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ELECTRICAL CONDUCTING COMPOSITION

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The present invention relates to an improvement in conducting compositions.

An object of the invention is to provide a composition of matter which is capable of rendering absorbent, normally non-conducting materials, such as paper and the like, conductors of electricity.

A further object is the provision of a composition which has relatively high electrical conductivity in the dry state.

A still further object is the provision of a composition which is in the form of a solid solution of a low melting mixture of ionizable salts in a polyhydroxylic material which is normally a solid and in which the salts ionize to a considerable extent.

A more particular object is the provision of a composition which comprises a eutectic mixture of salts of highly ionizable nature in mannitol.

Another object is the provision of a composition of a low melting mixture of salts and a polyhydroxylic body, in which the salts are ionized, which contains a wetting or dispersing agent to assist in obtaining rapid and complete impregnation of the absorbent material to be treated.

The above and other objects will be more fully explained hereinafter.

There are a number of applications in the arts in which it is desirous to render a normally non-conducting material, such as cloth or paper, conductive of electricity. An outstanding example of such an application is in the field of recorders in which a web of paper or the like is passed between electrical contacts, one of which is usually a traversing stylus, and upon the passage of current between the contacts a mark is produced upon or in the web by means of a color change in a sensitive chemical coating on one face of the web or in the web. The coatings used are such that the passage of current through the paper between the electrodes produces an electrochemical change or a thermo-chemical change, the heat for which is developed by the passage of the current, which either produces a color which contrasts with the unaffected portion of the web or else destroys the color at the point of passage of current, thereby giving rise to a contrast with the unaffected portion of the web. In some instances the color changing composition is impregnated into the web so that the color change is actually in the web. In other cases the color changing composition is merely coated as a layer upon one surface of the web so that the visible contrast is located only at one surface. It will be apparent, however, that in either case the prime essential is to enable the current to pass through the web between the electrodes. The most practical material known for use as this web, both from a standpoint of economy and its desirable physical properties, is paper. However, paper is normally a non-conducting substance.

In the earliest attempts to use paper webs in recorders, the web was simply run through an aqueous bath of a conductive salt such, for example, as sodium nitrate. The resulting wet web contained a solution of the highly ionized salt in water and upon passage between the electrodes it afforded a medium of good conductivity. The disadvantages of using a wet bath of this sort in connection with the recording apparatus are obvious. The mechanism was complicated by the necessity of providing for this bath. The wet web was substantially weakened and had to be handled very carefully. After recording, the web had to be dried before it could be handled or, in case it carried a message, before the message could be delivered. Another defect with the wet web system consisted in the fact that the portion of the web which remained between the electrodes for substantial periods of time in which no messages were being recorded would dry out and become non-conductive and it was necessary to make provision for discarding this dried portion of the web before the next message could be received.

Attempts were also made to make a conducting web which would retain sufficient moisture so that ionizable salts would be maintained in conducting condition. Such expedients as the incorporation of hygroscopic agents such as glycerine or calcium chloride have this effect. The webs thus impregnated, however, had a further disadvantage that they were always in moist condition and could not be permanently dried. Where it was desirable to retain the web or to deliver the web in the form of a message, this wet condition was a substantial defect. In addition to this defect such webs varied widely in conductivity with changes in the relative humidities encountered in use.

In order to produce a dry sheet of low hygroscopicity it was proposed to use a solid solution of an ionizable salt in a normally solid solvent in which the salt ionized. However, for most practical purposes this expedient was unsatisfactory because of the very high resistance of the resulting paper.

The present invention produces a composition which has relatively high conductivity when impregnated into paper or the like and dried, Generally, the invention contemplates a solid solution of a low melting mixture of highly ionizable salts in a polyhydroxylic body in which they ionize. In particular the eutectic mixtures of highly ionizable salts in polyhydroxylic bodies, preferably the normally solid hexitols (straight-chain hexahydroxyhexanes), have especially good conductive characteristics. Quite unexpectedly it was discovered that a solid solution of a eutectic mixture of two salts in a hexitol such as mannitol had a conductivity between three and four times better than a solid solution of either one of the single salts in the same polyhydroxylic material. It was further discovered that in general a eutectic mixture of three highly ionizable salts in a hexitol was more conductive than the binary eutectic mixture of any two of the component salts in solid solution.

According to the invention, a mixture of salts in such proportions as to contain a substantial quantity of the eutectic mixture is employed as the solute in a solid solution. The solvent is the polyhydroxylic material. Numerous highly ionizable salts can be used, such as, for example, sodium nitrate, potassium nitrate, ammonium nitrate, ammonium chloride, ammonium sulfate, lithium nitrate, 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. Of the polyhydric materials the hexitols have been found particularly useful although other normally solid polyhydroxylic materials in which the salts ionize can be used. Of the hexitols, mannitol, sorbitol and dulcitol are of particular value. Sorbitol, being more hygroscopic than mannitol or dulcitol, is not as satisfactory for compositions in which low hygroscopicity is essential but it is otherwise quite satisfactory in the composition.

The following examples are intended as illustrative only and are given in order to indicate to those skilled in this art some of the ways in which the invention can be carried out.

Example 1

20 g. of the eutectic mixture of KNO_3 and $NaNO_3$ composed of 10.26 g. KNO_3 and 9.74 g. $NaNO_3$ were added to 20 g. mannitol and 20 g. sorbitol and the mixture made up to a volume of 200 ml. with water. Samples of paper were dipped into this composition, passed through a wringer to remove excess solution and dried five minutes at 110° C. The paper was impregnated with 25 lbs. to the ream. The resistance of the impregnated paper to the passage of current between electrodes placed at opposite sides was 6.0 megohms at 20% relative humidity.

Example 2

20 grams of a binary mixture consisting of 9.4 grams KNO_3 and 10.6 g. $NaNO_3$ were added to 20 g. mannitol and 20 g. sorbitol and the mixture made up with water to 200 ml. volume. Samples of paper were dipped into this composition, passed through a wringer to remove excess solution and dried for five minutes at 110° C. The resistance of the impregnated paper to the passage of current between electrodes placed at opposite sides was 8.0 megohms at 20% relative humidity.

In this example the proportions of the salts do not correspond exactly to the eutectic but there is an excess of $NaNO_3$ present. The proportions, however, are such that the two salts are present in substantially the amounts required to form the binary eutectic.

Example 3

For comparison with Examples 1 and 2, 20 g. $NaNO_3$, 20 g. mannitol and 20 g. sorbitol were made up with water to a solution of 200 ml. volume. Samples of paper were dipped into the solution, passed through a wringer to remove excess solution and dried for 10 minutes at 110° C. The resistance of the paper so treated, determined by the same method and under the same conditions as those employed in Examples 1 and 2, was 30.0 megohms.

Example 4

20 grams of a ternary eutectic mixture containing 15.15 g. NH_4NO_3, 1.02 g. NH_4Cl and 3.83 g. $NaNO_3$ were mixed with 40 g. mannitol and the mixture made up with water to a solution of 200 ml. volume. Samples of paper were impregnated with this solution to the extent of 26 lbs. solids per ream. The samples of impregnated paper were then dried for five minutes at 110° C. The dried samples had a resistance of 0.4 megohm at 20% relative humidity.

In this example mannitol alone was used as solvent and the salts were employed in the exact eutectic proportions.

Example 5

20 g. of a ternary mixture containing 14.96 g. NH_4NO_3, 1.5 g. NH_4Cl and 3.54 g. $NaNO_3$ were mixed with 20 g. mannitol and 20 g. sorbitol and the mixture made up with water to a solution of 200 ml. volume. Samples of paper were impregnated with this solution to the extent of 26 lbs. solids per ream. The samples of impregnated paper were then dried for five minutes at 110° C. The dried samples had a resistance of 0.8% megohm at 20% relative humidity.

In this example the salts are not in the exact eutectic proportions but are close enough to give a low melting mixture and to produce a relatively highly conducting composition in hexitols.

Example 6

20 g. of the same ternary mixture as employed in Example 5 were mixed with 40 g. mannitol and 0.6 g. di-octyl-sodium-sulfonsuccinate (Aerosol O. T.) and the mixture made up with water to a solution of 200 ml. volume. Samples of paper were impregnated with this solution to the extent of 26 lbs. solids per ream. The samples were dried for five minutes at 110° C. The dried samples had a resistance of 0.4 megohm.

In the above example mannitol alone was used as the solvent for the solid solution and a wetting agent was employed to assist in the impregnation of the paper.

Example 7

25 g. of the ternary mixture of NH_4NO_3, NH_4Cl and $NaNO_3$ as employed in Example 5, and 50 g. of mannitol were made up with water into 150 ml. of solution. Samples of paper were pretreated by dipping into a solution of 5 ml. di-octyl-sodium-sulfonsuccinate (Aerosol O. T. 10%) in 150 ml. water. The paper was dried, then impregnated with the conducting composition, dried, and finally calendered between hot rolls at 250–260° F. The samples of paper so treated had a resistance of 0.2 megohm.

Example 7 shows first of all a variation in the manner in which the wetting agent is incorporated into the final paper. In general where a wetting agent is used it has been found preferable to pre-treat the paper with it before impregnating with the solution of the conducting composition. A particular advantage to the use of the wetting agent is in the obtaining of uniform impregnation which gives uniform conductivity throughout the sheet. In case the sheet is to be used for the purpose of a recorder, this uniform conductivity is of the greatest importance.

Example 7 introduces another step in making the treated paper. After the conducting composition has been applied in the form of a solution and the impregnated paper dried, the samples are passed through heated calendering rolls which are maintained at a temperature sufficient to exceed the melting point of the conducting composition. In this way the composition is melted and run in the paper so that it becomes homogeneous and extends uniformly throughout the paper. This hot calendering step has been found of great advantage in obtaining uniformity of conductivity throughout the paper.

Where the calendering of the sheets is conducted at a high temperature, satisfactory results are obtainable without the use of any wetting agent.

The compositions set out in the above examples are colorless and can be added to white paper or cloth or the like without causing any change in appearance thereof. In the case of a paper which is to be used for recording, the conductive paper resulting from treatment according to one of the examples is then coated with a lacquer containing the color changing material. This lacquer forms no part of the present invention but numerous compositions known in the prior art are available for the purpose.

The proportion of mannitol or other polyhydroxylic material to the salt mixture is capable of variation. In the examples given the ratio is two parts of the polyhydroxylic solvent to one part of the salt mixture. However, it is to be understood that this ratio can be varied within rather broad limits and will depend ultimately upon the particular use to which the paper is to be put, the type of the paper, the weight to which it is impregnated and other factors which will be apparent to those skilled in this art. In the case of impregnation according to the examples, the ratio of two parts of polyhydroxylic material to one part of the salt mixture has been found preferable although compositions containing other ratios have very good conductive properties. For example, ratios of polyhydroxylic material to salt mixture of 4 to 1 down to 1 to 2 have good conductive properties.

As shown in several of the examples, in place of the exact eutectic proportions of the salts it may be desirable in some instances to use an excess of one or more over the proportions called for by the eutectic. In such cases, however, there will be substantial amounts of the eutectic mixture present and the excess of salt will act as an impurity in the mixture. It is to be understood that the invention is not limited to the exact eutectic proportions but that proportions of the salts such as to give substantial amounts of the eutectic mixture are operative.

The invention has been described particularly with reference to binary and ternary salt systems but it will be apparent to those skilled in the art that it is equally applicable to more complex systems, for example, systems containing four or five salt components. Likewise some of the systems of salts give more than one eutectic point with different proportions of the component salts, all of which eutectic points are below the melting point of the lowest melting component salt. It is to be understood that the invention is not restricted to the lowest melting eutectic available for a given system but that any of the eutectic compositions can be used in the invention.

The examples above have illustrated the use of single polyhydroxylic materials and mixtures of two of them. The invention is applicable not only to mannitol or sorbitol or mixtures of these two but also to the other hexitols and other normally solid polyhydroxylic materials in which the salts are ionizable, such for example as pentaerythritol, glucose, sucrose, and others. These materials can be used singly or in any desired combination with each other or with the hexitols. It will be understood that with certain of the salt mixtures better results will be obtained with some of these polyhydroxylic materials than with others, and for a particular use some combinations will be found better than others.

With regard to the salts, it may be pointed out that in the case of use of the combination with a recorder it is necessary to take into consideration the chemical nature of the color changing composition and then to select combinations of salts which do not have an adverse effect upon this substance or which would tend to inhibit the color changing action when the current is passed.

It is to be understood that the invention is not limited to application in recorders but that the invention furnishes a conducting composition of general application. The composition is particularly useful in rendering absorbent, normally non-conducting materials, such as paper and cloth, conductive of electricity. The invention will therefore be found useful in many cases where it is desired to render cloth or paper electrically conductive.

I claim:

1. An electrical conducting composition consisting essentially of a solid solution of highly ionizable salts, substantially in the proportions of a eutectic mixture of said salts, in normally solid polyhydroxylic organic material in which the salts are ionized.

2. An electrical conducting composition consisting essentially of a solid solution of two highly ionizable salts, substantially in the proportions of a eutectic mixture of said salts, and normally solid polyhydroxylic organic material in which said salts are ionized.

3. An electrical conducting composition consisting essentially of a solid solution of a mixture of two highly ionizable salts, substantially in the proportions of a eutectic mixture of said salts, in a hexitol in which said salts are ionized.

4. An electrical conducting composition consisting essentially of a solid solution of a mixture of three highly ionizable salts, substantially in the proportions of a eutectic mixture of said salts, in a normally solid polyhydroxylic organic material in which said salts are ionized.

5. An electrical conducting composition consisting essentially of a solid solution of a mixture of three highly ionizable salts substantially in the proportion of a eutectic mixture of said salts, in a hexitol in which said salts are ionized.

6. An electrical conducting composition consisting essentially of a solid solution of a mixture of ammonium nitrate, ammonium chloride, and sodium nitrate, substantially in the proportions

of a ternary eutectic mixture thereof, in mannitol.

7. A normally solid electrical conducting composition comprising a mixture of ammonium nitrate, ammonium chloride, and sodium nitrate substantially in the proportions of a ternary eutectic mixture thereof, and mannitol in the proportion of about two parts mannitol to one part of the said eutectic mixture.

8. A normally solid electrical conducting composition comprising a mixture of at least two highly ionizable salts substantially in the proportions of a eutectic mixture thereof, and a hexitol in which said salts are ionized, said hexitol being present in the proportion of from 4 parts to 1 part of salt mixture to 1 part hexitol to 2 parts salt mixture.

9. An electrical conducting composition consisting essentially of a solid solution of at least two highly ionizable salts, substantially in the proportions of a eutectic mixture of said salts, in a normally solid polyhydroxylic material in which said salts are ionized, said polyhydroxylic material being selected from the class consisting of polyhydric alcohols and sugars.

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