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RECORDING MATERIAL

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Data supplied by measuring instruments of all types can be recorded on strips or sheets of paper or other suitable material which carries a superficial layer of a material which, upon pressurable contact with a stylus, is wholly or partially compacted or removed from the suitably colored support. It has been proposed to use for this purpose dark paper strips covered with a so-called blushed-film which upon pressurable contact with an object loses its light colored and opaque appearance and shows the dark paper surface therebehind. The paper strips can thus be used to receive a continuous record applied by means of a pressure stylus. Recording material of this type however is not suitable for certain purposes, particularly when the strip has to be repeatedly handled, which usually involves pressurable contact with objects other than the recording stylus, so that the record becomes obscured or disfigured with spots or marks rendering its interpretation difficult or impossible.

It is an object of the present invention to provide a recording material of the blushed film type which is very little sensitive to pressure and therefore can be handled without particular attention to record obscuring disfiguration through accidental contact. Another object is to provide a recording material of the above mentioned type whose blushed film is affected for intended recording purposes upon contact with a heated recording stylus rather than pressure exerted thereon, whereby the optimum temperature can be adjusted to suit given requirements such as stylus construction. Still another object of the invention is to provide material of this type which is inexpensive, easy to manufacture, durable, quite insensitive to pressurable contact but easily responding to a heated recording element, and which has good keeping qualities. Recording paper of this type is particularly suitable for purposes of electrocardiographs because they avoid the usual photographic processes heretofore used in this field. In electrocardiography, it is particularly important that the record strips can be handled quickly and without regard to their susceptibility to unavoidable pressurable contact with the hospital or sickroom environment.

In its main aspect, the invention consists in applying to a support such a strip of paper a very thin coat of blushed film of a color contrasting with that of the support, applied from solution of a film forming material in a volatile

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solvent, the solvent being compatible with water and having considerably higher vapor pressure than water, this film having only little sensitivity to pressure but considerable and adjustable sensitivity to heat; this reduced sensitivity to pressure and adjustably increased sensitivity to heat is due, in accordance with other aspects of the invention, to the exclusion from the blushed film of any softening admixture or of such admixtures other than a primary plasticizer, to the use of primary plasticizers having a vapor pressure lower than approximately that of diethyl-phthalate, and to the use of primary plasticizers, that is plasticizers which are solvents for the film forming material. In an additional aspect, the invention permits predetermination of the effective stylus temperature sufficient for satisfactory recording, by adjusting the admixture including omission, of plasticizers of the above mentioned type.

Microscopic examinations of blushed film as obtained by the process described below shows that the film contains numerous microscopic bubbles throughout the entire body. These very small hollow spaces give the film a light appearance called blushing, white if the layer is undyed. In order to make the blushing disappear from the coating thus rendering the latter visible, it is merely necessary to eliminate the minute bubbles throughout the resin. The blushing obtained according to this invention differs from that which involves actual inclusion of water. The blushing which is thus produced and maintained on varnished and shellaced surfaces by actual presence of water does not disappear upon the application of heat or pressure, but only upon removal of the water; on the other hand, the blushing according to the invention although it will not disappear on prolonged exposure to dehydrating conditions because it is not caused by the presence of water, responds to the application of heat but not to pressure of degrees corresponding to usual accidental contact with a stylus or other apparatus components.

Blushed coatings according to the invention may be prepared by dissolving resin, more particularly film forming thermoplastic linear polymeric resin, in a solvent having a vapor pressure in excess of that of water and further diluting the resin solution with water, or a water-solvent mixture. The solvent must be one which is miscible with water while the resin must be substan-

tially insoluble in water. If enough water is added to a solution of a resin, the resin will precipitate, therefore less water than is required to precipitate the resin should be added. If the desired recording temperature, preferably applied with a stylus or similar device, is fairly high depending on the solid constituent used, the solution is prepared free from any plasticizing addition. For adjustably lowering the recording temperature, a plasticizer of the particular type to be discussed is added in variable amounts, depending upon the desired marking temperature of the stylus.

The water containing solution obtained as described above is applied to a suitable support such as paper in the form of a thin film, by roller coating, spraying, printing, floating, but preferably by a knife coating process. Acetone, a preferred solvent, may be employed, which evaporates and precipitates the resin almost immediately after coating in the form of a white surface.

For the purpose of providing an easily readable record, the blushed film is preferably placed upon colored, such as red or black, paper. When so placed, a heated stylus applied lightly to the surface of the coating will cause a red or a black line to appear. However, it is not necessary to use colored paper. A dye may be incorporated in the film mixture which, upon deposition on the paper, will assume a light color of the hue of the dye. When marked with the heated stylus, a line of darker color of the same hue is produced.

Several resinous materials which blush in an acetone-water solution include ethyl cellulose, cellulose acetate, cellulose nitrate, cellulose caprate, cellulose acetate-propionate, cellulose acetate-butyrate, benzyl cellulose, polymethyl methacrylate and polystyrene.

As mentioned above the marking temperature of film entirely lacking a plasticizer is rather high, especially if cellulose acetate is used as solid component. It was found that this temperature may be lowered to predeterminable degrees without impairing the desirable high pressure insensitivity, if selected amounts of plasticizers of the primary type are added which are solvents for the film forming material and which have a vapor pressure lower than approximately that of diethyl phthalate, that is about 2.0 mm. at 150° C. Dibutyl phthalate, having a vapor pressure of 1.1 mm. was found to be very suitable. Plasticizers of the secondary, mechanical or lubricant type, such as glycerin, fatty acids, salts or esters of such acids or other oily, fatty or waxy materials, although they might affect the pressure sensitivity, are of no value for adjusting the temperature sensitivity of the blushed film.

The range of temperatures which are operative with blushed material of this type is between about 80° F. and 340° F.; the blushing will disappear when a stylus heated to a temperature within this range is applied to the coating, thus causing a visible and clearly defined mark. Because the resins named above do not have sharp melting points, it is not necessary to heat them to their melting point. Ethyl cellulose, for instance, has a melting point of 220° C. and a marking temperature of about 120° C.

As a water miscible solvent for resins having a considerably higher vapor pressure than water, acetone has been found to be most desirable methyl alcohol and methyl ethyl ketone are practical, although not particularly desirable for use with ethyl cellulose.

As primary plasticizers according to the invention, dioctyl phthalate was found to be very effective with ethyl cellulose, but also tricresyl phosphate, diamyl phthalate, dicapryl phthalate, dibutoxyethyl phthalate, tributyl citrate, butyl phthalyl butyl glycolate and dibutyl sebacate; with cellulose acetate, ortho and paratoluene ethyl sulfonamide is effective but also such primary plasticizers as methyl phthalyl ethyl glycolate or methoxyethyl phthalate.

These and other objects, aspects and features are further illustrated by the following examples of practical embodiments of the invention.

Example I

Dissolve:	Grams
Ethyl cellulose N-100	10
in	
Acetone	90
Add:	
Di-2-ethylhexyl phthalate	1.5
Acetone (50% solution in water)	40

This solution is coated on red paper and dried. The resulting film softens sufficiently under the stylus to produce satisfactory markings at about 115° C. If no primary plasticizer is added, the paper marks satisfactorily, but at the somewhat higher temperature of about 120° C. If in the above formula 15 g. di-2-ethylhexyl phthalate are added to 85 g. ethyl cellulose (10% in acetone as above), the marking point is at about 97° C. If 25 g. di-2-ethylhexyl phthalate are added to 75 g. ethyl cellulose (10% in acetone) the marking point is at about 85° C.

Example II

Dissolve:	Grams
Ethyl cellulose	10
in	
Acetone	52.5
Add to this solution:	
Acetone	37.5
Water	15.0

Apply the resulting solution to red paper in a thin film and dry. The white, glossy film produced is quite adhesive and marks at 120° C.

The addition of 2.5 grams of dioctyl phthalate (known to the trade as "D O P") to the acetone-ethyl cellulose solution lowers the marking point to 80° C.

Example III

Dissolve:	Grams
Cellulose acetate	15
in	
Acetone	60
To this solution add:	
Acetone	25
Water	30

The resulting solution is applied to red paper in a thin film and dried. The film is white and glossy and marks at 170° C. The addition of 2.5 grams of a mixture of ortho and para toluene ethyl sulfonamide (known to the trade as "Santicizer 8") lowers the marking temperature at 160° C.

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Example IV

Dissolve:	
Methyl methacrylate -----	Grams 20
in	
Acetone -----	70

To this solution add:

Acetone -----	10
Water -----	5

Apply to a support as before; the marking point is 139° C.

Example V

To the composition of Example II, add 0.5 gram of the dye "National oil black 34341." The resulting solution is coated on white paper. The coating is light lavender in color and marks with a deeper color to give a distinct line. The marking point is 120° C.

It should be understood that the present disclosure is for the purpose of illustration only and that this invention includes all modifications and equivalents which fall within the scope of the appended claims.

I claim:

1. A heat-sensitive, dry, non-tacky recording material comprising a backing having an opaque blushed coating characterized by the presence therein of numerous microscopic hollow spaces, said coating consisting essentially of a water insoluble film-forming thermoplastic material selected from the group consisting of cellulose esters and ethers, polymethyl methacrylate and polystyrene and from 15% to about 33% of a compatible primary plasticizer having a vapor pressure lower than about 2.0 mm. at 150° C., said coating being free from secondary plasticizers and substantially insensitive to pressure, but capable of becoming translucent in response to heat received from a stylus heated to a temperature of at least 80° C., thereby to provide a

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visible contrast with the surrounding opaque unheated area.

2. A heat-sensitive material as defined in claim 1, further characterized in that said thermoplastic film-forming material consists essentially of cellulose acetate.

3. A heat-sensitive material as defined in claim 1, further characterized in that said thermoplastic film-forming material consists essentially of cellulose acetate and a toluene alkyl sulfonamide plasticizer.

4. A heat-sensitive material as defined in claim 1, further characterized in that said thermoplastic film-forming material consists essentially of ethyl cellulose.

5. A heat-sensitive material as defined in claim 1, further characterized in that said thermoplastic film-forming material consists essentially of ethyl cellulose and a compatible alkyl phthalate plasticizer.

6. A heat-sensitive material as defined in claim 1, further characterized in that said thermoplastic film-forming material consists essentially of methyl methacrylate.

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