

Nov. 29, 1960

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2,962,382

SHEET RECORDING MATERIAL AND METHOD OF MAKING SAME

Filed Feb. 25, 1958

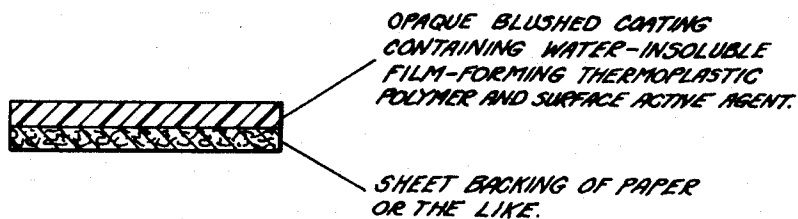


*Fig. 1.*

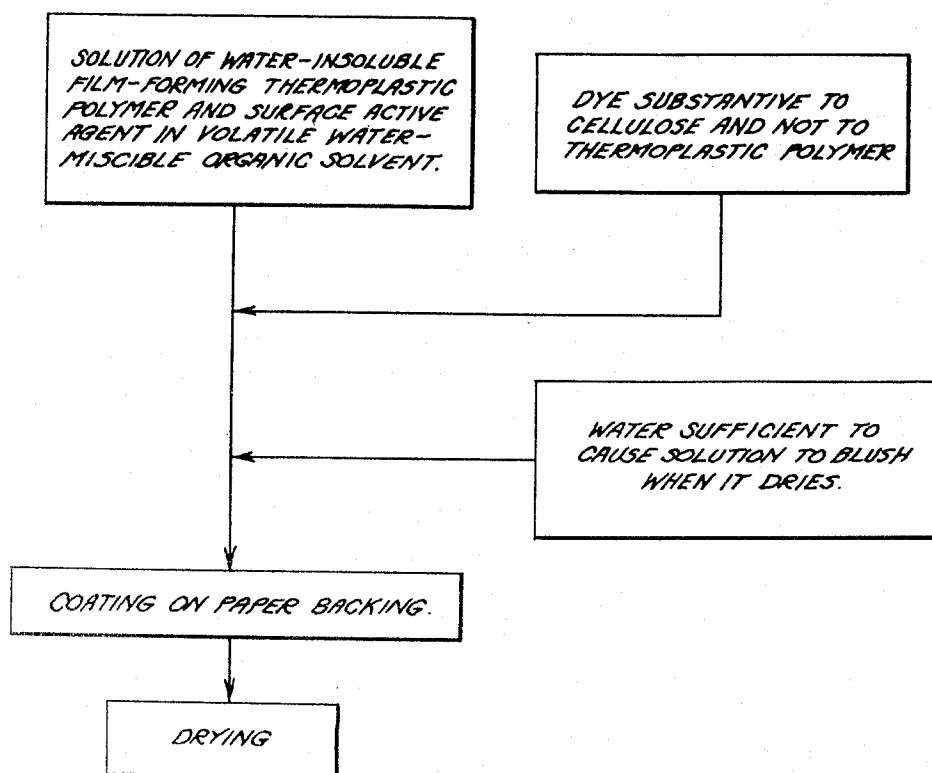


*Fig. 2.*

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2,962,382

## SHEET RECORDING MATERIAL AND METHOD OF MAKING SAME

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Filed Feb. 25, 1958, Ser. No. 717,323

13 Claims. (Cl. 117—36)

This invention relates to sheet recording material and pertains more specifically to paper or the like carrying a coating of an appearance contrasting with that of the paper base or backing sheet and sensitive to pressure so that pressure applied to the coating by a stylus or other marking instrument leaves a visible and permanent mark on the sheet material, the mark being the color of the backing sheet.

One object of the present invention is to provide sheet recording material of improved pressure sensitivity suitable for use in making a plurality of copies simultaneously without the use of carbon paper.

Another object is to provide a sheet recording material which displays improved pressure sensitivity over a wide temperature range and which can be used with a heated stylus if desired as well as with an unheated stylus.

Still another object is to provide a method of making sheet recording material in which the backing sheet is dyed a color contrasting to the color of the coating simultaneously with the application of the coating.

Other and further objects will be apparent from the description which follows.

It has now been found that an improved recording material can be prepared by coating a backing such as paper or any other suitable sheet backing material with a blushed coating comprising a water-insoluble, film-forming, polymeric composition containing a surface active agent. In a preferred embodiment of the invention a waxy lubricant for the polymeric material is also included in the composition, this lubricant preferably being high in melting point; i.e., having a melting point above 100° C. It is also possible to include in the composition a dye which preferentially dyes the backing sheet while leaving the polymeric material substantially undyed, so that the opaque colorless coating contrasts with the color of the backing. This feature is not essential, however, and if desired the coating composition may be applied to a backing sheet which has previously been dyed or otherwise colored the desired shade. Indeed, a colorless transparent backing sheet may be employed. In any event, the finished sheet recording material bears an opaque coating the appearance of which contrasts with that of the underlying base sheet; this coating, when subjected to pressure in localized areas, as by a stylus, becomes translucent in these areas to reveal the underlying base sheet.

In the drawings:

Fig. 1 is a schematic cross-sectional view of one embodiment of the recording sheet of the present invention; and

Fig. 2 is a flow sheet representing one embodiment of the method of the present invention.

A simple test may be employed for determining pressure-sensitivity. A stylus having a hemispherical tip with a diameter of 0.010 inch is drawn across the sheet recording material at a speed of one inch per second. The load on the stylus urging it against the sheet is increased in one-gram increments, the smallest load which

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produces a visible mark being taken as a measurement of sensitivity. The sheet recording material of the present invention has a sensitivity ranging from 3 grams to 15 grams, measured by the foregoing test. Sheet recording material having a sensitivity less than about 3 grams is difficult to handle because of its tendency to smudge or to mark accidentally during handling, while material having a sensitivity greater than about 15 grams is too insensitive to be capable of producing the desired number of simultaneous copies. Preferably, the sheet recording materials of the present invention have a sensitivity of 5 to 12 grams by the foregoing test.

Among the water-insoluble, film-forming, polymeric materials which may be employed for coating the backing to provide the sheet recording material of the present invention are ethyl cellulose, cellulose acetate, cellulose nitrate, cellulose acetate-propionate, cellulose acetate-butyrate, and polyethyl methacrylate, all of which materials are thermoplastic in nature. In some cases it is desirable to include a plasticizer for the polymeric material, particularly when the latter normally possesses high hardness. All of these film-forming polymeric organic materials are water-insoluble and are soluble in one or more water-miscible volatile organic solvents. Cellulose acetate and ethyl cellulose have been found to give particularly good results and are therefore preferred.

The film-forming polymeric material (together with plasticizer therefor if desired) is dissolved in a water-miscible volatile organic solvent having a boiling point below that of water. Among the common solvents which may satisfactorily be employed are acetone, methyl alcohol, and methyl ethyl ketone, as well as mixtures. Of these, acetone is preferred because of its low cost and high volatility. The amount of solvent used may vary widely and will depend primarily upon the thickness or viscosity desired, which in turn depends upon the thickness of the coating desired, the porosity of the backing sheet, the type of coating device used, and other factors well known to the art.

While such solutions of film-forming polymeric materials in a volatile solvent may readily be diluted by the addition of water, then coated on paper or other sheet backing material and dried to provide an opaque blushed pressure-sensitive coating, the sensitivity of such materials is quite poor, ranging as high as 25 to 30 grams even when plasticizer and/or waxy lubricant is present. The addition to the film-forming polymeric material of a quantity of surface active agent up to 100% by weight, in the absence of plasticizer and/or waxy lubricant, produces very little effect upon pressure-sensitivity of a sheet recording material made therefrom. Only when the amount of surface active agent reaches 150% or more by weight of the polymeric material is it effective by itself to improve the sensitivity to 15 grams or less. However, when the surface active agent is employed in conjunction with a waxy lubricant for such polymeric material, a coating containing as little as 16% of surface active agent, 4% of waxy lubricant and 80% of polymeric material displays a sensitivity of 15 grams, a sensitivity far less than can be obtained with either a waxy lubricant or a surface active agent alone in an amount of 20% with 80% polymeric material, indicating that the waxy lubricant and the surface active agent have a synergistic effect. It should be noted that although the foregoing composition contains only 16% by weight of surface active agent, this amounts to 20% by weight based on the weight of the polymeric material.

Although any of the well-known surface active agents may be employed for this purpose, such as any of the cationic, anionic or non-ionic surface active agents, it

has been found that best results are obtained by employing a cationic or non-ionic surface active agent which includes a long polyoxyalkylene chain.

Among the surface active agents which are effective the following may be listed as representative. Anionic agents: soaps, e.g., sodium oleate, sodium stearate, the sodium salt of coconut oil fatty acid, etc.; alkyl sulfates, e.g., sodium lauryl sulfate; alkyl benzene sulfonates, e.g., sodium alkyl benzene sulfonate. Cationic agents: acid salts such as acetic acid salts of the n-alkyl amines, e.g., acetic acid salts of laurylamine or tallow amine; fatty imidazolines, e.g., the sodium salt of 1-coco-5-hydroxyethyl-5-carboxymethyl imidazoline, and other imidazolines substituted with long chain (12-20 carbon atoms) alkyl groups in the 1-position; stearamido propyl dimethyl-beta-hydroxyethyl ammonium phosphate; quaternary ammonium salts such as dimethyl distearyl ammonium chloride. Non-ionic agents: ethylene oxide condensates of long chain fatty acid amides; ethylene oxide condensates with hydrophobic bases formed by condensing propylene oxide with propylene glycol; ethylene oxide condensates with bases formed by condensing propylene oxide with ethylene diamine; ethylene oxide condensates with higher fatty acids such as lauric acid; sorbitan esters of fatty acids, e.g., sorbitan monolaurate, sorbitan monopalmitate; ethylene oxide condensates with alkyl-substituted phenols, e.g., iso-octyl phenoxy polyoxyethylene ethanol, nonyl phenoxy polyoxyethylene ethanol.

While any waxy solid material may be employed as the waxy lubricant, it is desirable to employ one which is as high melting as possible in order to make the sheet recording material suitable for use over as wide a range of temperature as possible. Preferably the waxy lubricant has a melting point above 100° C. Among suitable materials are carnauba wax, candelilla and esparto waxes, ozocerite, and synthetic waxes such as bis-ethylenestearamide, which is sold under the trade name Acrawax C. Water-insoluble metal soaps, i.e., polyvalent metal salts of long chain (12-20 carbon atoms) fatty acids are also effective waxy lubricants; representative of such materials are zinc laurate, zinc stearate, aluminum stearate, lead oleate, barium stearate, calcium stearate, and the like. The waxy lubricant must be one which is water-insoluble and which is also insoluble in the acetone or other volatile organic solvent employed for the film-forming polymeric material. The waxy lubricant is dispersed in the solution of polymeric material in finely divided form, the individual wax particles preferably being sufficiently fine to pass a No. 270 screen (U.S. Standard Sieve Series). The waxy lubricant, when present, may vary in amount up to 50% or even 60% by weight of the total mixture of film-forming polymeric material, surface active agent, and waxy lubricant.

Secondary plasticizers for the film-forming polymeric material may also be included in the composition as indicated above and tend to enhance the pressure sensitivity of the finished product. Whenever plasticizers for the polymeric materials are employed, it is preferred to use secondary plasticizers only, since primary plasticizers tend to prevent the blushing of the coating when it is dried.

The amount of water required to cause the solution to blush will vary somewhat depending upon the nature of the solvent and of the materials dissolved, but optimum results usually will be obtained by adding from 8% to 15% of water, based on the weight of the total coating composition including the volatile solvent.

The coating composition may be left colorless and may simply be applied to a backing such as paper which has been dyed or otherwise colored to the desired shade. However, it is also possible to combine the step of dyeing or coloring the backing with the step of applying the coating composition to the backing by incorporating in the coating composition a dye which is substantive to cellulose and which dyes it in preference to the film-

forming polymeric material of the coating composition. For example, when the backing is paper and the film-forming polymeric material is cellulose acetate, there may be introduced into the coating composition a small amount of a dye such as Fastusol red-violet LRLA or Fastusol blue LBRRA ex. conc. CF, both of which may be obtained from General Dyestuff and both of which preferentially dye the paper backing while leaving the cellulose acetate substantially colorless.

In making the sheet recording material of the present invention, the desired film-forming polymeric material and surface active agent are first dissolved in a water-miscible organic solvent such as acetone to provide a clear solution. To this solution is added, if desired, the waxy lubricant in the form of dispersed finely-divided particles and the preferential dye, and there is stirred into it approximately 8% to 15% by weight of water. The solution is then coated upon paper or other suitable backing by means of a knife coater, roll coater or any other conventional coating device, and it blushes as it is allowed to dry either at room temperature or at moderately elevated temperature (up to 200° F.). In any event, whether a dye be present or not, the composition dries on the backing to produce an opaque, substantially colorless coating, the appearance of the coating contrasting markedly with the appearance of the backing, which may be transparent or opaque. If opaque, the backing may previously have been colored or may preferentially absorb the dye present in the coating composition. In order to facilitate and enhance the differential dyeing effect as well as to promote uniformity of the product, it has been found desirable to include in the coating composition a high boiling (100°-150° C.) water-miscible organic solvent, for example, a polyether such as Carbitol (diethylene glycol ethyl ether) or Shellacol in an amount from 5% to 15% by weight based on the weight of the volatile organic solvent. While the weight and thickness of the coating and the type of paper or other sheet material employed as the backing are not critical, it has been found that eminently satisfactory results are obtained by employing as the backing a paper which weighs approximately 10 to 20 pounds per ream (24" x 36"—500 sheets). The weight of the coating applied to the backing may vary considerably, but best results have been obtained by employing a coating which when dry weighs 3 to 6 pounds per ream (20" x 25"—500 sheets).

The following specific examples will serve to illustrate more clearly the nature of the invention, but are not intended as a limitation on the scope thereof.

#### Example 1

|                                                               | Parts by weight |
|---------------------------------------------------------------|-----------------|
| Cellulose acetate.....                                        | 8.00            |
| Acrawax C.....                                                | 4.40            |
| 55 Tergitol NPX (alkyl phenyl polyethylene glycol ether)..... | 8.70            |
| Carbitol.....                                                 | 6.50            |
| Acetone.....                                                  | 58.00           |
| 60 Water.....                                                 | 14.25           |
| Fastusol red-violet LRLA.....                                 | 0.15            |

The Acrawax C employed in this composition was in finely-divided form (passing a No. 270 screen) and was insoluble in both water and acetone, the water being added last. The composition was coated on white paper by means of a reverse roll coater operating at room temperature, the dry weight of the coating being approximately three pounds per ream. After completion of the drying step the outer face of the coating was a smooth, opaque, substantially white mass, whereas the backing preferentially absorbed the dye, becoming a brilliant red-violet very shortly after the drying step.

The resultant sheet recording material when subjected to pressure by a stylus exhibited a distinct, readily visible mark in the areas touched by the stylus, the coating be-

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coming translucent in these areas to reveal the color of the backing, which contrasted with the substantially white or faintly pink opaque face of the coating in the zones not subjected to stylus pressure. The pressure-sensitivity of this recording material, as measured by the test described above, is 12 grams.

The extremely high pressure-sensitivity of this material is demonstrated by the fact that up to sixteen legible copies can be made with it simultaneously in an electric typewriter without the use of any carbon paper. In addition, the composition exhibits a remarkably uniform pressure-sensitivity over a very wide range of temperatures being useable at any temperature within the range  $-30^{\circ}$  to  $+260^{\circ}$  F. Despite this great sensitivity, however, the coating is non-blocking and exhibits remarkable resistance to rub-off or accidental marring of the surface.

## Example 2

A composition was prepared which was identical with that of Example 1 except that the amount of Acrawax C was reduced to 2.0 parts by weight and the dye was omitted, the composition being coated on colored paper. The product exhibited a sensitivity of 13 grams.

## Example 3

A composition was prepared as described in Example 2 except that the amount of Acrawax C was increased to 8.0 parts by weight. The blushed film on paper exhibited a sensitivity of 6 grams.

## Example 4

A composition was prepared as described in Example 2 except that the Acrawax C was completely omitted and the amount of Tergitol NPX was increased to 12.0 parts by weight. The sensitivity of the product was 15 grams.

## Example 5

The following composition was prepared, in which the parts are by weight:

|                        | Parts |
|------------------------|-------|
| Cellulose acetate..... | 8.0   |
| Zinc stearate.....     | 0.4   |
| Tergitol NPX.....      | 1.6   |
| Acetone .....          | 58.0  |
| Carbitol .....         | 6.5   |
| Water .....            | 14.0  |

The water was added last. The composition was coated on colored paper by means of a reverse roll coater at room temperature and dried to produce a blushed coating. A smooth white opaque film resulted on the surface of the paper. The product exhibited a sensitivity of 15 grams. When the zinc stearate was increased to 3.4 parts and the Tergitol was increased to 13.0 parts by weight, the product exhibited a sensitivity of 5 grams. When 8.0 parts of zinc stearate and 8.0 parts of Tergitol were present along with 8.0 parts of cellulose acetate, the sensitivity of the product was 10 grams.

## Example 6

The following composition was prepared, in which the parts are by weight:

|                      | Parts |
|----------------------|-------|
| Ethyl cellulose..... | 8.0   |
| Acrawax C.....       | 4.4   |
| Tergitol NPX.....    | 8.7   |
| Acetone .....        | 58.0  |
| Carbitol .....       | 6.5   |
| Water .....          | 14.3  |

It was coated on colored paper and dried, the product exhibiting a sensitivity of 7 grams.

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## Example 7

The following composition was prepared, in which the parts are by weight:

|                        | Parts |
|------------------------|-------|
| Cellulose acetate..... | 8.0   |
| Acrawax C.....         | 18.0  |
| Tergitol NPX.....      | 8.7   |
| Acetone .....          | 58.0  |
| Carbitol .....         | 6.5   |
| Water .....            | 14.3  |

The solution was coated on colored paper and dried, the product exhibiting a sensitivity of 3 grams. When the amount of Acrawax present was decreased to 4.5 parts and the amount of Tergitol increased to 14.1 parts, the product had a sensitivity of 4 grams.

## Example 8

The following composition was prepared, in which the parts are by weight:

|                           | Parts |
|---------------------------|-------|
| Cellulose acetate.....    | 8.0   |
| Acrawax C.....            | 4.4   |
| Surface active agent..... | 8.0   |
| Acetone .....             | 58.0  |
| Carbitol .....            | 6.5   |
| Water .....               | 14.3  |

A variety of surface active agents were employed in the foregoing recipe including commercially available specimens of the anionic, cationic and non-ionic types as outlined hereinabove. The products obtained by coating colored paper with such compositions and drying exhibited sensitivities within the range of 3 grams to 15 grams, although products embodying the anionic surface active agents generally exhibited higher sensitivity values than did those made with other surface active agents.

Similar results were obtained by using surface active agents in amounts as high as 300% by weight of the polymeric material and with waxy lubricant present in amounts up to 60% by weight of the total mixture of polymeric material, surface active agent and waxy lubricant.

Although specific embodiments of the invention have been herein described, it is not intended to limit the invention solely thereto, but to include all of the obvious variations and modifications within the spirit and scope of the appended claims.

What is claimed is:

1. Sheet recording material comprising a backing having an opaque blushed coating of an appearance contrasting with that of the backing, said coating comprising a water-insoluble, film-forming, thermoplastic polymeric material together with from 20% to 300%, based on the weight of said polymeric material, of a surface active agent, and from 4% to 60% by weight, based on the total weight of polymeric material, surface active agent, and waxy lubricant, of finely divided waxy lubricant having a melting point above  $100^{\circ}$  C., said coating becoming translucent when subjected to a hemispherical stylus having a diameter of 0.010 inch under a load of 3 to 15 grams to reveal the appearance of the backing contrasting to that of said opaque coating.

2. Sheet recording material as defined in claim 1 in which said backing comprises a sheet of paper.

3. Sheet recording material as defined in claim 2 in which said polymeric material comprises cellulose acetate.

4. Sheet recording material as defined in claim 2 in which said polymeric material comprises ethyl cellulose.

5. Sheet recording material as defined in claim 3 in which said surface active agent comprises a non-ionic polyoxyalkylene compound.

6. Sheet recording material as defined in claim 5 in

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which said waxy lubricant comprises bis-ethylenestearamide.

7. Sheet recording material as defined in claim 5 in which said waxy lubricant comprises zinc stearate.

8. The method of making the sheet recording material defined in claim 1 which comprises adding to a solution of said polymeric material in a volatile water-miscible organic solvent, which solution contains said surface active agent and said waxy lubricant, sufficient water to cause said solution to blush when it dries, coating said backing with said solution, and drying.

9. The method of making sheet recording material which comprises adding to a solution of a water-insoluble, film-forming, thermoplastic, polymeric material and from 20% to 300% based on the weight of said polymeric material, of a surface active agent in a volatile water-miscible organic solvent a dye which is substantive to cellulose and not to said polymeric material and sufficient water to cause said solution to blush when it dries, coating a paper backing with said solution, and drying said coating, whereby said paper is differentially dyed with respect to said polymeric material.

10. Sheet recording material comprising a backing having an opaque blushed coating of an appearance con-

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trasting with that of the backing, said coating comprising a water-insoluble, film-forming, thermoplastic, polymeric material and from 150% to 300%, based on the weight of said polymeric material, of a surface active agent, said coating becoming translucent when subjected to a hemispherical stylus having a diameter of 0.010 inch under a load of 3 to 15 grams to reveal the appearance of the backing contrasting to that of said opaque coating.

11. Sheet recording material as defined in claim 10 in which said backing comprises a sheet of paper and said polymeric material comprises cellulose acetate.

12. Sheet recording material as defined in claim 10 in which said backing comprises a sheet of paper and said polymeric material comprises ethyl cellulose.

13. Sheet recording material as defined in claim 10 in which said backing comprises a sheet of paper and said surface active agent comprises a non-ionic polyoxy-alkylene compound.

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