

3,359,525

**ELECTRIC HEATING ELEMENT**

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This invention concerns electric heating elements which convert electrical energy into heat by means of electrical resistance, particularly electric heating elements comprising particulate carbon which are heat-stable at elevated temperatures.

Commercial heating elements comprising particulate carbon generally are not useful above 285° F. because of relatively rapid decomposition of the components, changed electrical resistance and loss of strength due to brittleness or softening. Heat resistant binders such as silica are used commercially to form dispersed carbon heating elements useful at elevated temperatures but these elements are inflexible, brittle, of low structural strength and are usually not useful at watt densities over 290 watts per square foot.

A strong heat-stable electric heating element which has a relatively long useful life at high temperatures has now been discovered. This element comprises (A) an electrically conductive heat generating unit comprising particulate carbon and having means for connecting said unit to an electric power source, and (B) an electrically insulating, heat conductive coating in adherent contact with the surfaces of said unit, said coating consisting essentially of an aromatic polyimide, aromatic polyamide, or aromatic polybenzimidazole.

These heat-stable heating elements have a relatively long useful life at temperatures up to about 600° F. and are useful as heat generating sheets in electric frying pans, warming trays, ovens, clothes dryers, toasters, water heaters, heating pads, electric blankets, space heaters, baseboard heaters, and wall panels; as heat generating strips for heating pipes and thawing ice; as heat generating rods, strands, ropes, filaments, etc. useful in most of the above applications and in other shapes and sizes required for special applications.

The phrase "heat stable" is used in this specification to designate an ability to resist degradation, brittleness, etc. at temperatures up to about 600° F. for a useful length of time. Useful life of heating elements of this invention when used in most of the above applications is determined by the ability of the heating elements to maintain their electrical resistance within 10% of initial resistance. At a surface temperature of 200° C. (392° F.), heating elements of this invention maintain electrical resistance within this limit for over 25,000 hours. At a surface temperature of 250° C. (482° F.) heating elements of this invention maintain electrical resistance within this limit for about 2,400 hours. Heat stability of heating elements of this invention at higher temperatures is shown in Table I.

Sheet, strip and small diameter rod configurations of the heating elements of this invention are both strong and flexible. Ease of assembly of the element into the end use product and versatility in design of end use products are especially important attributes of these flexible heating elements. Heating elements of this invention in two dimensional form such as sheets and strips are capable of converting electric power to heat at a rate of over 650 watts per square foot and can be produced with surface resistivities over a broad range, generally of about 30 to 5000 ohms per square as desired. Elements of this invention in two dimensional form having electrical surface resistivities of 50 to 100 ohms per square are most useful and have an excellent balance of strength and flexibility.

The phrase "two-dimensional" is used herein to designate forms of heating elements of this invention having relatively small thicknesses as compared with length and width and are therefore two-dimensional for practical purposes. Preferred essentially two dimensional embodiments of this invention are sheets and strips having thicknesses up to about 50 mils. The term "flexible" is used herein to designate the ability of two dimensional forms and small diameter rods of heating elements of this invention to be wound around mandrels of less than about 4 inches in diameter without cracking. Data showing the flexibility of a typical heating element of this invention is presented in Example 1.

Surface resistivity of conductive sheets and strips of elements of this invention is conveniently measured in ohms per square which is the resistance of a square element of any size. Surface resistivity in ohms per square multiplied by the thickness of the conductive material in centimeters is equal to the volume resistivity in ohm-centimeters of the conductive material which is a more widely known measure. Volume resistivity of conductive materials of this invention can be measured according to the procedure of ASTM D991-48-AT, Volume Resistivity of Electrically Conductive Rubber and Rubber-Like Materials. Heating elements of this invention having a total resistivity over an almost infinite range can be prepared by varying the dimensions of the heat generating unit.

Heating elements of this invention are also electrically insulated and are chemically inert to a wide variety of compounds and solvents.

Carbon in the form of pyrolytic graphite sheets and films is useful in making the (A) heat generating unit of this invention. Useful pyrolytic graphite sheets can be prepared by the process described by J. Pappis and S. Blum in the Journal of the American Ceramics Society 44: 592-7 (1961) in which graphite is deposited on a surface heated to about 2000° C. by decomposing gaseous hydrocarbons such as methane gas. The resulting sheet is composed of particulate carbon in randomly arranged graphite flake form and has structural stability and heat generating electrical properties.

A less expensive, more flexible and more easily manufactured heat generating unit useful in making the heating elements of this invention comprises particulate carbon dispersed in a heat-stable binder. The conductive carbon blacks used in the trade to impart anti-static properties to rubber and plastics are useful as particulate carbon for this type of heat generating unit. Oil furnace, gas furnace, and thermal blacks including acetylene black which have a carbon content of at least about 98% are preferred because heating elements having the best combination of electrical and structural properties result. Other forms of carbon such as lampblack, charcoal, coke and ordinary graphite can also be used. Dispersed carbon heating elements having the best conductivity and strength are prepared from carbon blacks having the highest electrical conductivity. Oil furnace carbon blacks are sometimes classified as conductive, super conductive, or extra conductive, all of which are useful in the heating elements of this invention.

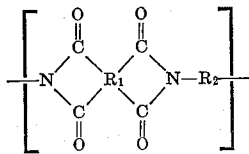
The quantity of carbon black in these dispersed carbon heat generating units is dependent on the level of conductivity and strength desired and generally ranges from about 10% to 75% of the total weight of binder and carbon. Best conductivity and strength are obtained with 10% to 45% by weight of extra-conductive carbon black on this basis.

Heat generating properties of dispersed particulate carbon can be obtained with an extremely broad range of carbon particle sizes. Carbon black having a size range from about 9 to about 470 millimicrons (based on electron micrograph measurements), and graphite flakes hav-

ing a maximum dimension of up to 430 microns, are readily available and useful in this invention, but heat generating properties can be obtained with carbon particles beyond these size ranges.

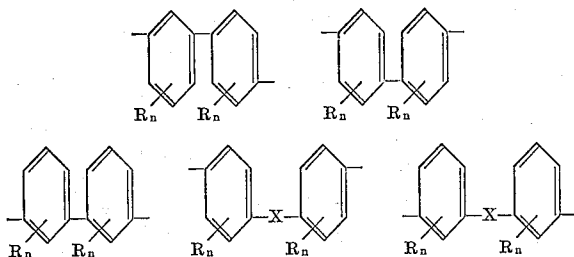
Typical heat-stable binders useful in these dispersed carbon heat generating units are the same aromatic polyimides, aromatic polyamides, or aromatic polybenzimidazoles useful as the (B) heat conductive coating of the heating elements of this invention, or other heat-stable polymers such as polyfluoroethylene, polyfluoropropylene, etc., or the inorganic binders such as silica, etc. Heating elements comprising binders of the aromatic polyimides, aromatic polyamides or aromatic polybenzimidazoles have the best flexibility, strength, and heat stability properties and are therefore preferred.

Aromatic polyimides useful as the heat resistant binders and the (B) insulating coating in this invention have the recurring structural formula

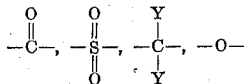


in which  $R_1$  is a tetravalent aromatic radical, the four carbonyl groups are attached to separate carbon atoms of the  $R_1$  radical and both carbonyl groups which are attached to a single nitrogen atom are attached to adjacent carbon atoms of the  $R_1$  radical, and  $R_2$  is a divalent aromatic radical. Typical aromatic polyimides useful in this invention are disclosed in copending United States patent application Edwards, Ser. No. 169,120, filed Jan. 26, 1962, now United States Patent No. 3,179,634, issued Apr. 20, 1965, and assigned to the assignee of the instant application, the disclosure of which is hereby incorporated into this specification by reference.

The term "aromatic" as used in this specification means a carbocyclic ring possessing resonance. Exemplary  $R_2$  divalent aromatic radicals have the following structural formulas



in which  $R$  is preferably a lower alkyl, lower alkoxy, or halogen group,  $n$  is a number from 0-4, inclusive, and  $X$  is preferably one of the groups of

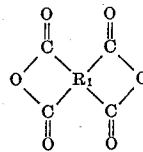


in which  $Y$  is a hydrogen or a lower alkyl group.  $X$  can also be a lower alkylene or lower alkylene diether group, a nitrogen atom, a silicon atom, a phosphorous atom, a dioxysilicon chain, a dioxyporphorus chain, or a combination of these, although these are somewhat less desirable.  $R$  can also be a lower carbalkoxy or other non-polymer forming group. All of these aromatic radicals are divalent and meta or para oriented, i.e., the unsatisfied bonds of the radicals (the "chain-extending bonds" when the radical is viewed in the repeating unit of the structural formula of the polymer) are meta or para oriented with respect to each other. One or more of the aromatic radicals can contain substituent groups as indicated and

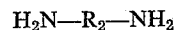
any aromatic ring can contain two or more of the same or different substituent groups. Preferable, however, are polymers in which the aromatic radicals are unsubstituted or contain only lower alkyl groups attached to any one ring. The term "non-polymer forming groups" refers to groups which do not form polymers during the polymerization reactions herein disclosed. The term "chain-extending bond" refers to any bond in the polymer which, if broken, would decrease the length of the polymer chain.

Tetravalent  $R_1$  aromatic radicals useful in this invention can be any of the above  $R_2$  aromatic radicals except for being tetravalent, but need not have the same configurations in any instance.

These polyimides can be prepared by reacting an aromatic dianhydride having the structural formula



in which  $R_1$  is a tetravalent aromatic radical and the carbonyl groups are attached to  $R_1$  in the manner disclosed above for the  $R_1$  radical of the polyimide structural unit with a diamine having the structural formula



in which  $R_2$  has the characteristics disclosed above for the  $R_2$  of the polyimide structural unit.

Typical aromatic dianhydrides useful in preparing the polyimides of this invention are:

- pyromellitic dianhydride;
- 3,3',4,4'-benzophenone tetracarboxylic dianhydride;
- trimellitic anhydride;
- 2,3,6,7-naphthalene-tetracarboxylic dianhydride;
- 3,3',4,4'-diphenyl tetracarboxylic dianhydride;
- 1,2,5,6-naphthalene tetracarboxylic dianhydride;
- 2,2',3,3'-diphenyl tetracarboxylic dianhydride;
- 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride;
- bis(3,4-dicarboxyphenyl)sulfone dianhydride;
- 3,4,9,10-perylene tetracarboxylic dianhydride;
- bis(3,4-dicarboxyphenyl)ether dianhydride;
- naphthalene-1,2,4,5-tetracarboxylic dianhydride;
- 1,4,5,8-naphthalene tetracarboxylic dianhydride;
- 2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic dianhydride;
- 2,7-dichloronaphthalene-1,4,5,8-tetracarboxylic dianhydride;
- 2,3,6,7-tetrachloronaphthalene-1,4,5,8-tetracarboxylic dianhydride;
- phenanthrene-1,8,9,10-tetracarboxylic dianhydride;
- 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride;
- 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride;
- bis(2,3-dicarboxyphenyl)methane dianhydride;
- bis(3,4-dicarboxyphenyl)methane dianhydride;
- bis(3,4-dicarboxyphenyl)sulfone dianhydride;
- benzene-1,2,3,4-tetracarboxylic dianhydride; etc.

The preferred dianhydride is pyromellitic dianhydride which is readily available and produces excellent polyimide binders and coatings.

- Preferred diamines for preparing the polyimides of this invention are 4,4'-diaminodiphenylether and 4,4'-diaminodiphenylmethane which produce the strongest polyimides. Other useful diamines are 4,4'-diaminodiphenyl ketone; metapenylene diamine; para-phenylene diamine; 4,4'-diaminodiphenyl propane; benzidine; 4,4'-diaminodiphenylsulfide; 4,4'-diaminodiphenylsulfone; 3,3'-diaminodiphenylsulfone; 2,6-diaminopyridine; bis-(4-aminophenyl)diethyl silane; bis-(4-aminophenyl) phosphine oxide; bis-(4-aminophenyl)-N-methylamine; 1,5-diaminonaphthalene; 3,3'-dimethyl-4,4'-diaminobiphenyl;

3,3'-dimethoxybenzidine; 2,4-bis(beta-amino-t-butyl)toluene; para-bis-(2-methyl-4-amino-pentyl)benzene; para-bis-(1,1-dimethyl-5-aminopentyl)benzene; m-xylylenediamine; p-xylylenediamine; and diamines disclosed as useful in the process described in Hill et al. U.S. Patent No. 3,006,899.

Polyimides prepared from dianhydrides having more than one aromatic nucleus and which are capable of stereo isomerism (for example 3,3',4,4'-benzophenone tetracarboxylic dianhydride) are useful in this invention. Aromatic polyisoimides such as are disclosed by pending United States patent application, Angelo, Ser. No. 325,479, filed Nov. 21, 1963, and assigned to the assignee of the instant application, can also be used in this invention and the disclosure of that application is hereby incorporated into this specification by reference.

The reaction for preparing the polyimides useful in this invention between the diamine and the dianhydride is usually conducted in two stages. First a polyamic acid is prepared by mixing the reactants in an inert organic solvent for at least one of the reactants and for the resulting polyamic acid under substantially anhydrous conditions and holding the mixture at a temperature below about 60° C. until at least 90% of the polyamic acid is formed. To form a heat generating unit, carbon particles are dispersed in the resulting polyamic acid solution, the mixture is cast or shaped into the form desired or coated onto a substrate, and the second stage of the reaction is carried out in a multi-zone oven which initially drives off most of the solvent at a relatively low temperature and then converts the polyamic acid to the polyimide at a higher temperature. Insulating coatings are formed by this same procedure except that carbon particles which would make the coating conductive are not added.

Preferred inert organic solvents for at least one of the reactants and for the resulting polyamic acid operable in this process are N,N-dimethylacetamide and N,N-dimethylformamide which are easily removed from the polyamic acid by evaporation. Other useful solvents include N,N-diethylformamide, N,N-diethylacetamide, N,N-dimethylmethoxyacetamide, N-methylcaprolactam, N-methylformamide, dimethylsulfoxide, N-methyl-2-pyrrolidone, tetramethylene urea, pyridine, dimethylsulfone, hexamethylphosphoramide tetramethylene sulfone, butyrolactone, N-acetyl-2-pyrrolidone, ketones such as methyl ethyl ketone, and nitro alkanes such as nitroethane, nitropropane, etc.

Solvent quantity should be at least 60% of the weight of the total polyamic acid solution for best results. For ease in dispersing carbon particles and in coating substrates, the solvent proportion is usually increased until the polyamic acid solution is about 10% to 20% by weight solids.

Inherent viscosities of the polyamic acids produced after the first stage of the above reaction can be about 0.1 to 5.0 as measured at 30° C. in a 0.5% by weight solution of the polyamic acid in N,N-dimethylacetamide. The best combination of strength and ease of preparation is obtained with polyamic acid inherent viscosities of 0.8 to 1.2 measured by this procedure. Inherent viscosities can be varied by varying the mole proportions of the reactants; higher viscosities are produced with equal molar amounts while the use of either reactant in large excess limits the extent of polymerization and results in a corresponding decrease in inherent viscosity. Reaction time and temperature can be varied and chain terminating agents such as phthalic anhydride can also be used to control inherent viscosity of these polyamic acids.

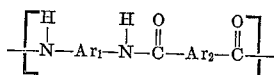
The second stage of the above reaction (conversion of the polyamic acid solution to a cured polyimide) requires heating to above about 150° C. (302° F.) to convert the polyamic acid to the polyimide. Heating is usually required for anywhere from a few minutes to several hours depending on the temperature and the diamine and dianhydride used. A preferred curing cycle involves a multi-zone oven in which the first zone is maintained at about

150° F. to 200° F. to drive off part of the solvent, the second zone is held at over 300° F. to drive off up to about 90% of the solvent, and the third zone is held at about 575° F. to 900° F. in which curing to the polyimide is accomplished. Dwell times in the first and second zones depend on the solvent used in the polyamic acid solutions; dwell time in the third zone is usually about 15 seconds to 30 minutes depending on temperature and reactivity of components.

Curing of the polyamic acid to polyimide can also be accomplished by adding a dehydrating agent such as acetic anhydride, propionic anhydride, butyric anhydride, etc.; by treatment with a carbodiimide such as dicyclohexylcarbodiimide which functions as a dehydrating and cyclizing agent; or by a combination of these methods. Polyimides having best heat stability result when curing is accomplished by the multi-zone heating procedure described above.

Increased heat stability of these polyimides can be obtained by crosslinking the basic polyimide structural units disclosed above. Crosslinking is accomplished by interpolymerizing a dianhydride having a ketone group attached to at least one aromatic ring carbon atom in the structural chain and crosslinking the structural chains through these ketone groups with excess diamine radicals. The preferred ketone-containing dianhydride useful for crosslinking is benzophenone tetracarboxylic dianhydride. Further details of crosslinking polyimides along with additional reactants are contained in copending patent applications, Chalmers Ser. No. 320,819 and Chalmers et al. Ser. No. 320,937, both filed on Nov. 1, 1963, and assigned to the assignee of the instant application, the disclosures of which are hereby incorporated into this specifications by reference.

The aromatic polyamides useable as the binder and as the insulating coating in the heating elements of this invention have the recurring structural formula



in which both Ar<sub>1</sub> and Ar<sub>2</sub> are aromatic as that term is defined above.

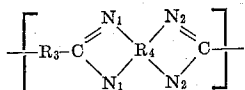
An interfacial polymerization process can be used to prepare these polyamides. This process consists of dissolving an aromatic diacid halide in an organic solvent and copolymerizing said halide with an aromatic diamine according to the procedure described in Hill et al., U.S. Patent No. 3,006,899. The diacid halides and diamines described by Hill et al. are also useful in forming binders and insulating coatings of the heating elements of this invention. Typical diacid halides include isophthaloyl chloride, terephthaloyl chloride; 4,4'-oxybenzoyl chloride; 4,4'-sulfonyldibenzoyl chloride; 4,4'-dibenzoyl chloride; 3,3'-dibenzoyl chloride; corresponding bromides and fluorides, etc.

The diamines previously disclosed for preparing polyimides useful in this invention as well as the diamines disclosed in U.S. Patent No. 3,006,899 can also be used for preparing these polyamides. Inherent viscosities of polyamides useful in this invention are usually about 0.1 to 5.0. Best strength and flexibility of the heating elements results from polyamides having inherent viscosities of 0.8 to 1.2.

The polyamides are dissolved in one of the solvents previously disclosed as useful for dissolving the polyamic acids of this invention and either mixed with conductive material to form the heat generating unit or coated on a heat generating unit by dipping, etc. to form the protective insulating coating and the solvent is then driven off in a single stage oven at not over 300° F. to form the heating elements of this invention.

Aromatic polybenzimidazoles useful as binder and as

the insulating coating in the heating elements of this invention have the recurring structural formula



in which both  $R_3$  and  $R_4$  are aromatic as that term is defined above, the four nitrogen atoms are attached to separate carbon atoms of the  $R_4$  radical with both nitrogen atoms represented by  $N_1$  attached to adjacent carbon atoms of the  $R_4$  aromatic radical and both nitrogen atoms represented by  $N_2$  also attached to adjacent carbon atoms of the  $R_4$  radical.

The powder polymerization process described by H. Vogel and C. S. Marvel in *Journal of Polymer Science*, 50: 511 (New York, 1961) can be used to prepare the polybenzimidazoles used in this invention. In this process the starting materials are mixed and heated in an inert atmosphere at about 250° C. to 290° C. until a solid cake or foam is formed. This solid cake or foam is powdered and held under a high vacuum for several hours at a temperature of about 400° C. to form a polymer having an inherent viscosity of about 0.1 to 5.0. The polymer is then dissolved in *N,N*-dimethylformamide or any of the solvents previously disclosed for use with the polyamic acids and coated onto the heat generating unit of this invention. Curing is accomplished in the multizone oven described above for the polyimide.

Starting materials for preparing these polybenzimidazoles are an aromatic tetraamine and a diester of an aromatic dicarboxylic acid. Typical tetraamines which can be used are 3,3',4,4'-tetraaminodiphenyl; 1,2,4,5-tetraaminobenzene; 4,4',3,3'-tetraaminobiphenylmethane; 4,4',3,3'-tetraaminobiphenyloxide; 1,2,5,6-tetraaminonaphthalene, etc.

Useful diesters include diphenyl isophthalate; diphenyl terephthalate; diphenyl-2,2'-biphenyl-dicarboxylate; diphenyl-4,4'-biphenylmethane-dicarboxylate; diphenyl-4,4'-diphenyloxide-dicarboxylate; diphenylnaphthalate; dimethylnaphthalate; diethylnaphthalate; dimethyl isophthalate; dimethyl terephthalate; dimethyl-4,4'-biphenylmethane; and other aliphatic or aromatic diesters of aromatic diacids. Diphenyl esters of aromatic diacids are preferred because of ease of processing and best heat stability of the final polybenzimidazole.

Polybenzimidazoles can also be prepared from aromatic diamino carboxylates such as phenyl-3,4-diaminobenzoate; methyl-3,4-diaminobenzoate; ethyl-3,4-diaminobenzoate; and other aliphatic and aromatic esters of 3,4-diaminobenzoic acid; phenyl-2,3-diaminobenzoate; methyl-2,3-diaminobenzoate; ethyl-2,3-diaminobenzoate; and other aliphatic and aromatic esters of 2,3-diaminobenzoic acid; phenyl-3,4-diaminonaphthalate; methyl-3,4-diaminonaphthalate; phenyl-5,6-diaminonaphthalate; phenyl-6,7-diaminonaphthalate; and other aliphatic and aromatic esters of diaminonaphthalenic acids.

Polymerization of these diamino carboxylates occurs between the carboxylate group of one molecule and the amino groups of another molecule to form a polybenzimidazole structural unit as disclosed above having  $R_3$  and  $R_4$  radicals the same. Polymerization is accomplished by heating under an inert atmosphere in a manner similar to that disclosed above for forming the polybenzimidazoles from tetraamino compounds and diesters.

Heat generating units useful in making heating elements of this invention having an especially desirable balance of strength, flexibility, and electrical properties can be prepared by coating a flexible electrically insulated heat-stable substrate with a conductive coating comprising carbon particles dispersed in a polyimide binder. Coating can be done by ordinary dipping followed by removal of excess by means of a doctor knife, or by brushing, roll-

ing, etc. Any composition capable of retaining its physical properties at the contemplated temperature of use for a useful length of time satisfies the heat stability requirements of these substrates. Useful substrates include glass cloth, asbestos paper and aromatic polyamide fibril paper such as the aromatic polyamide fibril paper disclosed in U.S. Patent No. 2,999,788, the disclosure of which is hereby incorporated into this specification. Substrates of a porous nature such as glass cloth can be impregnated with conductive material by dipping to produce a unit having two heat generating surfaces electrically interconnected through the pores of the substrate.

Heat generating units useful in making strong but inflexible heating elements of this invention can be made by applying these adherent conductive coatings to insulated substrates like wood, fiberboard, plaster, etc. Coating on both sides of microporous or substantially impermeable substrates generally are not conductively interconnected through the substrate and require electrical leads to both sides.

Heat generating units useful in making heating elements of this invention can also be cast or extruded or otherwise formed directly from the carbon-binder mixture to form self-supporting sheets, rods, etc. The tensile strength of the resulting unit varies with the amount of carbon present but is usually about 10,000 p.s.i. for units having the preferred resistance range disclosed above.

Means for connecting the heat generating units to an electrical power source are provided by attaching to the heat generating units of this invention strips of conductive paint such as silver paint along the edges of the units and then stapling or conductively bonding copper foils thereto, by conductively bonding copper, silver-copper alloy, copper-zirconium alloy, or aluminum, or other metallic foil directly to the heat generating unit, by weaving metallic foil such as copper foil, aluminum foil, etc. along the edges, etc. Connecting means such as foil leads can also be bonded to the heat generating units of this invention by preparing a mixture of conductive material in polyamic acid solution, coating this mixture onto metallic foil and heating for up to 60 minutes at 200° C. to drive off the solvent and partially cure the polyamic acid to make a coating having less than 15% polyimide formation (i.e., the coating still retains its solubility in *N,N*-dimethylacetamide). The foil can subsequently be bonded onto the heat generating unit by curing the remaining polyamic acid to polyimide. Crosslinked polyimides prepared in accordance with the disclosures of Chalmers, Ser. No. 320,819, and Chalmers et al., Ser. No. 320,937, which have previously been incorporated into this specification by reference produce the strongest bonds between these foil leads and heat generating units. A preferred bond of this type comprises metallic powders such as silver, aluminum, etc. in an aromatic polyimide binder. Aromatic polyamide and aromatic polybenzimidazole binders can also be used to form these connecting means. Electrical wiring is soldered to these foils to complete the electrical connection.

About 0.1 to 2 mils of (A) insulating coating is usually sufficient to produce elements having excellent insulation, long life, and good flexibility. Heating elements having (B) insulating coatings in adherent contact with the surfaces of the heat generating unit and the connecting means or the heat generating unit alone are both useful although the former are most useful because of better overall insulation and protection. Heat transfer coefficients of aromatic polyimide coatings generally are about  $72 \times 10^{-5}$  cal./cm.<sup>2</sup>/° C./cm. which is slightly higher than the heat transfer coefficients of aromatic polyamides and aromatic polybenzimidazoles. Aromatic polyimide coatings are preferred because they produce heating elements having the best heating efficiency, flexibility, and heat stability.

The following examples serve to further illustrate preparation of the heating elements of this invention.

## Example 1

A polyamic acid solution is prepared by stirring 74.53 parts by weight of 4,4'-diaminodiphenyl ether into 678.90 parts by weight of N,N'-dimethylacetamide and slowly adding 78.75 parts by weight pyromellitic dianhydride over a 30 minute period at a reaction temperature of about 25° C. Up to 0.82 part of pyromellitic dianhydride are then added over an additional 30 minute period. Stirring is continued throughout the reaction which is carried out under a nitrogen atmosphere. A viscous solution of about 18.5% solids by weight is produced.

A conductive coating solution is prepared by grinding 38.7 grams of an extra-conductive oil furnace carbon black (particle size of about 27 millimicrons) in 521.5 grams of N,N'-dimethylacetamide in a one quart ball mill using  $\frac{3}{8}$ " steel balls for 47 hours. To this dispersion, 388 grams of the above polyamic acid solution are added, the mill is rotated for an additional 5 minutes, and finally 139.8 grams of dimethylacetamide are added and the mill is rotated for another 5 minutes. The resulting dispersion is fine and smooth, has a solids content of 10.2% by weight, and a viscosity (Brookfield, 20 r.p.m.) of 20.5 poises.

Glass cloth having 60 warp threads per inch and 58 fill threads per inch, 4 mils thick, and weighing 3.17 ounces/yard is impregnated and coated with the dispersion on a vertical coating tower by running the cloth through the solution, then between opposed 60 mil wire-wound rolls to remove excess coating, and then through a three stage vertical oven having the entrance zone at 200° F., the intermediate zone at 300° F., and the final zone at 700° F. The coated cloth is cooled and the complete cycle, starting with the dipping step, is repeated three times to form a conductive carbon coating in a heat resistant polyimide binder on each side of the cloth, each coating being about 0.5 mil thick and conductively connected to each other through the pores of the cloth. The resulting heating unit has a uniform resistance of about 62 ohms/square and a coating weight of about 1.9 oz./square yard.

The edges of this heating unit are masked with tape and a coating of the polyamic acid prepared above but diluted to 12% solids by weight by adding additional solvent is applied by dipping the heating unit in a solution of the polyamic acid and removing excess solution by passing the coated element vertically through opposed 60 mil wire-wound rolls.

The polyamic acid coating is then converted to the polyimide by baking 15 minutes at 150° F., 1 minute at 200° F., 15 minutes at 300° F., and finally 2 minutes at 750° F. After the 150° F. bake the masking tape is removed and leads of a conductive silver paint are brushed on the uncoated edges. The final polyimide coating is about 0.15 mil thick on each side and the thickness of the complete heating element is 5.3 mils.

These polyimide-coated elements have a tensile strength of about 150 pounds/inch. Heat stability is tabulated in Table I where resistances of uncoated and polyimide coated elements are compared under various aging conditions. Heating elements produced in accordance with this example but having thicknesses of 5 mils, 10 mils, 20 mils, and 50 mils can be wound around  $\frac{1}{32}$ ",  $\frac{3}{8}$ ",  $\frac{7}{16}$ " and 2" mandrels respectively without cracking or other adverse effect.

## Example 2

Prior to application of the insulating coating in Example 1, conducting leads are applied to a  $3\frac{1}{2}$ " wide and 18" long sheet of the heating unit of Example 1 by applying a  $\frac{1}{4}$ " wide strip of silver paint along the 18 inch edges. Copper foil strips 2 mils thick and  $\frac{1}{4}$ " wide are stapled to the conducting leads at 3" intervals. The complete unit is then coated with polyamic acid by dipping the unit in a 13% solids by weight solution made by slow-

ly adding 246.6 grams of benzophenone tetracarboxylic dianhydride to 160 grams of 4,4'-diaminodiphenyl ether in 1772 milliliters of dimethylacetamide solvent over a period of 1.5 hours, followed by addition of 13 grams of benzophenone tetracarboxylic dianhydride over another 1.5 hour period, under nitrogen and at 25° C., to produce a 20.1% solids by weight solution and diluting this solution to 13% solids by weight with additional N,N'-dimethylacetamide solvent.

Excess coating solution is removed as in Example 1. The coating is baked for 15 minutes at 150° F., cooled, and a second coat is applied. The coating is then converted to the polyimide by baking 15 minutes at 200° F., 15 minutes at 300° F., and 1 minute at 750° F.

The resulting heating element is then cut into six elements 3" wide and 3" between leads which are aged along with uncoated heating structures at various temperatures to produce the results tabulated in Table I.

## Example 3

Asbestos paper 15 mils thick is coated with the conductive coating dispersion prepared according to Example 1 by dipping and removing excess as in Example 1. The coating is baked for 5 minutes at 300° F. followed by 5 minutes at 510° F. and a second coating is applied by repeating the procedure. The heating unit is then baked 1 minute at 750° F. to form a conductive carbon coating having a polyimide binder.

Conductive silver paint and copper foil strips are applied to both sides of this heating unit by the procedure used in Example 2. The complete structure is then dipped in a 13% solids solution prepared by diluting the polyamic acid solution of Example 1 with N,N'-dimethylacetamide. The excess is removed and the unit is baked 15 minutes at 150° F. A second coating is applied by repeating the procedure and the coatings are then converted to the polyimide by additional bakes of 15 minutes at 150° F., 15 minutes at 300° F., and 1 hour at 400° F. The resulting heating element is 16 mils thick, has a tensile strength of 15 pounds per inch of width and can be wound around a 1" mandrel without cracking.

Heating units of this example without the insulating polyimide coating and elements with the insulating polyimide coating in the form of  $2\frac{3}{8}$ " by 3" rectangles with  $2\frac{3}{8}$ " between leads were aged along with the heating elements produced by Examples 1 and 2 to produce the results tabulated in Table I.

## Example 4

An aromatic polyamide (nylon) fibrid paper, 7 mils thick, prepared according to Example 103 of U.S. Patent 2,999,788 is processed according to the procedure of Example 3 to form a coated heating element having the heat stability described in Table I. The element has a tensile strength of 75 pounds per inch of width and can be wound around a 1" mandrel without cracking.

## Example 5

A polyamic acid solution is prepared by stirring 160.0 grams of 4,4'-diaminodiphenyl ether into 1772 milliliters of N,N'-dimethylformamide and slowly adding 246.6 grams of benzophenone tetracarboxylic dianhydride over a 90 minute period at a reaction temperature of about 25° C. During a second 90 minute period, an additional 13 grams of benzophenone tetracarboxylic dianhydride are added. Stirring is continued throughout the reaction which is carried out under a nitrogen atmosphere. A solution having about 20.1% solids by weight is produced.

The procedure of Example 1 is then followed except that this polyamic acid solution is used to form both the polyimide binder and the polyimide topcoat in place of the polyamic acid solution and its corresponding polyimide of Example 1.

Heat stability of the resulting flexible, strong heating



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