

1

3,412,358

SELF-REGULATING HEATING ELEMENT

Friedrich Hummel, Innsbruck, Austria, and Richard Bauer, Heidelberg, Germany, assignors, by mesne assignments, to Gulton Industries, Inc., Metuchen, N.J., a corporation of New Jersey

No Drawing. Continuation-in-part of application Ser. No. 349,498, Mar. 4, 1964. This application Sept. 9, 1966, Ser. No. 578,133

13 Claims. (Cl. 338—7)

ABSTRACT OF THE DISCLOSURE

An electrical resistance material is described which comprises a resistive substance, an insulating material and a non-conductive plastic carrier; the insulating material has a specific electrical resistance and thermal coefficient of expansion, respectively greater than that of the resistive substance and the insulating material also has a specific electrical resistance greater than 10^5 ohm-cm. and at least 10^5 times that of the resistive substance. The electrical resistance material may be formed into foils, plates, films or other shaped articles to provide a space heater that is self-regulating, in that it does not have to be controlled by interrupting the current, but adjusts itself automatically to limit its temperature in individual areas thereof according to the heat load in such individual areas by automatically varying its local resistivity in such areas.

This application is a continuation-in-part of our earlier application, Ser. No. 349,498 filed Mar. 4, 1964 now abandoned.

This invention relates to electrical resistance materials and electrical heating sheets obtained therefrom. More particularly, the electrical resistance materials of the present invention comprise a resistive substance for conducting electrical current, an insulating material and a non-conductive carrier material.

Electrical resistors which contain graphite, carbon black, metal particles or other conductive material which are solidified with a binder are known in the art. However, if these resistors are used for heating purposes, they require, for the purpose of controlling the temperature or keeping the temperature constant, special devices such as thermostats or the like, and may also require protective devices to prevent an overload of the resistors. Further, resistors containing graphite or carbon have a substantial disadvantage due to their negative temperature coefficient. Thus when graphite or carbon resistors are heated increased current flows causing the resistors to become still hotter. This is due to the fact that as graphite or other carbon materials become heated their electrical resistance is lowered resulting in an increased current flow. Should there occur a reduction of the dissipation of heat from graphite-containing resistors, such as due to blocking radiation or otherwise preventing heat dissipation from such resistors, there is a substantial danger that the resistors will become hotter and progressively heated to the point of melting or burning. This will result not only in the destruction of the resistors, but may result in starting a fire. Hence, because of this negative temperature coefficient of carbon, it was not heretofore considered possible to use carbon-containing resistors of large capacity and especially for heating purposes.

Even in the case of resistors having metallic particles and a positive temperature coefficient of resistance, when heat dissipation is impaired, the increase in electrical resistance caused by the resultant heating is frequently not sufficient to avoid burning or fusing of such resistors.

Accordingly, it is an object of the present invention to

2

provide an electrical resistance material for heating purposes having a positive temperature coefficient which is greater than the temperature coefficient of the resistive substance contained in the electrical resistance material.

It is a further object of the present invention to provide an electrical heating element in the form of sheets e.g. foils, plates, films or the like.

It is still a further object of the invention to provide an electrical heating element, which does not require the heating element to be controlled by interrupting the current supply, as by means of thermostat or the like, but which adjusts itself automatically to limit its temperature in individual areas thereof according to the heat load in such individual areas, by automatically varying its local resistivity in such areas.

Yet another object of the present invention is to provide an electrical heating element wherein the resistance value in individual areas thereof is automatically increased as the dissipation of heat from those areas is decreased.

An additional object of the present invention is to provide a self-regulating electrical heating element which contains a resistive substance having a negative temperature coefficient.

Other objects and advantages of the present invention will become apparent from the following description.

In accordance with the present invention an electrical resistance material is provided which consists of the following essential components: (1) one or more resistive substances, (2) an insulating material; and (3) a non-conductive carrier material. In addition if desired, a reinforcement material may also be employed, which imparts to the electrical heating element external strength and stability with respect to mechanical forces.

It has been found that for the three essential components of the electrical resistance material, the following characteristics are important.

The resistive substance may be one having either a negative or positive temperature coefficient. Any materials with relatively good electrical conductivity which do not vary substantially upon change in air or moisture conditions or temperatures of up to about 300° C. are suitable. Non-limiting examples of resistive substances include carbon materials such as graphite, carbon black and lamp black; metal particles such as a metal powder of copper, iron, zinc, magnesium, etc.; heating wire alloys such as constantan and Nickeline and alloys such as Monel metal and Phosphor-bronze. If desired the resistive material may be a mixture of two or more resistive substances.

The insulating material employed in the present invention must have the characteristic that its specific electrical resistance and its coefficient of thermal expansion are both higher than the specific electrical resistance and the coefficient of thermal expansion of the resistive substance. The insulating material should have a specific electrical resistance greater than 10^5 ohm cm. Preferably, the insulating material has a specific electrical resistance of at least 10^5 times that of the resistive substance. The selection of insulating materials having these characteristics is essential in order to obtain an electrical resistance material having a resultant positive temperature coefficient which is greater than the temperature coefficient of the resistive substance. The selection of insulating materials is not critical so long as they meet the criteria mentioned above. The insulating materials which may be employed may be either liquid, solid or tacky materials. Liquid insulating materials which have been found particularly suitable are electrical insulating oils including the following:

(a) Lubricating oils (a distillation product from crude oil, tar, or lignite products which are used for motors and

machines). These oils preferably have a flame point of at least 200° C. Examples of such lubricating oils are "Mobil Vactra Oil No. 2, No. 3 and No. 4." These oils have a viscosity (centistoke) ranging from 37 to 99 at 50° C.

(b) Transformer oils (a chemically neutral mineral oil which is normally used as insulating filling for electrical transformers) such as for example "Univolt" oils.

(c) Silicone oils (linear-polymeric methyl silicone) e.g. methyl polysiloxane. Preferably the silicone oil has a viscosity of 100° F. ranging from 100 to 20,000 centistokes.

(d) Paraffin oils (a petroleum fraction).

Also suitable as insulating materials are soft pasty materials such as natural or synthetic waxes and lubricating greases. Examples of waxes which may be employed include beeswax, carnaubawax, "Castorwax," etc. Also suitable are petroleum waxes, such as paraffin hydrocarbons and microcrystalline waxes. The lubricating greases which may be employed include homogeneous mixtures of a motor lubricating oil with a metal soap usually obtained from the reaction of a metal hydroxide with a fatty acid. An example of such a metal soap is the lithium soap of 12-hydroxy stearic acid.

The insulating material may also be a solid substance which is easily meltable below the operating temperature of the electrical resistance material. An example of such a material is acetyl cellulose sold under the trademark "Cellon." It is also possible to use as the insulating material a solid material such as glass powder, finely divided bentonite, flint, etc.

The non-conductive carrier material, which is a plastic, may be selected from any one of the following class of materials:

(a) Polymers of alpha-olefins such as polyethylene, polypropylene, polyisobutylene, polystyrene, etc.

(b) Copolymers obtained by polymerizing two different alpha-olefins such as defined in (a).

(c) Halogenated vinyl polymers and copolymers, such as, for example, polyvinyl chloride, copolymers of vinyl chloride with vinyl acetate, styrene, propylene, etc.

(d) Polyesters, preferably unsaturated polyesters. These polyesters are plastic materials derived from the polymerization of esters in the presence of a peroxide which acts as a hardener. These esters are obtained by reacting an unsaturated dicarboxylic acid with a divalent alcohol. Examples of suitable polyesters are "Palatal P5" and "Palatal P6."

(e) Polyamides, e.g. "Versamid." (A condensation product of dimerized and trimerized unsaturated fatty acids, in particular linolic acid with polyamines.)

(f) Other materials such as polyacrylonitrile, polymeric vinyl amines and phenol waxes may also be employed as the non-conductive carrier material.

The reinforcement material may include paper, glass fiber fabric, plastic material, textile fiber fabric (including fabrics of synthetic fibers) or the like.

There is a relatively wide range of proportions in which the resistive substance, insulating material and non-conductive carrier material may be employed. When the insulating material is in the liquid or pasty state at room temperature, preferably that material is present in the final electrical resistance material in an amount between about 7 and 25% by weight of the resistive substance. Furthermore, when the insulating material is in the liquid or pasty state, it has preferably a thermal coefficient of expansion of at least ten times that of the resistive substance and a specific electrical resistance of at least 10^5 times that of the resistive substance. When the insulating material is a solid, it is preferably employed in an amount between 50 and 100 percent by weight of the resistive substance. The reason for employing a greater quantity of the insulating material when solid than when liquid or pasty is that the solid material does not have a thermal coefficient of expansion as great as that of the liquid or

pasty material, and this factor is compensated for by employing more of the solid insulating material in the formulation.

The electrical resistance material of the present invention may be prepared in the following manner. The resistive substance which preferably exists in finely divided form (e.g. a granular powder) is admixed with the insulating material. The granular powder particles preferably have a particle size between about 0.002 mm. and 0.01 mm. It is also possible to employ a granular powder having particles present of up to 0.1 mm. in size but such particles should not be present in excess of about 10% of the total mixture of the resistive substance and insulating material. Thorough mixing is desirable in order to obtain a homogeneous composition comprising the resistive substance and the insulating material. In the resulting homogeneous composition the individual grains of the resistive substance are largely surrounded or enveloped by the particles of the insulating material. If the insulating material is a liquid, a doughy substance is produced by the mixing of the resistive substance with this material so that the individual particles of the resistive substance are enveloped by the insulating material. If the resistive substance employed is a carbon such as graphite, and is mixed with a liquid insulating material, the liquid material penetrates into the individual porous conducting particles of the graphite. The envelopment or surrounding of the individual particles of the resistive substance by the insulating material is not complete, as otherwise no flow of electric current would be possible. Therefore, in the mixture obtained by combining the resistive substance with the insulating material there is obtained a partial contact of the individual resistive particles of the resistive substance with one another throughout the mixture. This partial contact is sufficient for the current to flow through the individual particles.

The mixing of the resistive substance with the insulating material may be carried out in a fluid mixer, a drum mixer or Pfeleiderer (heatable) mixer. The time required for obtaining a homogeneous mixture is obviously dependent on the amount of material being admixed and the nature of the materials. The temperature employed during the mixing of the resistive substance and the insulating material depends on the particular insulating material being employed. The mixing temperature should be sufficiently high to melt the insulating material in order to obtain a homogeneous mixture.

The homogeneous mixture obtained by combining the resistive substance with the insulating material is then embedded in a non-conductive plastic carrier material. This carrier acts primarily as a mechanical support for the resulting electrical resistance material. The introduction of the mixture consisting of the resistive substance and the insulating material into the carrier material is achieved according to well known techniques such as by means of a ball mill or a heated mixing arrangement such as a mixing roller, a roll stand or the like. The technique employed for embedding the homogeneous mixture of resistive substance and insulating material in a non-conductive carrier is determined by the nature of the carrier and the homogeneous mixture. For example, if a solid plastic is used as the carrier, that carrier may be ground into fine particles. After grinding, the plastic particles are mixed at room temperature with the homogeneous mixture (resistive substance plus insulating material) in a ball-mill or the like. After this premixing, the mixture is rendered homogeneous by subjecting the mixture to heat treatment at a temperature of about 20 to 50° C. above the melting temperature of the plastic carrier. This heat treatment may be carried out by using heated mixing rollers which knead the mixture and renders it homogeneous. A Pfeleiderer kneader is suitable for this purpose. The resulting product is a granulate which may then be extruded, calendered, or otherwise suitably formed into sheets such as foils, plates, films, or the like.

The mixing of the non-conductive plastic carrier with the homogeneous mixture of resistive substance and insulating material may also be performed by dissolving the plastic in a solvent having dissolving power for the particular plastic being used but inert relative to the homogeneous mixture. Among solvents which are suitable for this purpose are xylene, toluene, benzene, cyclohexane, heptane, dioxane, chloroform, acetone, methylethylketone, tetrahydrofuran and like solvents. The dissolved plastic is added to the homogeneous mixture and homogenized in a fast vibrating ball mill or the like.

After the non-conductive plastic carrier material has been mixed with the homogeneous mixture consisting of the resistive substance and insulating material, the resulting electrical resistance material is shaped into a sheet in the form of foils, plates, or other shapes. Such sheets have excellent heating properties and may be placed on walls, floors, etc. to heat a room or used in electric blankets, food warming equipment, and the like.

The shaping is carried out according to techniques well known in the art. For example, an extruder, calender, or a plate press may be employed to shape the electrical resistance material of the present invention.

The forming of the electrical resistance material into sheets is to some extent dependent on the nature of the non-conductive carrier material. For example, when using a thermoplastic polyester as the carrier material it is preferable to use a double-recoil extruder with a nozzle having a broad slit. A suitable quantity of homogeneous granulate comprising the resistive substance, insulating material and carrier material is fed into the extruder. The heating of the extruder from the melting zone to the compression zone takes place with a substantially constant increase in temperature. The temperature in the melting zone is preferably about 20° C. above the melting point of the polyester and the nozzle temperature may be up to 100° C. above the melting point. The extrusion is carried out slowly in order to obtain flat sheets of uniform thickness. A suitable extrusion rate is between three and six meters per minute at a gauge-pressure of about 180 kg./cm.². The extrusion procedure is best suited for obtaining sheets having a thickness greater than 0.3 mm. and up to about 2 mm. To obtain sheets having a uniform thickness less than 0.3 mm., a calendering procedure of forming the electrical resistance material gives good results.

In forming sheets by calendering it is desirable to have the melting rollers at a temperature of between 60° C. and 120° C. above the melting point of the thermoplastic polyester. The rotary speed of the melting roller, extracting roller, pressing roller and cooling roller must be regulated so that the sheets will be stretched as little as possible during their formation. Stretching is to be avoided in order to obtain sheets having a more uniform electrical transmission. The minimum desirable thickness of calendered sheets is about 0.1 mm. and the maximum about 1 mm.

A press plate may also be employed to obtain heating sheets consisting of the electrical resistance material of the present invention. Heating sheets may be formed having a thickness ranging from about 1 mm. to 5 mm.

If an especially strong heating sheet, highly stable to mechanical forces, is desired, the electrical resistance material may be laminated onto a firm or flexible reinforcement material in the form of a layer having a thickness of several mm. The lamination of the electrical resistance material on the reinforcement material may be effected with the use of a suitable organic solvent, e.g., xylene, toluene, benzene, cyclohexane, etc. and/or by the application of heat. Alternatively, the reinforcement material may be impregnated with the electrical resistance material. Even without the use of a reinforcement material, the electrical resistance material can be shaped into freely supporting large area flat sheets which are externally firm and stable.

The electrical resistance material of the present invention, in the form of flat sheets such as foils, films, plates, or the like has been found to give excellent performance in the range of about 30 to 500 watts per square meter.

The following examples are illustrative of electrical resistance materials according to the present invention, and heating sheets made therefrom. In each example the important physical properties of the three essential components, i.e. resistive substance, insulating material and non-conductive carrier material, are given.

EXAMPLE 1

	Temperature Coefficient (deg. ⁻¹)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. ⁻¹)
Graphite and lamp-black 1.	-5×10^{-4}	8×10^2	0.24×10^{-4}
Lubricating oil		10^{16}	7.3×10^{-4}
Polystyrene		$>10^4$	2.0×10^{-4}

¹ A precise value of temperature coefficient of electrical resistance for carbon black cannot be given because this material is not uniform due to occluded air, and precise measurements of its technical properties therefore cannot be made. The temperature coefficient of the electrical resistance of carbon black, however, is somewhat of the order of magnitude of that of graphite.

The resistive materials, namely 3500 grams of graphite powder ("AF special" having a pure carbon content of 96% and an average particle size of 0.04 mm.—available from Kropmuhl) and 650 grams of lamp black ("Corax L" having a pure carbon content of 98%—available from Degussa Company) are mixed in a Pfeleiderer kneader at a temperature of about 50° C. with 350 grams of a lubricating oil (Mobil Vactra 2—available from the Mobil Oil Co.). This mixing was carried out until a homogeneous pasty mixture was obtained. This pasty mixture was then mixed for 24 hours at room temperature in a drum mill with 9620 grams of polystyrene ("475KH"—available from Badische Anilin-Soda Fabrik Co.) dissolved in xylene. This mixture is the electrical resistance material, which was coated onto a reinforcement material of paper, the coating having a thickness of about 0.002 mm. so that a thin sheet is formed having a thickness of about 0.3 mm. A piece of this sheet, 50 x 10 cm., was air dried at room temperature.

This finished heating sheet is provided with respective electrodes for connection to an electric circuit. Suitable electrodes may comprise strips of conductive foil along opposite edges of the heating sheet. The conductive foil may be secured to the heating sheet by a suitable conductive adhesive.

The heating sheet was connected to a voltage source of 220 volts. The heating sheet heats up to a maximum temperature of about 44° C. at a surrounding ambient temperature of 10° C. This maximum temperature of 44° C. substantially exceeded even when the surface of the heating sheet is blocked in a particular region or even if the entire area of the heating sheet is blocked to prevent dissipation of the evolved heat.

EXAMPLE 2

	Temperature Coefficient (deg. ⁻¹)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. ⁻¹)
Graphite and lamp black	-5.0×10^{-4}	8×10^2	0.24×10^{-4}
Lubricating oil		10^{16}	7.3×10^{-4}
Polypropylene		$>10^{13}$	3.4×10^{-4}

The resistive materials, namely 3500 grams of graphite powder ("AF special" having a pure carbon content of 96%) and 1500 grams of lamp black ("Corax L") are mixed in a fluid mixer (3000 rotations per minute at 60° C.) with 500 grams of a lubricating oil (Mobil Vactra 2). This mixing was continued until a homogeneous paste

was obtained (about 60 minutes). To this mixture there was added in the fluid mixer 6000 grams of finely ground polypropylene ("Hostalen PPH"—available from Farbwerke Höchst). After sufficient mixing a homogeneous granulate was obtained. This granulate was introduced into a double recoil extruder having a nozzle of 40 cm. regulated to a slit size of 0.4 mm. The temperature progressively increased in the extruder from 170° C. in the melting zone to 220° C. in the compression zone of the recoil.

A piece of this extruded heating sheet, 50 x 10 cm., having a thickness of 0.4 mm., was connected to a voltage source of 220 volts in the same manner as described in Example 1. The sheet heated up to a maximum operating

The resulting homogeneous pasty mixture is placed into a press-frame. The press is heated to 110° C. in order to achieve hardening of the polyester carrier. The initial pressure in the press is between 5 and 10 kg./cm.² and after about 3 minutes it is increased to 50 kg./cm.². About 30 minutes are required to harden the electrical resistance material. The heating sheets formed are tempered overnight at 80° C. In order to obtain a defined heating sheet thickness, the sheets are subsequently passed through a roller-grinding machine and ground to the desired layer-thickness.

Heating sheets were also prepared according to the present invention having the components set forth in the following examples.

EXAMPLE 4

	Temperature Coefficient (deg. -1)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. -1)
2,500 g. graphite (Same as in Example 1) ..	-5.0×10 ⁻⁴	8×10 ⁻²	0.24×10 ⁻⁴
600 g. transformer oil (available from Mobil Oil Co.) ..		>10 ¹⁴	6×10 ⁻⁴ -8×10 ⁻⁴
5,800 g. Versamid (available from Schering AG) ..		>10 ¹²	3.5×10 ⁻⁴

temperature of 40° C. at a surrounding ambient temperature of 10° C.

EXAMPLE 3

	Temperature Coefficient (deg. -1)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. -1)
Graphite and lamp black ..	-5.0×10 ⁻⁴	8×10 ²	0.24×10 ⁻⁴
Lubricating oil ..		10 ¹⁵	7.3×10 ⁻⁴
Polyester ..		>10 ¹²	3.0×10 ⁻⁴

The homogeneous mixture of the above resistive substance, insulating material and carrier were coated onto a reinforcement material of paper, the coating having a thickness of .002 mm. A piece of this heating sheet, 50 x 10 cm., was connected to a voltage source of 220 volts in the same manner as described in Example 1. The sheet heated up to a maximum operating temperature of 24° C. based on a surrounding ambient temperature of 10° C.

EXAMPLE 5

	Temperature Coefficient (deg. -1)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. -1)
3,300 g. graphite (Same as in Example 1) ..	-5×10 ⁻⁴	8×10 ⁻²	0.24×10 ⁻⁴
and 940 g. iron powder (carbonyl-iron powder available from Badische Anilin-Soda Fabrik) ..	6.4×10 ⁻³	1086×10 ⁻⁴	0.38×10 ⁻⁴
520 g. beeswax ..		20×10 ⁻¹⁴	4.5×10 ⁻⁴
5,800 g. "Versamid" ..		>10 ¹²	3.5×10 ⁻⁴

3500 grams of graphite powder ("AF Special") and 1500 grams of lamp black ("Corax L") were mixed in a fluid mixer at 60° C. with 500 grams of lubricating oil (Mobil Vactra 2). This mixing was carried out for about 60 minutes until a homogeneous mixture resulted. This mixture was combined with 6000 grams of a polyester varnish ("Palatal P5" available from Badische Anilin-Soda-Fabrik) and 200 grams of benzoylperoxide as a hardener, and stirred. This mixture was then fed into an apparatus known as a "three-roller" in order to obtain

The homogeneous mixture of the above resistive substance, insulating material and carrier were coated onto a reinforcement material of paper, the coating having a thickness of .002 mm. A piece of this heating sheet, 50 x 10 cm., was connected to a voltage source of 220 volts in the same manner as described in Example 1. The sheet heated up to a maximum operating temperature of 16° C. based on a surrounding ambient temperature of 10° C.

EXAMPLE 6

	Temperature Coefficient (deg. -1)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. -1)
3,300 g. graphite (Same as in Example 1) ..	-5×10 ⁻⁴	8×10 ²	0.24×10 ⁻⁴
and 650 g. lamp black (Same as in Example 1) ..		20×10 ¹⁴	4.4×10 ⁻⁴
450 g. beeswax ..			
9,620 g. polystyrene ("475 KH" available from Badische Anilin-Soda-Fabrik) ..		>10 ¹⁴	2.0×10 ⁻⁴

a homogeneous pasty mixture. The friction rollers in this apparatus are kept cooled with water in order to keep the loss of solvent from the varnish as low as possible. This avoids adherence of the carrier material to the friction rollers which generate local temperature increases and if not cooled would result in evaporation of the solvent.

The homogeneous mixture of the above resistive substance, insulating material and carrier were formed into a heating sheet of the same size and thickness as in Example 1 which was connected to a voltage source of 220 volts in the same manner as described in Example 1. This sheet heated up to a maximum operating temperature of 27° C. based on a surrounding ambient temperature of 10° C.

EXAMPLE 7

	Temperature Coefficient (deg. $^{-1}$)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. $^{-1}$)
3,300 g. graphite (Same as in Example 1) and 940 g. iron powder (carbonyl-iron powder available from Badische Anilin-Soda Fabrik).....	-5×10^{-4}	8×10^2	0.24×10^{-4}
525 g. methyl silicone oil (M1000—available from Wacker-Chemie).....	6.4×10^{-3}	$.086 \times 10^{-4}$	0.39×10^{-4}
5,800 g. "Versamid".....		10^{15}	16×10^{-4} 9.6×10^{-4} 3.5×10^{-4}

The homogeneous mixture of the above resistive substance, insulating material and carrier were formed into a heating sheet of the same size and thickness as in Example 1 which was connected to a voltage source of 220 volts. This sheet heated up to a maximum operating

15 The homogeneous mixture of the above resistive substance, insulating material and carrier were formed into a heating sheet of the same size and thickness as in Example 1 which was connected to a voltage source of 220 volts. This sheet heated up to a maximum operating temperature of 25° C. based on a surrounding ambient temperature of 10° C.

EXAMPLE 10

	Temperature Coefficient (deg. $^{-1}$)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. $^{-1}$)
4,000 g. iron powder (Same as in Example 7).....	6.4×10^{-3}	$.086 \times 10^{-4}$	0.38×10^{-4}
520 g. beeswax.....		20×10^{14}	4.5×10^{-4}
5,800 g. polyester ("Leguval E90"—available from Farbenfabriken Bayer).....		10^{12}	3.0×10^{-4}

temperature of 33° C. based on a surrounding ambient temperature of 10° C.

The homogeneous mixture of the above resistive substance, insulating material and carrier were formed into

EXAMPLE 8

	Temperature Coefficient (deg. $^{-1}$)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. $^{-1}$)
3,500 g. graphite (Same as in Example 1) and 650 g. lamp black (Same as in Example 1).....	-5×10^{-4}	8×10^2	0.24×10^{-4}
600 g. methyl silicone oil (Same as in Example 7).....		10^{15}	16×10^{-4} — 9.6×10^{-4}
9,620 g. polyvinyl chloride (Vinnol P100—available from Wacker-Chemie).....		10^{13}	0.5×10^{-4} — 0.6×10^{-4}

The homogeneous mixture of the above resistive substance, insulating material and carrier were formed into a heating sheet of the same size and thickness as in Example 1 which was connected to a voltage source of 220 volts. This sheet heated up to a maximum operating tem-

50 a heating sheet of the same size and thickness as in Example 1 which was connected to a voltage source of 220 volts. This sheet heated up to a maximum operating temperature of 27° C. based on a surrounding ambient temperature of 10° C.

EXAMPLE 11

	Temperature Coefficient (deg. $^{-1}$)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. $^{-1}$)
3,500 g. graphite (Same as in Example 1) and 1,500 g. lamp black (Same as in Example 1).....	-5.0×10^{-4}	8×10^2	0.24×10^{-4}
500 g. lubricating oil (Same as in Example 1).....		10^{16}	7.3×10^{-4}
5,000 g. polypropylene (Same as in Example 2).....		10^{13}	3.4×10^{-4}

perature of 33° C. based on a surrounding ambient temperature of 10° C.

The homogeneous mixture of the above resistive substance, insulating material and carrier were calendered

EXAMPLE 9

	Temperature Coefficient (deg. $^{-1}$)	Specific Resistance (ohm cm.)	Coefficient of Thermal Expansion (deg. $^{-1}$)
3,300 g. graphite (Same as in Example 1) and 650 g. lamp black (Same as in Example 1).....	-5.0×10^{-4}	8×10^2	0.24×10^{-4}
400 g. acetyl cellulose (Cellon available from Dynamit Nobel AG).....		2×10^{10}	3.27×10^{-4}
7,500 g. polyisobutylene (Oppanol B—available from Badische Anilin-Soda-Fabrik).....		10^{13}	3.4×10^{-4}

into a heating sheet, without any reinforcing material, having a thickness of 0.15 mm. A piece of this heating sheet, 1m. x 1 m., exhibits an electrical resistance of 220 ohms. This sheet allows for a voltage of 220 volts, a current of one amp. which corresponds to a heating performance of 220 watts.

While it is not desired to be limited to any theories of operation, it is believed that the following explanation of how the electrical resistance material of the present invention provides a self-regulating heating element will aid in understanding and appreciating the present invention. As previously explained, the electrical resistance material must have a positive temperature coefficient which is greater than the temperature coefficient of the resistive substance contained in that material. In order to achieve this result, it is necessary to use an insulating material in the electrical resistance material and that insulating material must have a higher specific electrical resistance and a greater coefficient of thermal expansion than the resistive substance. On heating of a sheet such as a foil plate, film or the like shaped from the electrical resistance material of the present invention, the insulating material which has a greater coefficient of thermal expansion than the resistive substance, will always expand more than the resistive substance whose individual particles are enveloped by the insulating material. As previously explained, the resistive particles in the electrical resistance material are in a more or less efficient electrical contact with each other which permits the flow of current. If the temperature of the electrical resistance material is increased, the insulating material will expand more than the resistive substance and as a consequence of such thermal expansion, the individual resistive particles become more and more removed from each other, thereby reducing the number of contact points between such particles so that the transition resistance between the particles increases according to the degree of temperature rise. Therefore, the total resistance of the electrical resistance material is not solely determined by the inherent resistance of the particles of the resistive substance (with a negative temperature coefficient) but by a combination of that resistance and the transition or contact resistance between the individual particles of the resistive substance, which has a greater coefficient of positive character, producing an overall self-regulating effect.

Accordingly, if the electrical resistance material of the present invention is heated by electrical current and a corresponding temperature rise of that material is produced, the total resistance of that material increases due to the increase of the transition resistance.

If the insulating mass is a solid substance (e.g. glass powder), then, upon heating the electrical resistance material, the contact between the individual particles of the resistive substance is diminished by the expansion of the glass powder particles due to the fact that those particles are pushed away from each other. Hence, as these particles push away from each other and have less contact points, it becomes more difficult for the current to flow, which increases the resistance of the electrical resistance material in those portions where the ability of the current to flow has been reduced. When using a liquid or paste-like insulating material, such material expands between the individual particles of the resistive substance upon heating of the resistance material by electric current.

In this way the resistance value of the electrical resistance material adjusts itself from place to place according to the temperature prevailing at each particular place. Therefore, the electrical resistance material regulates its resistance value upon heating by electric current in such a manner that overheating and hence burning or other damage is completely prevented, because in every region of the electrical resistance material the resistance value automatically adjusts itself so that the current consumption and hence the heat produced at

that particular region does not permit the temperature thereof to increase beyond a desired maximum value. Thus, the electrical resistance material or a heating sheet made therefrom maintains a regulated temperature regardless of change in surrounding conditions.

If, for example, in a heating sheet made from the electrical resistance material, a reduction of the heat transfer from the material should occur due to any circumstances such as by placing a piece of furniture in front of the sheet, the current consumption through the sheet is reduced by the sheet itself until an equilibrium between the resistance value, temperature, current consumption and heat transfer again establishes itself in the interior of the electrical resistance material. Therefore, a heating sheet, for example, one square meter which is blocked in one region would exhibit the same resistance over the entire remaining area, but would possess a higher resistance value in that locally blocked region, due to which, only a slight and readily permissible temperature increase (if at all) would occur at the blocked region.

After the removal of the blockage from such a region of the heating sheet, the temperature would reduce, so that the resistance value in that region would drop again to the same value as the remaining area of the heating sheet. This drop in resistance value is due to the fact that the removal of the blockage allows for normal dissipation of heat, and as a consequence, the insulating material contracts, thereby increasing the contact between the individual resistive particles which in turn decreases the resistance value of the heating sheet to that of the unblocked area of the sheet. After disconnecting the electric current, the resistance value of the heating sheet decreases to its starting value as it cools, and the insulating material retracts to its original condition.

Numerous modifications of the present invention are possible. For example, it is possible to first combine the insulating material and the carrier material, and to mix this mixture with the resistive substance. This is particularly feasible when a solid material such as glass powder is used as the insulating material. Obviously, other electrodes are suitable for connecting the heating sheet to the electrical circuit. For example, the electrodes may be embedded in the heating sheet, clamped to the heating sheet or the like.

While certain preferred embodiments of the invention have been described herein, it is to be understood that the invention is not limited thereto, but is defined by the appended claims.

What is claimed is:

1. An electrical heating element consisting essentially of a substantially flat sheet of electrical resistance material, and opposed spaced electrodes each at a respective one of the opposed edges of said sheet for connection with an electric current source, said electrical resistance material during the passage of electric current there-through automatically increasing and decreasing the resistance of individual areas of said sheet in accordance with the dissipation of heat from said individual areas, said material comprising (1) a finely divided resistive substance selected from the class consisting of a carbon material, an alloy and a metal, (2) an insulating material which is an oil and is present in said heating element in an amount between about 7 and about 25 percent by weight of said resistive substance, said oil having a specific electrical resistance greater than 10^5 ohm cm. and at least 10^5 times that of the resistive substance and said oil having a greater coefficient of thermal expansion than said resistive substance, and (3) a substantially inert non-conductive plastic carrier, said resistive substance and said oil being substantially uniformly distributed in said sheet, said resistive substance being substantially enveloped by said oil and said heating element having a positive temperature coefficient of resistance

which is greater than the temperature coefficient of said resistive substance.

2. An electrical heating element according to claim 1 wherein said resistive substance is present in said heating element in a quantity of at least 28% by weight based on the total weight of said oil, said resistive substance and said non-conductive carrier in said electrical resistance material.

3. An electrical heating element according to claim 1 wherein said oil is selected from the class consisting of lubricating oils, transformer oils, silicone oils and paraffin oils.

4. An electrical heating element according to claim 2 wherein said non-conductive carrier is selected from the class consisting of polymeric alpha-olefins, polyesters, polyamides and polyvinylhalides.

5. An electrical heating element according to claim 2 wherein said non-conductive carrier is a polymeric alpha-olefin and said resistive substance is a finely divided carbon material.

6. An electrical heating element according to claim 5 wherein said finely divided carbon material is a substantial porous material.

7. An electrical heating element according to claim 6 wherein the polymeric alpha-olefin is a polystyrene.

8. An electrical heating element according to claim 6 wherein the polymeric alpha-olefin is a polypropylene.

9. An electrical heating element consisting essentially of an electrical resistance material and opposed spaced electrodes, said electrical resistance material during the passage of electric current therethrough automatically increasing and decreasing the resistance of individual areas of said heating element in accordance with the dissipation of heat from said individual areas, said electrical resistance material comprising (1) a finely divided resistive substance comprising at least one member selected from the class consisting of a carbon material, an alloy and a metal, (2) an insulating material which is an oil and is present in said heating element in an amount between about 7 and about 25 percent by weight of said resistive substance, said oil having a specific electrical resistance greater than 10^5 ohm cm., and at least 10^5 times that of said resistive substance, said oil having a greater coefficient of thermal expansion than said resistive substance, and (3) a substantially inert nonconductive carrier, said resistive substance and said oil being substantially uniformly distributed in said electrical resistance material, said resistive substance being substantially enveloped by said oil said heating element having a positive temperature coefficient of resistance which is greater than the tem-

perature coefficient of said resistive substance, and said heating element having one of its three orthogonal dimensions much greater than at least one other of such dimensions.

10. An electrical heating element consisting essentially of a substantially flat sheet of electrical resistance material and opposed spaced electrodes each at a respective one of the opposed edges of said sheet for connection with an electric current source, said electrical resistance material during the passage of electric current therethrough automatically increasing and decreasing the resistance of individual areas of said sheet in accordance with the dissipation of heat from said individual areas, said electrical resistance material comprising (1) a finely divided resistive substance selected from the class consisting of a carbon material, an alloy and a metal, (2) an insulating material comprising glass powder, said glass powder being present in said electrical resistance material in an amount between about 50 and about 100% by weight of said resistive substance, and (3) a substantially inert non-conductive carrier, said resistive substance being substantially uniformly distributed in said heating sheet and said heating sheet having a positive temperature coefficient of resistance which is greater than the temperature coefficient of the resistive substance.

11. An electrical heating element according to claim 1 wherein the oil is a lubricating oil, the non-conductive plastic carrier is a polymeric alpha-olefin, and the resistive substance is at least one carbon material.

12. An electrical heating element according to claim 1 having a thickness between about 0.1 mm. and about 5 mm.

13. An electrical heating element according to claim 5 wherein the non-conductive carrier is polyethylene.

References Cited

UNITED STATES PATENTS

2,526,059	10/1950	Zabel et al.	252-511 X
2,683,673	7/1954	Silversher	252-514 X
2,861,163	11/1958	Asakawa	338-224 X
3,056,750	10/1962	Pass	252-511
2,744,981	5/1956	Spears	338-114 X
3,111,495	11/1963	Murphy et al.	252-511
3,243,753	3/1966	Kohler	338-28 X

FOREIGN PATENTS

495,360 8/1953 Canada.

LEON R. ROSDOL, *Primary Examiner.*

J. D. WELSH, *Assistant Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,412,358

November 19, 1968

Friedrich Hummel et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, after line 9, insert -- Claims priotiry, application, Germany, Mar. 5, 1963, E 24,436 --.

Signed and sealed this 14th day of April 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents