as the sole color-forming ingredients, the record material will be white in color, and application of localized pressure will produce a dark blue mark thereon, but this mark may fade upon continued exposure to light under conditions of high humidity. On the other hand, if the crystal violet lactone be omitted and tetramethylbenzidine and kaolin be used as the sole color-forming reactants, the pressure-sensitive record material produced will be normally white, and application of localized pressure thereto will produce a green mark, which deepens in color upon aging and does not fade as readily as the mark produced by crystal violet lactone and kaolin alone, under conditions of high humidity.

This pressure-sensitive record material is not substantially affected by the amount of atmospheric humidity ordinarily encountered, although the mark may fade somewhat if subjected to high humidity for a long-continued period of time. However, this pressure-sensitive record material does not become stained or discolored by exposure to high humidity for long periods of time, and retains its ability to respond to the application of localized pressure, and to produce the mark of distinctive color, under such conditions. This is thought to be due to the fact that the record material does not include any hygroscopic ionizing media. Consequently, the structure of the record material is not altered or modified due to the absorption of water from the atmosphere.

An embodiment of this invention successfully used for making pressure-sensitive record material such as described above, using casein as the solid insulating medium and kaolin, crystal violet lactone, and tetramethylbenzidine as the color-forming reactants, is as follows: 200 grams of kaolin were made into a slurry with 200 grams of water, to which 0.3% by weight of sodium metaphosphate was added as a dispersing agent. A casein solution was formed by dispersing 20 grams of casein in 139 grams of cold water and stirring for fifteen minutes. This dispersion of casein in water was then heated to 60 degrees centigrade, and 5 grams of commercial 28% ammonium hydroxide solution were added and the solution stirred for fifteen minutes while hot, after which it was allowed to cool to room temperature. One-half of the casein solution thus formed was thoroughly mixed with the kaolin slurry. 5.1 grams of crystal violet lactone and .9 gram of tetramethylbenzidine were then dissolved in 50 cc. of 3.7% hydrochloric acid solution, having a specific gravity of 2.5° Bé. at 20°/4 centigrade. To the other half of the casein solution, 5 grams of commercial 28% ammonium hydroxide solution were added, and the acidified solution of crystal violet lactone and tetramethylbenzidine was added slowly to this portion of the casein solution, with continued stirring, for about an hour. The portion of the casein solution containing the kaolin was passed through a homogenizer, or other means for mixing and thoroughly dispersing the particles of kaolin in the casein solution, and the two portions of casein solution, one containing the kaolin and the other containing the the crystal violet lactone and the tetramethylbenzidine, were then mixed thoroughly and applied as a coating to the base web of paper. This coating was then dried on the paper in the usual manner. The resulting record material had a light bluish-white color approaching white.

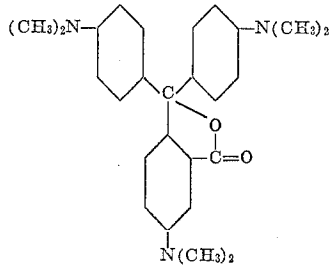
It should be noted that the mixing of the ammoniacal kaolin-containing portion of the casein solution with the other portion of the casein solution, containing the crystal violet lactone and the tetramethylbenzidine, results in an alkaline mixture, in which the crystal violet lactone and the tetramethylbenzidine are precipitated in extremely fine particles.

In case gelatin is substituted for casein as the solid insulating medium, the procedure described above is modified, in that the gelatin is first dissolved in water at a temperature above 40 degrees centigrade, and this gelatin solution is then divided into two equal parts, to one of which the slurry of kaolin and water is added as before. The other part of the gelatin solution is made sufficiently ammoniacal to neutralize the precipitate the crystal violet lactone and the tetramethylbenzidine when the hydrochloric acid solution of these ingredients is added thereto. These two portions of the gelatin solution are then mixed, and the mixture is applied as a coating to the paper and then dried. It should be noted that, when gelatin is used as the solid insulating medium, the gelatin solution should be kept at a temperature above 40 degrees centigrade throughout the entire procedure.

In case methyl cellulose is used as the solid insulating medium in substitution for the casein, a solution is prepared by dissolving about 5 parts by weight of methyl cellulose (of any viscosity between 2000 and 4000 centipoises at 68 degrees Fahrenheit) in about 50 parts by weight of water, and this solution is divided into two equal parts. To one portion of the methyl cellulose solution, the slurry of kaolin and water is added, in the ratio of 40 parts by weight of kaolin to one part by weight of methyl cellulose, and mixed, as described in connection with the use of casein. The other portion of the methyl cellulose solution is rendered sufficiently ammoniacal to precipitate the crystal violet lactone and the tetramethylbenzidine from the hydrochloric acid solution thereof, when the latter is added to and mixed with this portion of the methyl cellulose solution in such proportions that the ratio by weight of kaolin to crystal violet lacton and tetramethylbenzidine in the coating will be 100 to 3. The two portions of the methyl cellulose solution are, then, thoroughly mixed and applied as a coating to the paper, which coating is dried.

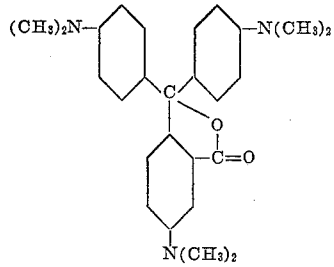
actant so as to be an electron acceptor when in adsorption contact with said organic reactant.

7. 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 reactant 3,3 bis(p - dimethylaminophenyl) - 6 - dimethylamino phthalide, having the stucture

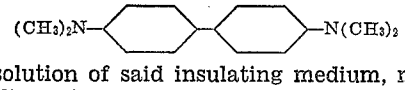


in a solution of said insulating medium, mixing said dispersions, coating a base web with the mixture of said dispersions, and evaporating the solvent therefrom, leaving on the base web a coating of solid insulating medium having said solid reactant particles interspersed therethrough at random, the first reactant being an inorganic compound upon which the second reactant is adsorbable, said first reactant being so selected as to react in the absence of an ionizing medium to form a distinctive color when brought into adsorption contact with the second reactant, and said 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.

8. 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 reactant which is a mixture of the compound 3,3 bis(p - dimethylaminophenyl) - 6 - dimethylamino phthalide, having the structure



and the compound tetramethylbenzidine, having the structure

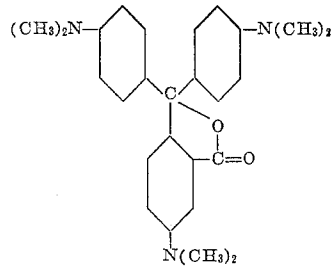


in a solution of said insulating medium, mixing said dispersions, coating a base web with the mixture of said dispersions, and evaporating the solvent therefrom, leaving on the base web a coating of solid insulating medium having said solid reactant particles interspersed therethrough at random, the first reactant being an inorganic compound upon which the second reactant is adsorbable, said first reactant being so selected as to react with the second reactant, in the absence of an ionizing medium, to form a distinctive color when brought into adsorption contact with the second reactant, and said first 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.

9. The process of claim 8, in which the first color-forming reactant is kaolin.

10. The process of claim 9 in which the solid insulating medium is casein.

11. 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 reactant in a solution of said insulating medium, said 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 and said second color-forming reactant being a mixture of the compound 3,3 bis(p - dimethylaminophenyl) - 6 - dimethylamino phthalide, having the structure



and the compound tetramethylbenzidine, having the structure



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 therethrough at random, the first one of said reactants being an inorganic compound selected so as to react in the absence of an ionizing medium to form a distinctive color when brought into adsorption contact with the second reactant compound, and the inorganic reactant being in fine particle form and 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.

12. The process of claim 11 in which the inorganic color-forming reactant is kaolin.

13. The process of claim 12 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:

UNITED STATES PATENTS

Number	Name	Date
2,505,471	Green	Apr. 25, 1950
2,505,481	Green	Apr. 25, 1950