United States Patent Office 2,776,251 Patented Jan. 1, 1957

2,776,251

ELECTRICAL RECORDING MEDIUM

Robert S. Schwartz, Great Neck, N. Y., assignor to Faximile, Inc., New York, N. Y., a corporation of Delaware

No Drawing. Application November 3, 1953, Serial No. 390,096

13 Claims. (Cl. 204—2)

This invention relates to recording media of the type which are subjected to an external application of heat to render the medium markable electrically.

While not limited thereto, the invention is particularly useful in the art of electrical recording wherein it is desirable to pass a recording current through a conductive record medium containing an electro-responsive marking compound. In recorders operating on this principle, the recording current is applied to two cooperating electrodes, and a conductive sheet or tape, which may be impregnated paper or cloth, is drawn between the electrodes. Marks are made on the conductive medium by electrochemical change.

Paper, being white and inexpensive, is very desirable for record purposes. However, paper is normally nonconductive and must be impregnated with suitable chemicals to make it electro-conductive and suitable for use in electrical recorders. Perhaps the most successful of the recording papers in use at the present time are the types impregnated with aqueous electrolytes and a marking compound such as disclosed in patents to J. V. L. Hogan et al., 2,339,267, and E. R. Wagner, 2,358,839. These papers are eminently suitable for most recording applications but have the characteristic that they must be maintained with the proper moisture content during storage until actually recorded on by recording apparatus.

Another type of electro-graphic recording paper is known and is disclosed in patent to R. B. Gibney, 2,530,956. This type of paper is fabricated as a composite sheet of several layers. One layer, the recording layer, is impregnated with a solid compound consisting of acetamide, alone or in combination with propionamide or formamide. Another layer is impregnated with the same amide or amides and an ionizable organic dye, the ions of which migrate to the recording layer when the solid impregnant is melted by the passage of an electric current therethrough, to produce a characteristic mark. In recording paper of this type there is the disadvantage that at least two layers are required to form the composite sheet. The acetamide which forms the basic impregnant sublimes or evaporates readily at normal ambient temperatures and pressures so that the paper must be stored in a sealed container to remain operative.

In moist types of recording papers such as disclosed in Patent 2,358,839 mentioned above, and in patent to Solomon 2,419,296, the papers are impregnated with a variety of marking compounds and may include as optional ingredients small quantities of urea or thiourea as antioxidants or color intensifiers. Quite unexpectedly, applicant discovered that it is possible to provide a wholly dry, white recording medium employing only a single layer sheet or tape of paper or cloth impregnated with only urea and/of thicurea and an electro-responsive substantially colorless marking compound. An ionizable salt may be added to the impregnant for a purpose to be described. The recording medium is markable electrically only by being first heated until the impregnant is molten, and the medium is then subjected to a suitable electrical

voltage between electrodes. The recording medium is characterized by its extreme stability when stored under varying conditions of temperature and humidity and prolonged exposure to the ambient atmosphere.

It is therefore a principal object of the invention to provide a dry recording medium which can be rendered conductive only by heating and is then electrically markable.

It is a further object to provide a white, dry, single layer porous recording medium impregnated with urea and/or thiourea, with or without an ionizable salt, and with a substantially colorless electro-responsive marking compound.

It is a further object to provide a dry recording medium containing an impregnant which medium is electro-conductive and electrically markable only when heated to at least the melting point of the impregnant, and which retains its markability on prolonged exposure to varying ambient atmospheric conditions.

It is a further object to provide a dry recording medium impregnated with a solid material which does not require special packaging for storage prior to use.

It is a further object to provide a novel impregnant composition for a recording medium.

It is a further object to provide a recording medium which may be employed in an intermittently operated recorder without portions of the medium which are exposed during the idle period becoming inoperative.

It is a further object to provide a recording medium which is "dry," in the sense of being solid as well as non-aqueous, prior to and subsequent to marking.

For a description of a recording apparatus and method suitable for the recording medium of this invention reference is had to my Patent 2,662,803.

It is thus far apparent that the dry recording paper of the present invention is radically different from known dry recording papers of the type which involve a carbonized body and a thin gray coating which is blasted off in the recording process. The present paper is white throughout and it permits of recordings including the white end of the tone scale rather than being limited to a tone scale from gray to black. The present paper is also relatively low in cost by reason of utilizing standard paper stock, and is relatively non-inflammable.

In addition to urea and/or thiourea, the normally solid impregnant may include a highly ionizable salt to increase conductivity of the impregnant when in the molten condition. Any of numerous highly ionizable salts can be used such as, for example, sodium nitrate, potassium nitrate, ammonium nitrate, ammonium chloride, ammonium sulfate, and sodium chloride. Recitation of these examples of such salts is not to be taken as limiting the invention, which is applicable generally to all highly ionizable salts both inorganic and organic.

It is to be emphasized that the normal functioning of the impregnant of this invention does not require the presence of moisture to any degree whatever. On the contrary the recording paper containing the impregnant is useful in the wholly "bone dry" state since it only requires the application of sufficient heat to melt the impregnant to render the recording paper electrically markable.

The impregnant may be formed by melting urea and/or thiourea and adding a relatively small amount of the salt. Or the urea and/or thiourea and the salt may be dissolved in an appropriate common solvent which may then be removed by evaporation leaving the dry, white impregnant as an electrolyte.

In making a normally-dry recording medium which, at elevated temperatures, is markable responsively to electric currents, a suitable white substantially colorless marking compound is added with the salt to the molten urea

or urea and/or thiourea. Electro-responsive marking compounds fall into at least two categories: those depending on electro-chemical change, an example of which is catechol; and those depending on thermo-chemical change, an example of which is lead thiosulfate. Catechol is normally a white crystalline compound which turns black when in an electrolyte subject to electric current from an iron electrode having a positive polarity. Lead thiosulfate is also white and it turns black when heated to about 200 deg. C. This heat may be provided in an elemental area by the passage of current through an electrolyte containing the lead thiosulfate, and therefore it properly may be called an electro-responsive marking compound. It will be understood that when a thermo-chemical type marking compound is employed in a normally-solid electrolyte, the electrolyte is rendered molten and thus conductive by the application of an appropriate amount of heat, and then a marking current is passed through the molten electrolyte with the result that additional heat is generated locally which turns the locally-present lead thiosulfate black. The heat below 150 deg. C. applied to melt the electrolyte does not in any way affect the color of the lead thiosulfate.

As an example of the manner in which a sheet of recording paper containing urea and an ionizable salt is rendered electro-conductive when heated, the following experiments may be performed.

TEST I

About 24 g. of urea and 3 g. of potassium nitrate are added to 20 milliliters of water and heated to boiling. A piece of absorbent paper stock is immersed in the hot solution, removed, and allowed to cool and dry. The resistance of the dry impregnated paper as then measured by applying two probes of an ohmmeter to opposite sides of the paper will be found to exceed one megohm, so that the paper may be considered substantially non-conductive. If the paper is now placed on a hot plate having a temperature of about 120 deg. C., the paper will assume a "wet" appearance and have an electrical resistance in the order of from 500 to 20,000 ohms depending on the contact pressure and spacing on one side of the paper of the two ohmmeter probes. The paper remains conductive as long as it is kept in a heated state. When the paper is allowed to cool, the electrical resistance again exceeds one megohm.

Test I may be performed with the impregnant consisting of thiourea and an ionizable salt or with a mixture of urea and thiourea and an ionizable salt. The electrical resistance of the paper when the impregnant is molten will generally be found to be highest when thiourea is used without urea. Mixtures of urea and thiourea will generally produce resistances intermediate in value between urea used alone and thiourea used alone. In general higher temperatures will be required to melt the impregnant as the proportion of thiourea is increased. Test I may be performed without the addition of potassium nitrate or any other ionizable salt, so that the impregnant consists of urea and/or thiourea alone. The range of resistances of the paper when the several impregnants are molten will generally be higher than when the ionizable salt is used, with the highest resistance obtained by use of thiourea alone. The reason that the test can be successfully performed without use of an ionizable salt is believed to be that urea and/or thiourea when heated until molten break down in such a manner as to create free ions which render the paper support electroconductive.

Advantage is taken of the electroconductive characteristics of urea and/or thiourea when molten in the present invention. The following examples are intended as illustrative of ways in which the invention can be demonstrated:

Example I

About 8 g. of urea and 1 g. of potassium nitrate are

added to 10 milliliters of water and heated to boiling. About 2 g. of lead thiosulfate is added to the water solution. Lead thiosulfate is a thermo-chemical type of marking compound. A piece of absorbent paper stock is immersed in the hot solution including dispersed lead thiosulfate, removed, and allowed to dry. The dried paper is then placed on a hot plate having a temperature of about 120 deg. C., whereupon it will assume a "wet" appearance. One terminal of a 45-volt dry battery is then connected to the metallic hot plate and the other electrode connected to a stylus. When the stylus is touched to or drawn over the paper, an intense black mark is left on the paper. The electric current passing through the paper generates heat locally to transform the lead thiosulfate into a black compound. Electrical conductivity by melting the electrolyte in the paper is, of course, a prerequisite to the passage therethrough of marking current.

A suitable recording medium can be obtained by use of a mixture of thiourea and urea or of thiourea alone in accordance with Example I instead of urea alone. The relative proportions of urea and thiourea in the mixture if used have not been found to be critical. The intensity of the black mark will generally be less as the proportion of thiourea is increased because the higher resistance of the molten impregnant results in a weaker marking current. Also higher temperatures will generally be required to melt the impregnants containing thiourea.

Example II

About 20 g. of urea is melted at about 130 deg. C., with 0.3 g. of catechol. Paper impregnated with this solution has a slight pinkish tinge and when heated until the impregnant is molten has a resistance of about 100–10,000 ohms, measured as described in Test I. It will be noted from the above that no ionizable salt is added to the impregnant. When current is passed through the heated paper from an iron stylus connected to the positive terminal of a 45-volt battery to a hot plate contacting the paper and connected to the negative terminal of the battery, the stylus traces a dark black mark on the paper.

Example II brings out the fact that urea is sufficiently electroconductive in the molten state without the addition of a highly ionizable salt to render the recording medium electrically markable. It will be noted that no water is employed in the impregnant of Example II. If desired the urea and catechol may be dissolved in about 30 milliliters of water and heated to boiling to form the impregnant.

A suitable recording paper may be obtained by employing a mixture of urea with thiourea or by employing thiourea alone in accordance with Example II instead of urea alone. The relative proportions of urea and thiourea in the mixture if used have not been found to be critical. The marking currents will generally be weaker because of the increased range of resistance of the molten impregnants containing thiourea. Also higher temperatures will be required to melt the impregnants containing thiourea. To obtain an intensity of mark closer to that obtained by use of urea and catechol alone, a higher voltage must be applied.

The present invention thus provides a means of control in the fabrication of the recording medium to adapt it for use in recorders operated at temperatures considerably above the melting point of urea. Addition of thiourea to the urea or substitution of thiourea for the urea will result in a recording medium in which the melting point of the impregnant is closer to that of the operating temperature of the recorder. Furthermore, the voltages available in the recorder may be excessively high for a recording paper containing urea and an ionizable salt. By omitting the salt or reducing the quantity used, and by adding thiourea to the urea or using it instead of the urea, the electrical resistance of the recording medium can

be accommodated to the particular marking voltages available at the recorder.

The several examples described above are not to be construed as limiting the invention. It will of course be understood that the recording paper, when manufactured in quantity may be made continuously by passing the paper stock through an impregnating bath and drier.

One of the important advantages of a recording medium constructed in accordance with the teaching of this invention is that the same sheet may be heated and recorded on any number of times. Expressed another way, the medium is electrically markable when heated to the melting point of the impregnant regardless of having been so heated previously. The sensitivity of the medium is not destroyed by a developing or "fixing" process. Yet each recorded mark is permanently fixed in the impregnated fibers of the support at the instant that the mark is made. The continued sensitivity of the recording medium makes it valuable for special applications such as in the instrumentation field where it may be desirable to make a comparison record of values taken at one time with values taken at a previous time.

In order to demonstrate the stability of recording paper embodying the invention, samples of dry recording paper were made employing impregnants containing acetamide and propionamide which are amides whose use in recording media is taught in the prior art. Urea and thiourea may also be considered as amides since both compounds are amide derivatives of carbonic acid. It was found that recording media containing these prior art amides were unstable, or had other objectionable characteristics as discovered in the tests described below. Samples of impregnated recording paper prepared as described in Example I were formulated as follows:

SAMPLE A

Actamide, 20 g.
Potassium nitrate, 0.3 g.
Catechol, 0.3 g.

SAMPLE B

Acetamide, 20 g.
Propionamide, 2 g.
Potassium nitrate, 0.3 g.
Catechol, 0.3 g.

In addition, samples of recording paper were prepared as described in Examples I and II respectively. The samples each included as an electrolyte urea, thiourea, or a mixture of urea and thiourea, with and without an ionizable salt, in addition to a marking compound.

TEST FOR EFFECTS OF PROLONGED EXPOSURE

The several samples of recording paper formulated as described above were each heated on a hot plate set at 130 degrees C. and tested for markability at 45 volts. Black marks of different intensities were produced on all samples when an electrode was touched to and was drawn over each sample of paper. The several samples were then exposed to normal varying ambient atmospheric conditions for a period of twenty days. Again each sample was heated on a hot plate of 130 degrees C. and tested for markability at 45 volts as above. Black marks were produced on all paper samples containing urea and/or thiourea when an electrically positive iron electrode was touched to and was drawn over the papers. No mark was produced on any of the sample papers containing acetamide. It was found that the amide content of these papers had sublimed or evaporated to the extent that no marking was possible when tested for markability at 45 volts in accordance with the method of Example I.

OBSERVATIONS AND CONCLUSIONS

The above test clearly demonstrated that the physical condition of the papers containing urea and/or thiourea were substantially unaffected by conditions of prolonged exposure to varying ambient atmospheric conditions, and their markability, when tested in accordance with Example I by externally heating until the impregnant was molten and then applying an electrical voltage was unimpaired. It was furthermore found that the urea and/or thiourea in these papers sublimed or evaporated to such a small extent under open storage conditions that the markability of the papers was not impaired. The amide content of the papers containing either acetamide or a mixture of acetamide with propionamide under conditions of prolonged exposure to ambient atmospheric conditions sublimed or evaporated to the extent that marking by external heating and application of an electrical potential in accordance with Example I was not possible.

It must be emphasized that it is essential to the invention that the impregnant of the recording medium be such that the recording medium will remain operative upon prolonged exposure to varying ambient atmospheric conditions. Thus the rate of sublimation or evaporation of the impregnant is a critical factor. The rate of sublimation or evaporation is of course directly related to the inherent vapor pressure. It will be noted that urea, thiourea, and mixtures thereof all have inherent vapor pressures less than acetamide.

The invention has been described by reference to specific examples, but this has been done by way of explanation and not limitation, and the scope of the invention is to be construed by reference to the appended claims.

One particularly important extension of the invention is in connection with certain impregnants for recording paper containing the particular amides having inherent vapor pressures less than acetamides disclosed in my copending applications Ser. No. 350,757, filed April 23, 1953, and Ser. No. 355,843, filed May 18, 1953. Among these amides are chloroacetamide, cyanoacetamide and other hydrogen substitution products of acetamide; also acetanilide, benzamide, paratoluene sulfonamide, N-ethyl sulfonamide, butyramide, and other primary and secondary amides having at least four carbon atoms. Urea or thiourea or a mixture of urea and thiourea may be used to replace part or all of the ionizable salts used in any of the impregnants including the amides mentioned above, when it is desired to produce a recording medium having a higher resistance when the impregnant is molten than is otherwise obtained by use of ionizable salts.

This application is a continuation-in-part of my copending application Serial No. 102,135, filed June 29, 1949, now abandoned.

What is claimed is:

1. A white dry recording medium comprising a porous sheet impregnated with a major quantity of urea and a substantially colorless electroresponsive marking compound, said medium being substantially non-conductive electrically at temperatures below the melting point of urea, and having high electrical conductivity and electrical markability only at temperatures above the melting point of urea.

2. A white dry recording medium according to claim 1, wherein the impregnant further includes thiourea.

3. A white dry recording medium comprising a porous sheet impregnated with a major quantity of urea, a highly ionizable salt, and a substantially colorless electroresponsive marking compound, said medium being substantially non-conductive electrically at temperatures below the melting point of urea, and having high electrical conductivity and electrical markability only at temperatures above the melting point of urea.

4. A white dry recording medium according to claim 3, wherein the impregnant further includes thiourea.

5. A white dry recording medium comprising a porous sheet impregnated with a major quantity of an amide selected from the group consisting of urea and thiourea, and a substantially colorless electroresponsive marking compound, said medium being substantially non-conductive electrically at temperatures below the melting point of the amide and having high electrical conductivity

and electrical markability only at temperatures above the melting point of the amide.

6. A white dry recording medium according to claim 5, wherein the impregnant further includes an ionizable salt.

7. A white dry recording medium according to claim 5, wherein the impregnant includes another amide having an inherent vapor pressure less than that of acetamide.

8. A white dry recording medium according to claim 7, wherein the impregnant further includes an ionizable salt.

9. A white dry recording medium according to claim 7, wherein the said other amide is a hydrogen substitution product of acetamide.

10. A white dry recording medium according to claim 7, wherein the said other amide is selected from the group consisting of acetanilide, benzamide, para-toluene sulfonamide, N-ethyl sulfonamide, and butyramide.

11. A white, dry recording medium according to claim 7, wherein said other amide is selected from the group consisting of chloroacetamide and cyanoacetamide.

12. A white, dry recording medium according to claim 7, wherein said other amide is a primary amide having at least four carbon atoms.

13. A white dry, recording medium according to claim 7, wherein said other amide is a secondary amide having at least four carbon atoms.

References Cited in the file of this patent

UNITED STATES PATENTS

2,358,839	Wagner	Sept. 26, 1944
2,419,296	Solomon	Apr. 22, 1947
2,530,956	Gibney	Nov. 21, 1950