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3,425,858

HEAT SENSITIVE RECORDING MATERIAL

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No Drawing. Filed June 7, 1965, Ser. No. 462,040
U.S. Cl. 117—36.8
Int. Cl. B41m 5/18

7 Claims

ABSTRACT OF THE DISCLOSURE

A heat-sensitive recording material comprises a base material having a surface with a smooth uniform coating thereon in intimate adhered contact therewith. The coating is white in color and is made upon drying of a mixture including alkaline magnesium hydroxide, phenolphthalein, a suitable solvent, a binder and sufficient acid to produce an adequate pH to provide a white color to the mixture. The phenolphthalein and magnesium oxide cooperate to effect a change in the color of the coating to red in the area of the coating engaged by a heated marking member effective to heat the coating in said area to a predetermined temperature. The proportion by weight of magnesium oxide to phenolphthalein is with the range of 1:15 to 15:1.

The present invention relates to a recording material and a method of manufacture thereof, and particularly to a heat-sensitive recording material having a base with a coating thereon which upon the application of heat changes in color, and to a method of manufacturing the heat-sensitive recording material.

It has been discovered that a heat-sensitive material having a good shelf life and providing a clear sharp mark when contacted by a heated stylus is provided by a base coated with a material having an indicator of alkalinity and a material which becomes alkaline upon the application of heat thereto. The material which becomes alkaline causes the indicator to effect a color change when it becomes alkaline. The mixture, in accordance with the present invention, includes an indicator and an oxide of an alkaline earth or an oxide of an alkaline metal. The oxides of the alkaline earth and the alkaline metal tend to form hydroxides and are incorporated in the coating so as to form the hydroxides when heated. The indicator then indicates the presence of the hydroxide by turning red.

Preferably, phenolphthalein and magnesium oxide, as well as a binder and a suitable solvent, are used in the mixture. The phenolphthalein serves as the indicator. The mixture is uniformly applied to a base material and dried so as to provide a dry cohesive coating adhered thereto in intimate contact and which is heat sensitive. The coating is preferably white and when contacted by a heated implement, such as a stylus, changes to a red color in the area contacted by the heated stylus due to the phenolphthalein indicating the alkalinity thereof.

The phenolphthalein and magnesium oxide, when mixed together with a suitable solvent, may provide a red mixture. This red color of the mixture renders the mixture unsatisfactory for coating a base material for providing a heat-sensitive material. This is overcome by preferably adding an acid to the mixture of phenolphthalein and magnesium oxide which provides a mixture with a pH equal to that of phenolphthalein and which has a white color. The acid which is preferably used in the mixture is such which will become an integral part of the coating, even though the coating is dried on the coating base and which will, when heated, evaporate, returning the coating to an alkaline state which, it is believed, tends to aid the color change of the coating due to the removal of the acid upon the application of heat. Acetic acid has

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been found to be quite satisfactory in providing the necessary neutralization and also for evaporation purposes when the coating material is contacted by a heated stylus. The nature of the present invention will be further apparent from a description of the preferred embodiment thereof which follows.

The present invention is preferably embodied in a recording material which is adapted to be marked by a heated stylus. The recording material includes a base material with a heat-sensitive coating on the base material and which changes in color to provide a mark where engaged by a heated implement, such as a heated stylus. The base material may comprise any suitable material, such as cardboard, metal foil, plastic film, or cloth. However, preferably it comprises a paper having a suitable quality so as to properly receive the coating thereon.

The coating on the material includes a sensitive indicator of alkalinity which changes in color to indicate alkalinity, and a material which becomes alkaline on the application of heat thereto. When the coating is heated and the material changes to an alkaline state, the indicator changes in color to indicate the alkaline state. The indicator is phenolphthalein, while the material which becomes alkaline on the application of heat includes an oxide of an alkaline metal or an oxide of an alkaline earth. Such oxides have a strong tendency to form hydroxides which, of course, are alkaline.

Preferably, due to the fact that the oxides of the alkaline metals are difficult to handle, the oxides of the alkaline earths are used in the coating mixture, such as beryllium oxide, magnesium oxide, barium oxide, calcium oxide, and strontium oxide. However, lithium oxide may be used, which of course does come within the alkaline metal group. Preferably, magnesium oxide is utilized because it renders the coating stable at relatively low temperatures, such as room temperatures. The magnesium oxide does, however, have a high tendency to form a hydroxide when heated somewhat in the presence of any substance, such as water or water vapor, containing an OH radical, and turns alkaline when combined with a radical OH. The magnesium oxide when incorporated in the dry coating combines with an OH radical only when heated.

The coating on the base material thus preferably includes phenolphthalein and magnesium oxide, and a coating including these materials reacts upon the application of heat thereto to provide a color change and thereby a mark is provided on the blank in the area where heat is applied to the blank. It is believed that where the dry coating is contacted by a heated implement, the molecules of magnesium oxide combine with the radical OH and come into close contact with the molecules of phenolphthalein and resonate at a frequency to effect a color change. The coating material also includes a suitable binder to provide a cohesive coating, and other additives may be added, as described hereinbelow.

The coating is formed of a number of materials which are mixed to form a coating mixture which is applied to the base. These materials include the phenolphthalein, magnesium oxide, and binder, as mentioned above. The binder may take many forms and may comprise polystyrene, vinylidene chloride, or vinyl acetate, or any of the polymers or copolymers that melt at relatively low temperatures. Preferably, the binder is polystyrene with metacrylonitrile. The binder should be such that it will not change the properties of the phenolphthalein and magnesium oxide. These materials are mixed with a suitable solvent so as to provide the coating mixture. Acetone is preferably used as the solvent, but other solvents could be used which would dissolve the binder and phenolphthalein without affecting the properties thereof or detrimentally affecting the reaction or color change.

The following table contains the relative quantities of each of the preferred materials which are included in the coating mixture and the preferred range of parts by weight of each ingredient:

Ingredient	Parts by weight	Range of parts by weight
Phenolphthalein.....	3	.001-15
Magnesium oxide.....	10	1-15
Binder.....	9	5-20
Solvent.....	80	60-100

The proportions of the ingredients set forth in the above table are preferred and may be varied. The amount of the oxide of the alkaline earth may vary depending upon the strength of the hydroxide which it forms. For example, barium oxide forms a rather strong hydroxide in the sense that it is quite alkaline; thus, the amount thereof may be lower than the amount of magnesium oxide. The amount of solvent and binder can be changed to provide a coating of the desired viscosity for easy uniform application to the base material, and the amount of phenolphthalein and magnesium oxide may be varied within the range depending upon the desired sensitivity of the coating. The more isolated the phenolphthalein and magnesium oxide from other substances, the more sensitive is the coating and the easier to mark. The more intimately the phenolphthalein and magnesium are in contact, the lower the temperature required to mark the material. The binders, of course, are only to increase cohesion of the coating.

The most desirable method of making the coating mixture begins with the weighing of the proper amount of magnesium oxide and phenolphthalein and the mixing of the phenolphthalein and magnesium oxide with acetone. The magnesium oxide and phenolphthalein are both in powdered form and are white in color. When mixing the phenolphthalein and magnesium oxide in the acetone, only the phenolphthalein dissolves therein. The more sensitive type of phenolphthalein in the mixture turns deep red as it comes into close contact with the small particles of alkaline magnesium oxide. If the mixture turns red, it is necessary to add a few drops of a suitable acid in order to counteract the alkalinity of the mixture. This alkalinity may also be counteracted by coating the base material with the red or rosy mixture and exposing the coating to acid vapors.

Since the alkalinity may be different for different mixes, depending upon the materials added to the mixture and the degree of impurities therein, the amount of acid which may have to be added to the mixture in order to provide a neutral mixture will vary. The amount of acid which should be added is such as to provide an adequate pH to the mixture so that the phenolphthalein does not turn red, thus providing a white mixture which may be coated onto the base material to provide a white coating thereon. The amount of acid required may be quite extensive, depending upon the alkaline earth used. Any suitable acid may be utilized, but preferably an acid, such as acetic acid, having a relatively low boiling point is extremely satisfactory for this purpose for a reason to be described hereinbelow.

After the phenolphthalein and magnesium oxide have been mixed together with the acid, as necessary, the binder is dissolved in a solvent and mixed with the mixture of phenolphthalein and magnesium oxide and acid. The resulting mixture is then coated onto a suitable base material and dried thereon in intimate adhered contact therewith providing a cohesive dry coating on the base material. The drying time and temperature may vary but preferably drying for two hours at room temperature has been found satisfactory. The drying should be such as to evaporate substantially all of the solvent; however, it is well if the acid in the mixture remains therein and is not evaporated or driven off entirely. The acid, or at least

some portion thereof, will remain in the coating due to adsorption thereof by the other materials of the mixture.

A suitable plasticizer may be added to the coating mixture in order to increase the plasticity of the coating and also affect or diminish the friction of the stylus as it travels over the paper and thus serves as a lubricant. Castor oil, for example, is a satisfactory additive and small portions thereof may be utilized for this purpose. Other plasticizers, such as other organic oils may also be used, which may be dissolved with the phenolphthalein and not adversely affect the coating mix.

The coating may be contacted by a heated stylus in selected areas and, where contacted, provides a mark which is red in color and contrasts extremely well with the white appearance of the coating where not contacted by the heated stylus. The red color will readily appear if the coating is heated above about 75° C. The red color is provided, it is believed, due to the formation of a hydroxide in the coating and the phenolphthalein indicating this formation. The magnesium oxide when heated in the dry state of the coating combines with a radical OH from water molecules possibly contained in the oxide and/or vapor in the air and becomes alkalized. The molecules of the alkalized magnesium oxide and phenolphthalein come into closer contact and resonate in a frequency range to provide the red color. The temperature of the stylus may be such as to evaporate some included acid from the mixture, and the evaporation of the acid tends to return the coating to an alkaline condition and accentuates or aids the change to the red color.

The recording material constructed in accordance with the above may be readily manufactured and has a good shelf life. Moreover, when used in applications where the material and stylus move relatively, the speed of relative movement may be highly satisfactory. Furthermore, the mark provided is extremely sharp and clear. Very important is the fact that any mark effected is a permanent mark due to the fact that the state of alkalinity which provides the mark remains, and since the marking is performed in a dry state of the coating, a permanent state of resonance is effected and produces a permanent deep red color.

A heat-sensitive material embodying the present invention may be manufactured in different ways, and the coating of a base material, as described above, is preferable. The heat-sensitive material may also be prepared by incorporating in the paper during the manufacture thereof the alkaline earth or alkaline metal material. At a later time phenolphthalein may be dissolved in a suitable solvent and this solution may be applied to the paper, either on one or both sides thereof. When the paper is heated, the alkaline earth combines with a radical OH and the phenolphthalein indicates the presence thereof by effecting a color change, as described above. Such a mark will penetrate the paper due to the fact that the entire paper is alkaline where heated.

While the preferred embodiment of the present invention has been described in considerable detail hereinabove, it should be understood that certain changes and modifications thereof may be made by those skilled in the art to which it relates and that the invention is not intended to be limited to the specific embodiments described, but it is intended to cover all changes coming within the scope of the appended claims.

Having described my invention, I claim:

1. A heat-sensitive recording material comprising a base material having a surface with a smooth cohesive uniform coating thereon and substantially covering said surface in an intimate adhered contact with said surface, said coating having a given color and consisting essentially of phenolphthalein and magnesium oxide which cooperate to effect a change in the color of the coating upon the application of heat thereto wherein the proportion by weight of magnesium oxide to phenolphthalein is within the range between 1:15 to 15:1.

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2. A heat-sensitive recording material comprising a base material having a surface with a smooth cohesive uniform coating thereon in an intimate adhered contact with said surface, said coating being white in color and consisting of phenolphthalein, alkaline magnesium oxide, a binder, and an acid which evaporates upon the application of heat to the coating, the proportion by weight of magnesium oxide to phenolphthalein being within the range of 1:15 to 15:001, and said phenolphthalein and magnesium oxide cooperating to effect a change in the color of the coating to red in the area thereof heated to above 75° C.

3. A heat-sensitive recording material as defined in claim 2 wherein said acid comprises acetic acid.

4. A heat-sensitive recording material as defined in claim 3 wherein said binder comprises polystyrene with metacrylonitrile.

5. A heat-sensitive recording material comprising a base material having a surface with a smooth uniform coating thereon in intimate adhered contact therewith, said coating being white in color and made upon drying of a mixture including alkaline magnesium oxide, phenolphthalein, a suitable solvent, a binder and sufficient acid to produce an adequate pH to provide a white color to the mixture, and said phenolphthalein and magnesium oxide cooperate to effect a change in the color of the coating to red in the area of the coating engaged by a heated marking member effective to heat the coating in said area to a predetermined temperature, the proportion

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by weight of magnesium oxide to phenolphthalein being within the range of 1:15 to 15:001.

6. A heat-sensitive recording material as defined in claim 5 wherein said acid comprises acetic acid.

7. A heat-sensitive recording material comprising a base material having a surface with a smooth uniform coating thereon substantially covering and in intimate adhered contact with said surface, said surface including an alkaline earth oxide which combines with a radical OH when heated in the presence of a substance containing an OH radical and thereby becomes alkaline on the application of heat thereto and an indicator which changes in color upon contact with the alkaline alkaline earth oxide so that the coating changes in color in the area where heated, the ratio of said alkaline earth oxide to said indicator being within the range of 1:15 to 15:001.

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U.S. Cl. X.R.

117—155; 346—76, 135