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PRESSURE SENSITIVE RECORD MATERIALS

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Serial No. 38,547

28 Claims. (Cl. 282—28)

This invention relates to pressure-sensitive record material, and more particularly pertains to such material having minute particles of two kinds of substances which are color reactive on contact, one of the substances being in liquid form and the other being in solid form, the particles of the two substances being arranged in proximity in profuse numbers but insulated from contact by material rupturable when pressure is applied, which pressure acts to bring the two kinds of substances together at the points of rupture to produce a distinctively colored localized mark.

The record material of this invention although adapted for response to stylus pressures, is particularly adapted for response to pressures applied in impact printing operations such as by the striking or pressing of type thereagainst and in that respect is an improvement over the record material of Barrett K. Green's copending application, Serial No. 784,938, filed November 8, 1947, for Pressure Sensitive Record Material, now Patent No. 2,505,470.

The record material disclosed therein required the bringing together, by pressure, of two kinds of solid particles embedded in a rupturable solid insulating film. The low mobility of such solid particles rendered that record material more sensitive to pressures caused by drawing a stylus thereover than to pressures derived from the impact of type. This novel record material also is an improvement over that record material disclosed in United States Letters Patent No. 2,299,693, patented on October 20, 1942, on the application of Barrett K. Green. That patent discloses pressure-sensitive record material, especially adapted for impact work, such material including a rupturable insulating medium in which are interspersed liquid droplets of two kinds which react on contact to form color. The liquid droplets included solid color-forming materials dissolved in an ionizing medium, glycerine, which reacted to produce color on contact by interchange of ions. Any liquid ionizing medium available for use in such a system is hygroscopic making the record material unduly sensitive to moisture.

The present invention provides a record material with exceptional response to impact pressures and one having remarkable stability as no ionizing liquid is required. The liquid used to dissolve the active color ingredient in the liquid reactant substance is a non-ionizing inert oily type of material which is non-hygroscopic and is used solely to dissolve the active ingredient and to obtain easier release and greater mobility of the droplets when the supporting film is ruptured. Because of the mobility of the released liquid droplets at points of rupture of the insulating medium, the new record material is highly sensi-

tive both to drawing and to impact pressures yet it is resistant to destructive influences encountered in ordinary enviroment and normal handling operations. Thus, the new record material combines the best characteristics of known pressure responsive record materials by providing a novel liquid-solid reactant structure.

The principal object of the 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, said material including color-forming substances of two kinds, one being solid and the other being liquid, the two substances normally being held insulated from reaction contact by a rupturable insulating medium until marking pressures rupture the insulating medium at points of pressure to bring about local contact of the two substances to produce a mark.

Another object of the invention is to provide a record material in which one of the color reactant substances is dissolved in a non-ionizing oily liquid which may be dispersed as droplets in a rupturable solid insulating film so as to be readily available and mobile locally to make contact with the other solid reactant material when released by rupture of the film.

Another object of the invention is to provide such a record material which is highly sensitive to impact pressures such as are met with in typewriter or letterpress work and for this effect the two color reactants are arranged in separate overlying layers on a web so that marking pressures vertically applied to the said layers will cause penetration of the color reactant substance of one layer into that of the other layer.

Further objects and objects relating to details and economies of production, will definitely appear from the detail description to follow. The objects of this invention have been attained by the several embodiments thereof described in detail in the following specification. The invention is clearly defined and pointed out in the appended claims.

In the preferred form of this invention the liquid droplets of color reactant are dispersed in a film-forming substance which is applied as a coating to a paper web and dried thereon leaving the liquid droplets entrapped therein. The solid color reactant particles, acting as adsorbents, are likewise dispersed in a film-forming substance which is applied as a second overlying coating. Both films are rupturable to force the reactant substances together.

Of the reactant materials employed, the liquid droplets contain an organic substance which is an electron donor aromatic compound having a double bond system which is converted to a more highly polarized conjugated form upon taking part in an electron donor-acceptor adsorption chemical reaction, giving it a distinctive color, and the solid particles are of an inorganic substance which is an acid relative to the organic substance so as to be an electron acceptor when in adsorption contact therewith. The solid material is in fine particle form in order to furnish a large reactant surface per unit area of the record material, which enhances the depth of color produced in the record material.

The film-forming substances are derived from hydrophilic colloid materials that form pressure-rupturable films.

Although in the preferred form of the invention a single kind of solid reactant particle substance is used, such as Attapulgus clay, or attapulgite, it is within the scope of the invention to mix two or more kinds of solid reactants together, such as magnesium trisilicate and attapulgite, or to mix attapulgite with sodium aluminum silicate zeolites, which together act as adsorbents upon which color reactant adsorbates dissolved in the liquid droplets may be adsorbed.

Likewise the adsorbate substance may include one or more kinds of reactant such as crystal violet lactone, which is 3,3 bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, and tetrachloro malachie green lactone mixed together and dissolved in the oily liquid.

The web used as a support may be paper or other material suitable as a record base. For instance, either cardboard, glass, metal or wood may be used if desired. The total thickness of the pressure-sensitive film need be no greater than from .001 to .002 of an inch so it may be supported on very thin paper stock. By placing a number of such thin-coated paper sheets in superimposed relation in a typewriter a number of printed copies of typewritten material may be made without the use of a typewriter ink ribbon or carbon manifold paper as is now the common practice.

As it is difficult, if not impossible, to show the exact structure of this coating by use of a drawing none accompanies this specification.

In the following examples, there will be described embodiments of this invention by which the objects of the invention have been successfully attained.

Example 1.—The following embodiment of this invention constitutes the best mode of applying the principles thereof as contemplated up to the present time and may be considered the preferred embodiment. It comprises a base web of paper, or the like, on one surface of which two coatings are applied, the first or undercoating being an insulating film in which are entrapped a profuse number of liquid droplets in which a color reactant substance is dissolved. These droplets are, on the average, of the order of from 1 to 5 microns in diameter and are spaced apart, on the average, a distance of the order of ½ micron. The preferred thickness of this first coating, when dry, is of the order of .001 of an inch.

The first coating is made by dissolving one part by weight of animal gelatin, having an isoelectric point of pH 8 and a jelly strength of 275 grams as measured by the Bloom gelometer, with three parts by weight of water heated to 150° Fahrenheit.

Into four parts by weight of the gelatin solution there is dispersed, or emulsified, three parts by weight of a solution of crystal violet lactone in chlorinated diphenyl.

This solution of crystal violet lactone, which

is 3,3 - bis(p - dimethylaminophenyl, - 6 - dimethylamino phthalide, in chlorinated diphenyl is made by dissolving three parts by weight of the crystal violet lactone in ninety-seven parts by weight of chlorinated diphenyl which has a chlorine content averaging 48 per cent by weight. This chlorinated diphenyl solution is heated to the temperature of the gelatin solution before it is added thereto and emulsified.

The emulsion is applied while still hot, or if allowed to cool after reheating to 150° F. and is dried either under normal atmospheric conditions or by artificial means such as a hot air blast or on a heated drying drum such as is commonly used in paper coating machines. It is considered that drying under normal atmospheric environment gives a somewhat better water resistance to the dried film or coating in which the chlorinated diphenyl solution droplets are entrapped.

The dried undercoating is next treated to drive the droplets out of the top surface layer and into the interior of the film so as, in effect, to form an impermeable surface skin thereon. This is accomplished by wetting the surface with water at room temperature, that is from 70°–80° Fahrenheit, which water has had added thereto 1 per cent by weight of formaldehyde and 0.1 per cent by weight of a wetting agent such as dioctyl ester of sodium sulfosuccinate. The wetting should be allowed to persist for several minutes and thereafter the film is dried in a low humidity atmosphere. The surface wetting may be accomplished by floating the coated paper on the water, coated face down, or by carrying it on a partially submerged drum with the coated surface facing outwardly. The formaldehyde may be omitted, if desired.

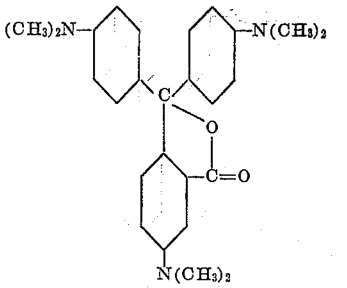
The second, or overcoating, then is applied to the dried undercoating. In making the second coating 20 per cent, by weight, of paper coating starch in water is cooked at 200° Fahrenheit for 15 minutes and cooled to room temperature. Separately, 1 part by weight of attapulgite is dispersed in three parts by weight of water by use of a ball mill or equivalent. Four parts, by weight, of the attapulgite dispersion is mixed with one part, by weight, of the starch solution. The resultant mixture is applied, at room temperature, as an overcoating to the prepared paper having the gelatin coating dried thereon. This starch-clay overcoating is applied in any convenient manner, as by a paper coating machine. This overcoating when dry should have a thickness of the order of .0005 of an inch.

The thickness of the undercoating and the overcoating may be varied somewhat without interfering greatly with the sensitivity of the material, such variation range being of the order of 25 per cent in either direction.

This record material when finished has a substantially white appearance and produces a dark blue mark which sharply defines the area of pressure or impact.

The impact of a marking instrument on the surface of this record material locally releases the oily droplets from the gelatin film and forces them into contact with the overlying attapulgite particles. The needle-like crystal aggregate structure of attapulgite prevents any substantial masking of it by the starch binder, thus leaving the attapulgite available to adsorb the color reactant crystal violet lactone from the released oil. Therefore, in this coating system the attapulgite solid particles are held in a non-masking or non-insulating binder whereas the oil-carried other reactant is protected as entrapped droplets in the gelatin insulating film.

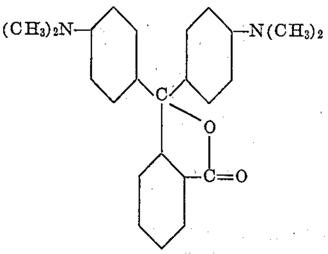
The compound crystal violet lactone has the structure



and the process of making it is described 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." An application for reissue of said patent is now pending.

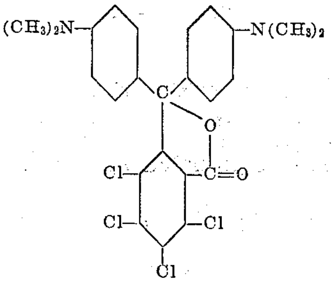
While not nearly as good as the arrangement of the layers or films just described, it is within the broad aspects of the invention to apply the adsorbent-bearing film or coating first on the paper and next to apply the crystal violet lactone-bearing film as an overcoating.

Example 2.—Another embodiment of the invention is the use of malachite green lactone, that is to say 3,3 bis(p-dimethylaminophenyl) phthalide, having the structure



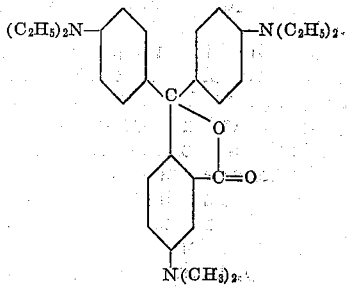
in place of the crystal violet lactone of Example 1 and in the same amount. This gives a substantially white record material producing a green mark when the pressure is applied. This green color is not as intense as the blue given by crystal violet lactone.

Example 3.—Another embodiment of the invention is the use of tetrachloro malachite green lactone, that is to say 3,3 bis(p-dimethylaminophenyl) 4,5,6,7 tetrachloro phthalide, having the structure



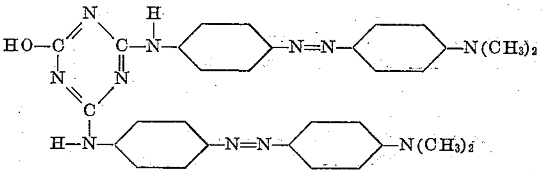
in place of the crystal violet lactone of Example 1 and in the same amount. This gives a substantially white record material producing a green mark when pressure is applied.

Example 4.—Another embodiment of the invention is the use of 3,3 bis(p-diethylaminophenyl)-6-dimethylamino phthalide, having the structure



in place of the crystal violet lactone of Example 1 and in the same amount. This gives a substantially white record material producing a blue mark when pressure is applied.

Example 5.—Another embodiment of the invention is the use of 2,4 bis[p-(p-dimethylaminophenylazo) anilino]-6-hydroxy sym. triazine, having the structure



in place of the crystal violet lactone of Example 1 but using only one-sixth as much by weight. The normal color of this record material is dark yellow and upon pressure being applied it turns to a bluish gray.

In Examples 1 to 4 inclusive the attapulgite can be replaced with a synthetic zeolite material of the sodium aluminum silicate type preferably having a maximum particle size of 10 microns and used in essentially the same amount by weight as specified in Example 1 for the attapulgite. For use with the zeolite type of adsorbent, gelatin, methyl cellulose, polyvinyl alcohol, and casein may be substituted for the starch of Example 1 as a binder.

In Examples 1 to 5 inclusive, whether attapulgite or the sodium zeolite is used, there may be substituted for the starch a mixture of starch, casein, and a synthetic latex made of butadiene-styrene copolymer material. In such a binder when dried with the attapulgite or zeolite material therein, the amount of starch should be 7 per cent, the amount of casein should be 1 per cent, and the amount of latex should be 7 per cent all by weight with respect to the weight of the attapulgite or zeolite material. In making such a binder a starch solution is made as described in Example 1 and allowed to cool. Next one part of casein is dispersed in two parts of cold water, by weight, and allowed to swell for one-half hour, after which seven more parts of cold water and 1/10 of a part of ammonium hydroxide of 25° Beaumé are added. This casein dispersion is heated on a water bath of 165° Fahrenheit for 15 minutes and then allowed to cool. The latex used contains 45 per cent of solids in water. The attapulgite or zeolite material to be used is dispersed in water as set out in Example 1 except the water contains 0.2% of sodium pyrophosphate. To 10 parts by weight of the dispersed adsorbent, eliminating the weight of the water, is added 3.5 parts by weight of the starch solution, 1.6 parts by weight of the latex, and 1 part by weight of the casein solution. This binder material is characterized by greater adhesion to the adjacent coating and by excellent properties as far as the access of the adsorbent material to the action of the liquid color reactant droplets is concerned.

In Examples 1 to 5 the attapulgite may be replaced with an equivalent amount of halloysite, and in Examples 1 to 4 the attapulgite may be replaced by an equivalent amount of magnesium trisilicate. Mixtures of the adsorbents will do as well as the individual adsorbents.

With respect to the zeolite material the sodium of the specified sodium aluminum silicate may be replaced with other cations such as nickel, copper, iron, zinc, mercury, barium, lead, cadmium and potassium to give zeolites with equivalent or better color reactant qualities.

The exchangeable calcium cations on natural attapulgite may be replaced by other cations to give workable adsorbents in the same way as noted for the zeolites. In addition hydrogen may be substituted for the calcium exchange cations of attapulgite.

The adsorbent material should be accessible to the liquid droplets containing the color reactant material to be adsorbed thereon and the action of the coating binder tends to mask the exterior surface available on such adsorbent particles. The needle-like aggregates of attapulgite and the porous structure of zeolites, contain interiorly active surfaces, not masked by the binder, which are left available for adsorbing the color reactant in the liquid droplets and, hence, these types of adsorbents are particularly suited for the novel structure which is the subject of this invention. Halloysite and magnesium trisilicate seem to be of such structure as has available interior adsorbent surfaces and therefore are given as substitute materials to act as the adsorbent material of the system.

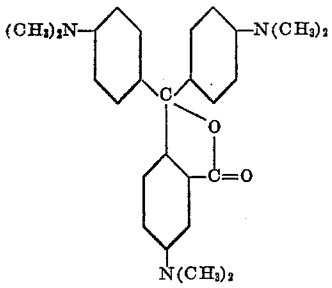
The methods and process of making the pressure-sensitive record material as disclosed herein are disclosed and claimed in the copending application of Barrett K. Green and Robert W. Sandberg, Serial No. 38,548, filed July 13, 1948.

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

What is claimed is:

1. Pressure-sensitive record material including the combination in a coating on a base web of color-forming substances of two kinds, one kind being solid and the other kind being liquid, said liquid kind being held insulated from contact with the solid kind by being profusely dispersed in minute droplets in a solid rupturable film on the exterior of which is deposited a film bearing particles of the solid kind, the application of localized pressure to the record material rupturing the film at points of application and there bringing the color-forming substances together, whereby a distinctively colored mark is produced by mere application of localized pressure, the liquid substance including 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 donor-acceptor adsorption chemical reaction, giving it a distinctive color, and the solid substance being an inorganic material in fine particle form providing a large adsorbent surface area and said inorganic material being an acid relative to the organic compound and acting as an adsorbent therefor so as to be an electron acceptor when the organic compound is in adsorption contact therewith.

2. The record material of claim 1 in which the liquid color-forming substance includes as the active ingredient 3,3 bis(p-dimethylaminophenyl)-6-dimethylamino phthalide having the structure



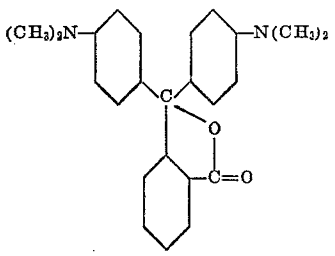
3. The record material of claim 2 in which the solid color-forming substance is attapulgite.

4. The record material of claim 1 in which the solid color-forming substance is attapulgite.

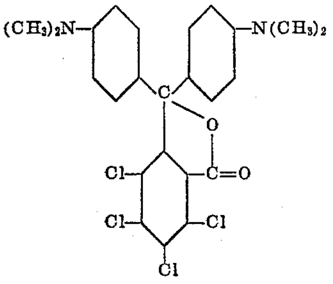
5. The record material of claim 1 in which the liquid color-forming substance is dispersed as droplets in a gelatin film.

6. The record material of claim 1 in which the liquid color-forming substance is dispersed in minute droplet form in a gelatin film supported by a base web, and in which the solid color-forming substance is dispersed in fine particle form in a binding coating applied over the gelatin film.

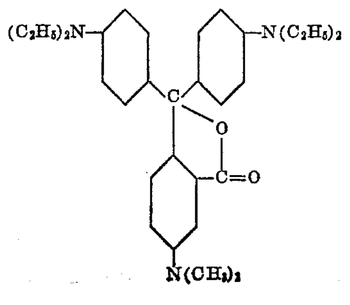
7. The record material of claim 1 in which the liquid color-forming substance includes as the active ingredient 3,3 bis(p-dimethylaminophenyl) phthalide having the structure



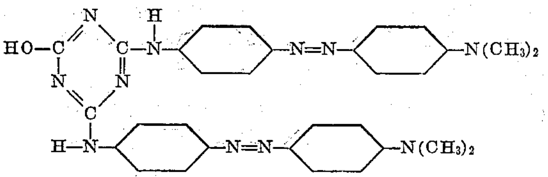
8. The record material of claim 1 in which the liquid color-forming substance includes as the active ingredient 3,3 bis(p-dimethylaminophenyl) 4,5,6,7 tetrachloro phthalide having the structure



9. The record material of claim 1 in which the liquid color-forming substance includes as the active ingredient 3,3 bis(p-diethylaminophenyl)-6-dimethylamino phthalide having the structure



10. The record material of claim 1 in which the liquid color-forming substance contains as the active ingredient 2,4 bis[p-(p-dimethylaminoazo) anilino]-6-hydroxy sym. triazine, having the structure



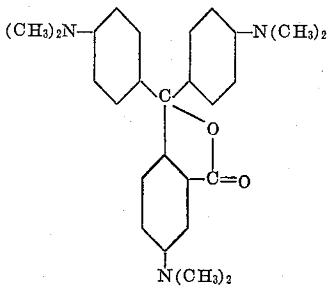
11. The record material of claim 1 in which the liquid color-forming substance includes an oily, non-evaporating solvent for a solid color-forming reactant carried therein in solution.

12. The record material of claim 11 in which the liquid color-forming solution is dispersed in minute droplets in a thin rupturable gelatin film coated on a supporting web.

13. The record material of claim 12 in which the solid color-forming substance is carried dispersed in a binder film coated on top of the gelatin film.

14. Pressure-sensitive record material including the combination of a supporting web; a continuous rupturable solid insulating film applied thereto said film containing dispersed therethrough a profusion of minute liquid color-forming inclusions; and a coating on the outer surface of the insulating film, said coating containing a profuse number of solid color-forming particles which, when brought into contact with the liquid inclusions by application of localized pressure to the record material which ruptures the insulating film and coating, react with said liquid inclusions to form a distinctively colored mark at said points of localized pressure, the liquid inclusions include 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 donor-acceptor adsorption chemical reaction, giving it a distinctive color, the solid particles being an inorganic substance of such fineness as to provide a large adsorbent surface area, said inorganic substance being an acid relative to the organic compound so as to be an electron acceptor when in adsorption contact with said organic compound, and the film being derived from a hydrophilic colloid material.

15. The record material of claim 14 in which the liquid color-forming substance includes as the active ingredient 3,3 bis(p-dimethylaminophenyl)-6-dimethylamino phthalide, having the structure



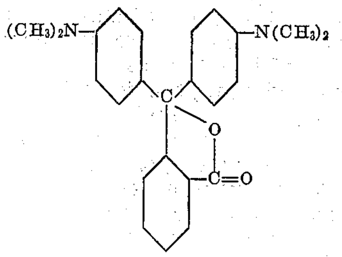
16. The record material of claim 15 in which the solid color-forming substance is attapulgite.

17. The record material of claim 14 in which the solid color-forming substance is attapulgite.

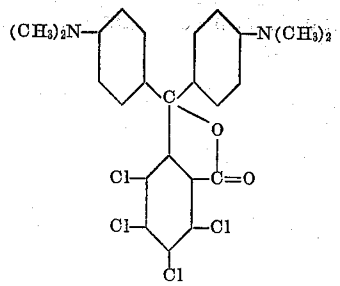
18. The record material of claim 14 in which the liquid color-forming substance is dispersed as droplets in a gelatin film.

19. The record material of claim 14 in which the liquid color-forming substance is dispersed in minute droplet form in a gelatin film supported by a base web, and in which the solid color-forming substance is dispersed in fine particle form in a binding coating applied over the gelatin film.

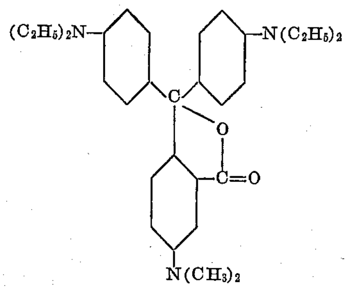
20. The record material of claim 14 in which the liquid color-forming substance includes as the active ingredient 3,3 bis(p-dimethylaminophenyl) phthalide having the structure



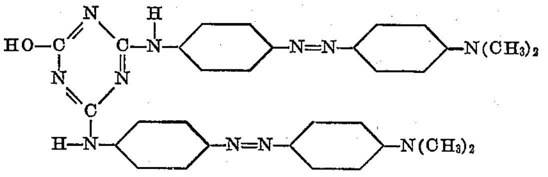
21. The record material of claim 14 in which the liquid color-forming substance includes as the active ingredient 3,3 bis(p-dimethylaminophenyl) 4,5,6,7 tetrachloro phthalide having the structure



22. The record material of claim 14 in which the liquid color-forming substance includes as the active ingredient 3,3 bis(p-diethylaminophenyl)-6-dimethylamino phthalide having the structure



23. The record material of claim 14 in which the liquid color-forming substance contains as the active ingredient 2,4 bis[p-(p-dimethylaminoazo) anilino]-6-hydroxy sym. triazine, having the structure



24. The record material of claim 14 in which the liquid color-forming substance includes an oily, non-evaporating solvent for a solid color-forming reactant carried therein in solution.

25. The record material of claim 14 in which the supporting web is paper.

26. A pressure-sensitive record material including the combination of a web of paper; a ruptur-

able thin solid film coated on one side of the paper to which it is adherent, said film having dispersed internally thereof a profusion of minute discrete liquid inclusions of a material which produces a color when in contact with a certain class of color-forming solid substances; and a rupturable coating on said film containing a profuse number of minute solid particles of one or more of the class of said color-forming substances embedded therein, localized pressure on said record material rupturing the film and coating to bring together locally at the pressure points the solid particles and liquid inclusions to form a distinctively colored mark, the liquid inclusions including 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, the solid particles being fine to provide a large adsorbent surface area, said solid particles being an acid relative to the organic compound so as to be an electron acceptor when the organic compound is in adsorption contact with it, and the film being derived from a hydrophilic colloid material.

27. The structure of claim 1 wherein the liquid inclusions contain more than one kind of color reactant.

28. The structure of claim 27 in which one of the color reactants in the liquid inclusions is 3,3 bis(p-dimethylaminophenyl)-6-dimethylamino phthalide and another color reactant in the same inclusions is 3,3 bis(p-dimethylaminophenyl) 4,5,6,7, tetrachloro phthalide.

BARRETT K. GREEN.
ROBERT W. SANDBERG.

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