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PROCESS FOR MAKING A MOISTURE SENSING
ELEMENT FOR DRY CLEANING AND ARTICLE

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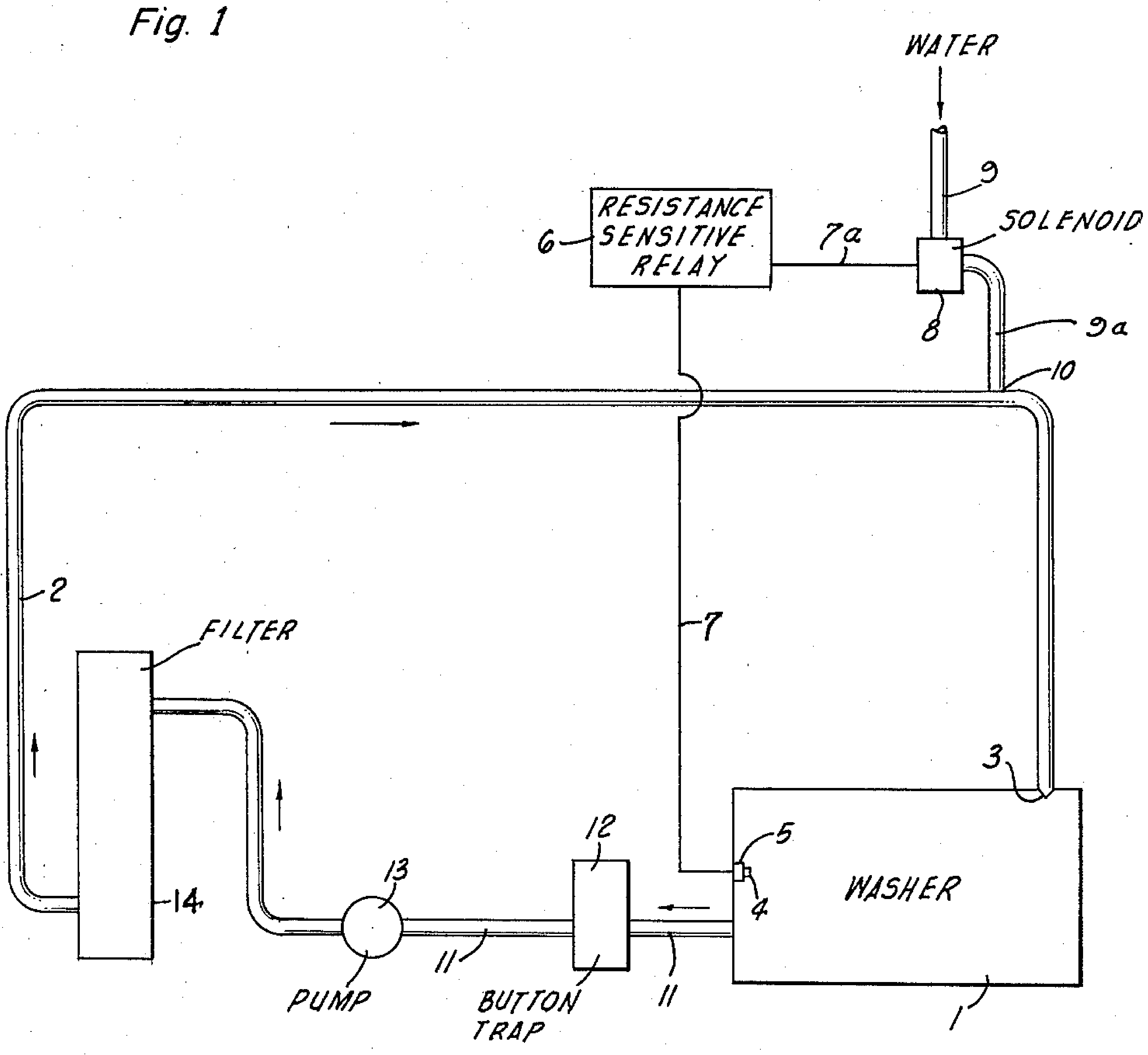
Fig. 1



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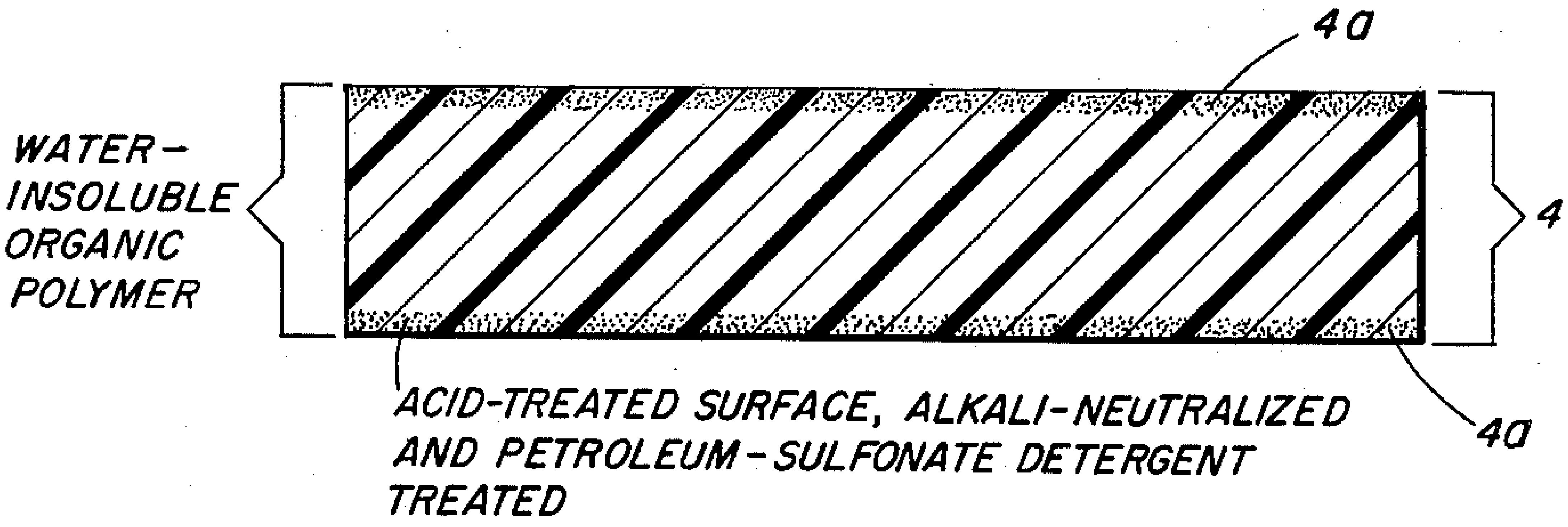

FIG-2

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# PROCESS FOR MAKING A MOISTURE SENSING ELEMENT FOR DRY CLEANING AND ARTICLE

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7 Claims. (Cl. 117—213)

The present invention relates to methods and apparatus for dry cleaning fabrics, garments and the like without injury thereto. More particularly, it relates to processes of the type which are carried out by the careful regulation of water absorption by garments to be drycleaned by the control of relative humidity within a washer. Still more particularly, the invention is directed to methods for the utilization of a sensing element, more particularly defined hereinafter, for relative humidity determination directly placed in the dry cleaning solvent.

The present application is a division of our copending application, Serial No. 587,620, filed May 28, 1956, now United States Letters Patent 2,949,336, issued on August 16, 1960.

The term "relative humidity (R.H.) within the solvent or garment" as used in this specification may be defined as the ratio of the vapor pressure of water in the solvent or garment to the vapor pressure of pure water at the same temperature as that of the solvent or garment. As is customary, the degree or value of relative humidity is expressed as percent R.H. In this description R.H. values in the solvent above about 80% may be defined as "free water" and R.H. values below about 80% may be defined as "bound water."

In the dry cleaning of fabrics and garments for the removal of ground-in soils and sweet stains, it is known that the amount of moisture pick-up by such fabrics or garments as determined by the relative humidity within the cleaning solvent plays a very considerable effect in removing various types of soils and stains. For example, too little water will remove little, if any soil. Excessive moisture will also deleteriously effect garments or fabrics in the form of possible shrinkage, wrinkling and color loss. Usually, for best overall results, the relative humidity within both the solvent and garment has been maintained at from about 60% to about 80%. The relative humidity within a dry cleaning system may be altered by varying the "free water" content in the washing zone. For instance, water may be prevented from entering that zone. Conversely, if it were desired to increase the relative humidity of the cleaning system, entry of water is permitted. As a practical matter, it has been demonstrated previously that solvent relative humidity and garment moisture pick-up must be accurately established and maintained. Otherwise, the efficiency of the cleaning operation for purposes of removing soils, stains and like is markedly low. To the present, such control, if possible, has been singularly difficult to attain.

In the past, many proposals have been suggested for controlling relative humidity within a dry cleaning washing zone. Unfortunately, each has had its shortcomings. One procedure suggested was to precondition soiled garments to a known moisture content and then add them to a cleaning solvent of some controlled moisture value. At best this procedure will give only an approximation of the solvent relative humidity due to the difficulties in preconditioning garments to predetermined uniform low relative humidities. Further, such garment drying technique is not commercially feasible. A drying operation is both costly and impractical, since many stains are set by heat and are rendered exceedingly more difficult to remove, if at all.

Another method recently developed for dry cleaning is the use of humidity gages to measure the relative humidity of the air above the cleaning solvent in the dry cleaning washer. This procedure utilizes the principle of passing the stream of air from the washer over a humidity sensor or sensing element fixed in a gage housing at a point above the solvent. Again, such a procedure does not adequately control both the solvent and garment relative humidities without the constant attention of the dry cleaning operator. Even where such attention is given, nevertheless there remains inherently a hiatus in sensing element response between changes in relative humidity of solvent and relative humidity of the air above the solvent. Also, for example, if a hair hygrometer or other animal membrance hygrometer is used, such sensors respond to a bulk moisture effect on the membrane or hair. The response will show hysteris values which make such measurements ineffectual. Accordingly, this general procedure does not lend itself to commercial exploitation.

A still further method which has been suggested for controlling solvent R.H. is to measure the conductivity of the dry cleaning solvent. However, such measurements are not entirely accurate, for the reason that the introduction of water into the washing zone cannot be readily measured by conductivity. This may be explained by the fact that water may affect the conductivity of many solvent-detergent cleaning mixtures in different ways. For example the conductivity of the solvent may increase in a linear manner as water is first added to the system. This increase in conductivity in linear only until the free water level (about 80% R.H.) is reached. However, above this level, the R.H./conductivity curve which at low moisture content proceeded in a linear fashion usually inverts to show a maxima above 80% R.H., the conductivity actually decreasing with added moisture. Thus, when water is added to a cleaning system, conductivity measurements of the solvent are usually unreliable because beyond a RH of about 80%, the conductivity reading may actually indicate a R.H. less than 80% due to the aforementioned inversion phenomenon. Therefore, when garments are being subjected to large amounts of water, the conductivity reading may be interpreted as showing an R.H. value below 80%, although the garments are being irrevocably injured. This situation can be compensated for by providing smaller additions of water to thereby regulate the conductivity of the solvent such that the R.H. is not permitted to exceed 80% at any time either before garment addition or during washing. However, such amounts of water can be preent in the cleaning system as bound or less available water, physically bonud to the solvent-detergent mixture. Moisture in the cleaning zone is therefore limited both by the quantity of water which a particular solvent/detergent system can dissolve at activities below 80% as well as by the physical state of that water. As such, this cleaning system cannot supply the requisite quantity of water at a rate to affect the surface of the garment for purposes of efficient removal of soils and sweet stains. Accordingly conductivity measurements of solvents for purposes of determining R.H. are unreliable and ineffectual in modern dry cleaning operations which employ solvent/ detergent cleaning solutions.

Expenditures of money, time and effort have been spent to provide accurate methods for controlling R.H. in a washer unit. To the present all such previously disclosed methods have fallen short of their goal.

A principal object of the invention, therefore, is to provide suitable means for regulating the quantity of both bound and free water in the cleaning system within predetermined levels. Another object of the invention is the provision for accurately controlling a dry cleaning solvent R.H. and garment R.H. level at from about 60–80% in the washing chamber without initially either predrying the garment or regulating the moisture content in the solvent, prior to garment addition to the washer. Still another object is the provision for the regulation of solvent R.H. and garment R.H. directly in the washing chamber without resort to the determination of the moisture content either in the air above the solvent or in the solvent prior to its entry into the washing chamber. These and other objects are accomplished in a simple and straight-forward manner.

Briefly, accurate control of water addition both to soiled garments and to commercial cleaning solution comprising a detergent charged organic solvent, can be attained by the provision of a detergent activated, chemically surface-modified dielectric sensing element placed directly in the washing zone. In this manner, the sensing element acts as an analogue of the garment surface so as to indicate its R.H. status and to predict the terminal R.H. of the garment under a constant rate of moisture addition. We have unexpectedly discovered that an inert, integral and ionic modified-surface dielectric element acts accurately as a sensor in a detergent charged hydrophobic solvent when placed directly in a washer or washing zone. This is unexpected because such sensing elements are generally worthless or at best ineffective in a hydrophobic environment. Therefore, according to the process of the present invnetion, an inert, integral, modified-surface sensing element when placed in a washing zone so as to regulate R.H. within that zone, will readily and quickly detect R.H. changes therein so as to permit efficient cleaning of garments within shortened time periods. It is an important advantage of the invention that a safe and efficient dry cleaning method is for the first time attained in shortened time periods. Without limiting the invention to any particular theory, our novel method may be explained by the fact, that water, which is essential in modern dry cleaning operations, can be introduced rapidly into the washer at a regulated rate so as to attain a desired relative humidity range within the washer for effecting safe dry cleaning and insuring a safe terminal R.H. of the garments. However, since the rate of water addition is rapid, the detergent charged solvent cannot apparently bind all of the introduced water, the solvent thereby becoming saturated. Only a portion of the introduced water may be bound to the solvent detergent mixture and the remainder is available as free water to effect cleaning of the garments. The importance of a suitable sensing element comes into prominence in detecting free water and in determining how the available free or unbound water is affecting the garments during the cleaning operation. The use of our element whose moisture response is a surface effect, gives a true recording of the free moisture effect on the garments' surfaces. It appears that the sensing surface which responds to the moisture level in the washer is analogous to the garment surface. Moisture introduced into the system at a constant rate raises the bulk moisture content of the garments. Our surface sensor predicts the state of the surface of the garment by responding to the excess available moisture in the washing zone. This excess develops due to lower rates of absorption by the garments at higher moisture levels. The sensing element responds more rapidly than does the garments, thus preventing the introduction of excessive quantities of water.

Necessity in our process for recleaning of only insignificant percentages of the garments evidences the efficiency of the sensor in its ability to register the R.H. status of the cleaning system, particularly with reference to the terminal R.H. of the garment.

Any of a large variety of dielectric sensing elements may be used in the process of the present invention provided the elements are inert in the cleaning solvent and characterized by their ionically modified surfaces. Further, they may be also defined by resistance characteristics. In general, the use of elements which record resistances of between about 0.02 megohm per square of sensing surface and about 100 megohms per square of sensing surface as determined in an organic cleaning solvent of 75% R.H. is particularly advantageous. A sensing element may be prepared from a variety of organic materials. Illustrative of the latter are water-insoluble solid resins or polymers such as for example, the epoxy resins, polyethylene, polypropylene, copolymers of polystyrene, polyesters, urea-formaldehyde, melamine-formaldehyde, cellulose esters and ethers, and phenol-formaldehyde resins. The surfaces can be chemically modified to an ion-active state as by sulfonation, carboxylation or phosphonylation. The electrical resistance of the surface will vary according to the degree of exposure to the surface chemical modifiers. For example, it has been found that the longer the chemical treatment, the lower the resistance of the element, and conversely, the shorter the treatment, the higher the resistance. The element is then exposed to a surface active reagent, such as petroleum sulfonate, to activate the element for purposes of moisture response in hydrophobic solvents. Alternatively, activation of the element can be accomplished in situ by insertion of the surface modified element into a charged solvent system. Of all the sensing elements above mentioned, surface sulfonate epoxy resins are especially well adapted for use as a humidity sensing element.

The preparation of various sensing elements is given by way of illustration in the following examples and such examples are not intended to be taken as limitations upon the invention.

*Example A*

To 60 grams of Shell's Epon 828 (a diglycidyl ether of bisphenol which is a viscous liquid at room temperature having a viscosity of 5000–15,000 cps. and an epoxide equivalent of 175–210) is added 3 grams of diethylenetriamine and stirred at room temperature until a clear solution is obtained. The clear solution thus treated is poured on an inert stainless steel plate and the cast solution is cured at 80° C. for eighteen (18) hours. The cured epoxy resin is next stripped from the stainless steel plate and cut into one half inch squares. Each square is sulfonated by incorporating the latter in a mixture of one gram of chlorsulfonic acid and 160 grams of anhydrous carbon tetrachloride at 70° F. for about two minutes. The so sulfonated resin is immersed in diethyl ether and rinsed several times with additional diethyl ether. It is then dried and rinsed with distilled water to remove excess acid. The resin is neutralized with a 5% aqueous sodium carbonate solution. Excess sodium carbonate is then removed with water and electrodes are attached to a thus treated epoxy resin surface and the resistance is measured by usual methods using A.C. currents. The resistance registers one megohm per square at 75% relative humidity and 0.5 megohm per square at a relative humidity of 85%, when placed in a solution of perchloroethylene containing 4% petroleum sulfonate.

*Example B*

A cured phenol-formaldehyde resin of one-half inch squares is sulfonated following the procedure of Example A in every material detail. The element which shows that its surface was sulfonated possesses in the solvent-detergent medium of Example A an electrical resistance of 0.5 megohm per square at 75% relative humidity and 0.17 megohm square at 85% relative humidity.

*Example C*

A cured mica-modified phenol formaldehyde resin is prepared in two strips of one inch squares. These are sulfonated in fuming sulfuric acid for 2 minutes at 80° C. The surface-sulfonated element is next drowned in diethyl ether, removed and rinsed several times in the latter solvent to remove any residual acid. The elements are rinsed in water and neutralized with dilute aqueous sodium carbonate and excess carbonate is removed with water. The element is then immersed in a 1% solution of petroleum sulfonate in Stoddard's solvent at 40° C. for 24 hours. Electrodes are attached to the so-activated element and its resistance is measured in Stoddard solvent. It is found that the electrical resistance at R.H. 75% is 0.6 megohm per square and 0.2 megohm per square at 85%. A cross linked polystyrene resin can be substituted for the phenol-formaldehyde resin above. Similar properties are obtained.

*Example D*

Polyethylene square of three-quarters inch is sulfonated in a mixture comprising one gram of chlorosulfonic acid, 160 grams carbon tetrachloride and 20 grams of dioxane for 76 hours at 20° C. After sulfonation, the resin is washed first with ether and then with water to remove residual acid. To insure complete acid removal, the washed resin is treated with a dilute aqueous potassium carbonate solution followed by treatment with water. When the element is exposed to the detergent charged solvent of Example C, its resistance is determined as at 2.7 megohms per square at relative humidity of 80%.

*Example E*

A strip of commercially available cellulose acetate is partially deplasticized by extracting the latter in perchloroethylene solvent. Resulting deplasticized cellulose acetate is then immersed at 70° F. in 50% aqueous monoethanolamine for one hour. It is then washed to remove the monoethanolamine. The so treated resin is next wetted with monochloroacetic acid and air dried over night in the presence of said chloroacetic acid solution. The surface carboxylated resin is next immersed in 50% sodium hydroxide at 30° C. for 40 minutes. The resin is neutralized in acetic acid and the latter removed by washing in sodium chloride solution and, finally, the surface modified resin is washed with water. The element is immersed in a detergent charged solvent as in Example C. It shows a resistance of 2.8 megohms per square at 75 R.H. and 0.25 megohm per square at R.H. of 85%.

Substituting phosphoric acid for the chloracetic acid employed above will result in a phosphonylated surface modified resin in showing similar properties as obtained in this example.

The sensing elements prepared in accordance with the procedures set forth above may be removably mounted on an inert plug adapted to be inserted into a washing chamber. The plug will contain a pair of electrical terminals, which are in direct contact with the sensing element surface. The sensing element may be pressure fitted to electrical contacts of the plug.

The invention will be further described with reference to the accompanying drawings, FIG. 1 is a flow sheet which constitutes one mode for practicing the invention. FIG. 2 is a cross-section of the novel sensing element. Thus, a dry cleaning plant embodying the principal features described above is diagrammatically illustrated below.

Referring now to the drawing, a washing chamber is generally designated at **1**. Filtered solvent is fed through line **2** and then through an opening **3** into the washing chamber. A sensing element **4**, such as prepared in Example A, above, and as shown in FIG. 2, is mounted on a plug **5**. The sensing element as shown in cross-section of FIG. 2 comprises an integral, surface modified water-insoluble organic polymer **4** as prepared by acid treatment of the polymer surface **4***a*, followed by alkali-neutralization and petroleum sulfonate detergent treatment. Thereafter, the plug is removably attachable to the washing chamber by providing matching threads (not shown) on the plug and in the opening of the washing chamber. The sensing element is linked to a resistance sensitive relay **6** through wires in cable **7** attached also to plug **5**. A relay **6** then actuates solenoid valve **8** through wires **7***a* when the resistance of the element is above the controlling value. Thus water introduced into the solenoid valve through line **9** will flow through line **9***a* into line **2**. By spraying the water into line **2** as at nozzle **10**, intimate mixing with solvent will occur readily. In the interim, solvent in the washing chamber is withdrawn through a button trap **12** by means of pump **13** and fed through filter **14**. Solvent is next returned to the washing zone **1** through line **2**.

The following examples for controlling the amount of moisture addition to a cleaning system are presented to facilitate a better understanding of the invention. It will be noted that the R.H. of the garment phase will not exceed 80% although the R.H. of both the solvent and garments are not necessarily the same at the same time.

*Example 1*

To a dry cleaning washer unit of 30 pound capacity as in FIGURE 1, is added 30 gallons of perchloroethylene solvent which circulates at a rate of 30 gallons per minute between the filter and washer during the washing cycle. Since the R.H. of the cleaning system is less than 60%, water is injected into the solvent line entering the washer at the rate of 6 oz. per minute. The solvent is charged with 4% by volume of a commercial (petroleum sulphonate) detergent. A 4% solution of this detergent in perchlorethylene will normally register a R.H. equivalent of 75% with about 0.15% total water and will not dissolve more than 0.2–0.4% water dependent upon temperature and impurities. Since 6 oz. of water per 30 gallons of solvent is equal to 0.15% water by volume, this 75% R.H. value is therefore exceeded by the incoming solvent.

The washer is provided with an epoxy sensing element as prepared in Example A above. This element possesses a resistance of 0.2 megohm when in equilibrium with the detergent charged solvent containing a moisture equivalent of 75% R.H., but in air the element will have a resistance of 2.0 megohms at a R.H. of 75%.

The cleaning cycle comprises a wash cycle of 15 minutes and extraction cycles of two minutes before and after a rinse cycle of three minutes. After which time the garments are removed for drying and deodorization.

30 pounds of mixed woolens are introduced into the above described washer. The pump fills the washing zone with solvent. This is circulated during the 15 minute washing cycle. Moisture is allowed to enter the solvent up to 0.8 megohm resistance of the aforementioned sensing element. The R.H. of the garments before introduction into the washer was measured and determined to have a regain value equivalent to a R.H. of 40%. The solenoid is activated by the relay to allow water to be injected and after three minutes the resistance of the sensor decreased from an original resistance in the solvent of 3 megohms to 0.8 megohm or 60% R.H. at which point the relay is regulated to shut off the water supply. Thereafter, for the next twelve minutes water intake is regulated to maintain a resistance of 0.8 megohm. Total water added to the cleaning system is 30 ozs. A terminal regain or water pick-up of the garments equivalent to a R.H. of 65% is attained. Examination of the garments after rinsing and extraction indicate that the garments showed no wrinkling of linings and complete removal of all surface stains.

*Example 2*

The procedure of the foregoing example is repeated except that the resistance of the sensor is regulated to 0.2 megohm (R.H. 75%) by controlling the water input. Another load of mixed woolen and cotton garments having an initial regain of 50% R.H. is charged to the washer.

Water fed into the washer, during the wash cycle is as follows:

| Controlled moisture time in min.— | Water addition |
|---|---|
| 0–3 | on |
| 3–4 | off |
| 4–6 | on |

Within 6 minutes, the controlled addition of water is terminated by a timer and washing cycle is completed. The total water added is 30 ozs. and terminal regain of the garments is equivalent to 70% R.H. Excellent cleaning of soil and stains is attained.

*Example 3*

In this example, an 85 pound petroleum washer which contains approximately 60 gallons of solvent during washing cycle and having a flow of solvent through the washer of 55 gallons per minute is used. Water is injected into the solvent line at the rate of 8 oz. per minute. Commercial grade solvent-soluble, dry cleaning detergent containing a mixture of petroleum sulfonates and polyethylene oxides of nonylphenol having an average molecular weight of 400 is added to the solvent to supply a 5% concentration therein. A load of 85 pounds of silk dresses are added to the washer which operated during a normal cleaning cycle of 30 minutes followed by extraction cycles of 3 minutes before and after a 3 minute rinse. A sensing element comprising a sulfonated cross-linked polystyrene as prepared in Example C above having a resistance of 0.3 megohm at 70% R.H. equivalent solvent is inserted into the washing zone before washing commences. Moisture is added into the solvent feed. It is terminated when a resistance of 0.5 megohm is attained. However, the moisture control is operated for merely 15 minutes of the normal 30 minute cleaning cycle for excellent cleaning results. In this run, the quality of the cleaning was so high that 5% of the load required recleaning whereas the usual practice using a 30 minute cleaning cycle is to reclean 20% of the load or more.

The original moisture content of the silks was equivalent to a 40% regain but terminal regain at the end of the cleaning cycle is 73%. The following sequence of moisture addition was recorded as shown in the table below:

| Controlled Moisture Time In Minutes | Water Addition | Total Water Added |
|---|---|---|
| 0–5 | on | 56 oz. |
| 5–6 | off | |
| 6–7 | on | |
| 7–8 | off | |
| 8–9 | on | |
| 9–15 | off | |

Here again, almost 100% washing efficiency is achieved.

*Example 4*

A 450 pound washer containing 300 gallons of Stoddard's solvent and charged to 1½% of a commercial mixture of anionic, nonionic and cationic detergent. Water is introduced directly into the washer at the rate of 45 oz. per minute. This washer was provided with an epoxy resin sensor prepared in accordance with Example A above which has a resistance of 1.5 megohms at a solvent relative humidity of 75% R.H. and a resistance of 0.25 megohm at a solvent relative humidity of 85% R.H. The addition of water is set so as to terminate at 0.3 megohm resistance or about 80% R.H.

A load of 400 pounds of woolen pants at a R.H. of 25% initial regain is introduced to the washer containing 300 gallons of solvent without circulating solvent through the washer. The washer was run for 15 minutes in accordance with the following schedule:

| Controlled Moisture Time In Minutes | Water Addition | Total Water Added |
|---|---|---|
| 0–9 | on | 585 oz. |
| 9–11 | off | |
| 11–15 | on | |

Although the R.H. of the solvent is set for 80%, total regain of the garments in terms of R.H. is 70%. This is due to the interchange rate of this type of washer and the control sequence is set to compensate for different type washers. Substantial complete washing is attained.

A large variety of solvents may be employed for example, Stoddard's solvent, carbon tetrachloride, trichloroethylene and perchloroethylene are in common use. Of these, perhaps Stoddard's solvent is used most prevalently. However, perchloroethylene is rapidly gaining in popularity because of its non-flammable characteristics. Nonetheless, any of the solvents enumerated above may be used in the process of the invention.

The detergents which are used in conjunction with the solvents listed above are the anionic detergents, such as the petroleum sulfonates or non-ionics such as the alkylaryl polyglycol ethers and alkylol amides or mixtures of both as exemplified herein. Any of the commercially available detergents can be used. Of these, the petroleum sulfonates are preferred.

The amount of detergent agent may be varied widely but in general from about 0.25% to 10% by weight of the solvent yields satisfactory results. However, larger or smaller proportions may be used.

We claim:

1. A petroleum sulfonate detergent-activated, integral, ionic surface-modified dielectric material selected from water insoluble organic polymers characterized by its inertness to hydrophobic solvents and having an electrical resistance of not less than about 0.02 megohm per square of sensing surface but not more than about 100 megohms per square when said dielectric material is exposed to a organic solvent medium having a relative humidity of 75%.

2. A petroleum sulfonate detergent activated integral, ionic surface-modified dielectric material of claim 1 comprising a sulfonated epoxy resin, characterized by a resistance of one megohm per square of sensing surface at 75% relative humidity.

3. A petroleum sulfonate detergent-activated integral, ionic surface-modified dielectric material of claim 1 comprising a carboxylated cellulose acetate characterized by a specific resistance of 2.8 megohms per square of sensing surface at 75% relative humidity.

4. A petroleum sulfonate detergent activated integral, ionic surface-modified dielectric material of claim 1 comprising a sulfonated phenol-formaldehyde resin characterized by a resistance of 0.5 megohm per square of sensing surface at 75% relative humidity.

5. A petroleum sulfonate detergent activated integral, ionic surface-modified dielectric material of claim 1 comprising a sulfonated polyethylene characterized by a resistance of 2.7 megohms per square of sensing surface at 75% relative humidity.

6. A process for the preparation of an integral, ionic surface-modified dielectric water insoluble organic material which comprise the steps of: subjecting said organic dielectric to surface chemical modification with sufficient acid selected from the group consisting of chlorosulfonic acid, sulfuric acid, monochloracetic acid and phosphoric acid for a time sufficient to insure a resistance of not more than about 100 megohms per square and not less than about 0.02 megohm per square, removing all excess acid by washing with ether and then with water, thereafter washing with dilute alkali, then washing the so-washed

element with water, and subjecting the element to the action of a petroleum sulfonate detergent in a hydrophobic solvent.

7. A process for the preparation of an integral ionic surface-modified epoxy resin prepared by reacting a bisphenol with a diglycidyl ether which comprise the steps of subjecting said resin to the action of chlorosulfonic acid for a period not exceeding two minutes at about 70° F., drowning the thus-sulfonated resin in diethyl ether, then rinsing the resin with water and neutralizing residual acid with dilute sodium carbonate, removing said residual carbonate with water, and subjecting the element to the

action of a petroleum sulfonate detergent in a hydrophobic solvent.

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