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HYGROMETER ELEMENTS

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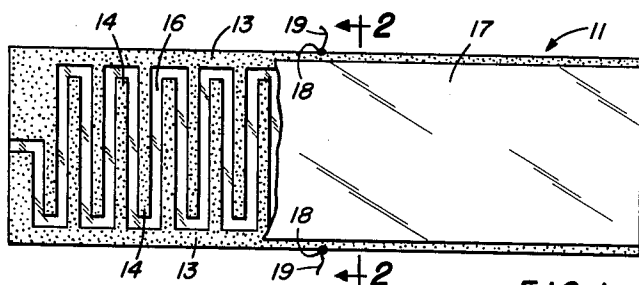


FIG. 1

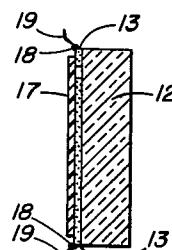


FIG. 2

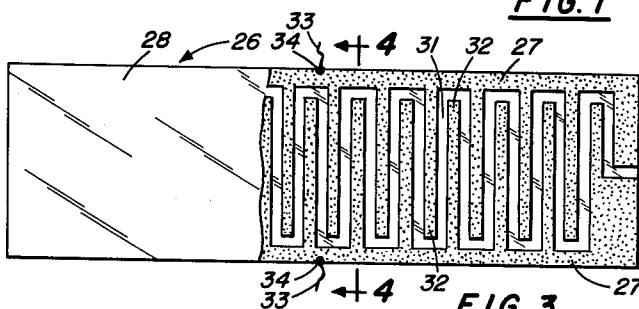


FIG. 3

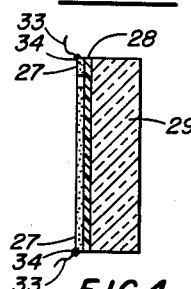


FIG. 4

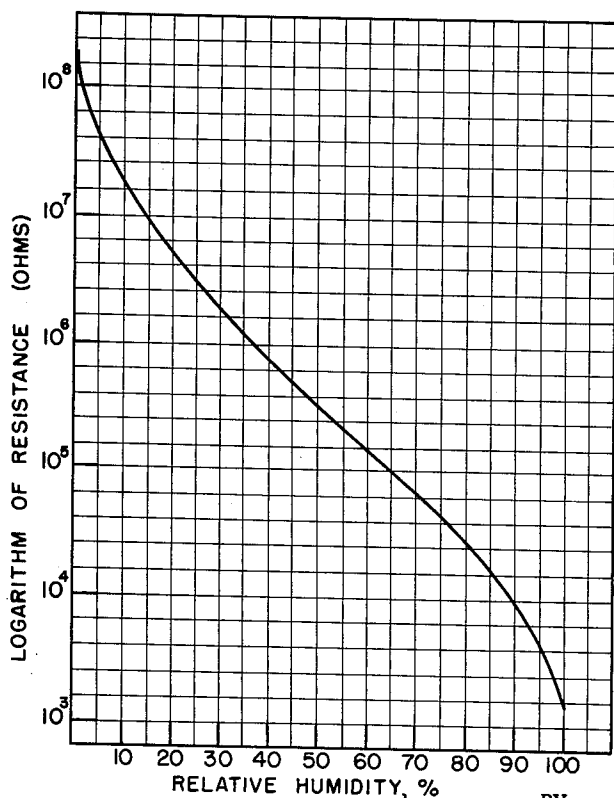


FIG. 5

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HYGROMETER ELEMENTS

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

The present invention relates to electric hygrometer elements and more particularly to electric hygrometer elements incorporating particular humidity-sensitive materials.

Since the electrical resistance of humidity-sensitive materials is altered in some relationship to the change in relative humidity of the atmosphere about it, it is well-known in the art that by measuring such changes in resistance humidity determinations can be made.

This invention has been the outgrowth of investigations directed toward producing an electric hygrometer for use in radiosondes and similar devices. To be adaptable to such use the response time must be very small in order to record the rapid changes in humidity during ascents at speeds in excess of 1000 feet per minute. Further, for radiosonde use, the response times at low temperatures are critical. As the temperature decreases the lags in response increase and in the case of humidity-sensitive materials in which the change in electrical resistance is dependent on the transfer of water into or through the material (volume conductivity) such time lags may well be so great as to render the readings of little value.

Among the prior art methods of measuring humidity by means of humidity sensing devices employing changes in electrical resistance are the following:

(1) Aqueous salt solutions such as lithium chloride, calcium chloride and zinc chloride, or solutions of acids such as sulfuric or phosphoric acids are mixed with one or more binders such as polyvinyl acetate, polyvinyl alcohol, gelatin, pectin and agar-agar and such mixture subsequently deposited by dipping or spraying on an insulator having metallic electrodes mounted thereon. The concentration of the salt solution, and hence the conductivity, changes with relative humidity.

(2) A plastic binder, such as hydroxyethyl cellulose, is mixed with the following: a humectant-type plasticizer such as polyethylene sorbitol; a non-ionic dispersing agent such as alkyl aryl polyether alcohol, and a conductor such as powdered carbon. The resulting mixture is deposited by dipping, spraying, or painting on an insulator having electrodes mounted thereon. The plastic binder expands and contracts with changes in relative humidity changing the distances between the conducting particles and hence changing the overall resistance.

(3) Natural or synthetic fibers (such as cotton, silk, nylon or rayon) or fabrics made from natural or synthetic fibers (such as cloth, paper or asbestos) or natural organic materials (such as human or horse hair) are impregnated with saturated aqueous solutions of salts such as lithium chloride or calcium chloride with or without binders. The resistance of the impregnated material varies with relative humidity.

(4) Wicks of fabric such as glass wool are impregnated with a saturated solution of salt such as lithium chloride and a bifilar wire winding is wound around such an impregnated wick. The wick is heated automatically by passing an electric current between the parallel wires until the temperature of the wick and the temperature of the saturated salt solution is such that there is no gain or

loss of moisture from or to the ambient atmosphere. The temperature of the wick, measured by a resistance (or by a liquid-filled thermometer in the center of the wick) is a measure of the vapor pressure of the ambient atmosphere and is, therefore, a measure of the relative humidity.

(5) Porous materials such as paper, leather, regenerated cellulose, underfired clay, plaster of paris or brick all of which absorb water vapor have been used. The resistance of such materials varies with relative humidity.

(6) Non-porous insulating materials such as glass, quartz, porcelain and plastics are also used since the surface resistivity of such materials varies with relative humidity.

(7) Evaporated films of potassium metaphosphate, sodium carbonate, calcium sulfate, cuprous iodide, potassium sulfate or sodium chloride deposited on an insulating base are used to measure relative humidity.

As to the disadvantages of the prior art methods, methods (1) through (5) have poor response times. The reason for this slow response to changes in relative humidity is that the water vapor has to be absorbed into or diffused through a volume of material (volume conductivity). Method (6) is not reproducible and involved instrumentation has been required since the resistances to be measured are very high. Method (7) has the disadvantages that very high resistances must be measured requiring special instrumentation; that the lower limit of relative humidity that can be measured is set by the surface resistance of the substrate, and further that prolonged exposure to high relative humidities results in undesirable shifts in the resistance-relative humidity relationship.

Thus, an object of the invention is to provide a hygrometer incorporating particular humidity-sensitive materials thereby having a resistance range which can be conveniently handled without the use of special circuitry and without limitations due to the parallel resistance of the substrate.

A further object of the invention is to provide a hygrometer incorporating particular humidity-sensitive materials thereby enabling the attainment of low resistance but very thin films of such materials.

Another object of the invention is to provide a hygrometer of high sensitivity and precision.

Still another object of the invention is to provide a hygrometer capable of rapid response times even at low temperatures (below -40°C.).

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same become better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

FIG. 1 shows a plan view of a preferred embodiment of the invention with a portion thereof broken away;

FIG. 2 shows a section taken on line 2—2 of FIG. 1;

FIG. 3 shows a plan view of a modification of the device with a portion thereof broken away;

FIG. 4 shows a section taken on line 4—4 of FIG. 3, and

FIG. 5 shows a curve indicating relative humidity plotted as a function of the logarithm of the resistance variation of the hygrometer element.

Referring now to the drawings and FIGS. 1 and 2 in particular, the humidity sensitive element 11 comprises a base or substrate member 12 which may be made of glass, quartz, polystyrene or similar plastics or other electrically insulating materials. It would be possible as well to use an electrically conducting material such as a metal providing that it be covered by a thin electrically insulating layer. The substrate is cleaned chemically using water, detergents and organic solvents, the latter being applied by dipping or by the use of a vapor degreaser.

The conducting or electrode materials 13, 13 which are adhered to the substrate 12 can be any of a number of conducting materials such as metals, alloys of metals, solid solutions or combinations of metals. The electrodes 13, 13 can be in the form of parallel strips or can be formed in configurations specially designed to adjust the resistance values of the device. Palladium, gold, silver, and chromium have, for example, been deposited by evaporation. In the preferred embodiment shown, the closely-spaced intermeshing comb electrode configuration was formed by a fine-line etching process. An evaporated film of chromium (or other suitable material) is deposited on the substrate. This film is covered by a photosensitive resist. This resist is exposed to ultraviolet light through a photographic negative of the electric pattern. The resist is then developed and the unwanted resist washed off leaving a fine line of electrode film exposed. This fine line is removed by electroetching the film in an electrolytic solution.

One pattern successfully employed is of the general configuration shown in FIG. 1 in which each of the two combs 13, 13 have 122 teeth 14, each tooth being 0.008 inch wide and $\frac{1}{16}$ inch long. The separation 16 between the intermeshed teeth is 0.006 inch and the overall length of the pattern is $\frac{3}{16}$ inch.

By employing such a closely-spaced electrode configuration and in effect providing very long electrodes separated by a very small distance the net result is to markedly reduce the electrical resistance of the hygrometer.

The humidity-sensitive material 17 is deposited on the substrate by vacuum evaporation or sublimation although deposition can be made by chemical or other means. Actually the prime requisite is the recognition and employment of a series of criteria in the selection of the humidity-sensitive material.

In isolating these criteria the theoretical approach has been to consider the layer of sensitive material a solid variable resistor and to consider the dependence of the resistance of this solid on relative humidity as being the result of interaction between the solid and water vapor.

The water vapor molecule is a dipolar molecule (i.e., the centers of gravity of the positive and negative charge do not coincide) having a large permanent dipole moment (the product of the magnitude of either charge by the distance between the centers of gravity of the charges). Substances can be considered to consist of atoms, molecules, and ions. An atom, molecule, or ion may be polarized by induction in an external electric field. The induced dipole moment is proportional to the electric field intensity. The proportionality constant, α , is called the polarizability of the particle. The water vapor-resistor system may therefore be considered to consist of polar and polarizable molecules of water vapor and polarizable atoms, molecules, or ions of the resistor material.

It can be shown that the water vapor molecules and the particles of the resistor will be mutually attracted by "intermolecular" forces. The forces involved are the "van der Waals forces." The van der Waals forces are attributed to three effects: the orientation effect, the induction effect, and the dispersion effect.

The van der Waals forces are the forces which are effective in physical adsorption. Physical adsorption is the weak interaction between solids and gases in which the gas "condenses" on the surface of the solid. In addition to physical adsorption there is the possibility of chemical adsorption, a strong interaction similar to chemical reaction. Chemical adsorption is characterized by irreversibility in most cases and slow response. These two characteristics make chemical adsorption unsuitable for an electric hygrometer; therefore, physical adsorption systems only will be considered.

In physical adsorption of gases on solids, molecules in the gas or vapor become "attached" to, adsorbed on, the surface of the solid. Physical adsorption takes place at very great speed and is reversible (i.e., water vapor ad-

sorbed at high relative humidities is removed, desorbed, at low relative humidities).

The generalization can now be made that the ability of a substance to adsorb water vapor by physical adsorption depends upon the magnitudes of the permanent multipole moments and the polarizabilities of the particles of the substance. This generalization is applicable to nonionic substances (metals, for example) as well as ionic substances, and to liquids and gases as well as the solid state. Therefore, an important result of the investigation of the resistor-water vapor interaction is the establishment of the polar and polarizable nature of the adsorbing substances as important criteria to consider in the selection of materials for use in humidity sensors.

Many materials experience changes in surface electrical conductivity when exposed to humid air, i.e., when water vapor is adsorbed or desorbed. This property can be exploited in producing an hygrometer in which the very desirable characteristics, extremely rapid response and reversibility, of physical adsorption are inherent. In practical cases of physical adsorption in which response is not found to be practically instantaneous, the slow step in the process is diffusion. Since rapid response is essential in radiosonde hygrometers, the use of a very thin film of the adsorbing material providing very short diffusion paths would minimize the effect of diffusion, if it were present.

From the preceding, some criteria can be set up for the selection of materials to be used in the form of thin films as the sensitive materials for electric hygrometers. These criteria are presented below:

Electronic Polarizabilities (Units 10^{-24} cm.³)

Barium fluoride	3.976
Cesium fluoride	3.664
Cadmium iodide	14.61
Cuprous chloride	4.628
Thallium iodide	12.238
Strontium sulfate	6.500

Equivalent Conductances of Separate Constituent Ions (Units Ohm⁻¹ @ 0° C.)

Silver	32.9
Chlorine	41.1
$\frac{1}{2}$ Barium	33
$\frac{1}{2}$ Calcium	30
$\frac{1}{2}$ Lanthanum	35
$\frac{1}{2}$ Sulfate	41

Decomposition Temperature

Thallium iodide	Dissociates at 139° C.
Barium fluoride	None listed
Silver iodide	Dissociates at 552° C.
Cesium fluoride	None listed
Strontium sulfate	Dissociates at 1580° C.

Vapor Pressure of the Material

All of the materials covered specifically herein have high enough vapor pressures that evaporation can proceed at conveniently low source temperatures i.e.

Cesium fluoride	1 millimeter of mercury at 712° C.
Cadmium iodide	1 millimeter of mercury at 416° C.
Cuprous chloride	1 millimeter of mercury at 546° C.

Ease of Evaporation

All of the materials have been conveniently evaporated from molybdenum "boats" without requiring excessive power and without excessive reaction with the boat material. Films of suitable thicknesses have been deposited in conveniently short times.

Adhesion of the Material to the Substrate

The materials covered herein adhered well enough to the substrate to allow the films to be used without special handling procedures. Barium fluoride, for example, adhered well enough to the glass substrate to allow immersion in water without removal of the film.

Temperature Coefficient of Expansion

The temperature coefficient of expansion of the film should not be incompatible with that of the substrate. The smaller the differential between the coefficient of expansion of the substrate, the smaller the strain to which the bond between film and substrate will be subjected as the result of fluctuations in temperature. The coefficient of the film is dependent on the conditions under which the evaporation is made and is therefore subject to some adjustment.

The conditions existing in the vacuum chamber before, during, and after the evaporation (deposition) determine the initial structure and physical properties of evaporated thin films. Recognition of the influence of these conditions and the setting up of controls over them will enable one to produce films reproducibly and with some predetermination of structure and properties. The following is a list of some of the influencing parameters and conditions which can be controlled or at least measured throughout the film production process and subsequent treatment:

- (1) Nature of the substrate.
- (2) Temperature of the substrate during the evaporation.
- (3) Residual pressure in the evaporator.
- (4) Composition of the residual gas in the evaporator.
- (5) Heat treatment of film and substrate after evaporation.
- (6) Temperature of the evaporating source.
- (7) Size and geometry of the evaporating source.
- (8) Duration of the evaporation.
- (9) Source-to-substrate distance.
- (10) Angle between the evaporated "beam" and the substrate.
- (11) Number and nature of nuclei or centers of nucleation on the substrate.
- (12) Thickness of the film.

Structure of the Deposited Film

The structure of evaporated films depends upon the conditions under which the evaporation is made. However, some materials form films which are inherently unsuitable to this application due to porous structure, granulation, or some other unfavorable characteristics. The barium fluoride films and others of the materials covered specifically herein have satisfactory structure as indicated by rapid response and low hysteresis.

Porosity of the Films and Solubility

These two properties are used to indicate the unsuitability of a material. That is, if the film is porous it will be unsuitable due to excessive hysteresis, irreversibility, and excessive response times; if the film is easily soluble in water, the resistance of the hygrometer will change permanently upon exposure to humid air and the film might wash off the substrate. These properties are, therefore, not positive, but negative criteria.

Solubilities of materials in water are tabulated in handbooks, etc., and can serve as a guide in eliminating materials. However, since evaporated films have properties which are not the same as those of the bulk materials, the solubilities of the films can be different than those of the bulk materials.

Solubilities of some of the materials covered by this application are listed below:

(Units grams per 100 milliliters)

Barium fluoride.....	0.17 at 10° C.
Cerous fluoride.....	insoluble in cold water
Thallium iodide.....	0.0064 at 20° C.
Strontium sulfate.....	0.0113 at 0° C.

Electrical Resistance-Relative Humidity Characteristics of the Resulting Device

It is preferable for use in radiosondes that the hygrometer have a resistance range compatible with the

radiosonde circuitry and also high sensitivity. By selection of materials based on the criteria discussed above, hygrometers with suitable resistances and sensitivity can be produced. The resistance can be further lowered by using a suitable electrode configuration.

Having applied the above criteria the following materials have been isolated, tested and found successful: barium fluoride cerous fluoride, didymium fluoride, lanthanum fluoride, neodymium fluoride, cesium iodide, cadmium iodide, cuprous chloride, thallium iodide, lead iodide, strontium sulfate and lead sulfide.

As an indication of the greatly improved performance of materials selected by the above developed criteria the following are response times reported for barium fluoride hygrometers: at approximately 25° C. the response times are of the order of 0.1 second; at -20° C., about 1.5 seconds; and at -40° C., about 3 seconds. Since for a radiosonde use, the response times at low temperatures are critical this data will indicate the suitability of the present hygrometers for such an application.

The following serves to illustrate the production of a typical humidity-sensing device as is shown in FIGS. 1 and 2. A glass plate 12 such as a standard microscope cover slide glass is cleaned by standard procedures and placed in the vacuum chamber of a vacuum evaporator (not shown). A glow discharge is maintained at a pressure of approximately 20 microns of mercury for about 20 minutes in the vacuum chamber to further clean plate 12. A thin film of metal such as palladium or chromium is deposited on the plate by vacuum evaporation or sublimation and a closely-spaced electrode comb configuration 13, 13 is produced by the fine-line etching process described above. A humidity-sensitive material (selected from the group disclosed above) such as barium fluoride is heated in a vacuum chamber and a thin film 17 of the material is deposited over the exposed glass plate 12 and the electrode configuration 13, 13 by vacuum evaporation or sublimation. The electrical resistance of the device varies with relative humidity and this resistance can be measured by contacting electrodes 13, 13 at contacts 18, 18 with leads 19, 19 connected to a resistance measuring device (not shown).

In the modification 26 shown in FIGS. 3 and 4 electrodes 27, 27 are placed over the humidity sensitive layer 28 which in turn covers the surface of substrate 29. Since the performance of the selected humidity-sensitive material depends upon surface "attachment" or adsorption of the molecules of water vapor, the results obtained in the case in which the electrodes are placed over the humidity-sensitive material are in substantial accord with the results obtained in the case in which the humidity-sensitive material is deposited over the electrodes. However, due to the care which must be taken to avoid damage to layer 28 during the placement of electrodes 27, 27 the construction disclosed in FIGS. 1 and 2 are the preferred construction.

The portion of the humidity-sensitive layer 28, exposed in gaps or separations 31 between electrode teeth 32 serves to register changes in moisture content of the atmosphere. Leads 33, 33 attached to electrode contacts 34, 34 connect to a resistance measuring device (not shown).

If a device such as is disclosed in FIGS. 1 and 2 employing a barium fluoride film is tested and a calibration curve is prepared therefor in which the logarithm of electrical resistance is plotted against the relative humidity, the resultant curve will be that shown in FIG. 5. It can be seen that the electrical resistance of the device varies through more than four degrees of magnitude throughout the range of relative humidity. In this manner the magnitude of variation in resistance which gives the device high sensitivity can be seen. Such high sensitivity enables measurement of this resistance (and thereby the corresponding humidity) without the need for special circuitry. In addition the precision of measure-

ment is increased. It has further been found that the hysteresis effects of such a device are very small, adding to the attainment of satisfactorily repeatable relative humidity indications.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claim the invention may be practiced otherwise than as specifically described.

What is claimed is:

In an electric hygrometer element having an electrically non-conductive surface, a pair of electrodes mounted on said surface, a humidity-sensitive material arranged as an adherent film in the gap between said electrodes and in electrical contact with said electrodes, said material having an electronic polarizability in the range between about 3×10^{-24} cm.³ to 18.0×10^{-24} cm.³ and having

conductances of constituent ions in the range between 18 ohm^{-1} and about 52 ohm^{-1} , the improvement in said combination of a very thin film of barium fluoride arranged as the adherent film in the gap, said film being non-granular, non-porous and difficultly soluble in water, whereby on exposure of said film to moist atmosphere a rapidly responsive indication of humidity is obtained.

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