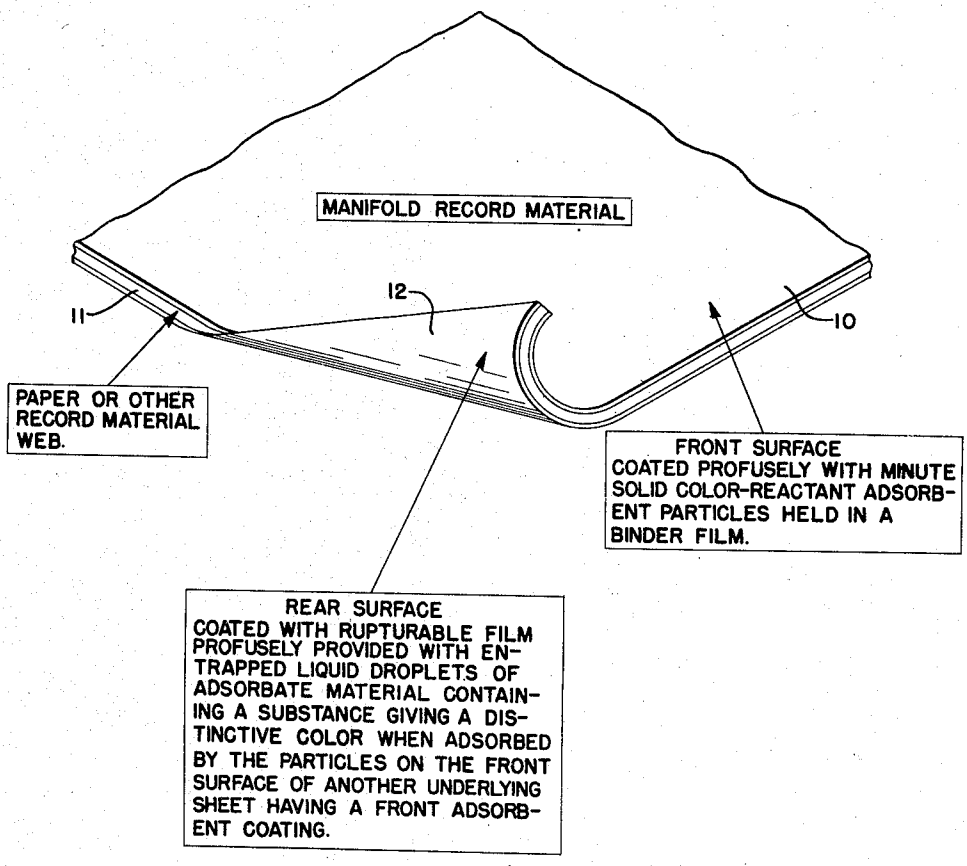
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MANIFOLD RECORD MATERIAL AND PROCESS FOR MAKING IT

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MANIFOLD RECORD MATERIAL AND PROCESS FOR MAKING IT

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2 Claims. (Cl. 282—28)

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This invention relates to manifold record material and to a process for making it, and more particularly pertains to such record material which acts both as a receiving sheet and a transferring sheet and, hence, is suitable for use in a stack or pile wherein an original entry made on the top sheet by impact or pressure is reproduced on the top surface of each under sheet without the necessity of using interleaved transfer sheets.

This application is a division of pending United States application, Serial No. 41,756, filed by applicants herein, on July 31, 1948.

It is, of course, recognized that heretofore it has been possible to transfer from the back of an entry receiving sheet to an under sheet, without the use of interleaved transfer sheets like carbon paper, by simply coating the back of the receiving sheet with a carbon transfer composition or the equivalent. Such a sheet coated on the back with ordinary carbon transfer composition smudges and dirties the under sheets or the operator's hands. Moreover, being coated with colored marking materials, ordinarily of dark appearance, such sheets are not attractive.

The novel transfer sheet which is the subject of this invention is smudge-proof and pleasing in appearance, being white on both sides or white on the receiving side and a pleasing color on the back side, as the material transferred to the under sheet causes color therein only by reason of a color reaction between the transferred material and the sensitized receiving surface, producing a distinctively colored mark on the receiving surface without changing the appearance of the back of the sheet from which such transfer is made. The receiving surface is such that, although it is sensitized, it may be used as the surface on which the original entry is made by writing, typing or printing.

The color reaction which causes the distinctively colored marks to appear at points of pressure on the under sheets is of the type known as an adsorption color reaction wherein a color reactant material changes color when adsorbed on a suitable adsorbent material, without the presence of any ionizing medium.

The reactant material which changes color is 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 surface chemical reaction, giving it a distinctive color, and the adsorbent material is an inorganic substance which is an acid relative to the organic compound so as to be an electron acceptor when in adsorption contact therewith. The adsorbent material is in fine particle form to provide a large

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adsorbent surface area per unit area of the record material, and the organic compound is carried in a fluid so it is more readily mobile to make adsorption contact with the adsorbent.

In our co-pending application for United States Letters Patent Serial No. 38,547, filed July 13, 1948, there is disclosed a pressure sensitive record material producing color by the same type of color reaction except the record material disclosed therein was coated on one side only with the two color reactants superimposed in proximity but insulated from each other by a pressure rupturable film. Any pressure or blow on such a sheet produces color.

In the present invention the individual sheet is immune to any pressure or impact, it being necessary to bring two such sheets into superimposed relation where the back surface of one sheet rests on the front surface of another sheet of the same material before a color reaction can be caused by pressure.

The color reactant on the sensitized receiving surface is the inorganic reactant in small solid particle form profusely dispersed in a binder coating so that the particles are available for contact by the color reactant droplets transferred from the back of the superimposed sheet by pressure. The transfer coating is a rupturable film having profusely dispersed therein small droplets of an inert oily solvent in which the second color reactant is dissolved, said droplets being expelled locally at points of pressure.

Therefore, it is an object of this invention to provide a sheet of record material which has on a front receiving surface a coating containing small solid particles of a first color reactant material and which has on the rear surface a pressure rupturable coating which has profusely dispersed therein minute liquid droplets containing a second color reactant which produces a distinctive color when in contact with the first color reactant, the droplets being extrudable locally from the coating on pressure being applied so as to come in contact with the receiving front surface of an underlying sheet of the same kind, there to produce a distinctively colored mark.

Another object of the invention is to provide a process for making such record material.

Further objects and objects relating to details and economies of production 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 specifications. The invention is clearly defined and pointed out in the appended claims.

The drawing is a schematic showing on a large

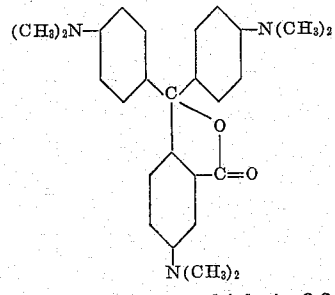
scale of a portion of a piece of the novel record material.

The sheet or web used as a base for the coatings preferably is thin paper although other materials of similar utility suitable for writing or printing may be employed.

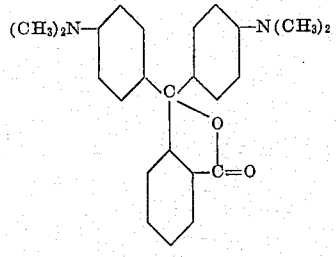
The sensitized receiving surface of the sheet contains as the active ingredient a material upon which the active ingredient of the liquid droplets received from the bottom of an overlying sheet may be adsorbed, the adsorbate in the liquid and the adsorbent being selected so as to produce a color upon adsorption taking place.

Among the most satisfactory adsorbents from an economic and functional standpoint is magnesium trisilicate. This material may be applied to the sheet by use of a white or colorless binder to give a white surface which will receive ink or other marking fluid as well as being adsorptive with respect to the adsorbate in the liquid received from the rear surface coating of an overlying sheet. Thus, the novel manifold sheet may be used as a top sheet as well as an intermediate or bottom sheet of a stack.

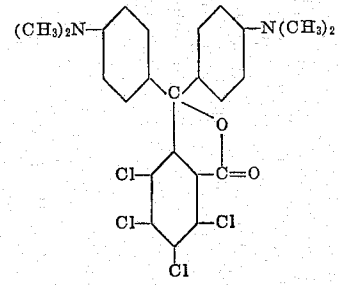
The color reactant adsorbate carried in the rear surface film of the novel manifold sheet is present therein dissolved in minute droplets of an oily, non-evaporable, inert liquid medium, preferably a chlorinated diphenyl and may consist of one or more color reactants such as crystal violet lactone, which is 3,3 bis(p-dimethylaminophenyl)-6-dimethylamino phthalide, having the structure



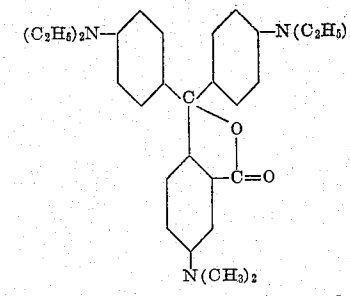
malachite green lactone, which is 3,3 bis(p-dimethylamino-phenyl) phthalide, having the structure



tetrachloro malachite green lactone which is 3,3 bis(p-dimethylaminophenyl)-4-5-6-7 tetrachloro phthalide, having the structure



and 3,3 bis(p-diethylaminophenyl)-6-dimethylamino phthalide, having the structure



The adsorbate color reactant dissolved in the inert oily liquid medium is held as minute droplets profusely dispersed in a solid pressure-rupturable film, preferably of gelatin derived from an emulsion in which gelatin in water forms the continuous phase, which is dryable to form the film, and in which the oily solution forms the discontinuous phase.

The adsorbent may be applied to the sheet by the use of an ordinary paper coating starch binder.

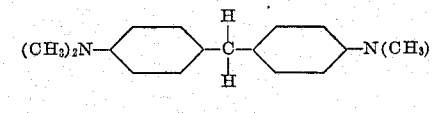
This manifold sheet is an improvement on the manifold sheet disclosed in Barrett K. Green's United States Patent No. 2,374,862 issued on May 1, 1945, which was useful only as an overlying sheet and which was not sensitized to receive data from an overlying sheet. The present improvement provides a record material sheet having the dual features of being sensitized to receive data from an overlying sheet and of transferring it to an under sheet. The novel manifold sheet is smudge-proof on both sides and is not subject to discoloration by handling as the reactants are on opposite sides of the sheet.

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, called the transfer surface or rear surface, a coating is applied which becomes a solid pressure-rupturable insulating film in which are entrapped a profuse number of minute liquid droplets in which a color reactant substance has been 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 coating forming the transfer surface, when dry, is of the order of .001 of an inch.

The transfer 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 gelatin solution there is dispersed, or emulsified, three parts, by weight, of a solution of crystal violet lactone, which is 3,3 bis(p-dimethylaminophenyl)-6-dimethylamino phthalide, mixed with an equal weight of bis(p-dimethylaminophenyl) methane being known as methylene base and having the structure



The solution of crystal violet lactone and methylene base is made by dissolving 1½ parts, by weight, of crystal violet lactone and 1½ parts, by weight, of methylene base in 97 parts, by weight, of chlorinated diphenyl which has a chlorine content averaging 48 per cent by weight. This 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° Fahrenheit, 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 transfer coating is next treated to drive the droplets from the top surface portion of the film into the interior of the film so as, in effect, to form a surface skin thereon. This is accomplished by wetting the surface of the dried film with water at room temperature, that is from 70°–80° Fahrenheit, which water has 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 followed by a drying operation in a low humidity atmosphere, either at room temperature or at an elevated temperature as high as 180° Fahrenheit. The surface wetting may be accomplished by floating the coated paper on the water, coated side down, or by carrying it around a partially submerged drum with the coated surface facing outwardly.

Onto the front receiving surface of the sheet is coated the adsorbent color reactant material in a binder. In making the adsorbent 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 magnesium trisilicate is dispersed in three parts, by weight, of water, by use of a ball mill or equivalent. Four parts, by weight, of the magnesium trisilicate dispersion is mixed with one part, by weight, of the starch solution. The resultant mixture is applied to the sheet, at room temperature, in any convenient manner, as by a paper coating machine. This adsorbent coating, when dry, should have a thickness of about .0005 of an inch.

The coating thickness specified may be varied by 25 per cent, or more, without interfering with the sensitivity thereof.

This record material, in the unused state is substantially white on both sides and the droplets of color reactant when expressed by pressure onto the absorbent surface of another like sheet will produce a dark blue mark, which intensifies on standing, defining sharply the area of applied pressure. The droplet size is so small that the mark appearing on the adsorbent surface caused by drawing a line on an overlying sheet appears as a continuous line, and not as a series of dots.

The compound crystal violet lactone may be made by the process described in United States Letters Patent No. 2,417,897, issued March 25, 1947, on the application of Clyde S. Adams, although the compound is incorrectly named in that patent as 3,3 bis(p-dimethylaminophenyl)-6-dimethylaminophenyl phthalide. A reissue of that patent to correct the name was made on August 17, 1948, under No. Re. 23,024.

Example 2.—Another embodiment of the invention is in the substitution of 1½ parts by weight of crystal violet lactone for the methylene base of Example 1, making 3 parts, by weight, of crystal violet lactone. The color produced is the same as in Example 1.

Example 3.—Another embodiment of the invention is the use of malachite green lactone, which is 3,3 bis (p-dimethylaminophenyl) phthalide instead of the crystal violet lactone of Example 2. This provides a substantially white record material giving a green color when adsorbed on magnesium trisilicate but it is not as intense as the blue of crystal violet lactone.

Example 4.—Another embodiment of the invention is the use of an equal weight of tetrachloro malachite green lactone, that is to say 3,3 bis(p-dimethylaminophenyl) 4,5,6,7 tetrachloro phthalide, in place of the crystal violet lactone of Example 2. This provides a substantially white record material giving a green color reaction.

Example 5.—Another embodiment of the invention is the use of an equal weight of 3,3 bis(p - diethylaminophenyl) - 6 - dimethylamino phthalide, in place of the crystal violet lactone of Example 2. This makes a substantially white record material giving a blue color reaction.

In Examples 1 to 5, inclusive, 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 adsorbent particles 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 adsorbent material.

In making the binder containing casein and latex, a starch solution, as described in Example 1, is made and allowed to cool. Next, 1 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, by weight, of cold water and $\frac{1}{10}$ of a part, by weight, of ammonium hydroxide of 25° Beaumé are added. This casein dispersion is heated on a water bath at 165° Fahrenheit for 15 minutes and then allowed to cool. The latex to be used should contain approximately 45 per cent of solids in water. The adsorbent material particles to be used are dispersed in water as set out in Example 1 except the water should contain 0.2 per cent, by weight, 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 paper and has excellent properties as far as the access of the adsorbent particles to the action of the liquid color reactant droplets expelled thereonto is concerned.

Referring to the drawing, **10** indicates the sensitized receiving surface coating containing the adsorbent color reactant, **11** indicates the supporting web, such as paper, and **12** indicates the transfer coating containing the liquid droplets in which the adsorbate color-reactant material is dissolved.

A particular system utilizing the novel mani-

fold record material disclosed herein is disclosed in our co-pending application for U. S. Letters Patent, Serial No. 41,757, filed July 31, 1948, wherein a stack of such sheets in superimposed relation is provided for use in making multiple copies through a single impression.

It is understood that the novel manifold record material described herein is susceptible of considerable variations without departing from the spirit of the invention.

What is claimed is:

1. A sensitized record material adapted to be used in conjunction with other record material of the same kind, in superimposed relation and faced in the same direction, to form a manifold pack, including a sheet of material suitable for a manifold record material base web, said sheet having a front receiving surface and a rear transfer surface; a coating on the front receiving surface of the sheet comprising a binder containing profuse numbers of minute solid particles of adsorbent material; and a pressure-rupturable coating on the rear transfer surface, having entrapped therein a profuse number of minute liquid droplets containing a substance which is adsorbable on material like the adsorbent particles in the coating on the front receiving surface and reactant therewith on contact to form a distinctive color, recording pressures on the front receiving surface through the adsorbent coating causing rupture of the coating on the rear transfer surface locally at the points of pressure there to release and extrude on the surface of the said ruptured coating droplets of the liquid, there available for adsorption on the receiving surface of an under sheet to produce a distinctively colored mark thereon, the adsorbent being magnesium trisilicate, and the adsorbable material being 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 surface chemical reaction with the adsorbent, giving it a distinctive color.

2. A process for making a sensitized record material sheet to be used in conjunction with other sheets of record material of the same kind, in superimposed relation and faced in the same direction to form a manifold pack, including the steps of coating one side of a sheet of material, suitable for a manifold web, with a film of binder material in which is profusely dispersed minute solid particles of an adsorbent material which is one of two substances which comprises an adsorbent and an adsorbate which produce color in contact; and the step of coating the other side of the sheet with an emulsion having a continuous phase dryable to a pressure-rupturable film and having a discontinuous phase of an inert oily liquid containing the adsorbate substance whereby upon drying the discontinuous phase is entrapped in the film as a profusion of minute droplets of liquid which may be released locally by pressure applied to the sheet, the adsorbent being magnesium trisilicate, and the adsorbate material being 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 surface chemical reaction with the adsorbent, giving it a distinctive color.

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No references cited.