

[54] **HUMIDITY CONTROL MEANS AND PACKAGES CONTAINING THE SAME**

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206/.5, 312/31.1

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[58] Field of Search **239/53 X, 55, 54, 36 X,**
239/34; 206/.5; 312/31.01, 31.02, 31.03,
31.04, 31.05, 31.06, 31.1

[56] **References Cited**

UNITED STATES PATENTS

3,578,545	5/1971	Carson et al.	239/53
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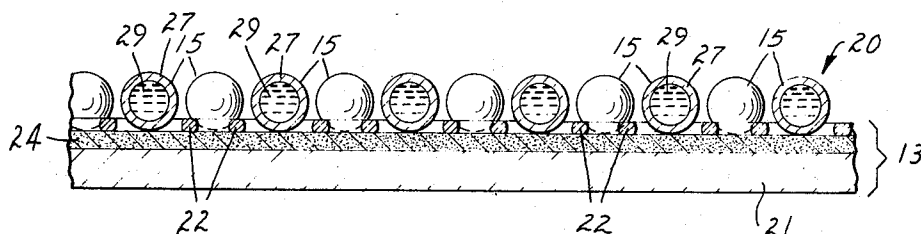
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[57] ABSTRACT

The disclosed humidistasis (i.e., humidity control) means comprises a sheet-like carrier with a partially exposed layer of water-containing capsules adhered thereto. The water-containing capsules are preferably spheroids less than about 3,000 microns in diameter and have vapor-transmissive walls. Prior to use, the humidistasis means can be stored in a moisture-tight bag. In use, the humidistasis means is preferably adhered to an inside surface of a container, thereby providing a humidistatic environment for dehydration-sensitive materials.

11 Claims, 4 Drawing Figures



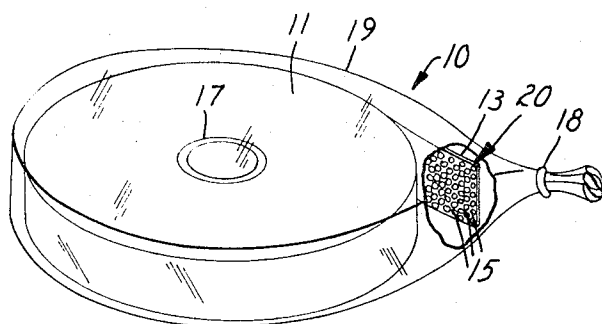


FIG. 1

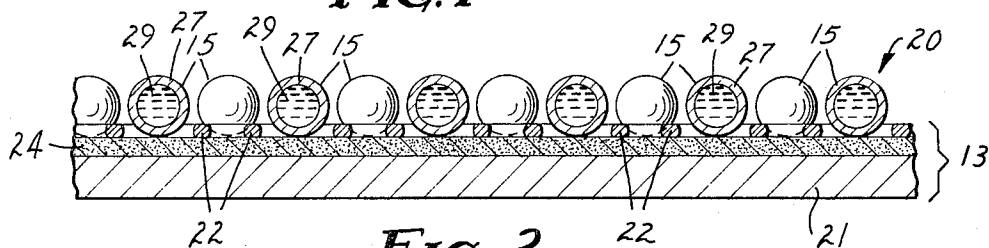


FIG. 2

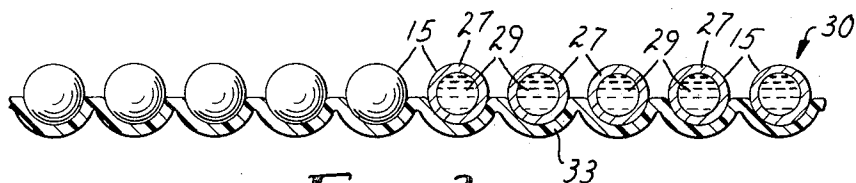


FIG. 3

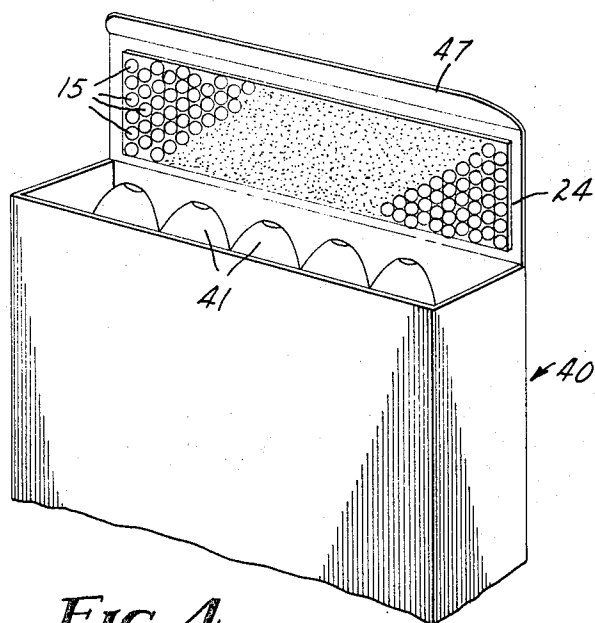


FIG. 4

HUMIDITY CONTROL MEANS AND PACKAGES CONTAINING THE SAME

FIELD OF THE INVENTION

This invention relates to humidistatic or hygrostatic means which remove or emit water in order to control or maintain a humidity level in an environment which can contain perishable or dehydration-sensitive material. An aspect of this invention relates to a package containing a humidistatic means, wherein the humidistatic means can be stored for long periods of time prior to use. A further aspect of this invention relates to the use of the humidistatic means in a package containing dehydration-sensitive material requiring some degree of humidity control, e.g., perishable goods or articles containing material sensitive to excessively low or excessively high humidity conditions.

DESCRIPTION OF THE PRIOR ART

It has long been recognized that certain materials, e.g., foods (including confections and produce), tobacco products, cut flowers and other plant life, articles such as photographic film, and other goods which are perishable or sensitive to excessively dry conditions should be stored within a humidistatic environment. Thus, humidity control or humidistasis is an important field unto itself, particularly as it relates to packaging.

One very common problem in the art of humidistasis (i.e., keeping humidity within prescribed bounds) is encountered when one attempts to provide conveniently packaged perishable or dehydration-sensitive goods with an adequate shelf life through the use of a means for replacement of moisture losses. Typically, it is inconvenient or undesirable to provide a package of tobacco products, fruits, vegetables, confections, films, etc., with an effective hermetic or moisture-tight seal. Typically, the contents of the package are, in effect, exposed to ambient relative humidity (R.H.) conditions potentially varying from a few percent R.H. (e.g., in heated warehouses during the winter) to over 90 percent R.H. Either extreme can be damaging to tobacco products, confections, and other goods which are at optimum quality only under very narrowly circumscribed R.H. conditions. For example, cigars are economically and efficiently packaged in small cardboard boxes encased or wrapped in cellulosic film, but the cellulosic wrapping is water vapor transmissive, thus permitting the water vapor to pass quite freely from the inside of the box to the ambient atmosphere or vice versa.

A second, somewhat related problem is encountered when goods are stored under purely temporary moisture-tight conditions. For example, pipe tobacco containers are subject to frequent opening and closing. Even if the container is well sealed while closed, the humidistasis is disturbed with each opening and must be re-established by some means; see, for example, U.S. Pat. No. 1,552,877 (Phillipps et al.) issued Sept., 1925, and U.S. Pat. No. 2,262,327 (McKinnon) issued Nov. 11, 1941.

A third problem is encountered even when the goods are kept under a substantially permanent moisture-tight seal. If the goods are to be kept at a preselected R.H. level, it is generally not practical to first introduce an atmosphere of controlled moisture content into the package prior to sealing and then maintain the sealed

package at a constant temperature. The usual prior art approach involves introducing a mechanical or chemical means within the package which can serve as a source and/or a sink for humidity, as the internal conditions (e.g., temperature) dictate. It has been suggested, for example, that an invert sugar solution, a Glauber's salt solution, a semipermeable envelope containing sodium bicarbonate, a mixture of Glauber's salt and borax, or the like can be used as the humidifying or humidistasis element; see, for example, U.S. Pat. No. 2,270,603 (Ridder), issued January, 1942, No. 2,329,908 (Johnson), issued September, 1943, and No. 3,320,697 (Larsen) issued May 23, 1967; see also O'Brien, "The Control of Humidity by Saturated Salt Solutions" in *J. Sci. Instruments*, March, 1948.

The demands placed upon a humidifying element by the manufacturer, grower, seller, or packager can be very severe. The water is preferably not bound up either too loosely or too securely within the humidifying element and preferably should be released or releasable at a variable rate, depending upon conditions within the package. If the R.H. within the package were to drop below, say, 10 percent, a very rapid release rate would be needed—yet not so rapid that the contents would be excessively moistened by a humidity surge or that the humidifying element would be irreversibly dried out and rendered substantially inoperative after a short period of storage.

Further demands upon the humidifying element are made by the techniques and specifications of packing and shipping goods. Water vapor pervious bags or porous chambers can add weight or occupy a great deal of space, thereby detracting from the amount of material storable in the package. For the typical package, the humidifying element would preferably have very little bulk. However, a small, light-weight element would perhaps be the most subject to humidity surges or rapid irreversible dehydration.

Furthermore, it is especially difficult to introduce a saturated salt (constant humidity) solution into a closed environment; the salt may precipitate out or the solution may not be convenient to enclose in a spill-proof, but humidistatically effective, container.

Techniques for encapsulating water or other fill liquids within solid shell walls have been available since about the mid-1950's. See Flinn et al., *Chem. Eng.*, Dec. 4, 1967, pages 171-178. Among the techniques for encapsulating aqueous liquids in capsules 10 to 4,000 microns in diameter is the process disclosed by Arens et al., U.S. Pat. No. 3,423,489, issued January 1969. Ordinarily, the water is sealed into the capsules and cannot be gotten out without rupturing the capsule walls, but capsules with a slow, apparently constant water vapor release rate have been made; see Example XXIV or the Arens et al patent. A controlled soil-moistening capability has been noted when the soil is mixed with so-called water-in-air emulsions or "powdered water," i.e., water encapsulated within silane-treated, fumed silicon dioxide particles.

The application of water encapsulation technology to solve the problems of humidistasis is not straightforward. First, the capsules are fragile and ought to be protected from breakage. Second, the capsules should ideally be disposed so as to permit maximum exposure and should be able to release or absorb water vapor at a rate responsive to the demands of the system. Realization of this ideal would be contrary to the reason-

able expectations of the humidistasis art. Experience with humidifying elements such as saturated blotters or sponges suggests that the element might be subject to excessively rapid dehydration under low ambient humidity conditions (e.g., less than 10 percent R.H.). This difficulty would appear to apply with great force to water-containing capsules. The amount of water in each individual capsule is very small. If this small amount is lost, the capsule could become totally dry and inoperative as a humidifying element.

Accordingly, this invention contemplates providing a humidistatic element comprising water-containing capsules which release water vapor to an environment at a very high rate when the environment is characterized by a low relative humidity, but which release or absorb water vapor at a slow rate (or remain at equilibrium) when the environment is characterized either by high humidity or by the desired preselected relative humidity. This invention further contemplates a structure for providing a layer, preferably a monolayer, of water-containing capsules whereby the structure maximizes the exposure of the individual capsules and yet produces them from breakage or dislodgement. This invention further contemplates a combination comprising a layer of water-containing capsules adhered to a backing means, whereby the combination includes a means to prevent loss of moisture from the capsules until they are used in a packaging operation.

BRIEF SUMMARY OF THE INVENTION

It has now been found that water-containing capsules with water vapor transmissive walls can be included in a humidifying or humidistasis element with the result that the element has a demand-response capability extremely well suited to the preservation of perishable or dehydration-sensitive materials and articles. By "water-containing capsule" is meant a discrete amount of an aqueous liquid completely surrounded by a solid wall of wax, natural or synthetic gum or polymer, inorganic material, or the like. The "aqueous liquid" comprises a significant amount of water or a water phase, but can contain less than 50 wt. percent water, as is the case with an aqueous saturated KOH solution. Typically, aqueous solutions or liquids of this invention contain at least 10 percent by weight of water. The preferred form of capsule is a substantially spherical droplet of water or aqueous liquid at least 10 microns in diameter, but less than about 0.5 ml. in volume, surrounded and encapsulated by a substantially spherical, water vapor transmissive wall. For convenience of packaging, each capsule preferably contains about 5×10^{-7} to about 5×10^{-2} ml or cc of fill liquid, the fill liquid comprising at least about 50 percent by volume of the capsule. The demand-response capability appears to be the result of the vapor permeable walls which can apparently release or absorb water vapor by any one or a combination of mechanisms. The simplest mechanism appears to be gas-through-solid diffusion, in this case water vapor diffusing through the solid, but thin, capsule wall. The driving force for this mechanism is a non-equilibrium condition characterized by differences in partial pressure of water vapor on opposite sides of the capsule wall. Other more complicated mechanisms appear to be involved also, particularly when the capsule is full. One such mechanism appears to involve wicking of liquid water through or into pores, cracks, or irregularities in the inner surface of the capsule wall (by cap-

illary action or some similar effect) followed by evaporation of the water thus entrapped. The preferred capsules used in this invention have porous walls and are preferably capable of a slow, substantially constant net release rate. The "net release rate" is the rate measured while the capsules are losing more water than they absorb. The rate can be expressed as a percent loss of the total encapsulated water per unit time, i.e., $100\Delta W/W\Delta t$, where W is the total amount of encapsulated water and t is time. In some embodiments of the invention, capsules with at least two net release rates are used, a fast rate predominating so long as the capsule has released less than about 20 to 60 percent by weight of its contents, and a slow net rate predominating at least after the capsule has released more than 60 percent by weight of its contents, e.g., more than 10 wt. percent for the "slower" capsules and more than 55 percent for the "faster" ones. The fast net rate can usually be accurately measured during the first 24 to 48 hours of a reproducible test wherein the capsules are permitted to release water vapor to an ambient atmosphere fixed at 5.5 percent R.H. The test conditions can be provided by a dessicator containing saturated sodium hydroxide. Ambient temperature conditions for the test are preferably in the range of 20° - 25° C. The slow net release rate can typically be measured after about the twentieth day in the 5.5 percent R.H. atmosphere or after about the fifth day in a 97 percent R.H. atmosphere, conveniently provided by a potassium dihydrogen phosphate solution. The capsules themselves can contain aqueous salt solutions, so that they will reach an equilibrium vapor release/absorption condition in a given R.H. environment. If the percent water released vs. time curve has a linear (constant rate) portion, the constant fast vapor release rate should preferably be less than about 15 wt. percent of encapsulated water per day at 5.5 percent ambient R.H. If the curve is nonlinear, the capsule half life should preferably exceed three days, i.e., at least 3 days of release time should be required to obtain a net release of 50 percent by weight of the encapsulated water. The slow net release rate has been found to be substantially constant and is less than 5 percent by weight per day of encapsulated water; at 97 percent R.H. the slow release rate is preferably less than 2.5 percent per day. By selecting appropriate deliquescent or hygroscopic fill liquids, the net release rate can be set at zero (i.e., equilibrium) or as slow as desired, even in a low ambient R.H. atmosphere. It can reasonably be assumed that at equilibrium the rates of vapor release and vapor absorption are equal.

In the preferred structures of this invention, the capsules are firmly adhered to a backing or carrier which can be cut into wide or narrow sheets or strips of any desired size which can, if desired, be coiled into overlapping convolutions for storage prior to use. The capsule-containing sheets are preferably stored in moisture-tight bags or containers, wherein the capsules reach equilibrium after losing, at most, a few percent of their contents. In use, these sheets can be removed from their moisture-tight containers and inserted in or integrally bonded to the inside of a container such as a shipping carton, package, overwrap, twist-tied bag, or the like, which container need not be moisture-tight unless either a substantially saturated or a precisely determined level of humidity is to be maintained within it. The preferred carriers or backings for the capsules

include a vacuum-formed layer of organic polymer or a pressure-sensitive adhesive on a tape backing or release liner.

DESCRIPTION OF THE DRAWING

This invention can be more clearly understood by referring to the accompanying Drawing, wherein:

FIG. 1 is a perspective view of a storage stable humidifying or humidistasis means of this invention with parts broken away.

FIG. 2 is a cross-sectional view, greatly enlarged, of one embodiment of a humidifying or humidistasis means of this invention.

FIG. 3 is a cross-sectional view, drawn to the same scale as FIG. 2, of another embodiment of a humidifying or humidistasis means of this invention.

FIG. 4 is a perspective view of the upper portion of an open package, illustrating the use of a humidistasis element of this invention to help extend the shelf life of a tobacco product.

In the various figures of the Drawing, like numerals denote like elements of the described structure.

DETAILED DESCRIPTION OF THE DRAWING

A typical humidistasis means of this invention is illustrated by FIGS. 1, 2, and 4 of the Drawing, and an alternative embodiment of this means is illustrated in FIG. 3. FIG. 1 illustrates how a storage stable packaged humidistasis means 10 can be in the form of a humidistasis tape 20 wound into a roll 11 and stored in a moisture-tight bag 19. Tape 20 comprises a narrow, strip-like backing or carrier 13 to which capsules 15 have been adhered. Tape 20 is wound in overlapping convolutions upon a core 17 to form the roll 11. Roll 11 is stored in a substantially water-impervious bag 19 sealed with closure element 18. Bag 19 can comprise a film of thick (e.g., up to 4 mils or 0.1 mm) hydrophobic polymer or the like so that closing bag 19 with closure element 18 provides a moisture-tight environment for roll 11. Packaged humidistasis means 10 is a preferred form in which the humidistasis tape 20 can be sold to manufacturers, shippers, growers, packagers, and others who may be making up humidistatic packages.

An enlarged cross-sectional view of tape 20 is shown in FIG. 2, wherein it can be seen that capsules 15 comprise an aqueous fill liquid 29 surrounded and enclosed by a capsule shell wall 27, described in more detail subsequently. FIG. 2 also illustrates a preferred form of carrier strip or backing 13, which comprises a layer of pressure-sensitive adhesive (hereinafter referred to as PSA) 24 deposited as a coating upon a major surface of release liner 21 and a fabric-like capsule positioning means 22 adhered to the exposed major surface of PSA layer 24. Positioning means 22 is preferably a cloth mesh or scrim with hexagonal openings of approximately the same size as capsules 15. Means 22 helps to securely position capsules 15 in neat rows and columns, diagonal with respect to the length of tape 20, thus facilitating quality control over manufacture of tape 20 and also helping to guard against dislodgment or breakage of capsules. Capsules 15 are substantially spherical and are more than hemispherically exposed by virtue of being adhesively bonded substantially at their points of tangency with the exposed surface of PSA layer 24. In practice, a few percent of the area of the shell walls 27 can be embedded in PSA layer 24.

This small amount of embedding is, however, adequate to securely anchor capsules 15, particularly with the additional reinforcement of positioning provided by means 22. As will be apparent from the subsequent discussion of FIG. 4, means 22 can be omitted from the structure of backing 13. Pressure-sensitive adhesive layer 24 is preferably of the type having sufficient integrity to be handled and used as a transfer adhesive; see, for example, Kalleberg et al., U.S. Pat. No. 3,062,683, issued Nov. 6, 1972. Thus, PSA layer 24 and release liner 21 comprise a conventional adhesive transfer tape. Removal of release liner 21 permits the adhesive transfer film 24 to be adhered directly to an inside surface of a shipping carton or container, e.g., the inside of lid 47 of cigar pack 40 (FIG. 4).

Thus, FIG. 4 illustrates a typical composite structure of the type shown in FIG. 2 in use. In FIG. 4, about 1 to about 3 grams of capsules 15 are adhered to lid 47 by means of PSA layer 24 to keep cigars 41 at the proper R.H. level. The capsules 15 are reasonably well secured to layer 24 and are not likely to be dislodged during shipment or handling of cigar pack 40; therefore, the positioning means 22 (FIG. 2) has been omitted from the humidistasis means used in humidifying the inside of cigar pack 40.

The humidistasis means 30, shown in FIG. 3, comprises a monolayer of capsules 15 through which a vacuum has been drawn, causing a hot, plastic polymer to be vacuum formed into a tough backing film 33. Adherence of the capsules 15 to the resulting vacuum-formed backing film 33 is particularly firm in this embodiment, and a capsule positioning means is generally superfluous. Capsules 15 are substantially hemispherically exposed. However, variations in exposure and contact with the backing film 33 from as little as 30 or 40 percent of the surface of the capsules exposed to as much as 80 or 90 percent exposed is not detrimental to either the moisture transmission or capsule anchoring features of the invention. As a general rule, however, in both embodiments 20 and 30, the capsules 15 are preferably at least hemispherically exposed.

A further alternative embodiment (not shown) involves the substitution of a double-coated tape for the adhesive transfer tape. Since the use of a double-coated tape involves an additional pressure-sensitive adhesive layer and an additional release liner, this embodiment is not preferred. When adherence to an inner surface of a container is not required, as, for example, in the case where the humidistasis element is inserted loose into the inside of a carton or container, the backing 13 can comprise a conventional pressure-sensitive adhesive tape with no adhesive transfer capability.

Either of the embodiments 20 or 30 of a humidistasis element of this invention can be cut into a narrow strip, wound upon a core in overlapping convolutions, and thereby formed into a compact roll which can be stored almost indefinitely by the packager or manufacturer (as in FIG. 1) until ready for use in a humidistatic package, e.g., of the type shown in FIG. 4.

During storage, the capsules 15 in tape roll 11 lose some water vapor to the environment within plastic bag 19. However, since substantially no moisture is lost from bag 19 to the ambient atmosphere, an equilibrium condition is soon reached. If capsules 15 contain a saturated salt solution, the equilibrium condition within bag 19 will be determined by the humidistatic effect of the solution. To cite two possible extremes, the atmosphere

inside bag 19 could level off at 97 percent R.H. for capsules which contain saturated aqueous potassium dihydrogen phosphate. Alternatively, the R.H. within bag 19 could actually drop to 5.5 percent if the aqueous fill in capsules 15 were saturated aqueous sodium hydroxide (in this case there would be some danger of rupturing some of the capsules due to stress on the inside of capsule walls resulting from the large water absorption). If the aqueous fill in capsules 15 is pure water, the equilibrium is reached at about 99 percent R.H.

The conditions of capsule equilibrium during storage are generally applicable to the performance of the capsules in use in a humidistatic package. As will be apparent from the foregoing discussion of the prior art, there are various uses for humidistasis means 20 or 30. The first type of use is illustrated in FIG. 4. Five-pack 40 is a moisture-pervious package which, under typical conditions of storage, is likely to permit net loss of moisture from cigars 41 to the ambient atmosphere external to pack 40. Capsules 15 on lid 47, after lid 47 has been closed, serve a humidity replacement function. The net rate of loss of moisture from cigars 41 is variable, and capsules 15 advantageously supply humidity at a controlled rate substantially in response to the demands of the system. For this type of moisture-replacement-on-demand, it is adequate and even preferred to use capsules 15 which contain substantially pure water rather than a saturated salt solution. However, saturated salt solutions can be used, e.g., saturated sodium chloride.

Humidistasis means 20 or 30 is also useful in tightly closed environments which are intermittently opened, e.g., to remove part of the contents. In this use, and in uses involving moisture-tight environments which are not intermittently opened, a desired equilibrium R.H. level within the environment can be prescribed within narrow limits by selecting an appropriate aqueous fill for capsules 15. Typically, the aqueous fill 29 is a saturated aqueous solution of one of the metal salts disclosed in O'Brien, *J. Sci. Instruments*, pp. 73-76 (March, 1948). If a fixed level of about 99 percent R.H. is desired, the aqueous fill 29 can be pure water. Humidistasis means of this invention are surprisingly efficient in restoring equilibrium R.H. conditions even when humidistasis is temporarily disturbed by intermittent opening and closing of a relatively moisture-tight container. A sealed moisture-tight environment not subject to even temporary disturbances can be provided by means known in the packaging art, e.g., wax coatings in or upon cartons or packages; polyolefin film overwraps, liners, or packages; heat-sealed polymeric films or aluminum/polyolefin laminates; etc.

For the typical five-pack of cigars, about 0.5 to 3 square inches (3.2 - 19 cm²) of humidistasis means 20 or 30 is adequate to protect the freshness of the cigars and insure a shelf life of a year or longer. For cigar boxes containing 50 cigars, larger humidistasis means are generally desirable, e.g., about 10 square inches (65 cm²).

The preferred capsules 15 are preferably made according to the teachings of Arens et al., U.S. Pat. No. 3,423,489, issued Jan. 21, 1969, the fill liquid being preferably a predominantly aqueous liquid which can contain, if desired, dispersoids or solutes such as dissolved inorganic salts. The shell material is preferably made from a mixture of 20 - 70 wt. percent polyethylene, 15 - 50 wt. percent natural or synthetic polyter-

pene or other amorphous organic resin, up to 40 wt. percent (preferably at least 2 wt. percent) of a wax such as a hydrocarbon wax, and, if desired, a minor amount of a suitable plasticizer or the like. This type of composition forms a single phase at elevated temperatures, but is subject to phase separation effects upon cooling. The separation of phases creates microscopic pores in capsule walls 27. These pores permit transmission of water vapor to and from the interior of the capsule by one or more vapor transport mechanisms.

FURTHER DESCRIPTION AND EXAMPLES

As will be apparent from the foregoing description, a variety of carrier means or backing means can be used in this invention, provided that the capsules are securely anchored to it and are sufficiently exposed for good moisture release. The carrier means itself can be any suitable sheet-like structure, including woven or non-woven webs, waterlaid sheets such as paper, polymeric film, metal foil or polymeric film coated with adhesive, a coherent adhesive (such as an adhesive transfer film), a sheet of foamed synthetic organic resin, or the like. Coherent, flexible carriers with an exposed major surface suitable for capsule anchoring are most useful, and planar carriers ("planar" meaning either a flat or curved plane), which can be cut to any desired width are preferred. The carrier means is preferably 10 - 2,500 microns (0.4 - 100 mils) thick, though up to about 5 mm (about 200 mils) can be used if the carrier is a thick layer of foamed synthetic resin, e.g. polyurethane foam. Corrugated or embossed carriers can be used.

When a cloth mesh or scrim is employed as in FIG. 2 of the Drawing, the openings in the scrim can be square, hexagonal, or the like, provided the widest dimension of the opening is slightly smaller or slightly larger than the diameter of the capsules positioned by the scrim. The scrim can be made from monofilament or multifilament fibers of nylon, polyester, or the like.

The water-containing capsules used in this invention are preferably made by the "biliquid column" technique of Arens et al., U.S. Pat. No. 3,423,489, issued Jan. 21, 1969. In the Arens et al. technique a jet or column of the liquid fill material is surrounded and enclosed by a concentric stream of shell forming material. This composite or "biliquid" stream is directed in a trajectory with a horizontal component such that the stream of shell-forming material constricts along its length into spheroids, each spheroid enclosing a core of the fill material. This process can produce capsules ranging in size from 10 to 4,000 microns in diameter. In the present invention, capsules less than 3,000 microns in diameter are preferred, and it is generally convenient to use capsules larger than 100 microns in diameter.

Although it is desirable in some embodiments of this invention to use a capsule fill comprising pure water, the viscosity of pure water is less than ideally suited for the Arens et al process of making capsules. Therefore, it is preferred to introduce a viscosity modifier or builder into the aqueous fill liquid to facilitate capsule manufacture. As pointed out in the Arens et al. disclosure, a few percent of a copolymer of maleic anhydride and methyl vinyl ether and/or a hydroxy terminated polyoxyethylene/oxypropylene copolymer can be used as a viscosity builder. Other conventional additives to

the aqueous fill include latex solids and strongly colored dyes, where desired. Up to about 90 percent by weight of the aqueous fill liquid can comprise a solute, a water-miscible liquid, a dispersoid, a suspensoid, or mixtures of these. For careful control of humidity in a reasonably moisture-tight container, it is preferred to use a saturated aqueous solution of a suitable solute which will stabilize the R.H. level at less than 99 percent. Among the solutes known to be useful for control of humidity by saturated aqueous solutions are various oxides and metal or ammonium salts. The oxide which has been most fully investigated is phosphorus pentoxide. Typical metal salts are the salts of elements of Group I-A and II-A of the Periodic Table and lead, zinc, and thallium. Typical ammonium salts include ammonium nitrate, ammonium dihydrogen phosphate, ammonium sulphate, ammonium chloride, etc. Aqueous solutions of water-soluble organic compounds such as urea have also been used in humidity control.

If the aqueous fill liquid contains one of the previously mentioned solutes, the viscosity modifier or builder should be selected with some care so as not to precipitate the solute or radically alter the water vapor pressure of the aqueous solution. For example, a saturated sodium chloride solution can be used in a closed atmosphere to maintain a relative humidity level of 75 - 77 percent. Some of the conventional viscosity builders do tend to precipitate sodium chloride or alter the vapor pressure of saturated NaCl. It has been found that high molecular weight polysaccharide gums made by fermentation, e.g. "Kelzan" (trademark of Kelco Company) or "Biopolymer XP-23" (trade designation of General Mills) do not have these undesired effects upon a saturated sodium chloride solution.

In making capsules useful in this invention, any suitable shell wall material (including synthetic polymers, hydrocarbon or ester waxes, natural or synthetic resins, gums, gelatinous materials, etc.) can be used, provided that the shell wall will permit moisture vapor to pass from the interior of the capsule without rupturing the capsule walls. One method for providing moisture transmission is to control the capsule-forming conditions so as to provide walls thin enough for vapor loss by diffusion. Another technique is illustrated by Example XXIV of Arens et al, wherein the aqueous contents of the capsule diffused into a 40 percent R.H., 23° C. environment at a rate of 0.2 percent per day, thus providing a half life of 241 days for the capsule contents. The pores in the walls of the capsules made according to this technique were, however, in the nature of cracks and were generally grosser than the type of porous structure preferred for capsule walls in this invention. Cross cracks or pores in capsule walls are generally not too detrimental when the capsule contains substantially pure water. However, if the capsule contains a saturated salt solution, solute can leak out of the capsule wall in solution and be deposited outside the capsule, where it will no longer have a humidistatic effect upon the ambient atmosphere.

Accordingly, it is preferred that capsules used in this invention have shell walls which are free of gross flaws, cracks, etc., which are large enough to be seen by the naked eye. Stated another way, flaws or pores in the capsule wall should not be large enough to permit outflow of an aqueous liquid by mechanisms other than capillary action. In addition to loss of solute, severe leaks can result in the capsule fill having a half life of

only a day or two. Once empty, capsules with grossly flawed walls are generally not able to reabsorb water.

Another technique for providing moisture transmissive water-containing capsules involves the use of silane-treated fumed silicon dioxide. This material, which is an extremely fine powder, is so hydrophobic that it tends to surround and encapsulate droplets of water, thus forming "water-in-air" emulsions or "powdered water." Hydrophobic, silane-treated, fumed silica is obtainable from Cabot Corporation, Boston, Massachusetts, under the trademark "Silanox." When "Silanox" is mixed with relatively large quantities of water under high shear conditions, the water appears to be converted to a free-flowing powder which comprises, for example, 61 percent air, 34 percent water, and 5 percent "Silanox" by volume. Moisture is lost from this "powdered water" or "water-in-air emulsion" at a substantially constant rate for a given R.H. According to "Silanox" literature, an "emulsion" of 90 percent water, 10 percent "Silanox" lost about 5 percent of the water per day for the first 10 days in a 0 percent R.H. ambient atmosphere — a half life of 10 days. From the tenth to the fifteenth day, an additional 20 percent of the water was lost. Under 10 percent R.H. conditions, the rate of loss was 4 percent per day for the first 5 days, slowing to 3 percent per day or less for the next 10 days, resulting in a half life of about 15 days. The 47 percent R.H. curve showed a rate of 3 percent per day or less, the 15-day loss being about 35 percent. Under 85 percent R.H. conditions, the loss rate was only about 0.7 percent per day. Thus though "Silanox" is particulate, it appears to form a porous, hydrophobic wall about droplets of water, and the resulting structure behaves like water-containing capsules with moisture transmissive walls.

The preferred technique for providing the capsule shell walls for vapor transmissivity involves the Arens et al process with selection of the shell wall-forming materials such that these materials will have certain liquid phase and solid phase relationships, that is: At least a first solid phase comprises a first material, and a second solid phase comprises a second material, the first and second materials being miscible and capable of forming a single phase when both materials are in a liquid state, but capable of forming separate phases upon being cooled to a solid state. The percent of contraction in volume upon being cooled is greater for the first material as compared to the second material, and it appears that contraction of the first material, upon cooling of the shell-forming composition, contributes to the formation of micropores which extend completely through the resulting capsule wall. An example of the combination of materials which produces this microporosity is a mixture of an olefinic polymer, an amorphous organic resin, a wax, and, optionally, a few percent of a plasticizing material such as mineral oil.

In the Examples which follow, typical shell-forming compositions and their net water vapor release rates will be illustrated. These non-limiting Examples will also serve to illustrate the principle and practice of this invention.

EXAMPLE A

WATER VAPOR-RELEASING CAPSULES

Nine lots of capsules averaging 2,000 microns in diameter were made from aqueous fill liquids and

polyolefin-containing shell-forming materials according to the teachings of Arens et al., U.S. Pat. No. 3,423,489. The nine lots of capsules are designated hereinafter as Lot A-1 through Lot A-9. In Lots A-1, A-2, and A-7, the aqueous liquid fill material was 97 percent by weight of water, 3 percent by weight of a viscosity-building copolymer of maleic anhydride and methyl vinyl ether ("Gantrez" [trademark]). In Lots A-3, A-4, A-5, and A-6, the aqueous liquid fill material was 85 percent water, 15 percent polyoxyethylene glycol. The aqueous liquid fill material for Lots A-8 and A-9 was made from water thickened with a high molecular weight polysaccharide gum made by fermentation ("Kelzan," trademark of Kelco Company), in which sodium chloride was dissolved.

The procedure for making the liquid fill for Lot A-8 was as follows: Three liters of a 0.1 percent (by wt.) "Kelzan" in water solution was prepared and allowed to stand overnight with some mixing. Then 1.2 kg of NaCl was added, and the solution was mixed for 2 hours. The solution was then allowed to stand for one hour. The majority of it was decanted into a vacuum receiver and degassed at 27 mm Hg pressure. Three drops of "Triton X 200" were added before mixing had ceased. "Triton X 200" is the sodium salt of an alkyl-aryl polyether sulfonate in isopropanol.

The liquid fill for Lot A-9 was prepared by mixing 0.056 lb. of the "Kelzan" with 28 lbs. of water to give a 0.2 wt. percent "Kelzan" solution. Twelve pounds of NaCl were then mixed in to provide the desired solution.

The shell-forming materials for all nine lots were blended to form a single molten phase at elevated temperatures which cooled to a solid, vapor pervious shell during capsule manufacture. All of these blends were made from the following materials:

1. Polyolefin: Polyethylene "AC 617" (trade designation of Allied Chemical Co. for a low molecular weight polyethylene, melting point = 102° C., specific gravity = 0.92)
2. Amorphous resin: "Wingtack-95" (trademark of Goodyear Tire and Rubber Co. for amorphous hydrocarbon resin with softening point of 95° C. and a specific gravity of 0.93)
3. Wax: "Shellwax 700" (trademark of Shell Chemical Co. for hydrocarbon wax, melting point = 84° C., specific gravity = 0.94 at 15° C.)
4. Plasticizer: Mineral oil

Capsules made according to this Example were checked for gross flaws by soaking them in solution-type black ink. Stained gross flaws or darkened capsules were noted, and only a few percent of the capsules were found to have flaws readily visible to the naked eye. (The flawed capsules can be discarded for purposes of this invention.) The proportions of shell-forming materials in parts by weight are set forth below:

Capsule Lot	PARTS BY WEIGHT			
	Poly-olefin	Amorphous Resin	Wax	Mineral Oil
A-1	60	15	25	2
A-2	55	15	30	2
A-3	45	35	20	2
A-4	45	40	15	2
A-5	40	35	25	2
A-6	45	20	35	2
A-7	40	35	25	2
A-8	45	40	15	2
A-9	40	35	25	2

The above capsule shell formulations for Lots A-1 through A-9 were formulated and used in the Arens et al process by following the teachings of German laid-open Pat. application 2,019,724 (Hofacker) published Nov. 5, 1970.

Capsules of Lots A-1 through A-7 were placed in desiccators containing

a. saturated NaOH (5.5 percent ambient R.H.) and

b. saturated KH_2PO_4 (97 percent ambient R.H.).

All desiccators were kept at 20° to 25° C.

For all lots except Lot A-4 (which had a substantially linear cumulative-percent-water-release vs. time, even at 5.5 percent R.H.), at least two, generally three, different rates of release at 5.5 percent R.H. were noted. Typically, there was a fast initial rate of release, which was extrapolated back to time = zero (total amount of encapsulated water released = 0 percent). This initial rate is referred to in the following table as the " t_0 rate," " t " being time in days. A slow release rate was observed during the fifteenth to the twenty-fifth day. This rate is called t_{20} , since it was determined approximately by taking the slope of the cumulative-percent-release vs. time curve at $t=20$ (time = 20 days). A rate transitional between the t_0 rate and the t_{20} rate was typically observed at $t = 5$ days, referred to hereinafter as the t_5 rate. Rates of release at 97 percent R.H. were substantially constant for all capsule lots after the first few days; so for 97 percent R.H. only a time = 6 (t_6) rate is given. The 5.5 percent R.H. rates (t_0 , t_5 , t_{20}) are believed to be accurate to about ± 0.1 percent/day. The 97 percent R.H. rate (t_6) is believed to be accurate to about 0.05 percent/day.

35 Net Release Rates in % by Weight of Encapsulated Water Lost Per Day

Capsule Lot	t_0 rate at 5.5% R.H. (%/day)	t_5 rate at 5.5% R.H. (%/day)	t_{20} rate at 5.5% R.H. (%/day)	t_6 rate at 97% R.H. (%/day)
A-1	5.0	1.2	0.4	0.70
A-2	2.5	0.8	0.2	0.20
A-3	1.6	1.6	0.3	0.25
A-4	0.2	0.2	0.2	<0.05
A-5	3.6	2.6	0.4	0.50
A-6	9.2	3.8	0.2	0.25
A-7	3.2	2 to 3*	0.6	0.90

* t_5 for Lot A-7 fell on a portion of the curve where the slope was changing from about 2.8%/day to about 2%/day.

At 5.5 percent R.H., Lot A-6 had the shortest half life: 50 percent by weight of the total amount of water encapsulated within the test sample of Lot A-6 was released to the ambient atmosphere in 9.5 days. The half-lives of Lots A-1 through A-5 and A-7 at 5.5 percent R.H. were all longer than 25 days. The 5.5 percent R.H. half-life of Lot A-4 was the longest: 227 days (by extrapolation).

EXAMPLE B

ENCAPSULATION OF WATER WITH SILANE-TREATED FUMED SILICA

Ten grams of "Silanox" were mixed with 90 ml of a saturated aqueous solution of sodium chloride. The mixture was mixed in a high speed Waring blender for 30 seconds. A white flowable powder resulted, 4.6 grams of which were placed in a 250 ml. desiccator along with a Taylor "Humiguide." A constant relative

humidity of 73 percent was achieved within 24 hours. The Taylor "Humiguide" was not calibrated; therefore, 73 percent is not an absolute number, but it agrees fairly well with the theoretical value of 75 - 76 percent R.H.

During the humidistasis test in the desiccator, the temperature was kept at 71° - 73° F. The Taylor "Humiguide" had an initial reading of 66 percent R.H. at 73° F. Forty-eight minutes later the reading had dropped to a low point of 44 percent R.H. An hour after this low point was reached, the reading was up to 52.5 percent. The readings continued to rise steadily until, at seven hours elapsed time, the reading was 69.5 percent R.H. At 24 hours elapsed time the 73 percent R.H. value had been attained and remained within 1 percent of this value until the test was discontinued two days later.

EXAMPLE C

COMPARISON WITH HYDROPHILIC SPONGE

A hydrophilic sponge was made by the following procedure: 1,000 parts by weight of polyoxyethylene glycol of molecular weight 1,000 (sold under the trademark "Carbowax" 1,000) was reacted with 351 parts tolylene diisocyanate (an 80/20 mixture of the 2,4-2,6-isomers) under substantially anhydrous conditions for 2 hours to provide a hydrophilic diisocyanate prepolymer. The prepolymer dissolved in, and rapidly reacted with, water with considerable carbon dioxide evolution to form a hydrophilic foam. A portion of the foam was soaked in water and became saturated almost immediately. The saturated, spongelike foam was placed in desiccators under 5.5 percent R.H. and 97 percent R.H., as in Example A. Constant release rates were observed at both humidity levels. These rates were:

5.5 percent R.H.: 28 percent/day

97 percent R.H.: 4 percent/day (average of two curves)

Thus, the hydrophilic sponge had a tendency to dry out even at 97 percent R.H., as is illustrated by the half-life data:

5.5 percent R.H.: 50 percent by wt. of water released in <2 days.

97 percent R.H.: 50 percent by wt. of water released in <13 days.

EXAMPLE 1

CONSTANT HUMIDITY MEANS

The capsules of Lot A-8 (see Example A) were found to be in equilibrium with an ambient atmosphere controlled by a saturated salt solution in the following experiment:

Lot A-8 capsules were sealed inside a substantially moisture-tight chamber in the presence of a saturated aqueous NaCl solution, and the weight loss from the capsules was monitored. The weight loss was found to be negligible and was attributed to minor imperfections in the moisture tight seal.

A construction as shown in FIG. 2 of the Drawing was prepared using Lot A-8 capsules as the capsules 15 of the tape 20. This tape was found to be useful for storage of tobacco in moisture-tight containers.

EXAMPLE 2 INTERMITTENT DISTURBANCE OF HUMIDISTASIS

A 10-inch desiccator chamber was cleaned and thoroughly dried. A Taylor "Humiguide" which had previously been calibrated as reading about 9 to 10 percent low was placed in the chamber. Twenty-five grams of Lot A-9 constant humidity capsules of Example A were placed in an aluminum weighing dish in the middle of the support plate. The top was closed. The temperature of the desiccator, except as noted, was kept at 71° - 72° F. The following data were obtained:

Day	Time	Uncalibrated "Humiguide" Reading (% R.H.)
1st day	2:38 P.M.	13
	7:00 P.M.	57
	9:00 P.M.	60
2nd day	8:15 A.M.	64
	8:16 opened chamber and closed it (dry air introduced)	
	8:21 A.M.	57
3rd day	1:00 P.M.	54
	5:00 P.M.	59
	9:00 P.M.	62
	7:45 A.M.	65
	11:15 A.M.	63*
4th day	4:45 P.M.	63*
	10:20 A.M.	65*
	8:05 A.M.	63*
6th day	8:30 A.M.	65
	5:15 P.M.	64
8th day	8:50 A.M.	65
	7:59 A.M.	65
10th day	12:20 P.M.	63
	8:15 A.M.	65**
	7:25 A.M.	65**
	8:15 A.M.	65**
	8:45 A.M.	65**

*Temperature: 69° F. on part of 3rd day, 69° on 4th day, 70°F. on 6th day. **Corrected reading: 74.3% R.H.

These data demonstrate that the capsules can raise the relative humidity of a dry closed chamber to a given level and hold it there. It also demonstrates that the capsules can bring the environment back to its original condition if it is distributed by dry air.

The Lot A-9 capsules were applied to a tape and found to be useful for storing pipe tobacco in a humidifier which was subject to weekly openings and closings.

EXAMPLE 3

HUMIDITY-ON-DEMAND SYSTEM

The capsules of Lot A-6 (see Example A) were incorporated in a humidistasis means of this invention and were found to be useful for application to the inside of a shipping box for cut flowers. The capsules released water vapor on demand for a period of weeks.

What is claimed is:

1. Humidity control means comprising:

a sheet-like carrier means on one major surface of which is disposed a plurality of capsules 10-4,000 microns in diameter, said capsules comprising a shell wall fully surrounding and enclosing an aqueous fill liquid, said capsules being free of flaws or pores, in said shell wall, visible to the naked eye, said capsules being capable of releasing water vapor without rupture of said shell wall.

2. Humidity control means according to claim 1 wherein said capsules are less than about 3,000 microns in diameter and wherein said shell wall comprises at least a first solid phase comprising a first material

and a second solid phase comprising a second material, said first and second materials being miscible and capable of forming a single phase when both materials are in a liquid state, but capable of forming separate phases upon being cooled to a solid state, the percent of contraction in volume upon being cooled greater for the first material as compared to the second material, the first material being present in a quantity sufficient to provide micropores which extend completely through said capsule wall.

3. Humidity control means comprising:

a sheet-like carrier means and a plurality of substantially spherical capsules 10 - 4,000 microns in diameter, said capsules being adhered to a major surface of said carrier means at least at their points of tangency upon said major surface, each of said capsules containing about 5×10^{-7} to about 5×10^{-2} cubic centimeters of aqueous fill liquid fully surrounded and enclosed by a vapor-transmissive shell wall, at least 30 percent of the area of said vapor-transmissive shell wall being exposed to the ambient atmosphere to be controlled by said humidity control means, said capsules having the following water vapor release characteristics, determined under constant ambient relative humidity conditions:

an encapsulated water half life of at least three days at 5.5 percent ambient relative humidity and a substantially constant net release rate of less than about 2.5 percent by weight of the total amount of encapsulated water per day at 97 percent ambient relative humidity, said substantially constant net release rate being measured after the fifth day of 97 percent ambient relative humidity.

4. Humidity control means according to claim 3 comprising a monolayer of said capsules, said carrier means being a solid polymeric film vacuum formed upon one major surface of said monolayer of capsules.

5. Humidity control means according to claim 3 wherein said carrier means comprises a pressure-sensitive adhesive layer.

6. Humidity control means according to claim 5 wherein said carrier further comprises a cloth layer adhesively bonded to the same major surface to which

said capsules are adhesively bonded, said capsules being positioned within the openings between fibers of said cloth layer.

7. Humidity control means according to claim 3 wherein said humidity control means is enclosed within a container further containing dehydration-sensitive material.

8. Humidity control means according to claim 3 wherein said humidity control means is enclosed within a moisture-tight container.

9. Humidity control means according to claim 3 wherein said aqueous fill liquid is substantially entirely water.

10. Humidity control means according to claim 3 wherein said aqueous fill liquid comprises a saturated aqueous solution of a water soluble metal or ammonium salt.

11. A package containing a tobacco product and a humidistasis means, said humidistasis means comprising

a sheet-like carrier means adhesively bonded on one major surface to an inside surface of said package;

a plurality of capsules at least substantially hemispherically exposed to the inside of said container and adhesively bonded, at least at their points of tangency, to the exposed surface of said sheet-like carrier means, said capsules being less than about 3,000 microns in diameter and comprising a substantially spherical vapor-transmissive shell completely surrounding and enclosing an aqueous liquid, said capsules having the following water vapor release characteristics, determined under constant ambient humidity conditions;

an encapsulated water half life of at least three days at 5.5 percent ambient relative humidity and a substantially constant net release rate of less than about 2.5 percent by weight of the total amount of encapsulated water per day at 97 percent ambient relative humidity, said substantially constant net release rate being measured after the fifth day of 97 percent ambient relative humidity.

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