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DRY ELECTRICAL RECORDING MEDIUM

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This invention relates to recording media of the type which is 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 recording medium containing an electro-responsive marking compound. In recorders operating on this princple, 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 electro-chemical change.

Paper, being white and inexpensive, is very desirable for record purposes. However, paper is normally non-conductive 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 is the type impregnated with an aqueous electrolyte and a marking compound such as disclosed in patent to J. V. L. Hogan et al., 2,339,267. This paper is eminently suitable for most recording applications but has the characteristic that it must be maintained with the proper moisture content during storage until actually recorded on by recording apparatus.

Another type of electrographic recording paper is known and 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 amdies 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 in an acetamide vapor to remain operative. At ambient relative humidities exceeding 85% the paper becomes soft, weak, sticky and wrinkled because the amide content is extremely hygroscopic. The high humidity renders the paper unmanageable in conventional recorders and markability becomes either impaired or impossible.

Applicant's purpose has been to provide a dry, white recording medium employing a single layer sheet or tape of paper or cloth impregnated with one or more suitable amides, an ionizable salt, and an electro-responsive substantially colorless marking compound. The recording medium is markable only by being first externally heated and then subjected to a suitable electrical voltage between electrodes, one or which may be an element having an iron content. The recording medium is characterized by its extreme stability under conditions of high 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 external heating and is then electrically markable.

It is a further object to provide a white dry, single layer porous recording medium impregnated with a primary or secondary amide having at least four carbon atoms, an ionizable salt, and a substantially colorless electro-responsive marking compound.

It is a further object to provide a white, dry recording medium which is rendered electro-conductive only when externally heated and which remains wholly stable and markable under all humidity conditions.

It is a further object to provide a dry recording medium which is electro-conductive and electrically markable when externally heated and which retains its markability on prolonged exposure to ambient atmospheric conditions.

It is a further object to provide a dry recording medium impregnated with a solid amide 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.

For a description of a recording apparatus and method suitable for the recording medium of this invention reference is had to my copending application Serial No. 102,136, filed June 29, 1949, now Patent No. 2,662,803.

Generally the invention contemplates a recording medium such as paper or cloth impregnated with one or more amides having four or more carbon atoms, a highly ionizable salt, and a substantially colorless electro-responsive marking compound. The combination of amidle and salt is hereinafter designated as a "composite electrolyte." The composite electrolyte is normally solid, substantially non-hygroscopic and non-evaporating under normal ambient conditions. It includes as one ingredient a primary or secondary amide, which may be regarded as an incompletely substituted hydrogen substitution product of ammonia (NH_3), having a melting point above 20 deg. C. Primary, secondary and tertiary amides may be regarded generally as derivatives of ammonia in which one, two, or all three hydrogen atoms in ammonia (NH_3) have been replaced respectively by one, two, or three ($R \cdot CO$) or ($R \cdot SO_2$) groups as evidenced by standard works on the subject such as "Sidgwick's Organic Chemistry of Nitrogen," edited by Taylor and Baker, Oxford Press, 1937, page 136 et seq. Quite unexpectedly it was discovered that certain primary and secondary amides having four or more carbon atoms are for the purpose of this invention considerably superior to other amides having less than four carbon atoms. Tertiary amides such as methyl-acetanilide were found wholly ineffective for purposes of the present invention. Since one object of the invention is to provide a substance which is solid, dry and substantially non-evaporative at ordinary ambient temperatures, amides having a low melting point were found not suitable. Formamide is an example of such an unsuitable primary amide having less than four carbon atoms since it is a liquid at ordinary temperatures and subject to evaporation on exposure. Acetamide, another primary amide having less than four carbon atoms has also proven to be unsuitable since it is subject to extreme sublimation or evaporation on exposure and is objectionably hygroscopic in high humidity ambient conditions. Compositions of acetamide with propionamide and acetamide with formamide have been found to be similarly subject to sublimation or evaporation and are objectionably hygroscopic.

As a general rule normally solid primary and secondary amides containing four or more carbon atoms have been found to serve as satisfactory ingredients of the composite electrolyte of the present invention since they are

dry, solid, and substantially non-sublimating or non-evaporating at normal ambient atmospheric conditions. Among these amides are: acetanalide, para-toluene sulfonamide, butyramide, N-ethyl benzene sulfonamide, and benzamide. The listed amides are not to be taken as limiting the invention thereto since there is reason to believe other primary and secondary amides having four or more carbon atoms would also serve the purposes of the present invention.

In addition to an amide of the type described, the normally-solid composite electrolyte of this invention includes a highly ionizable salt. Numerous highly ionizable salts can be used, such as, for example, sodium nitrate, potassium nitrate, ammonium nitrate, ammonium chloride, ammonium sulfate, and sodium chloride. These salts are not to be taken as limiting the invention which is applicable generally to all highly ionizable salts both inorganic and organic. It will be understood that with certain of the salts better results will be obtained with some of the amides than with others, and for a particular use some combinations will be found better than others. Commercial grades of amides may contain enough salts as impurities to provide electro-conductivity and it will be understood that the use of such impure grades falls within the scope of the present invention.

The composite electrolyte may be formed by melting the selected amide and adding a relatively small amount of the salt. Or the amide and the salt may be dissolved in an appropriate common solvent which may then be removed by evaporation leaving the dry, substantially white composite electrolyte.

In making a dry recording medium which at elevated temperatures is markable responsively to electric currents, a suitable electro-responsive marking compound is added with the salt to the molten amide. Electro-responsive marking compounds as contemplated herein are generally substantially colorless compounds which are either white or very light colored. They depend on electrochemical action to change to dark colors or may be heat sensitive so that they decompose to change to dark colors. Such compounds are all deemed electro-responsive since they will darken on passage of an electrical current through them. Among the marking compounds found suitable for purposes of the present invention are phenols having at least two hydroxy groups in the ortho position, such as catechol, pyrogallol, gallic acid, and tannic acid. Certain heat sensitive electro-responsive marking compounds which have been found suitable are lead formate, lead thiosulphate, and nickel formate. Still other suitable electro-responsive marking compounds are known in the art. Colored dyes are wholly unsuitable for the present invention since they cannot be used to impregnate completely the single porous layer which carries the impregnant without rendering it useless for marking purposes.

It may be pointed out that as regards the combination of an amide, a salt and a specific marking compound, the chemical nature of the marking compound should be taken into consideration and combinations selected which have characteristics appropriate to the requirements of the particular application involved. It must be emphasized that use of a colored marking dye embodied in a separate layer of a plural layer marking sheet is undesirable in the present invention, since a single layer white porous recording medium is required which is capable of repeated marking. Multi-layered sheets known in the prior art wherein one layer carries a colored dye and another layer carries an electroconductive impregnant are not capable of repeated marking electrically. A further advantage of combining a substantially colorless marking compound with the composite electrolyte is that manufacture of the recording paper is simplified since a single dip in the proper solution impregnates the paper. Multi-layered papers requires repeated dips or successive coating steps. The following example is intended as illustrative of the way in which the invention can be carried out employing primary and secondary amides having four or more carbon atoms:

EXAMPLE 1

About 10 g. of butyramide was melted at about 125 deg. C. with 0.1 g. of potassium nitrate and 0.2 g. of catechol. Paper impregnated with this melt has a resistance of 2,000 ohms when measured across heated electrodes, one inch in diameter pressing the paper therebetween with a pressure of 10 pounds per square inch. The dried paper was then placed on a hot plate having a temperature of about 120 deg. C., whereupon it assumed a "wet" appearance. One terminal of a 45-volt dry battery was connected to the metallic hot plate and the other electrode to a stylus containing iron. When the stylus was both touched to and drawn over the paper, intense black marks were left on the paper.

The procedure of Example 1 can also be used to demonstrate the markability of recording media containing one or more amides having four or more carbon atoms of which the following are examples:

Para-toluene sulfonamide
Benzamide
Acetanilide
N-ethyl benzene sulfonamide

Several additional samples of recording paper were made and tested employing certain other primary, secondary and tertiary amides. It was found that these recording media were ineffective, unstable, or had other objectionable characteristics as discovered in the tests described below:

EXAMPLE A

An ineffective recording medium was made by impregnating paper with a melt of 10 g. of methyl acetanilide (a tertiary amide which may be regarded as a completely-substituted hydrogen substitution product of ammonia), 0.1 g. of potassium nitrate and 0.3 g. of catechol. The paper had a resistance of 100,000 ohms when measured as in Example 1. No visible mark was produced when the paper was heated and 90 volts was applied across the heated paper through appropriate electrodes as in Example 1. There is reason to believe all other tertiary amides would prove similarly ineffective for the purposes of this invention.

EXAMPLE B

About 20 g. of acetamide, and 0.3 g. of potassium nitrate were heated together until molten. Roughly 0.3 g. of catechol was added to the melt, blotted to remove the excess liquid, and allowed to cool. The resulting sheet was white and apparently dry. The paper was heated and tested for markability as in Example 1. Black marks were produced on the paper both when an iron electrode was touched to and was drawn over the paper.

EXAMPLE C

About 20 g. of acetamide, 2 g. of propionamide (a primary amide having less than four carbon atoms) and 0.3 g. of potassium nitrate were heated together until molten. Roughly 0.3 g. of catechol was added to the melt. A piece of absorbent paper stock was immersed into the melt, blotted to remove the excess liquid and allowed to cool. The resulting sheet was white and apparently dry. The paper was heated and tested for markability as in Example 1. Black marks were produced on the paper both when an iron electrode was touched to and was drawn over the paper.

EXAMPLE D

A sample of recording paper was made as described in Example B employing 20 g. of acetamide, 2 g. of formamide and 0.3 g. of catechol. The paper was heated

and tested for markability as in Example 1. Black marks were produced on the paper both when an iron electrode was touched to and was drawn over the paper.

I. *Test for hygroscopic effects*

Several samples of recording paper were fabricated in accordance with Example 1. They were impregnated respectively with butyramide, benzamide, acetanilide, paratoluene sulfonamide, N-ethyl benzene sulfonamide, acetamide, acetamide with propionamide, and acetamide with formamide. The samples were placed in a closed humidity test chamber having a relative humidity of at least 85%, at 20 deg. C., and atmospheric pressure. After one hour's exposure in the test chamber the samples were removed. The papers containing amides having four or more carbon atoms were all slightly limp from moisture absorbed by the paper but they were all smooth to touch and unwrinkled. These papers were then heated on a hot plate set at 120 deg. C., and were tested for markability as in Example 1. Black marks were produced on all the papers containing amides having four or more carbon atoms both when an iron electrode was touched to and was drawn over the papers.

The papers containing acetamide were soft, sticky, weak and wrinkled from absorbed moisture when removed from the humidity test chamber. The acetamide papers were heated on a hot plate set at 120 deg. C., and tested for markability as in Example 1. The marks produced when an iron electrode was touched to and was drawn over the acetamide papers were irregular, spotty and objectionably light.

II. *Test for effects of prolonged exposure to the atmosphere*

Several samples of recording paper were fabricated in accordance with Example 1. They were impregnated respectively with the same amides as the papers tested for hygroscopic effects. The samples were then exposed to varying ambient atmospheric conditions of pressure, temperature and humidity for a period of twenty days. Each sample was then heated on a hot plate at 120 deg. C., and tested for markability as in Example 1. Black marks were produced on all paper containing amides having four or more carbon atoms both when an iron electrode was touched to and was drawn over the papers. No mark was produced on the papers containing acetamide. It was found that the amide content of the acetamide papers had sublimed or evaporated to the extent that no marking was possible in accordance with the method of Example 1.

III. *Observations and conclusions*

The above tests clearly demonstrated that the physical condition of papers containing amides having four or more carbon atoms fabricated in accordance with Example 1 were substantially unaffected by conditions of high humidity and of prolonged exposure to ambient atmospheric conditions, and their markability, when tested in accordance with Example 1 by externally heating and then applying an electrical voltage was unimpaired. It was furthermore found that the amides in these papers sublimed or evaporated to such a small extent under all humidity and storage conditions that the markability of the papers was not impaired. The papers containing acetamide were extremely hygroscopic under highly humid conditions, becoming too soft, weak, wrinkled, and sticky to be handled practicably in recording devices commonly used in the art. Under conditions of prolonged exposure to ambient atmospheric conditions the amide content of the acetamide papers sublimed or evaporated to the extent that marking by external heating and application of an electrical potential in accordance with Example 1 was not possible.

Of the amides found satisfactory as ingredients of the composite electrolyte for use in this invention will be noted that all were aliphatic or aromatic primary and secondary amides having four or more carbon atoms. Of the amides found unsatisfactory all were aliphatic primary amides, namely: acetamide, acetamide with propionamide, and acetamide with formamides. These are all amides containing less than four carbon atoms. Tertiary amides which may be regarded as completely substituted hydrogen substitution products of ammonia were found wholly unsatisfactory for purposes of this invention.

It must be emphasized that it is essential to the invention that the amide content of the recording medium be such that the recording medium will remain operative upon prolonged exposure to all ambient atmospheric conditions. Thus the rate of sublimation or evaporation of the amides is a critical factor to be observed in selection of suitable amides for the impregnant. All the amides found satisfactory for the purposes of the present invention have an inherent vapor pressure lower than that of acetamide. The rate of sublimation or evaporation is of course directly related to the inherent vapor pressure. Thus it may be regarded as essential to the present invention that amides selected as ingredients of the impregnant according to the present invention have an inherent vapor pressure lower than that of acetamide.

In practicing the invention described herein it is considered within the scope of the invention to fabricate a recording medium containing a plurality of amides having at least four carbon atoms as disclosed herein. It is likewise considered within the scope of the invention to include a minor quantity of the order of 15% of one or more amides having less than four carbon atoms in the impregnant together with a major quantity of the order of 85% of one or more amides having at least four carbon atoms. Each amide employed in the impregnant must have an inherent vapor pressure lower than that of acetamide and may be either a primary or secondary amide. Amides suitable as addition ingredients to supplement the content of amides having at least four carbon atoms are: urea, propionamide, and derivatives of acetamide such as chloroacetamide and cyanoacetamide.

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

I claim:

1. A dry, white recording medium markable electrolytically only when heated, comprising a single layer of dry porous material impregnated essentially with at least one amide having at least four carbon atoms and selected from the group consisting of acetanilide, benzamide, paratoluene sulfonamide, N-ethyl benzene sulfonamide, and butyramide, a highly ionizable salt, and an electro-responsive substantially colorless marking compound.

2. A recording medium in accordance with claim 1 including therewith a minor quantity of an amide having less than four carbon atoms and having an inherent vapor pressure lower than that of acetamide, the last mentioned amide being selected from the group consisting of primary and secondary amides.

3. A recording medium in accordance with claim 1 wherein the marking compound is a phenol having at least two hydroxy groups in the ortho position.

4. A recording medium in accordance with claim 1 wherein the electro-responsive marking compound is sensitive to heat so that when an electrical current is passed through the medium, the compound changes to a dark color.

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