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PRESSURE-SENSITIVE, HEAT-RESISTANT RECORDING
MATERIAL AND METHOD OF MAKING SAME
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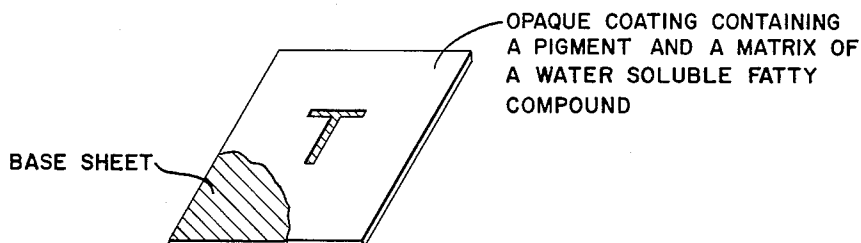


FIG. 1

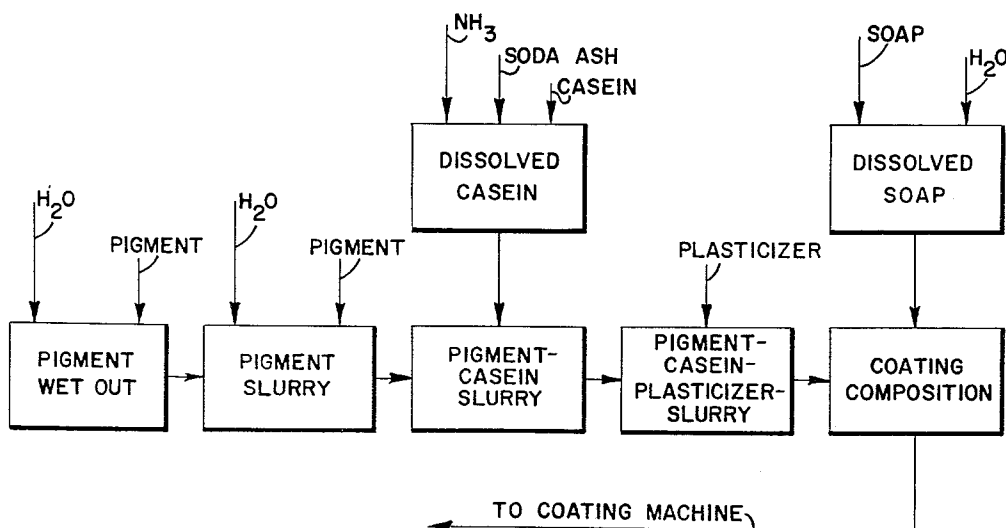


FIG. 2

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PRESSURE-SENSITIVE, HEAT-RESISTANT RECORDING MATERIAL AND METHOD OF MAKING SAME

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Continuation of application Ser. No. 720,019, Mar. 10, 1958. This application Dec. 10, 1959, Ser. No. 853,573 17 Claims. (Cl. 117—36.7)

This invention relates to pressure-sensitive, heat-resistant recording material and method of making same and, in particular, to such material in which a coating of pigment dispersed in a matrix is applied to a supporting web in combination with a coextensive undersurface of a color contrasting to that of the pigment, the interrelation of matrix and pigment being such that the coating is normally opaque, but becomes transparent wherever sufficient pressure is applied. For example, when sheets of material of this nature known as "autocopy paper" have been prepared with a white pigmented coating on a black undersurface, writing in black characters can be made to appear on one or a number of superposed sheets thereof by pressure of a stylus point or impact of typewriter keys without the use of carbon paper, ribbon, ink, crayon, or any other outside pigment means. While autocopy paper of the above-described properties is old, such known papers have all been prepared with coatings applied in a liquid solvent and suspension medium other than water, usually one of the organic solvents. Such solvents impose extra problems upon a manufacturer including added fire and explosion hazards and extra capital outlay for solvent recovery apparatus.

It is the object of this invention to provide a pressure-sensitive, heat-resistant recording material of the above-described properties prepared with a coating applied in water as a solvent and suspension medium.

What we have discovered is that, speaking generally, a suitable coating fluid can be prepared from proper amounts of pigments, water-soluble fatty compound, and water. Such a coating is transparent when applied wet and becomes opaque as it dries, having the color of the pigment particles which are distributed evenly through it embedded in the fatty compound as a matrix. When subjected to local pressure, as in writing, the dry coating becomes transparent again. The mechanism by which this happens is, we believe, that the coating as applied contains air which makes for air-pigment and air-soap interfaces that reflect and refract the incident light producing the opaque appearance. Under local pressure the coating is compacted and the air is forced out leaving the coating transparent.

The arrangement of the elements entering into this invention consists of a base sheet, preferably paper, of a color contrasting to the color of pigment in the coating and having a coating adhered thereto of a pigment dispersed in a water-soluble soap matrix. It will be understood that the base sheet could be of transparent material coated on its underside with our pressure-sensitive coating which was in turn coated with a color contrasting layer.

A coating according to our invention when properly compounded produces an economical, pressure-sensitive material which reproduces by compaction without transfer or chemical reaction, is water soluble, and can be applied on conventional paper coating apparatus such as a roll coater or a knife-blade coater. When coated on a sheet of paper, no color change is produced in the coating, nor is writing made by pressure thereon obliterated by heat, even up to temperatures that will scorch or ignite the paper. The essential elements of a coating liquid ac-

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cording to our invention are a pigment and a matrix former. The matrix former must be water soluble and must consist of a fatty compound, for example, either a water-soluble soap or a sulfonated oil or a mixture of the two. The pigment and matrix former are mixed with a sufficient quantity of water to produce the desired fluidity. We have found, in addition, that certain additives are desirable to increase the resistance of the applied and dried coating to chalking, to give it some resistance to accidental wetting, and to impart a certain brittleness to the coating so that the threshold of pressure to which it is sensitive will not be too low. In most cases the pH value of the liquid coating requires that such additives be alkali compatible. In addition, we have found in certain instances a small amount of plasticizer may be profitably added.

Various pigments can be satisfactorily used in the practice of this invention including silica, commercially available under the trade names "Hi-Sil" and "Santocel," calcium and magnesium silicates or mixtures thereof, for example, the product commercially available under the trade name "Silene," diatomaceous earth, commercially available under the trade name "Celite," magnesium carbonate, and the well-known satin white, which is slaked lime and alum. Other pigments which can be used according to this invention include aluminum silicate, calcium carbonate, commercially available under the trade name "Purecal," and barium sulfate, commercially available under the trade name "Blanc Fixe."

The pigment employed should be capable of obscuring the color of the base sheet by its light-scattering properties and should be capable of producing an opaque coating when laid down and high transparency when imaged. The pigment used should also be capable of being sensitive to pressure and become transparentized thereby but should not render the coating sensitive to heat. We have found that pigments having a refractive index below about 1.64 are operative in the practice of this invention. Pigments having a refractive index much above 1.64 lose their ability to be transparentized by the application of pressure and have generally been found to be inoperative.

The operative pigments, pigments having a refractive index below 1.64, have also been found not to be equivalent. Certain of these pigments work surprisingly better than others. We have found that the most advantageous pigments are magnesium carbonate, satin white, calcium and magnesium silicate, and calcium carbonate. Magnesium carbonate and satin white are highly superior pigments when used according to this invention. These pigments result in an original coating of high opacity and are easily deformable by pressure to yield an image of great contrast. The other pigments disclosed above perform less efficiently in one or more respects or require formula modifications in the way of increased adhesion or supplementary opacifiers.

Although pigments of various particle sizes can be used, we prefer to use a pigment having a particle size below about 5 microns.

The pigments can also be used in combinations if desired. In some instances, a small amount of a pigment having a higher refractive index such as titanium dioxide can be employed with the other pigments to advantage.

The matrix formers we have found are all water-soluble fatty compounds and specifically soaps and sulfonated oils are practicable and effective. The sulfonated oils may be used to replace soap entirely, but we prefer to regard them as extenders. The soaps we have found to be effective are the familiar potassium, sodium, and ammonium soaps of the usual saturated and unsaturated fatty acids and mixtures thereof, for example, the oleates and stearates.

As additives or "brittleness producers" we have used casein, animal glue, latex, sodium silicate, alpha protein, caramelized sugar, natural and modified starches, vinyl and acrylic resins, and emulsions of microcrystalline waxes. Generally speaking, these additives act as hardeners to the matrix former, imparting a certain brittleness to it. Their function is to raise the threshold of pressure sensitivity of the dry coating and to improve its resistance to chalking and accidental wetting. With some formulas a plasticizer is desirable to aid in making up the coating mixture and improving its utility.

These and other aspects of this invention will become apparent upon examination of the following descriptions of particular embodiments thereof and of the accompanying drawings.

FIGURE 1 shows the construction of the pressure sensitive, heat resistant recording material showing a portion thereof after being rendered transparent by the application of sufficient pressure so as to reveal the underlying base sheet at the point at which the pressure was applied.

FIGURE 2 is a flow sheet of Example 1 showing the various steps involved in the process.

As specific examples, we will describe in detail the compounding of three different coating mixtures according to our invention.

Example I

Ingredient:	Parts by weight (dry, calculated)
Pigment—	
Satin white	20
Titanium dioxide	5
Matrix former—soap, predominately sodium oleate	14
Hardener—Casein	2
Plasticizer—Glycerine	34

The completed liquid coating is made up in water as a solvent and suspension medium to contain 25 percent solids.

Procedurally, we wet out the titanium dioxide to 50 percent solids and add to it the satin white wet out to about 37 percent solids. Satin white is normally made wet and kept wet until used at about 37 percent solids. For this pigment ingredient the dry weights are on a basis of air dry with water of crystallization retained. We mix the pigment materials, adding sufficient extra water to make the mixture flowable. We next add the casein which has been previously cooked up, dissolved and modified by ammonia and soda ash according to customary and well-known methods. We next dissolve the soap by heating with all the remaining water, adding the resulting soap solution to the other ingredients to reduce foaming.

Example II

Ingredient:	Parts by weight (dry, calculated)
Pigment—Magnesium carbonate	20
Matrix former—Sulfonated castor oil (50 percent solids)	20
Hardener—Alpha protein	3

The completed liquid coating is made up in water as a solvent and suspension medium to contain 35 percent solids.

Procedurally, we first "slip" the magnesium carbonate in the water and then add the oil and protein, mixing thoroughly.

Example III

Ingredient:	Parts by weight (dry, calculated)
Pigment—Silicon dioxide (Hi-Sil)	20
Matrix former—	
Tallow soap, predominately sodium stearate	10
Sulfonated red oil (50 percent solids)	10
Hardener—"Ac 33" acrylic resin (50 percent solids emulsion)	5

The completed liquid coating is made up in water as a solvent and suspension medium to contain 26 percent solids.

Procedurally, we add a portion of the water to the oil and use the resulting mixture to wet out the silica. We then dissolve the soap in remaining water and add the soap solution to the pigment slurry, mixing thoroughly and adding the resin emulsion.

The proportion of the matrix former to the pigment can be varied quite widely depending mainly upon the particular pigment used. The limits of the concentration of the pigments are governed by the need to opacify and to yield a coating that is sensitive to pressure but insensitive to heat. We have found that the most advantageous area of performance is accomplished by maintaining between about 15 and 120 percent matrix on the pigment on a dry weight basis. The amount of pigment used also varies depending upon the particular properties desired in the finished product. Autocopy papers can be made which will be capable of producing different numbers of copies by varying the amount and type of pigment used. We have made satisfactory coatings over this entire range using various pigments. When using a soap matrix former and a satin white pigment we have found that substantial amounts of additives are necessary for satisfactory results at the ends of the range. Thus with 25 percent matrix former to pigment, the coating was very chalky and extra amounts of casein, as a binder and embrittler, and substantial amounts of glycerine as a plasticizer were needed. On the other hand, with 125 percent matrix former to pigment, the satin white had to be reinforced with titanium dioxide in order to cover and again lots of casein as hardener was required, but no glycerine at all. We prefer to use about 75 percent matrix former to pigment. With this proportion considerably less casein or other hardener is needed to achieve the desired pressure sensitivity threshold and no plasticizer. In all cases, the water requirements are adequately met if the fluidity of the mixture is adjusted to meet the requirements of the standard paper coating apparatus upon which it is to be used. When coating supporting sheets with our material, we have gotten satisfactory results with film thicknesses over the range 0.0002 to 0.001 inch, the optimum seeming to be over the range 0.0004 to 0.0006 inch.

This application is a continuation of our prior application Serial No. 720,019, filed March 10, 1958, now abandoned; which application is a continuation in part of our prior application Serial No. 484,262, filed January 26, 1955, now abandoned.

We claim:

1. Pressure-sensitive, heat-resistant recording material including a base sheet, a normally opaque coating having the property of becoming relatively transparent under writing pressure without becoming relatively transparent under heat up to about the charring temperature of paper and including a matrix formed of at least one essentially non-volatile water-soluble fatty compound and a pigment embedded in said matrix, said pigment having a refractive index of less than about 1.64 and being capable of producing an opaque coating when laid down and high transparency when imaged, and an undersurface of a color contrasting to the color of said pigment, said fatty compound being present in proportions between about 15 and 120 percent by weight based on the dry weight of said pigment.
2. The combination of claim 1 in which the coating includes a hardener.
3. The combination of claim 2 in which the coating includes a plasticizer.
4. The combination of claim 1 in which the fatty compound is a soap.
5. The combination of claim 1 in which the fatty compound is a sulfonated oil.
6. The combination of claim 1 in which the coating includes an alkali soap in the matrix, satin white in the

pigment, and a hardener including casein, and the under-surface is of a color contrasting to white.

7. The combination of claim 6 in which the base sheet is of paper with at least one side of dark color and the coating is applied to said side as a mixture of about 20 parts by weight satin white, 5 parts by weight titanium dioxide, 14 parts by weight sodium soap, 2 parts by weight casein, $\frac{3}{4}$ part by weight glycerine, and sufficient water to make a solution-suspension of about 25 percent solids.

8. The combination of claim 1 in which the proportion by weight of fatty compound to pigment in the coating is as the range 25-125 is to 100.

9. The combination of claim 1 in which the proportion by weight of fatty compound to pigment is as about 75 is to 100.

10. The combination of claim 1 in which the base sheet is of paper with at least one side of dark color and the coating is applied to said side as a mixture of 20 parts by weight magnesium carbonate, 20 parts by weight sulfonated castor oil, 3 parts by weight alpha protein, and sufficient water to make a solution-suspension of about 35 percent solids.

11. The combination of claim 1 in which the base sheet is of paper with at least one side of dark color and the coating is applied to said side as a mixture of 20 parts by weight silicon dioxide, 10 parts by weight sodium tallow soap, 10 parts by weight sulfonated red oil, 5 parts by weight acrylate resin, and sufficient water to make a solution-suspension of about 26 percent solids.

12. The process of making a pressure-sensitive, heat-resistant recording material which includes applying to a base sheet a normally opaque coating having the property of becoming relatively transparent under writing pressure without becoming relatively transparent under heat up to about the charring temperature of paper, said coating consisting of a solution-suspension in water of a mixture including an essentially non-volatile water-soluble fatty compound and a pigment, said pigment having

a refractive index of less than about 1.64 and being capable of producing an opaque coating when laid down and high transparency when imaged, said pigment being of a color contrasting to the apparent color of the surface of said base sheet to which it is applied, said fatty compound being present in proportions between about 15 and 120 percent by weight based on the dry weight of said pigment.

13. The process of claim 12 in which the solution-suspension includes water sufficient to make up at about 25 percent solids and the mixture consists of 20 parts by weight satin white, 5 parts by weight titanium dioxide, 14 parts by weight sodium soap, 2 parts by weight casein, and $\frac{3}{4}$ part by weight glycerine.

14. The process of claim 12 in which the amount of fatty compound in the mixture is from 25-125 percent of the amount of the pigment by weight.

15. The process of claim 12 in which the amount of fatty compound in the mixture is about 75 percent of the amount of pigment by weight.

16. The process of claim 12 in which the solution-suspension includes water sufficient to make up at about 35 percent solids and the mixture consists of 20 parts by weight magnesium carbonate, 20 parts by weight sulfonated castor oil, and 3 parts by weight alpha protein.

17. The process of claim 12 in which the solution-suspension includes water sufficient to make up at about 26 percent solids and the mixture consists of 20 parts by weight silicon dioxide, 10 parts by weight sodium tallow soap, 10 parts by weight sulfonated red oil, and 5 parts by weight acrylate resin.

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