

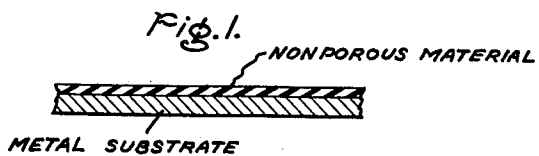
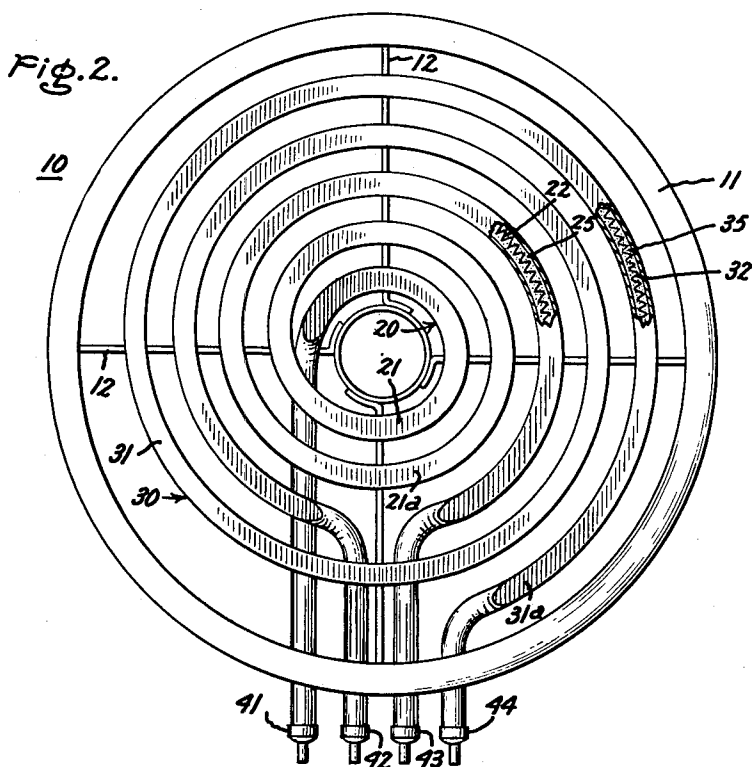
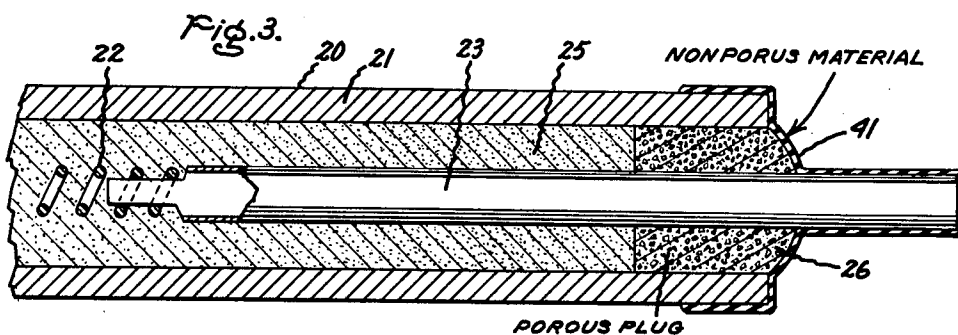
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3,197,728

ORGANOPOLYSILOXANE COMPOSITIONS

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3,197,728

ORGANOPOLYSILOXANE COMPOSITIONS

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Original application July 28, 1961, Ser. No. 127,681.
Divided and this application Jan. 6, 1965, Ser. No. 432,922

1 Claim. (Cl. 338—274)

This application is a division of my application Serial No. 127,681, filed July 28, 1961, entitled "Organopolysiloxane Compositions."

The present invention relates to heat unstable nonporous materials, to the employment of these materials in the treatment of a variety of substrates, and to the substrates treated thereby. More particularly, the present invention relates to certain organopolysiloxane compositions which can be readily applied to a variety of substrates to render the substrates impervious to moisture, and which thereafter can be readily removed therefrom.

In certain situations, it is often desirable to temporarily protect the surface of an object, particularly a metal object from the effects produced by exposure to water, or water vapor, such as rust and corrosion during the storage of the object. For example, a convenient method which can be employed to protect hardware is to treat it with an inert water insoluble material such as a hydrocarbon having a low vapor pressure. Although a hydrocarbon such as petrolatum can be easily applied to a metal substrate to render it temporarily corrosion resistant, it is often difficult to completely remove it. Methods such as wiping the treated surface with a dry cloth, dipping or immersing the treated object in an organic solvent can be employed in particular situations. Wiping and dipping procedures cannot be advantageously employed, when the object is irregular or the effects of an organic solvent cannot be tolerated throughout, such as when the object is part metal and part nonmetal, for example, plastic. Heating the object to melt the hydrocarbon so that it will run off the surface of the treated object can be employed but the risk of decomposing the hydrocarbon and forming a carbonaceous material on the metal surface also limits this approach. It would be desirable therefore to be able to treat a substrate such as the surface of a metal with a nonporous material to render such treated substrate impervious to water, and thereafter be able to remove the nonporous material therefrom in an easy and convenient manner.

A need also exists in various applications for an easily removable nonporous material to serve as a temporary humidity sealant. For example, in electric appliances such as electric stoves, where heating units of the sheathed conductor type are utilized, considerable effort has been devoted to overcoming problems caused by the accumulation of moisture from the atmosphere within the metal sheath. The aforementioned heating units generally comprise electrical resistance conductors surrounded by a dense mass of heat conducting refractory material within an outer metal sheath in the form of a spiral and have porous plugs at the terminals of the sheathed conductor to provide for breathing, such as illustrated in the co-pending application of Gunder Lien, Jr., Serial No. 773,217 filed November 12, 1958, and assigned to the same assignee as the present invention. These heating units often fail due to an accumulation of excessive moisture within the sheath as a result of normal breathing of the unit during storage over extended periods of time. Conventional sealants such as shellac, or various organic resins, etc. can be utilized to seal the porous plugs during the storage period but it is difficult to remove these sealants to restore normal breathing to the unit when the heating unit is ready for use.

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Accordingly, it is an object of the present invention to provide an improved nonporous material that can be readily applied to a variety of substrates, including metal substrates and porous substrates, so as to render the surface of the treated substrates resistant to the effects of water and water vapor over extended periods of time, where the aforesaid nonporous material can be thereafter readily removed from the surface of the treated substrate in an easy and convenient manner.

Another object of the invention is to provide an improved treated metal substrate resistant to the effects of water or water vapor over extended periods of time and where the surface of the treated metal substrate can be readily restored to its initial untreated state in an easy and convenient manner.

A further object of the invention is to provide for an electric heating unit of the sheathed resistance conductor type having an associated terminal extending from an end of the sheath and into the sheath through a porous plug of ceramic material secured in place, where the associated terminal extending from the end of the sheath and the porous plug is treated with an improved nonporous material so as to seal the end of the sheath to protect the electric heating unit against the entry of moisture through the porous plug during the storage of the electric heating unit prior to its initial use.

The present invention is directed to certain heat unstable nonporous materials comprising an organopolysiloxane, a silica filler and an acid treated absorbent material and to the employment of these materials in the treatment of a variety of substrates to impart moisture resistance thereto.

The invention will be better understood from the following description taken in connection with the accompanying drawings, and its scope will be pointed out in the appended claim.

In the drawings, FIG. 1 is an illustration of one embodiment of the invention showing a metal substrate treated with a nonporous material. FIG. 2 shows inner and outer heating units of the sheathed conductor resistance type incorporated within a hot plate assembly; FIG. 3 is an enlarged illustration of a terminal structure of a heating unit of the type in FIG. 2 treated with a nonporous material.

Referring further to FIG. 1, a metal substrate such as steel is shown with its surface treated with a nonporous material to render it resistant to water. The nonporous materials within the scope of the present invention are heat unstable materials that can be readily applied to a metal substrate in the form of a grease or can be dissolved in an organic solvent to provide for dip-coating techniques. The nonporous heat unstable material can be readily transformed into a free-flowing dry powder by application of heat. The nonporous heat unstable materials of the present invention comprise (A) 100 parts of an organopolysiloxane having the formula



(B) 5 to 75 parts of a filler, and (C) 1 to 75 parts of an acid treated absorbent material having an acid number in the range of from 1 to 500, and preferably 15 to 100, where R is a member selected from the class of monovalent hydrocarbon radicals and halogenated monovalent hydrocarbon radicals, and α is equal to from 1.95 to 2.2, inclusive.

The organopolysiloxanes of Formula 1 are well known in the art and are fluids that can vary at 25° C. from 0.65 centistoke to 500,000 centistokes or higher. Some of these fluids are shown in Patents 2,469,888 and 2,469,890—Patnode.

Included among the radicals represented by R of Formula 1 are for example, aryl radicals, e.g. phenyl, tolyl, naphthyl, etc. radicals; aralkyl radicals, e.g. phenylethyl, benzyl, etc. radicals; alkyl radicals, e.g. methyl, ethyl, propyl, butyl, octyl, etc. radicals; alkenyl radicals, e.g. vinyl, allyl, etc. radicals; cycloalkyl radicals, e.g. cyclohexyl, cycloheptyl, etc. radicals; and cycloalkenyl radicals, e.g. cyclohexenyl, cycloheptenyl, etc. radicals. In the organopolysiloxanes of Formula 1 it is preferred that each of the R radicals be the same and preferably methyl. However, there are organopolysiloxanes within the scope of Formula 1 where R radicals can be different and preferably are methyl and phenyl radicals. In those organopolysiloxanes of Formula 1 where R is a mixture of methyl and phenyl radicals, it is preferred that at least 50 to 75 percent of the total number of R radicals are methyl radicals.

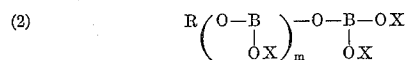
The fillers that can be employed to produce the nonporous heat unstable materials of the present invention are known to the art as silica fillers, preferably having a particle size between about .01 micron or less up to about 10 microns. Among the silica fillers operable in the present invention, are silica fillers which can contain or be free of hydroxyl radicals either in the form of adsorbed moisture or bonded to silicon atoms. These silica fillers may be additionally modified such as for example, by the introduction of silicon-bonded alkoxy radicals in place of some of the hydroxyl radicals. The preferred silica filler of the present invention is a fumed silica filler that has been treated with octamethylcyclotetrasiloxane in accordance with the teachings of Patent 2,938,009—Lucas. The fumed silica fillers can be made by fuming processes including the vapor phase burning of silica tetrachloride or ethyl silicate, an example of such silica filler being the product commercially available to the trade known as Cab-O-Sil. Examples of other silica fillers that can be employed are described in U.S. Patents 2,541,137, 2,610,167, and 2,657,149. Such fillers can be slightly acidic or alkaline depending upon the method of manufacture, such as by aerosol-aerogel process.

In addition to including a filler and an organopolysiloxane fluid as shown in Formula 1, the nonporous heat unstable materials of the present invention also contain an acid treated, finely divided, absorbent material.

This absorbent material is required in addition to the filler, to serve as a carrier for various mineral acids. Among the absorbent materials that can be rendered acidic and employed in the practice of the present invention are for example, the various clays, finely divided carbon such as charcoal, graphite, diatomaceous earth, etc. The term "clay" as hereinafter employed refers to hydrated alumina silicate and includes for example kaolin, montmorillonite, illite, attapulgite, allophane, high alumina clays, etc. The composition of these materials can vary over a range of from about 15% to 70% silicon dioxide and higher, 2% to 85% aluminum oxide and varying amounts of ferric oxide, magnesium oxide, water, etc. Specific examples are glacial clay, china clay, ball clay, fire clay, loess, adobe, slip clay, bentonite, fuller's earth, bauxitic clays, etc.

Various acids can be employed, to render the absorbent material acidic. Acids that can be employed for example, are the various mineral acids such as sulfuric, hydrochloric, etc. Highly ionic halogenated organic acids such as trichloroacetic can also be employed if desired. Any well known procedure can be employed to treat the absorbent material to render it acidic such as for example, immersing the absorbent material in a mineral acid and thereafter drying the treated product. The "acidity" or the amount of acid "carried" by the absorbent material can be readily determined by conventional titration procedures. A convenient manner, for example, by which the acidity of the treated absorbent can be determined is to calculate its acid number, i.e. the mg. of KOH/gm. of treated product.

Experience has shown that in order to achieve desirable compatibility between the organopolysiloxane fluid, filler and absorbent material utilized in the production of the nonporous materials of the present invention it is desirable to utilize a stabilizer in proportions of .1 to 5 parts per 100 parts of the organopolysiloxane of Formula 1. Suitable stabilizers are for example, organo borates having the formula



and cyclic borate esters



where m is a whole number equal to from 0 to 3, y is an integer equal to from 3 to 5, R is as defined in Formula 1 above and X is a member selected from the class of hydrogen and R. Specific examples of the organo borates of Formula 2 are triphenyl borate, trimethylborate, etc. A specific example of a borate ester in the scope of Formula 3 is trimethoxy boroxine.

In addition, polyalkylene glycol such as polyethylene glycol, polypropylene glycol and mixtures thereof that are alkoxy chain-stopped or hydroxy chain-stopped and have molecular weights in the range of 500 to 5,000, can also be employed in the practice of the invention as a grease stabilizer. For example, a polypropylene glycol can be employed, butoxy chain-stopped on one side and hydroxy chain-stopped on the other, having a viscosity in the range of from about 270 centistokes to 38,000 centistokes at 0°F.

In addition to the aforementioned ingredients, standard corrosion inhibitors such as zinc naphthanate, iron octoate, etc. can be added in amounts up to 5% by weight of the grease.

In the preparation of the nonporous heat unstable materials of the present invention the organopolysiloxane fluid, filler, acid treated absorbent material, and optionally other materials such as a stabilizer, etc. are blended in accordance with well known grease making procedures such as by milling, etc. until a uniform mixture is obtained. If desired, the viscosity of the resulting grease can then be cut with an inert organic solvent such as odorless mineral spirits, toluene, xylene, etc.

In forming the grease mixture, the various components of the mixture can be mixed together in any desired manner. It is preferred, however, to avoid mixing the stabilizer such as polyalkylene glycol directly with the acid treated absorbent material in the absence of the other components of the mixture.

The properties of the nonporous heat unstable materials of the present invention such as grease consistency, the rate of transforming the grease into an easily removable powder, etc. can vary widely depending upon the proportion of organopolysiloxane to filler utilized, viscosities of the organopolysiloxane employed in forming the mixture, amount and type of stabilizer incorporated into the mixture, the acidity and amount of the acid absorbent material utilized, temperature employed in heating the substrate to effect the transformation of the grease, etc. Accordingly, the rate of transforming the grease on the substrate to a powder can vary from a few minutes or less to many hours or more depending upon the combination of any two or more of the above factors.

Referring further to FIG. 2, an electric hot plate is shown at 10 comprising an outer supporting ring 11 carrying spiral like supporting structures 12, supporting inner and outer helical electric heating units 20 and 30 respectively and adapted to be incorporated in a conventional electric range or other heating appliance. The inner heating unit 20 comprises an elongated tubular metal sheath 21 and the outer heating unit 30 comprises an elongated tubular metal sheath 31. The metal sheaths 21 and 31 can be flattened at the top surfaces thereof as respectively indicated at 21A and 31A so as to define a substan-

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tially coplanar heating platform adapted to support a cooking utensil, or the like.

Referring further to FIG. 2, the inner heating unit 20 further comprises an elongated electric resistance conductor 22 wound in helical form and arranged within the sheath 21 spaced therefrom, as well as a pair of elongated treated terminal structures 41 and 43; these treated terminal structures shown in greater detail in FIG. 3 are respectively disposed in the opposite ends of the sheath 21; the outer heating unit 30 is identical to the inner heating unit 20 except for the configuration thereof, as previously described having treated terminal structures 42 and 44 respectively.

Referring further to FIG. 3, there is shown an enlarged interior view of a treated terminal structure 41 which is identical to treated terminal structures 42, 43, and 44; there is shown terminal 23 disposed interiorly of the adjacent end of the sheath 21 and spaced therefrom and electrically connected to the adjacent end of the resistance conductor 22 and the outer end of terminal 23 can be disposed exteriorly of the adjacent end of the sheath 21. A dense mass 25 of heat conducting refractory and electrical-insulating material is arranged within the sheath 21 and embedding the resistance conductor 22 and the inner end of the terminal 23 and retaining the same in spaced relation with the sheath 21. The mass 25 can comprise a highly compacted body of crystalline magnesium oxide. There is also shown porous plug 26 secured in place at the end of the sheath 21 and embedding the adjacent intermediate portion of the terminal 23. The plug 26 effectively seals the adjacent end of the sheath 21 against the entry of foreign solid material therein and against the loss of any of the dense mass 25 of material therefrom, while accommodating control breathing of air there-through into and out of the adjacent end of the sheath 21 during the normal use of the hot plate 10.

In the arrangement of a hot plate 10 in FIG. 2, the treated terminal structures 41, 42, 43 and 44 are brought out below the supporting ring 11 and project outwardly therefrom so as to provide a lower alignment of the exterior end of the respective terminals such as illustrated by 23, so that the respective terminals may be readily received in the usual connecting jacket or block, not shown, when the nonporous material has been removed therefrom, extending to the associated control switch and source of electric power supplied, also not shown.

The four treated terminal structures of the hot plate 10, as exemplified in FIG. 3, which shows the end portion of the metal sheath 21, the exterior face of porous plug 26 and the exterior portion of terminal 23, are treated with the nonporous, heat unstable material of the present invention by either dipping the untreated terminal structures of the respective heating units into an organic solvent solution of the heat unstable nonporous material, or the nonporous material can be suitably applied onto the surface of the respective terminal structures in the form of a grease in accordance with well known procedures. The thus finished hot plate 10 can be placed into storage prior to incorporation thereof into an electric range or other heating appliance without danger of migration of moisture in the respective ends of the sheaths 21 and 31 of the respective heating units 20 and 30 through the respective pairs of porous ceramic plugs, such as shown in FIG. 3 at 26. In fact, the thus finished hot plate 10 may be stored substantially indefinitely, without any deterioration thereof by virtue of the accumulation of moisture in the sheaths 21 and 31 of the respective heating units 20 and 30 incorporated therein.

Subsequent to the manufacture and storage of the hot plate 10, the extreme outer ends of the respective treated terminal structures 41, 42, 43 and 44 are unsealed, and the hot plate can be incorporated into an electric range; the exposed terminals can be inserted into cooperating jack points for the purpose of making the required electrical connections. However, at that time, the main por-

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tions of the treated terminal structures 41, 42, 43 and 44 are still substantially sealed and resistant to the effects of atmospheric moisture; whereby the opposite ends of the sheaths 21 and 31 of the respective heating units 20 and 30 are still sealed against the entry of moisture thereinto following the incorporation of hot plate 10 into the electric range mentioned. When the electric range is put into service, the nonporous material on the treated structures 41 to 44, is transformed into a free-flowing powder as a result of the heat produced by the normal use of the hot plate. The transformation of the nonporous material of the treated terminal structures 41 to 44, inclusive, to a free-flowing porous dry powder is entirely automatic, resulting from the mere initial use of the hot plate 10; accordingly, no particular action is required upon the part of the person installing the electric range.

In order that those skilled in the art may be better able to practice the invention, the following examples are given by way of illustration and not by way of limitation. All parts are by weight.

EXAMPLE 1

A grease was formed by milling in a standard grease mill, a mixture consisting of 87 parts of a polydimethylsiloxane having a viscosity of 350 centipoises at 25° C., 10 parts of fumed silica treated with octamethylcyclotetrasiloxane, 0.2 part of a polypropylene glycol having a viscosity of about 200 centipoises at 25° C., and 3 parts of a hydrous silicate of alumina having an acid number of 30. This clay had been treated with sulphuric acid by immersing it in a 1 N sulphuric acid solution, recovering the treated product and drying it.

A 40% solution of the above heat unstable nonporous material was prepared in odorless mineral spirits. A 40% solution of petrolatum having a penetration of 258 at 25° C. was also prepared using the same solvent.

A steel strip was dipped into the 40% solution of the heat unstable nonporous material and allowed to air dry. A steel strip was similarly treated with the petrolatum solution. The treated strips were then immersed in water.

After 30 days the strips were removed from the water and were allowed to air dry. The strip treated with the heat unstable nonporous material of the present invention was placed in an oven at 150° C. After 15 minutes it was removed. The strip was covered with a light dust that was easily removed by blowing. After the powder was blown off the surface, the strip was found to be free of any trace of the heat unstable nonporous material. The strip treated with the hydrocarbon solution in accordance with the above procedure had to be thoroughly wiped with a dry cloth before it was free of petrolatum. Close examination, however, indicated that the traces of the petrolatum were still present on the surface of the strip. Finally, after immersing in odorless mineral spirits, followed by a second wiping with a dry cloth, the last traces of the hydrocarbon were removed from the metal surface. Those skilled in the art would know that had the surface of the metal strip been irregular or inaccessible to direct wiping, it would have been even more difficult to completely remove the hydrocarbon from the metal surface.

EXAMPLE 2

A heat unstable nonporous material was made in the form of a grease by mixing together in a grease mill 100 parts of the dimethylpolysiloxane fluid of Example 1, 10 parts of fumed silica, 10 parts of carbon-black having an acid number of 40 that had been treated with sulphuric acid, and 1 part of trimethoxy boroxine. The resulting grease was smeared onto the surface of a metal strip at a thickness equal to that of about $\frac{1}{64}$ inch. A metal strip was also treated with an equal thickness of the petrolatum utilized in Example 1. The treated strips were then immersed in water for thirty days in accordance with the above procedure. The metal strip treated

with the nonporous heat unstable material of Example 2 was placed in an oven at 150° C. for 15 minutes. The strip was removed and it was covered with an easily removable dry powder. A metal strip that had been similarly treated with petrolatum had to be scraped with a spatula, dipped in odorless mineral spirits, followed by wiping with a dry cloth before all traces of the hydrocarbon were removed. It was found moreover, that the strips treated with the heat unstable nonporous material did not corrode after this thirty day period. The strip that had been dip-coated with the petrolatum solution, however, formed rust spots after 24 hours.

EXAMPLE 3

The porous plugs of a heating unit of the sheathed conductor type as shown in FIG. 2 containing a magnesium oxide refractory were treated with the heat unstable nonporous material of Example 1 by end dipping the terminal structure of the unit in a 40% solution of the material in naphtha. The treated heating unit and a similar untreated heating unit were placed in storage under atmospheric conditions for a period of about seven months. The heating units were then tested for moisture within the sheath by measuring the leakage current with a milliammeter across the sheath and the line at half minute intervals. Both units were tested before the storage period and no perceptible current leakage was found in either unit.

Table I below shows the results obtained with the treated and untreated heating units after seven months in storage, where time is in minutes.

Table I

Time	Milliamps Leakage	
	Treated	Untreated
0.5	0.60	0.70
1	0.90	5.0
1.5	0.65	20.0
2	0.85	15.0
2.5	0.70	16.5
3	0.50	0.50
3.5	0.	2.0
4	0.35	40.0
4.5	0.30	49.0
5	0.10	50.0
6	<0.10	35.0
7	<0.10	11.0

Based on the results, those skilled in the art would know that the valuable utility of the nonporous heat unstable materials of the present invention is clearly established. The results obtained, for example, by immersing the treated metal strips in water for 30 days, indicate that the heat unstable nonporous materials of the present invention are comparable to petrolatum, a conventional material used by the art to treat metal substrates to render them resistant to corrosion over an extended period of time. The heat unstable nonporous materials of the present invention, however, can be readily removed from the treated substrate surface when desired by simply heating it on the substrate to a particular temperature depending upon the rate at which it is desired to remove it therefrom. The removal of the resulting powdery residue can thereafter be accomplished in a relatively easy manner. Table I shows that the nonporous heat unstable materials of the invention can be advantageously utilized in the treatment of heating units of the sheathed conductor type. It was found moreover, that the leakage current between the sheath and the line in the untreated heating unit exceeded 100 milliamps at various times during the test. As shown in Table I, the leakage current observed on the treated heating unit was below 1 milliamp

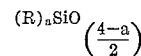
at all times. It was also found that after the test was complete, normal breathing was restored in the treated heating unit indicating the removal of the nonporous heat unstable material from the surface of the porous plug.

As a result of the above data, those skilled in the art would know that the nonporous heat unstable materials of the present invention can be employed in a variety of applications for the treatment of various substrates to render the substrates resistant to the effects of water or water vapor. The compositions of the present invention can be employed for example in treating various forms of hardware, including guns, tools, machine parts, etc. to render them corrosion resistant. In addition, various porous substrates such as ceramics, earthenware, various forms of masonry, etc. can also be treated in accordance with the practice of the invention.

While the foregoing examples have been limited to only a few of the very many variables within the scope of the present invention, it should be understood that the present invention is directed to a much broader class of heat unstable nonporous materials that can be applied to a variety of substrates. These heat unstable nonporous materials can be made by mixing the organopolysiloxane of Formula 1, a filler, an acid treated absorbent material, a stabilizer of Formulas 2, 3 or a polyalkylene glycol in accordance with the practice of the invention.

What I claim as new and desire to secure by Letters Patent of the United States is:

An electric heating unit comprising an elongated tubular metal sheath and elongated electrical resistance conductor arranged within said sheath and spaced therefrom, an elongated metal terminal disposed at one end of said sheath, the inner end portion of said terminal being disposed interiorly of one end of said sheath and spaced therefrom and electrically connected to the adjacent end of said resistance conductor and the outer end portion of said terminal being disposed exteriorly of said one end of said sheath, a dense mass of heat conducting and electrical insulating material arranged within said sheath and embedding both said resistance conductor and the inner end of said terminal and retaining the same in spaced relation with said sheath, a porous plug of ceramic material secured in place in one end of said sheath and embedding the adjacent intermediate portion of said terminal, said plug effectively sealing said one end of said sheath against the entry of foreign solid material thereinto and against the loss of any of said dense mass of material therefrom while accommodating control breathing of air therethrough into and out of said one end of sheath during the normal use of said unit, having the terminal structure of said heating unit consisting of the end portion of said sheath, the exterior face of said porous plug immediate to said end portion of said sheath, and said exterior end portion of said terminal, treated with a nonporous heat unstable composition comprising (A) 100 parts of an organopolysiloxane having the formula,



(B) 5 to 75 parts of a filler, and (C) 1 to 75 parts of an acid treated absorbent material having an acid number in the range of from 1 to 500, where R is a member selected from the class consisting of monovalent hydrocarbon radicals and halogenated monovalent hydrocarbon radicals and a is equal to from 1.95 to 2.2, inclusive.

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RICHARD M. WOOD, Primary Examiner.