Nov. 1, 1955 T. STEARNS ET AL 2,722,586

ELECTRIC HYGROSCOPE

Filed Nov. 24, 1951 2 Sheets-Sheet 1

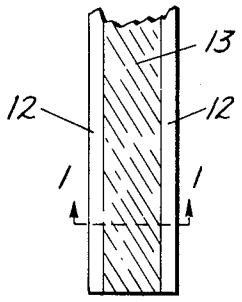


FIG. 1

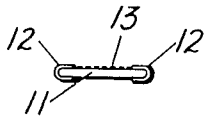


FIG. 2

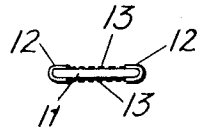


FIG. 3

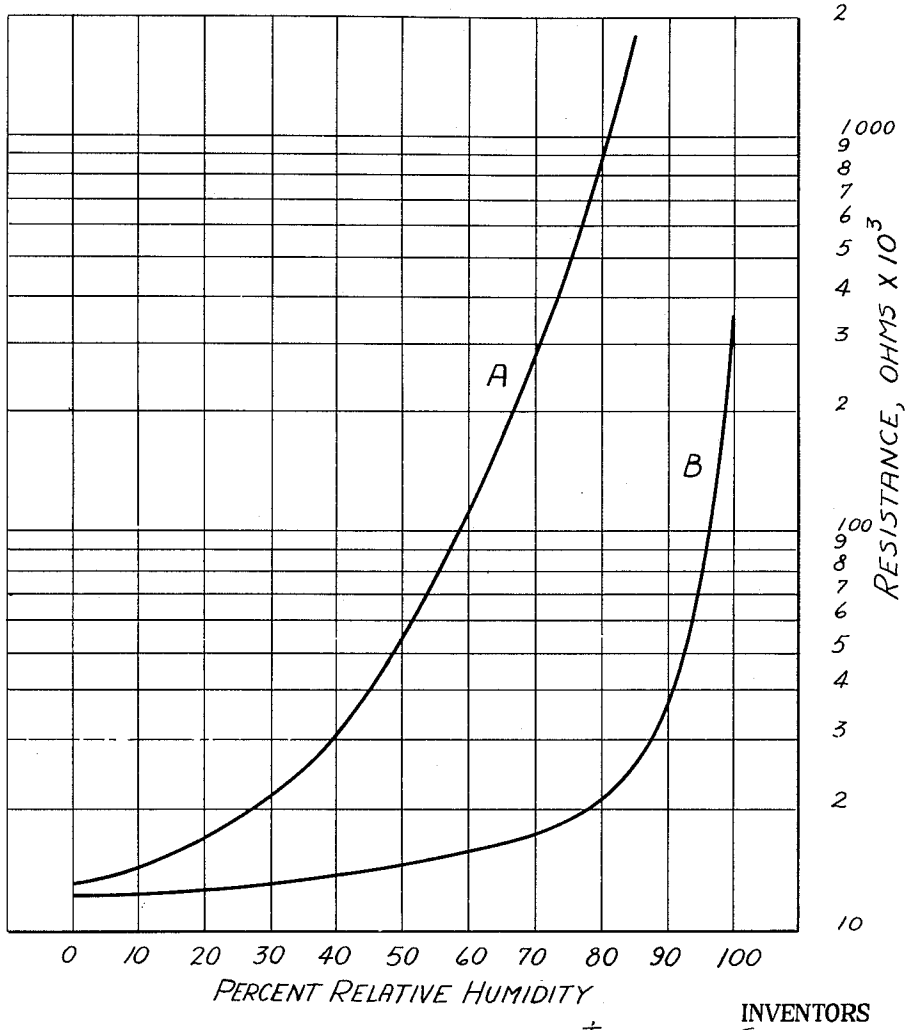


FIG. 5

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ELECTRIC HYGROSCOPE

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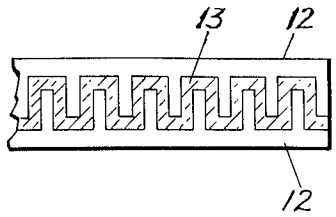


FIG. 4

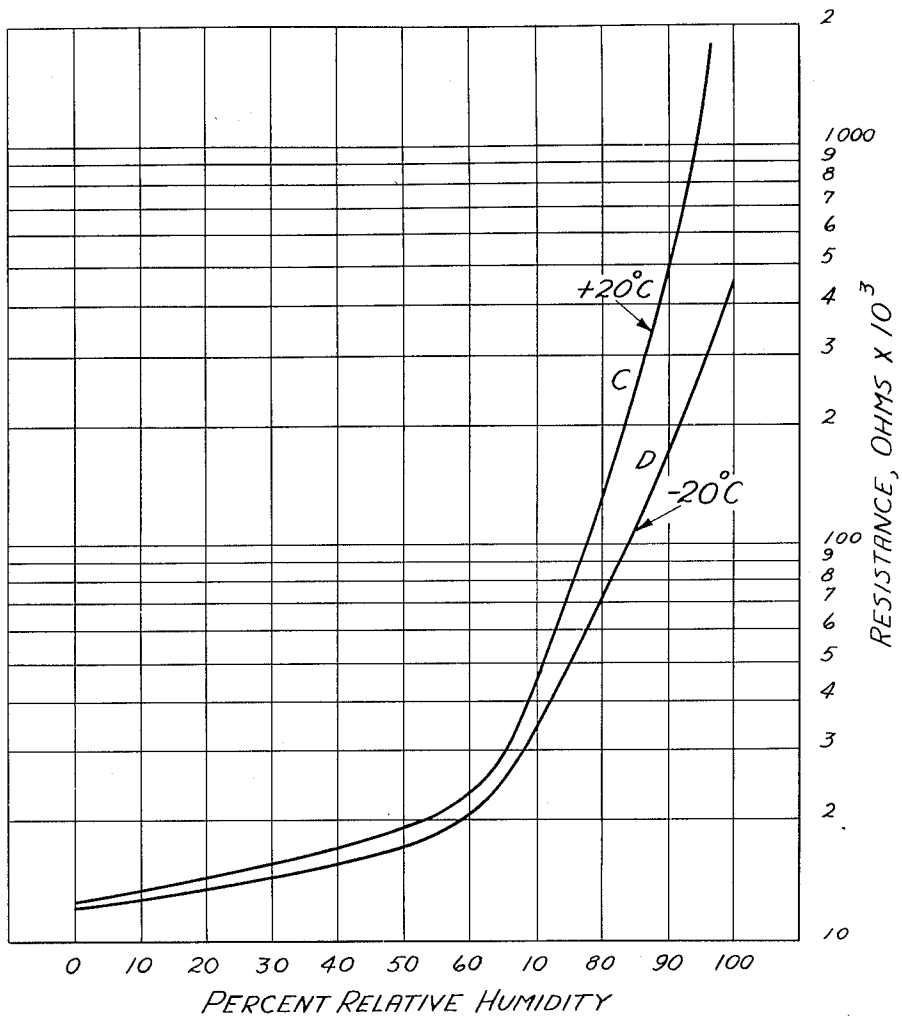


FIG. 6

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ELECTRIC HYGROSCOPE

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Application November 24, 1951, Serial No. 258,052

13 Claims. (Cl. 201—63)

This invention relates to instruments for measuring moisture content in various atmospheres and more particularly to the composition and formulation of a moisture-sensitive element for hygrometers.

The determination of moisture content by measuring the changing electrolytic conductivity of an inorganic hygroscopic salt such as lithium chloride is well known in the art as exemplified by the lithium chloride hygrometer sensing elements now used in balloon-borne weather indicating instruments. The use of these hygroscopic salts has several disadvantages and limitations. These normally include the presence of polarization effects, the probability of washing out at high humidities, inadequate sensitivities at low temperatures, instability over long periods of storage, and limited response rates. Therefore it is desirable to replace the element utilizing inorganic salts with a moisture-sensitive element which does not possess the above-listed disadvantages and limitations. Previous attempts to eliminate these disadvantages by using commercial carbon dispersion in gelatin films were not successful. The use of a moisture-sensitive film alone, such as gelatin, has been found to be impractical because of the extremely high resistance of the film.

The primary object of this invention is to provide a new type moisture-sensitive film for use in hygrometers, which film operates on the principle of electronic conduction rather than ionic conduction. Another object is the elimination of polarization effects in such hygrometer elements. A further object is the production of moisture-sensitive elements that are adequately and reliably responsive over wide ranges of humidity and temperature conditions, particularly at low temperatures, and resistant to washing out at high humidities. Still another object is the manufacture of a hygrometer element which has a rapid response to changing humidity and which will remain stable over long periods of storage. An additional object of this invention is the production of hygrometer elements with low temperature coefficients requiring small temperature corrections when used over a wide temperature range (—20° C. to room temperatures).

These objects along with others are accomplished by the procedure of the present invention which is described in detail below.

There are several accepted designs of bases or supports for water sensitive films, as well as numerous designs of spacing and configuration of the conducting edges. Two commonly accepted designs for the bases of and conducting edge patterns of hygrometers operating on the principle of changing electrical conductance with changing quantities of moisture in the film are illustrated in Figures 1, 2, 3, and 4. The use of the sensitive film described in this invention is not, however, limited to the types of bases and conducting edge pattern of hygrometers illustrated.

Fig. 1 is a plan view of a hygrometer element.

Fig. 2 is a cross-section view through a representative

portion such as section 1—1 of Figure 1, with a moisture-sensitive film on one side.

Fig. 3 is a cross-section view of a similar element having a moisture-sensitive film on both faces.

Fig. 4 illustrates another typical electrically conducting edge pattern.

Fig. 5 shows the performance curves of resistance vs. relative humidity for two elements as disclosed herein at +20° C. Curve A is for an element containing approximately 37% carbon. Curve B is for an element containing approximately 60% carbon.

Fig. 6 shows the performance curves of resistance vs. relative humidity for an element of the type disclosed herein containing approximately 52.5% carbon. Curve C is the performance curve at +20° C., while curve D is performance curve at —20° C.

The hygrometer element is made up of a base **11**, with electrically conducting edges, **12**, and a moisture-sensitive film, **13**, the electrical resistance of which changes as the relative humidity is changed. The moisture-sensitive film may be deposited on one side of the base, as shown in Fig. 2.

Fig. 3 is similar to Fig. 2 having a base **11**, with electrically conducting edges **12**, and a moisture-sensitive film **13** on both sides of base **11**. The moisture-sensitive film may be deposited by various methods but we prefer spraying. The advantages of the arrangement shown by Fig. 3 will become evident in the discussion on ranges of humidity which can be measured. The base, **11**, on which the moisture-sensitive film is deposited must be electrically non-conducting, remain dimensionally stable and not be sensitive to water or moisture. We prefer to use a base composed of a styrene polymer but any other material meeting the requirements may be used. The contacting or electrically conducting edge may be any good relatively stable electrical conductor. Such conductors may be applied by any suitable means such as mechanical application, spraying, sputtering, or evaporation. Tin, silver, gold or platinum, or even carbon, are all satisfactory for this purpose.

The objects of this invention are achieved by means of a new type electronically conducting moisture-sensitive carbon containing film, and the following discussion therefore will be directed primarily to this part of the hygrometer.

We have found that a moisture-sensitive film achieving the objects of this invention preferably should contain four basic components—a binder, a humectant-plasticizer for the binder, finely divided carbon, and a dispersing agent for the carbon.

The response of the element is dependent upon the moisture sensitivity characteristics of the binder, hence the choice of this component is of major importance. Film-forming materials whose moisture content varies with varying humidity are used as the binder. This binder or film-forming material must be as nearly as possible free of the electrolytic impurities which commonly occur in commercial materials. If ionically conducting materials are present in the film, the curve of resistance vs. relative humidity will show a reversal at some point, since the resistance of electronically conducting carbon containing film normally increases as the relative humidity increases. For ionic conductance, on the other hand, the resistance decreases as the relative humidity is increased. Thus, if ion-forming impurities are present, the resistance of the element will increase with electronic conductance as the relative humidity is increased to the point where the resistance of the ionic impurities is lower than the electronic resistance. When the relative humidity is increased beyond this point, the resistance of the element will decrease due to increasing ionic conductance.

Binders such as purified gelatin, polyvinyl alcohol, as

well as many other binders were investigated, but were found to be not preferred for one reason or another. Gelatin, for instance, is less sensitive at low temperatures though it may be satisfactory for elements where below zero temperatures are not encountered. Difficulty is also encountered with the purification of the gelatin. Methyl cellulose was not sufficiently responsive for high sensitivity. Polyvinyl alcohol showed more hysteresis at low temperatures than hydroxyethyl cellulose. In general, however, water-soluble, film forming materials substantially free from electrolytes may be used for a binder in this invention.

While most of the moisture sensitive materials may be employed for special purposes, we have found that substantially electrolyte free hydroxyethyl cellulose is the preferred binder. Hydroxyethyl cellulose is relatively easy to obtain substantially free from electrolytes and is quickly responsive and sensitive over wide ranges of humidity and temperature. Low electrolyte content of the hydroxyethyl cellulose may be obtained either by washing or dialyzing the material, by avoiding introduction of electrolytes when the material is manufactured, but preferably by a combination of these two methods. A suitable product can be made by dissolving substantially ashless cellulose in an aqueous solution of a quaternary ammonium hydroxide base such as benzyl trimethyl ammonium hydroxide and reacting the dissolved cellulose with ethylene oxide. The reaction product is precipitated in methyl alcohol, washed with methyl alcohol several times, dissolved in distilled water and dialyzed to further remove traces of electrolytes.

The constituent which serves as a hemectant and plasticizer must be one which, like the binder, varies in moisture content with varying humidity and also acts as a plasticizer for the binder. As a humectant this agent must assist in the water absorption characteristics of the binder and for a low temperature element, must remain sufficiently plastic at low temperatures. We have found that sorbitol derivatives, and particularly polyoxyethylene sorbitol possess the required properties. The humectant and plasticizer are incorporated with the binder by any convenient means as by mixing aqueous solutions of the two.

The type of carbon black used in the moisture-sensitive film is important. Effectiveness apparently depends upon the manufacturing method used. For example certain channel blacks are preferred and the best carbon black is determined by trial.

The dispersing agent is required to disperse the dry powdered carbon in water so that the carbon can be distributed properly in the moisture-sensitive film. This dispersing agent must be non-ionic and must effectively disperse the carbon black with a minimum amount of the dispersing agent. We have found that an alkyl aryl polyether alcohol such as the product formed by condensing octyl or octadecyl phenol with from 0.5 to 1.0 mol of formaldehyde and then reacting the product with from 10 to 20 mols of ethylene oxide meets these requirements for a dispersing agent. It has been found preferable to dialyze the dispersing agent before using it in the water-sensitive film.

If it is desirable to make a film most sensitive to lower relative humidities, lower percentages of carbon are used, while if the maximum sensitivity is required in the upper ranges of relative humidities, the higher percentages of carbon are used. The acceptable range of carbon in the film is equal to from 15 to 70 per cent of solids of the film, and preferably from 25 to 60 per cent of solids of the film. If a general-purpose element is desired which does not require great sensitivity at low humidities, we have found that about 52.5% carbon is to be preferred. This compromise may be achieved by making up a hygrometer element with a moisture-sensitive film containing about 52.5% carbon on one or both sides of the element. If an element which has high sensitivity in both low and high humidity ranges is required, it is preferable to use a low carbon concentration on one side and a high carbon concentration on the other. One side should contain from 15 to 40 per cent carbon and the other 50 to 70 per cent carbon by weight based on the weight of dry solids of the film.

It is essential not only to adjust the total carbon concentration but also to adjust the ratios of binder to the humectant-plasticizer and of carbon to dispersing agent.

If too much humectant-plasticizer is used the hysteresis may be larger than is desirable, while if too little is used, the low temperature sensitivity may be less than desired. The exact amount of humectant-plasticizer used is dependent primarily on the material used as the binder. The order of magnitude is generally between 1 to 4 parts of binder to 1 part of humectant-plasticizer, although as stated above, the particular ratio is dependent upon the binder used, and may in exceptional cases, fall outside this range.

The ratio of dispersing agent to carbon is maintained at approximately 1 part dispersing agent to 4 to 6 parts of carbon. The use of too much dispersing agent affects the performance characteristics of the moisture-sensitive film, while the use of too little results in non-uniformity of the film.

The choice of the percentage carbon to be used dictates the amount of dispersing agent and thereby guides the amount of binder and humectant-plasticizer which is required.

The following examples, which are to be considered as illustrative rather than limiting, will serve to explain the present invention in more detail.

Example 1

A dispersing agent was made by condensing 1 mol of octyl phenol with 0.75 mol of formaldehyde. This product was reacted with 15 mols of ethylene oxide. 37 grams of carbon powder were weighed into a beaker and 6.2 grams of the above dispersing agent were mixed together. After this mixture had been stirred to an even consistency, it was ball-milled for about 15 hours. The total solids of the final carbon paste amounted to about 10%.

To this carbon paste were then added 18.9 grams of polyoxyethylene sorbitol and 37.9 grams of electrolyte-free hydroxyethyl cellulose. Sufficient water (about 9,570 cc.) to make up a solution containing 1% total solids was added. This final mixture was sprayed on polystyrene blanks which had tin contact edges. Spraying was accomplished by means of an ordinary spray gun operating at 65 pounds per square inch gage placed 2 feet, 10½ inches from the element. The element was on a revolving wheel which allowed alternately spraying and drying until the resistance reaches about 10,000 ohms.

The elements thus produced had relatively good sensitivities down to —40° C., and could be stored for long periods of time without change in calibration.

Example 2

The mixing procedure was the same as described in Example 1. The proportions were varied to include 60 grams of carbon powder, 10 grams of dispersing agent as in Example 1, 10 grams of polyoxyethylene sorbitol and 30 grams of hydroxyethyl cellulose.

When the formulation described in Example 2 was sprayed on one side of an element to a resistance about 150,000 ohms, and the formulation described in Example 1 was sprayed on the other side of the element, the final resistance of the element being about 12,000 ohms, the resistance vs. relative humidity performance showed good sensitivity at low relative humidities, and an overall resistance range between 12,000 ohms and 1,000,000 ohms.

Example 3

The mixing procedure was the same as described in Example 1. The proportions were varied to include 52.5 grams of carbon powder, 8.7 grams of dispersing agent as

in Example 1, 12.9 grams of polyoxyethylene sorbitol and 25.9 grams of hydroxyethyl cellulose.

This formulation was sprayed on one or both sides of an element base with tin conducting edges.

The use in hygrometers of moisture-sensitive films, formed in the manner described in this invention, results in an instrument capable of measuring moisture over a wider range of relative humidity and temperatures and with less time lag than has been possible heretofore.

We claim:

1. A humidity responsive device comprising an electrically non-conducting, non-hygroscopic support, spaced electrical conductors, and a thin moisture sensitive film coated on said support, the electrical resistance of said film being responsive to humidity changes, said film being substantially free of electrolytes and comprising finely divided, evenly dispersed electrically conductive material throughout a humidity responsive binder and in contact with said conductors and with the moisture of the ambient atmosphere.

2. A humidity responsive device comprising an electrically non-conducting, non-hygroscopic support, spaced electrical conductors, and a thin moisture sensitive film coated on said support, the electrical resistance of said film being responsive to humidity changes, said film being substantially free of electrolytes, and comprising finely divided, evenly dispersed carbon black throughout a humidity responsive binder and in contact with said conductors and with the moisture of the ambient atmosphere.

3. The product in accordance wtih claim 2 wherein the carbon is present in a concentration equal to from 15 to 70 per cent of solids of the film.

4. The product in accordance with claim 2 wherein the carbon is present in a concentration equal to from 25 to 60 per cent of solids of the film.

5. A humidity responsive device comprisng an electrically non-conducting, non-hygroscopic support, spaced electrical conductors and a thin moisture sensitive film coated on one side of said support, the electrical resistance of said film being responsive to humidity changes, said film being substantially free of electrolytes, and comprising finely divided, evenly dispersed carbon black in a humidity responsive binder and in contact with said conductors and with the moisture of ambient atmosphere, said carbon being present in a concentration equal to from 15 to 70 per cent of solids of the film.

6. A humidity responsive device comprising an electrically non-conducting, non-hygroscopic support, spaced electrical conductors along opposed edges of said support and a thin moisture sensitive film coated on both sides of said support, the electrical resistance of said film being substantially free of electrolytes, said film comprising finely divided, evenly dispersed carbon in a humidity responsive binder and in contact with said conductors and with the moisture of ambient atmosphere, said carbon being present in a concentration equal to from 15 to 70 per cent of solids of the film.

7. The product in accordance with claim 6 wherein the carbon is present on one side of the support in a concentration of 15 to 40 per cent of solids of the film and in a concentration of 50 to 70 per cent of solids of the film on the other side of the support.

8. A humidity responsive device comprising an electrically non-conducting, non-hygroscopic support, spaced electrical conductors, and a thin moisture sensitive film coated on said support, said film being substantially free of electrolytes, and comprising finely divided, evenly dispersed carbon black in a water soluble binder and in contact with said conductors and with the moisture of ambient atmosphere, said carbon being present in a concentration equal to from 15 to 70 per cent of solids of the film.

9. The product in accordance with claim 8 wherein the binder is hydroxyethyl cellulose.

10. A humidity responsive device comprising an electrically non-conducting, non-hygroscopic support, spaced electrical conductors and a thin moisture sensitive film coated on one side of said support, said film being substantially free of electrolytes and comprising finely divided, evenly dispersed carbon black in hydroxyethyl cellulose, said carbon being present in a concentration equal to from 25 to 60 per cent of solids of the film.

11. The product in accordance with claim 10 wherein the film contains polyoxyethylene sorbitol as a plasticizer.

12. A humidity responsive device comprising an electrically non-conducting, non-hygroscopic support, spaced electrical conductors along opposed edges of said support and a thin moisture sensitive film coated on both sides of said support, said film being free from electrolytes and comprising finely divided, evenly dispersed carbon black in hydroxyethyl cellulose, said carbon being present on one side of the support in a concentration of 15 to 40 per cent of solids of the film and in a concentration of 50 to 70 per cent of solids of the film on the other side of the support.

13. A humidity responsive device comprising an electrically non-conducting, non-hygroscopic support, spaced electrical conductors along opposed edges of said support and a thin moisture sensitive film coated on both sides of said support, said film being free from electrolytes and comprising finely divided, evenly dispersed carbon black in hydroxyethyl cellulose plasticized with polyoxyethylene sorbitol, said carbon being present on one side of the support in a concentration of 15 to 40 per cent of solids of the film and in a concentration of 50 to 70 per cent of solids of the film on the other side of the support.

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