March 17, 1964 H. R. DALTON 3,125,458

PRESSURE AND HEAT SENSITIVE COATING COMPOSITIONS AND RECORDING BLANKS COATED THEREWITH

Filed May 20, 1960

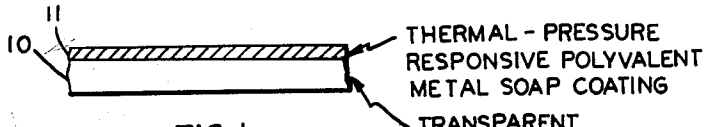


FIG.1

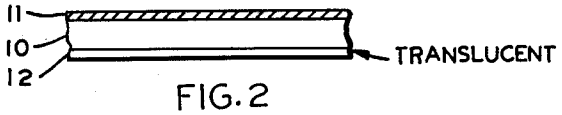


FIG.2

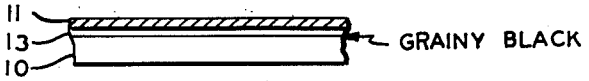


FIG.3



FIG.4

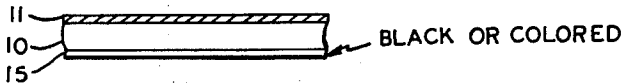


FIG.5

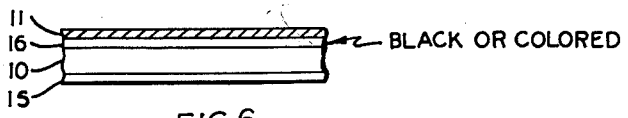


FIG.6

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PRESSURE AND HEAT SENSITIVE COATING COMPOSITIONS AND RECORDING BLANKS COATED THEREWITH

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This invention relates to coating materials and methods of preparation thereof, and more particularly it relates to such coating materials in the form of polyvalent metal soaps, and is in the nature of an improvement on the coating materials disclosed in applicant's prior Patents No. 2,313,808 and No. 2,313,810.

A principal object of the invention is to provide an improved polyvalent metal soap coating composition and method of preparation thereof.

Another principal object is to provide a polyvalent metal soap composition which can be used to coat paper, cloth, metal, plastic film and the like.

The invention also relates to a new coating composition for application as a substantially continuous non-transparent, i.e. relatively opaque, coating over a surface, the opacity of which coating can be partially or practically completely reduced in localized areas, for example wherever it is subjected to impact pressure such as by applying a writing stylus or typewriter bar.

The invention relates also to the method of preparing this new coating composition with its unique properties described hereinbelow and also to the method of preparing with such a coating composition an impact or pressure sensitive, as well as heat sensitive, recording blank.

For example, a recording blank made according to the invention has a coating which does not dust or flake off during use of the blank and does not require a protective covering film. In fact, the coating in some cases can be made so tough that it is self supporting and can be used as such.

A significant feature of the polyvalent metal soap content coating for recording blanks according to the invention, is that its hardness and response to impact or pressure can be controlled more readily and selectively than has been heretofore possible. By proper selection of resin binder and polyvalent metal soap this same convenient control is possible over the heat sensitivity of the recording blank.

A further feature of the invention relates to recording blanks of the heat sensitive or pressure sensitive kind, employing a polyvalent metal soap coating.

Other features and advantages not particularly enumerated will be apparent from the following detailed descriptions and the appended claims.

In the drawing,

FIG. 1 shows a recording blank having a light transparent backing and sensitive coating according to the invention;

FIG. 2 shows a modification of the recording blank of FIG. 1;

FIGS. 3, 4, 5, 6 show further modifications of the blank of FIG. 1.

Heretofore, the hardness of a coating containing particles of a polyvalent metal soap dispersed in the earlier used formulations could be controlled to some limited extent by the proportion of binder in the coating. Nevertheless such coatings had undesirable limitations. For example, increased proportions of binder not only made the coating undesirably harder and thus more rigid and less ductile, but also made it much less adhesive to the backing member and readily prone to cracking, dusting and flaking.

Such earlier coatings thus were restricted in scope of their utility by being inapplicable for many purposes and in certain uses.

The foregoing and other limitations, restrictions and shortcomings of the earlier used opaque coating compositions and of the recording blanks embodying such coatings are overcome by the coating compositions, methods and coatings of this invention.

Considered broadly, a typical method of preparing these advantageous coating compositions of this invention and the resulting coating compositions comprises mixing about thirty parts of a resin with a solvent for the resin, and water in an amount just slightly less than that which would precipitate the resin from solution, with about ten to eighty parts of a polyvalent metal soap in finely powdered form. The solvent for the resin must not be a solvent for the polyvalent metal soap, nor should the solvent, water mixture have any marked tendency to dissolve or form a gel with the polyvalent metal soap. The composition is then colloid, ball, roll milled or processed by any similar means until homogeneous. Generally from about one to two hours ball milling is sufficient time for the polyvalent metal soap to become homogeneously dispersed in the suspending vehicle.

The use of a plasticizer for the resin or resin blends is undesirable as most plasticizers have a solubilizing effect upon the polyvalent metal soap and will adversely effect the desirable whiteness or brightness of the dried coating. They also have a tendency to migrate from the coating so that its properties are constantly changing with time. Plasticizers are also objectionable because they affect rubber feed rolls in automatic recording blank feeding equipment so that they become soft. Coatings containing plasticizers are also likely to stick to rubber rolls and thus create a serious problem either with the rolls or in removing the coating from the paper at the place of contact.

The polyvalent metal soap of a fatty acid should be one that does not melt and will remain solid in discrete and non-transparent particle form, at the ambient temperatures prevailing in the environs wherein the coating compositions and the recording blanks embodying the same are to be used. Thus, there generally can be used any polyvalent metal soap of any polyvalent metal with any fatty acid having at least six carbon atoms, and beneficilly, say, from six to about twenty-four carbon atoms, so long as the soap does not melt at the highest ambient temperature in the locality where the coating or resulting coated product is to be used. The non-transparent particles of a satisfactory soap generally show under those conditions submicroscopic pores within the soap particles in the finished coating.

So far as presently indicated, such polyvalent metal soaps advantageously can be those of such fatty acid having up to and including eighteen carbon atoms, such as palmitic, stearic, hydroxystearic, lauric, oleic, sebacic, capric, caprylic acids and the like.

Accordingly it is a feature of the present invention to provide a coating dispersion of a polyvalent metal soap and a binder, using an organic solvent and water, to form a homogeneous solvent solution, as distinguished from an emulsion, in which the binder alone is soluble, but without materially affecting the desirable coating properties or other properties of the polyvalent metal soap, the dispersion being free from any plasticizer or substance that will modify the properties of the polyvalent metal soap or give to the dried coating the undesirable properties already mentioned.

The liquid suspending vehicle for the polyvalent metal soap must be a solvent for the binder or resin and should contain some water to form a homogeneous liquid suspending vehicle. Solvents to which water may be added

to form a homogeneous liquid suspending vehicle may be listed as follows: acetone, methyl alcohol, ethyl alcohol, dioxane, methyl ethyl ketone, ethyl ether, or a mixture of these. It is necessary that a greater portion of the solvent mixture have a considerably higher vapor pressure than water.

From the foregoing extended description and brief definition of the applicable liquid suspending vehicle, a person of ordinary skill in the art involved can tell from the identity of an organic solvent and general information as to its properties whether it is suitable. In some cases a few simple check tests may be needed to note whether some particular solvent or solvent combination is compatible and can dissolve the resin. After this determination, water can be added to the point where the mixture becomes cloudy, indicating that it is no longer homogeneous and is approaching the formation of an emulsion or suspension of the resin. Slightly less than this amount of water is the amount to use. Such tests can be made readily by a person of ordinary skill, and who would know how to make them for only merely simple physical steps are involved.

The invention as to these coating compositions is illustrated by, but not restricted to, the following examples:

Example 1

Thirty grams of ethylcellulose having an ethoxyl content of 47.5–49.0 percent, a substitution value of 2.42–2.53 ethoxyl groups per anhydroglucose unit and a viscosity of 100 cps. (5% solution in 80–20 toluene-ethanol) was dissolved in 300 grams of a 50 percent mixture of acetone and ethanol. To this was added the dispersion containing: 5 grams of Triton X–100 (Rohm & Haas—octylphenoxy polyethoxy ethanol) wetting agent, 200 grams of a 50 percent mixture of acetone-ethanol mixture, 60 grams water and 50 grams of calcium stearate made homogeneous by ball milling in a steel ball mill for one hour. The complete dispersion, after being filtered through a fine screen to remove any dirt and other foreign matter, was ready for coating.

Several methods of coating are suitable, e.g. coating rolls, doctor blade, wire wound doctor rod, air knife, and others.

The filtered coating composition, applied to a dark coated paper (25 lbs. 24" x 36"—500 sheets) and then dried, provides satisfactory useful coatings of from 0.15 to 1.0 ounce per square yard, depending on the coating device adjustment, after drying the coated paper at about 180 degrees F. The coating had a melting point of approximately 275 degrees F. and gave very satisfactory duplications of type impression through an ordinary bond paper. It gave good sharp impressions from a vibrating stylus of a facsimile machine.

Example 2

This example is the same as Example 1, except that 50 grams of zinc stearate was substituted for 50 grams of calcium stearate used in that example. The dried coating, however, had a melting point of approximately 225 degrees F.

Example 3

Thirty grams of 5–6 seconds nitrocellulose having a nitrogen content of 11.8–12.2 percent and a viscosity of 5–6.5 seconds (A.S.T.M. Spec. D301–33) was dissolved in a mixture of 120 grams of acetone and 400 grams of ethanol. To this was added 40 grams of water and 5 grams of Triton X–100. This gave a clear resin solution. 40 grams of magnesium stearate were added to this and the mixture ball milled and filtered as in Example 1.

The coating was applied as indicated in Example 1 and had a melting point of approximately 250 degrees F.

Example 4

Thirty grams of cellulose acetate having percent combined acetic acid of 54.0 to 55.0, and a viscosity of 60 to 80 seconds (time of fall of a 5/16" steel ball through 10" of a 20 percent solution of cellulose acetate dissolved in a solvent composed of acetone-ethanol in ratio of 90 to 10) was dissolved in 400 grams of 50 percent mixture of acetone-ethanol. 5 grams of Triton X–100 and 60 grams of water were then added to give a clear solution. To this was added 50 grams of zinc sebacate and the mixture milled and filtered as in Example 1.

The coating was applied as indicated in Example 1 and had a melting point of approximately 350 degrees F.

Example 5

This example is the same as Example 4, except that 10 grams of calcium stearate was substituted for 50 grams of zinc sebacate used in that example. The dried coating, however, had a melting point of approximately 250 degrees F., was much harder than that of Example 4, and gave a very fine trace with a stylus heated to 325 degrees F.

Example 6

This example is the same as Example 4 except that 70 grams of calcium stearate was substituted for 10 grams calcium stearate used in that example. The dried coating had the same melting point of approximately 250 degrees F., and was more pressure sensitive than the coating of Example 4. It gave very good sharp impressions from a vibrating stylus of a facsimile machine and very satisfactory impressions of type through ordinary bond paper.

The various coating compositions of these examples according to the invention can be applied to various types of supports or backing members, such as metallic foil, paper, plastic film, fabric, cardboard, coated paper, etc., to give a recording blank or medium for stylus or impact, or even thermo recording. For example, the dried and coated paper of each of the foregoing examples constitutes a recording blank and can be used either for pressure sensitive or for heat sensitive recording.

Then also, there can be certain types of modifications in the recording blanks from the physical aspect, to fit various types of contemplated uses. For example, as shown in FIG. 1, a recording blank is made by applying to a light-transparent or translucent backing member **10**, such as a translucent colorless or colored plastic, or a transparent plastic or a transparent plastic with a translucent coating on one surface of it, a layer **11** of a coating composition of this invention and evaporating the suspending vehicle and then drying that layer to form a substantially opaque mask. This combination provides a novel form of recording blank which can have either printed matter and/or designs formed in the polyvalent metal soap coating in response to any well known method of recording, for example, the pressure of a stylus or impact of a printing type bar, by heat, or the like.

As a result, the transparent or translucent backing is exposed at those particular areas where the opaque polyvalent metal soap coating was acted upon or rendered transparent by the pressure or thermo effect, thus enabling the blank to be used in light-projecting systems to project the recorded subject matter on a suitable screen, or for making copies as by the photographic or diazo or other methods.

The backing member **10** may be of translucent material, such as amber colored glassine paper, or a clear film printed or coated to have a grainy black or colored surface, bearing a dried coating of the composition of this invention. This provides a good recording contrast that enables the production of a clear and sharply projectable image.

Another effective type of recording medium is one made from a flexible backing member of paper, cardboard, and the like, with an applied and dried coating of the composition of the invention. Such backing member, before application of the coating composition of this invention, can be of any color or merely be dark in ap-

pearance or can bear a colored or dark coating on either or both of its surfaces. Then the application on one of its surfaces of a coating of a white or light colored coating composition of this invention, followed by drying, provides a recording blank having a white or light colored pressure or thermo-sensitive coating of the dried polyvalent metal soap deposited on the dark colored backing member.

Such a recording blank can be subjected to any suitable typing or printing pressure or other impact to remove from, or compress and thereby make transparent the polyvalent metal soap in any desired area of the coating of the invention. As a result, the contract between the thus exposed dark colored backing member areas and the untouched areas of the coating make the thus recorded subject matter easily readable.

Several recording blanks including certain of the types described hereinabove are schematically illustrated, with exaggerated thickness, in the accompanying drawings, wherein the coating material according to the invention is marked **11**.

FIG. 1 shows a recording blank with a pressure and thermo-sensitive coating **11** of a dispersion of a polyvalent metal soap held distributed through the dried binder which coating is spread on the upper surface of a light-transparent backing member.

FIG. 2 shows a recording blank, such as in FIG. 1, but with a translucent coating **12** on the underside of the backing member.

FIG. 3 shows a recording blank as in FIG. 1, but with the clear film **10** having a grainy black upper surface **13** to which the coating **11** of the invention is bound.

FIG. 4 represents a recording blank having its pressure-sensitive coating **11** carried on the upper surface of a colored or dark backing member **14**.

FIG. 5 illustrates a recording blank as in FIG. 1, but having a colored coating **15** on the underside of the transparent backing member **10**.

FIG. 6 shows a recording blank like that of FIG. 5, but having also on the upper surface of the backing member **10** another colored coating **16**, to which the coating **11** is affixed. The lower coating **15** may be omitted if desired.

While many resins may be found to function as indicated in an organic solvent-water system, those of primary importance are the esters and ethers of cellulose, such as cellulose nitrate, cellulose acetate, cellulose butyrate, cellulose acetate butyrate, ethyl cellulose, benzyl celluose, ethyl cellulose acetate, etc. A modifying resin may be used along with the cellulose derivative to improve, for instance, the adhesion of the film to some particular surface. Thus, in Example 4 the addition of 20 grams of Santolite MS (aryl sulfonamide-formaldehyde resin, manufactured by Monsanto Chemical Co.) produces a coating with improved adhesion to certain surfaces and also increases its hardness so that it becomes primarily a coating for heat sensitive recording blanks.

Also the addition of a small percentage of a pigment or dye to the formulations given will produce a colored coating which could be used to cover a surface which is white or of contrasting color to form a negative image or other desired effect.

While the invention has been explained in connection with certain preferred embodiments and utilizing certain specific materials, it will be understood that the invention is not limited thereto. For example, while use of heat is not mentioned for the preparation of the solutions or dispersions with the different cellulose derivatives, ordinarily ambient temperatures are wholly suitable. However, that does not preclude using heat, such as to assist in dissolving some of the solid resins in the selected solvents or when adding water to the various organic solvents to vary the amount as desired. Other cellulose derivatives than those named may also be found useful.

It has been found that the addition of water to the coating formulation as disclosed seems to have a multiple effect and that its use makes possible the production of stronger, more non-brittle, non-flaking coatings possessing improved whiteness, pressure sensitivity and thermo properties than has been heretofore possible through the use of either water additions to the resin system or the incorporation of a polyvalent metal soap therein. Although it is not known for a certainty, it would seem that the water has a dispersion effect upon the polyvalent metal soap and becomes closely associated with the polyvalent metal soap particles so that, upon drying, smaller air cells are formed to improve the whiteness or brightness of the coating together with producing a stronger bond between the resin and the soap particles. Rapid drying under all atmospheric conditions is also possible, probably because the water is held more tightly to the soap particles and remains in the coating long after all other solvents have been removed.

While the invention has been described in connection with its primary utility as applied to recording blanks, it will be understood that the coating materials of the invention are capable of a wide variety of other uses as for instance where a selectively responsive light-transmission coating is required.

What is claimed is:

1. A normally non-transparent liquid coating material which when dried on a backing support changes its light transmission properties in response to heat or pressure at localized areas, comprising a spreadable and homogeneous dispersion as distinguished from an emulsion of discrete non-transparent particles of a polyvalent metal soap of a fatty acid having at least six carbon atoms, wherein the dispersion vehicle includes a resin binder of a cellulose derivative dissolved in a volatile resin solvent which dispersion also includes water, the soap particles being insoluble in said solvent and constituting from fifteen percent to eighty percent by weight of the solid constituents of the dispersion, amount of water being slightly less than otherwise would precipitate the resin from its solution.

2. A normally non-transparent coating material according to claim 1 in which the said binder is chosen from the group consisting of cellulose ethers and cellulose esters and said dispersion constitutes a clear and homogeneous resin-solvent mixture.

3. A normally non-transparent coating material according to claim 1 in which said polyvalent metal soap has from six to approximately twenty-four carbon atoms.

4. A normally non-transparent coating material according to claim 1 in which said binder is cellulose nitrate.

5. A normally non-transparent coating material according to claim 1 in which said binder is cellulose acetate.

6. A normally non-transparent coating material according to claim 1 in which said binder is cellulose acetate butyrate.

7. A normally non-transparent coating material according to claim 1 in which said binder is ethyl cellulose.

8. A normally non-transparent coating material according to claim 1 in which said binder is ethyl cellulose acetate.

9. The method of coating a backing support with a normally non-transparent coating material which at localized areas changes its light transmission properties in response to heat or pressure, which comprises forming a homogeneous dispersion as distinguished from an emulsion by adding polyvalent metal soap of a fatty acid having at least six carbon atoms to a liquid dispersion vehicle comprising a cellulose derivative resin binder in a volatile solvent which includes added water in which solvent the metal soap is insoluble to form a spreadable mixture, wherein the soap particles constitute from fifteen percent to eighty percent by weight of the solid constituents of said mixture and the amount of water being slightly less than would otherwise precipitate the resin from its solution, drying the said mixture on a backing support to volatilize said solvent and to form on said support a non-transparent layer wherein the polyvalent metal

soap is present as discrete non-transparent particles, but which layer is capable of being rendered light transmissible in selected areas in response to heat and pressure thereat.

10. The method according to claim 9 in which said dispersion vehicle is substantially inert to said soap and also to the backing support on which the dispersion is dried, and the drying is effected at a temperature below that at which change in the physical characteristics of the coating occurs, and said dispersion is rendered homogeneous by agitating prior to spreading on said support.

11. A recording blank comprising a backing carrying on one side thereof a dried coating according to claim 1 which coating includes a colored pigment.

12. A recording blank comprising a backing support of opaque material having deposited thereon a dried coating according to claim 1.

13. A recording blank comprising a backing of transparent material having deposited thereon a dried coating according to claim 1.

14. A recording blank comprising a backing of transparent material having a translucent coating on one side and on the opposite side a dried coating according to claim 1.

15. A recording blank comprising a transparent backing having a dark colored coating thereon and superposed on said coating a dried coating according to claim 1.

16. A recording blank comprising a transparent backing having an opaque coating on one surface thereof and on the opposite surface a dried coating according to claim 1.

17. A recording blank comprising a backing of transparent material having both surfaces thereof provided with a colored opaque coating and superposed on one of said opaque coatings a dried coating according to claim 1.

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