United States Patent [19]

Kanaya et al.

[11] **3,808,403**

[45] **Apr. 30, 1974**

[54] **WATERPROOF ELECTRICAL HEATING UNIT SHEET**

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[22] Filed: **July 13, 1972**

[21] Appl. No.: **271,518**

[30] **Foreign Application Priority Data**

July 20, 1971 Japan 46-63483
Nov. 5, 1971 Japan 46-88082
Dec. 22, 1971 Japan 46-120681

[52] **U.S. Cl.** **219/528,** 219/543, 219/212, 219/549, 252/500, 338/211

[51] **Int. Cl.** **H05b 3/36**

[58] **Field of Search** 219/211, 212, 464, 528, 219/529, 543, 545, 549; 338/211, 212, 214; 252/500

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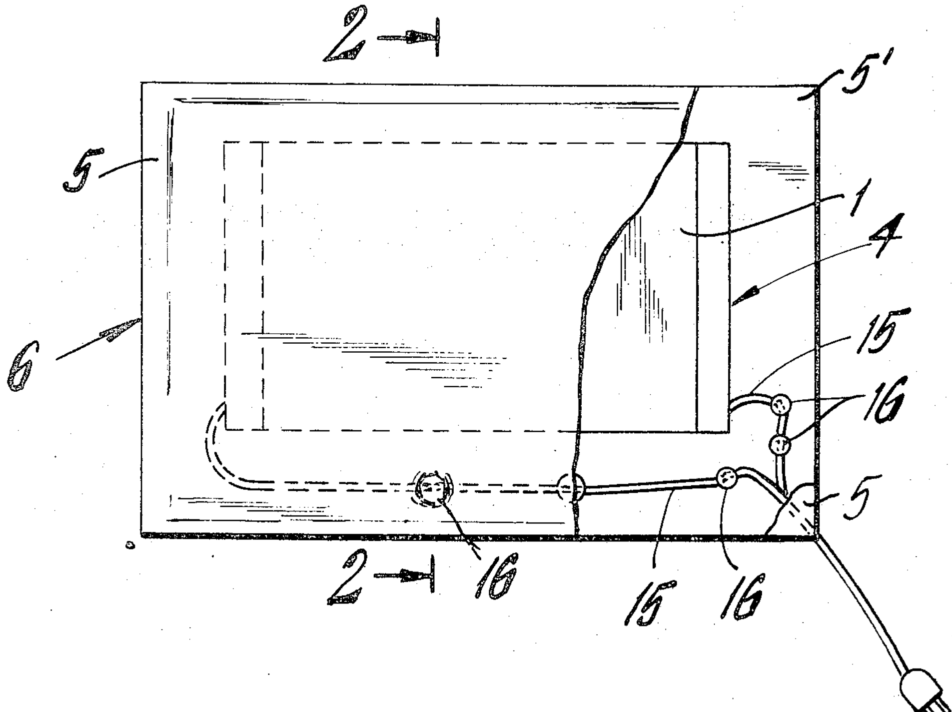
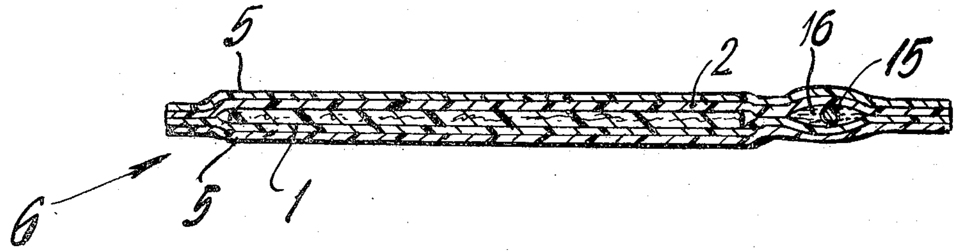
[57] **ABSTRACT**

A heating unit sheet composed of an electroconductive high molecular material and having a high degree of safety and excellent flexibility and which is useful in many various applications, equipped with electrodes and coated with insulating materials.

2 Claims, 15 Drawing Figures





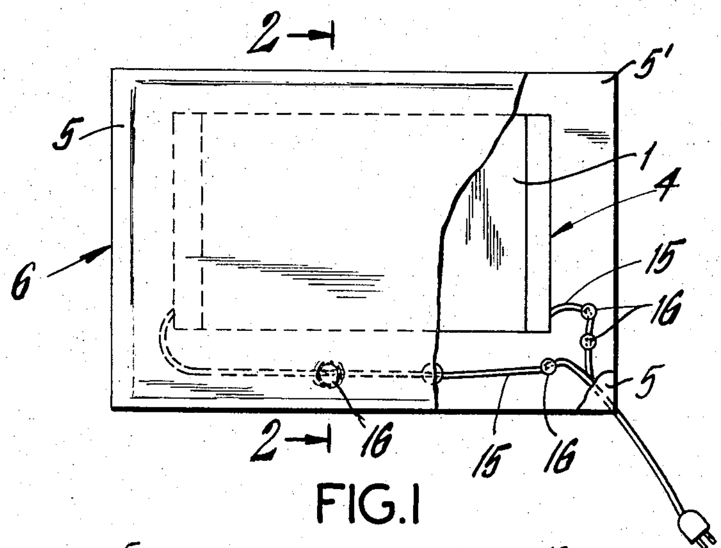


FIG.1

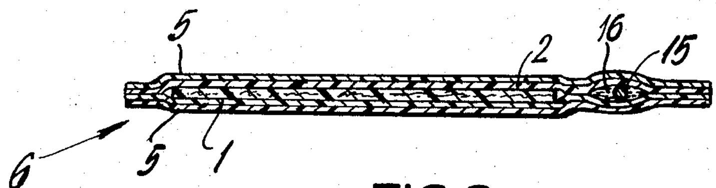


FIG.2

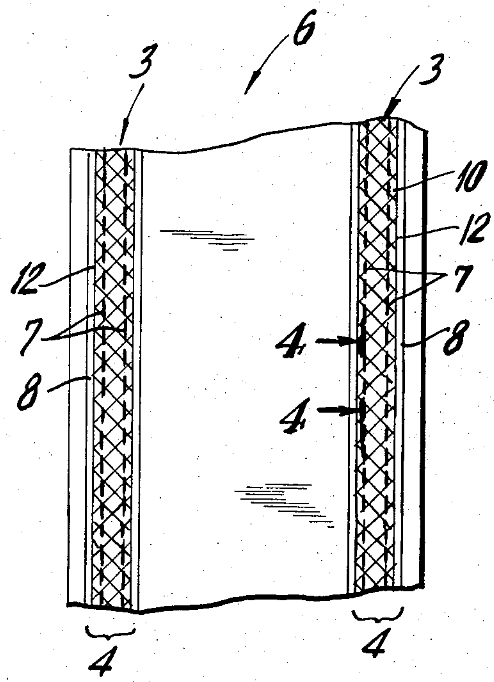


FIG.3

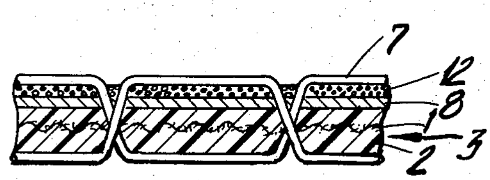


FIG.4

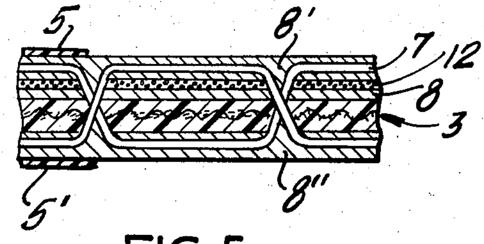


FIG.5

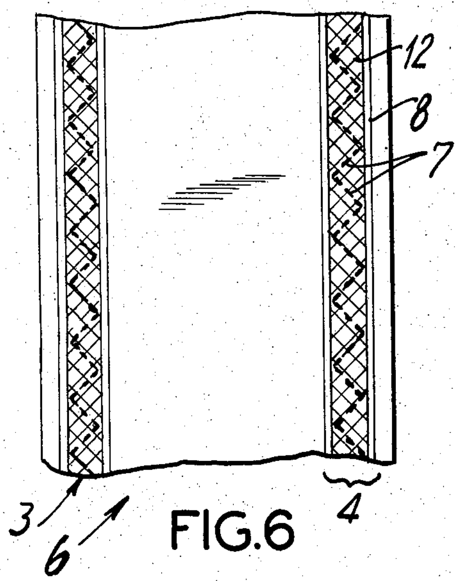


FIG.6

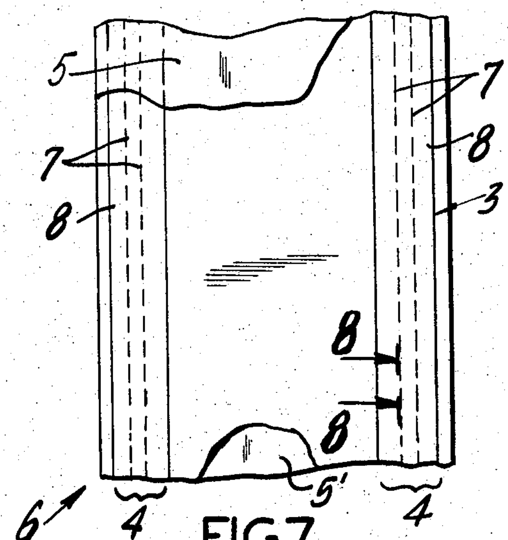


FIG.7

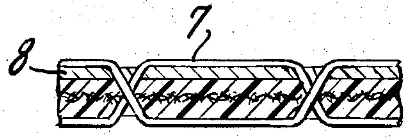


FIG.8

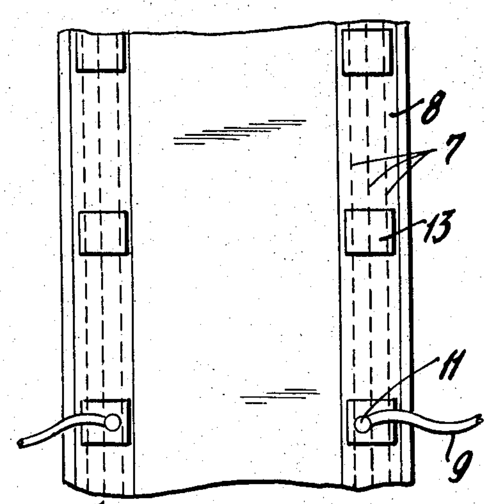


FIG.10

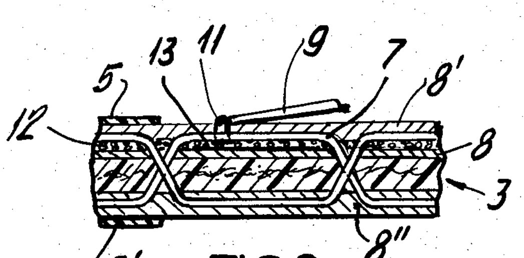


FIG.9

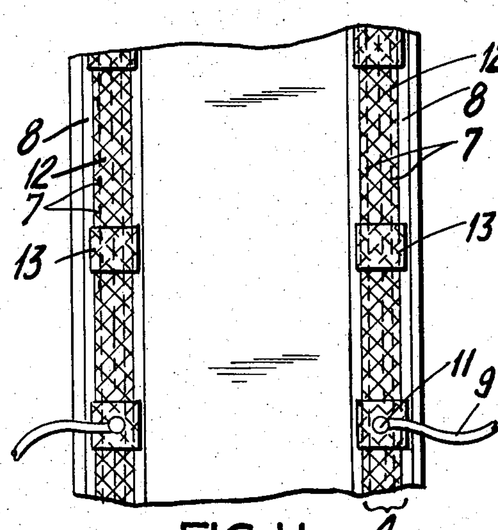


FIG.11

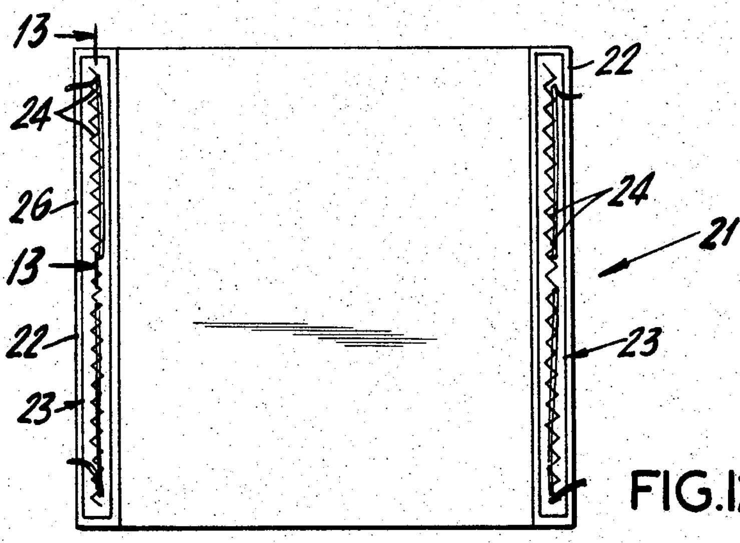


FIG.12

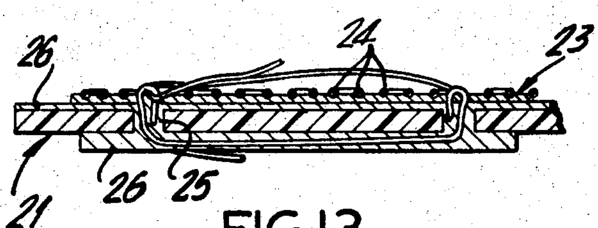


FIG.13

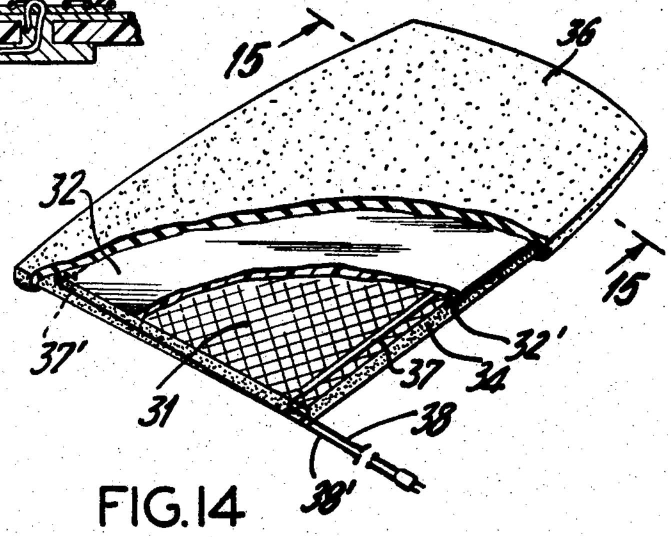


FIG.14

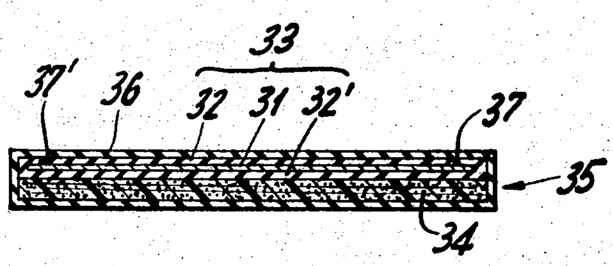


FIG.15

WATERPROOF ELECTRICAL HEATING UNIT SHEET

The present invention relates to a heating sheet on which a flexible high-molecular paint having electroconductive property is applied.

Heating sheets conventionally used include metal foils having a high electrical resistance and glass textures or asbestos paper on which an electroconductive paint, containing powders of carbon or metal, is applied and equipped with electrodes. Since these materials lack pliability and flexibility, they are likely to form cracks and be broken while in use.

Heating sheets may be incorporated in various materials used in applications, such as, walls, floors and ceilings; furniture, such as, stools and chairs; cars and trucks; live-stock breeding, such as, hog-raising and poultry farming; the marine industry such as, fish-raising in marshes, ponds and inland sea; agriculture, such as, for heating hot-beds and nursery beds; civil engineering works, such as, snow- and ice-melting of roads, runways, bridges, etc.; heat insulation for water supply pipes and other pipe lines and oven panels etc.; for warming clothing, such as, water-cloths, overcoats, jumpers, trousers and other personal effects, such as, gloves, shoes, slippers, and hosiery and many others.

However, the conventional heating sheets cannot be incorporated in many materials because of the poor flexibility of the heating sheets and furthermore, if cracks or defects are formed on the heating sheet, an abnormally large current may flow at the sites and evolve sufficient heat to cause a fire. Therefore, these heating sheets could not be used for incorporation in those materials which require flexibility, such as, clothes and small articles.

Particularly, when the heating sheet is incorporated in an aqualung, the working time in the water in connection with ocean- and lake-raisings can be remarkably lengthened and thus the heating sheet is very advantageous for future ocean developments and cold district developments where snowfalls and icing cause difficulties.

One of the objects of the present invention is to provide a heating sheet which is accident-free and superior in pliability and flexibility by equipping it with electrodes and wrapping the whole with an insulating materials which are superior in pliability and flexibility.

A further object is to provide a heating sheet which is accident-free and superior in pliability and flexibility.

Another object of this invention is to provide an electroconductive high molecular material for use as elements in a highly flexible and accident-free heating sheet.

The definitions of the terms "heating sheet" and "heating unit sheet" used in the present invention are; "heating sheet" means a sheet which evolves heat all over the surface in contrast to a linear heater such as nichrome wire, and not yet equipped with an electrode, and "heating unit sheet" means "a heating sheet" which is equipped with an electrode and further is electrically insulated.

The important points on which the present invention differs from the conventional heating sheets are:

1. High structure carbon is said to have good electroconductivity but it is so coagulative that the structure of carbon is likely to be nonuniform after application. This may cause the heating sheet to deteriorate due to the heat evolution locally induced on the surface. In this invention, high-dispersion grafted carbon which is produced by grafting a vinyl resin to oil furnace black is used.
2. The most important component of a flexible heating sheet is the base material for applying paint thereon. The base material is required to be thin enough and to have strength and resistance against bending to maintain flexibility. The surface must be uniformly uneven to assure uniform application of paint and hold an appropriate positing of volume to connect both side surfaces of the material. Further, the fibers themselves must be heat-resistant with high softening and decomposition temperatures and the product must be free from shrinkage and elongation. For these reason, high-melting synthetic fibers and the texture as referred to later are employed in the present invention.
3. In conventional heating sheet, most vehicles for paint have only poor ability to bind the carbon particles to each other and the carbon particles to the base material and poor thermal resistance. In this invention, however, use of cross-linking agent has led to success in forming a strong combination between grafted carbon particles.
4. The aging process of the coated film was necessary to make the electrical properties stable, but a long endured heating may often induce deterioration of the synthetic fibers which form the base material. An appropriated condition has been found in this invention, under which the treatment is completed in a shorter period at a high temperature and thus constant properties can be maintained for a long time.
5. A conventional flexible and highly resistant heating sheet can is difficult to combine with wires which lead electricity without introducing various mechanical and electrical problems. They have been solved in this invention particularly by the application of the thin electrodes.

As for the electrode of a conventional heating sheet, a thin metal strip or foil has been used and closely attached to the heating sheet by bonding, etc. Therefore, when the heating sheet with electrode is bent, the electrode cannot follow the bending and peeling-off or cracking of the electrode results which damages the electrical contact and excessive current flows through the portion, which portion is subjected to extraordinarily high temperatures as compared with other normal portions and is very often damaged.

According to the present invention, the electrode is of a soft and flexible structure and much less susceptible to damage by bending, and even when it is damaged, the extraordinarily high temperature melts the fibers and cuts off the circuit so that a high degree of safety is assured.

The heating sheet of this invention can be prepared by the following method.

An electroconductive high molecular paint which is prepared by dissolving in a solvent an electroconductive high molecular material superior in flexibility is applied in a thin layer onto the surface of a sheet that is superior in pliability and flexibility such as, for example, textures prepared of various kinds of high temperature-resistant synthetic fibers, such as nylon and Tetron fibers, and the resulting product is dried to form a thin film of the electroconductive high molecular material on one or both sides of the sheet. The application of the coating material referred to above may be carried out in any selected way of coating such as roll coater, doctor coater, dip coater and spraying coater. The thin film of the electroconductive high molecular paint formed on the sheet is then heated to accomplish the cross-linkage of the electroconductive high molecular paint and to obtain the electroconductive heating sheet. This heating sheet may be further heated at high temperatures to stabilize the electrical properties. Electrodes are fixed to the heating sheet being cut into appriciate size and the process to prepare a heating sheet with electrodes is completed. The heating sheet with electrodes can evolve heat when the electrodes are connected by lead wires to a power source. For the sake of safety in handling, the heating sheet with electrodes should be wrapped on both sides with an insulating sheet prepared from rubber or a flexible synthetic resin to obtain a heating unit sheet.

The method of synthesizing the electroconductive flexible high molecular material of the heating sheet will be explained as follows.

Vinyl monomers are heated in the presence of carbon black to carry out graft polymerization by the free radical initiation and polymerization of the vinyl monomers to each other, and vinyl polymers of relatively short chain lengths are chemically combined on active spots on the surface of the carbon black in a radial shape. As a result of the polymerization reaction, surface chemical properties of the carbon black particles are changed because of the plurality of vinyl polymer chains combined with the surface, and the particles acquire better dispersivility in organic solvents. Variation in the of vinyl monomer used makes possible different miscibility in the solvent. In addition, the high molecular substance can be made reactive by introducing certain functional groups into the vinyl monomers.

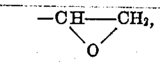
The vinyl monomers described above are expressed by the following formula of the general type:

$$CH_2{=}\overset{R}{\overset{|}{C}}{-}R'$$

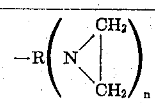
where R and R' mean a hydrogen atom and various substituents such as alkyl group, and the monomers include those which contain functional group such as acrylic and methacrylic acids, maleic acid anhydride, acrylamide, and those having no functional group such as esters of acrylic and methacrylic acids and maleic acid anhydride, acrylamide, methacrylamide, acrylonitrile, methacrylnitrile, vinyl acetate, styrene and derivatives thereof, vinyl ethers and vinyl pyridines.

The cross-linking agents which react with the above-mentioned functional groups include high molecular compounds having epoxy groups, metal organic compounds expressed by a general formula, $Me(OR)_n$, where R is an alkyl group having 1 – 16 carbon atoms, n is an integer of 2 – 4, and Me is a metal atom selected from the group consisting of Ti, Zn, Mg, Pb, Cu, Al and Cd, amine compounds and polyvalent alcohols. By combining the functional groups introduced into the vinyl polymers mentioned above with the cross-linking agents such as the high molecular compounds and the organometallic compounds referred to above, vinyl polymers polymerized on the surface of the grafted carbon particles can be cross-linked, and therefore the carbon black particles can be firmly combined both physically and chemically. Consequently, if electricity is passed through for long time the carbon black combined with vinyl polymers (electroconductive high molecular paint), shift of carbon black toward the electrode can be prevented. It is desirable to age the material at a temperature above the service temperature in order to obtain a film having better electrical stability.

It is possible that the heat treatment can be completed in a shorter time and the cross-linking reaction can also be completed to a necessary extent, even when a base texture sheet of synthetic fiber is used, under a heating condition in which the base texture is not thermally deteriorated, when the following electroconductive polymer compositions are used. These compositions comprise polymers having functional groups such as -OH, -COOH, $-NH_2$, =NH, -CONH,

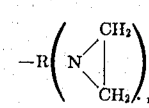


and $-SONH_2$ and the compounds used as cross-linking agents are expressed by the following general formula,



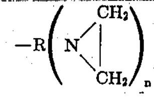
where R is an aliphatic, aromatic or alicyclic compound and n is an integer from 2 to 4.

Reactive compounds expressed by the general formula

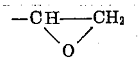


and having 2 to 4 terminal aziridine rings, which are employed as cross-linking agents in the present invention, include N,N'-tetramethylene-bis-ethyleneurea, N,N'-pentamethylene-bis-ethyleneurea, N,N'-hexamethylene-bis-ethyleneurea, N,N'-heptamethylene-bis-ethyleneurea, N,N'-octamethyleneurea, p-phenylene-bis-ethyleneurea, m-phenylene-bis-ethyleneurea, m-toluilene-bis-ethyleneurea, l-chloro-m-phenylene-bis-ethyleneurea, diphenyl-4,4'-bis-ethyleneurea, 3,3'-dimethyldiphenyl-4,4'-bis-ethyleneurea, 3,3'-dimethoxydiphenyl-4,4'-bis-ethyleneurea, diphenylmethane-p,p'-bis-ethyleneurea, tetramethylene-bis-ethyleneurethane, hexamethylene-bis-ethyleneurethane, nonamethylene-bis-ethyleneurethane, decamethylene-bis-ethyleneurethane, bis-phenyl-4,4'-bis-ethyleneurethane, p-phenyl-4,4'-bis-ethyleneurethane, p-phenyl-4,4'-bis-ethyleneurethane, p-cyclohexylethyleneurethane, lysine-bis-ethyleneurea, tetraaziridinyl-m-xylenediamine, tetraaziridinylmethyl-p-xylenediamine, diaziridinylmethyl-m-xylenediamine, diphenylmethane-4,4'-tetraaziridinylmethylenediamine, bis-phenyl-4,4'-tetraaziridinylmethylenediamine.

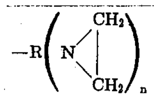
The above mentioned compounds expressed by the general formula,



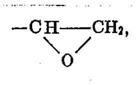
are readily subject to cleavage of the aziridine rings on heating and to react with functional groups such as -OH, -COOH, $-NH_2$, =NH, -CONH,



and $-SONH_2$. Since the compounds expressed by the general formula,

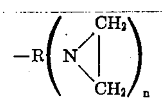


used as cross-linking agent and the polymers having functional groups such as -OH, -COOH, $-NH_2$, =NH, -CONH,



and $-SONH_2$ are contained together in the electroconductive polymer compositions of the present invention, reactions of the former compounds with the latter polymers can be most readily accomplished.

The polymers to be employed in the present invention as having those functional groups which react with the compounds expressed by the general formula



include following compositions, for example, graft carbon polymer composition having the functional groups mentioned above prepared by graft polymerization of carbon with vinyl monomers, mixture compositions prepared by mixing polymers having the functional groups above with carbon powder and compositions prepared by combined use of the graft carbon polymer composition.

It is also an object of the present invention to provide flexible heating sheets which can be used for more than 2,000 hours at 120° C, and it is desirable to use a texture fabric of, synthetic multifilament fibers with a thermal decomposition or softening temperature higher than 250° C Spun threads are not uniform in thickness and do not possess a smooth surface or elongation resistance). The texture should be plain woven, 0.10 to 0.15 mm thick, and carry 20 to 65 percent, preferably 40 to 60 percent, by volume of porosity, and a tensile strength of texture greater than 10 kg/cm.

If the volume of porosity exceeds 65 percent, the applied carbon is apt to fall out and in addition, a serious change of resistance occurs. On the contrary, for the volume of porosity less than 20 percent the applied carbon is likely come off and, irrespective of the of smoothness, plain weaving is difficult to perform. In conclusion, therefore, the permissive range is 20 to 65 percent, preferably 40 to 60 percent.

Appropriate choice of the volume of porosity permits better adhesion of the coated film of grafted carbon paint since a portion of the pain penetrates through the pore to the other side.

For example, 75 denier multifilament threads of polyester fibers having a strength of 5 g per unit denier are woven in 110 and 98 threads per inch in the longitudinal and lateral direction, respectively. The volume of porosity of this texture is about 50 percent. Less number of threads in the lateral direction by 10 percent is used because 10 percent shrinkage occurs during the processing. Though polyester fibers are the most suitable, any other heat resistant fibers may be used if the above requirements, are met. Regarding the structure of the textures, any weaving method can be used if the obtained volume of porosity, thickness and smoothness satisfy the required conditions. The above texture is required before use to be subjected to heat setting for 30 to 60 sec. at a temperature by 5° to 10° C below the softening temperature of the fibers to assure the dimensional stability of the fibers. For example, they are set for 45 sec. by introducing them into an oven at 225° C. Furthermore, it is necessary before the grafted carbon paint is applied that the said texture should be dipped in a suitable organic solvent (preferably the same solvent as used for the paint) to remove bubbles inside the texture.

The present invention also provides a new idea for placing electrodes on the heating sheet. As a preferred embodiment, 34 copper wires of 0.01 mm^2 cross-sectional area knitted in a flat ribbon of 6 mm broadness are used. Plating the copper wires with tin is more useful. At first, electroconductive silver paint is applied in the shape of 1 cm broad band at the ends of the heating sheet, dried by heating and the ribbon electrodes mentioned above are placed on the portions and attached by sewing in zigzag with electroconductive thin threads and then pressed with rollers. The ribbon electrodes from the heating sheet are combined and connected with external leads. The electrodes thus formed are extremely thin (about 0.1 mm) and so flexible as not to affect bending. Cracks and breaking do not cause any trouble owing to the flexible structure.

The capacity for current of the ribbon-shaped knitted electrodes above is 3.4A. When a larger capacity is required, the thickness and number of the wire and width of the ribbon should be increased to meet the requirement. Electroconductive thin wires refer to very thin wires of copper, silver and others and tape-shaped thin copper foils wrapping a cotton thread, which serve to pass the electric current to the other side.

The heating sheet with electrode may be covered not only with a flexible insulating material to make a flexible heater but also with a rigid insulating material to use as a flat plate heater.

As the insulation materials, rubber sheets, rubber coated sheets and synthetic resin sheets such as vinyl chloride sheets, polyethylene sheets, polypropylene sheets, polyurethane sheets, polyamide sheets, polyethylene telephtalate and ethylene-vinylacetate copolymer sheets may be used, and also liquid rubber and soft casting resins such as methane, and silicone-rubber may be used.

A preferred embodiment of the present invention is described with reference to the examples illustrated in the attached drawings in which:

FIG. **1** is a fragmented plan view of the heating sheet with electrodes of the present invention;

FIG. **2** is a sectional view of the heating sheet with electrodes taken along lines **2—2** of FIG. **1.**

FIG. **3** is a fragmented plan view showing the heating element;

FIG. 4 is a sectional view showing the electrodes and the structure of the heating sheet taken along lines 4—4 of FIG. 3;

FIG. 5 is a sectional view similar to FIG. 4;

FIGS. 6 and 7 are fragmented plan views showing a further heating sheet with electrodes;

FIGS. 8 and 9 are sectional views showing the electrodes and the structure of the heating sheet with FIG. 8 taken along lines 8—8 of FIG. 7 and FIG. 9 depicting an assembled sheet;

FIGS. 10 and 11 are fragmented plan views showing a still further heating sheet;

FIG. 12 is a plan view of a further heating sheet with electrodes;

FIG. 13 is a sectional view taken along lines 13—13 of FIG. 12 showing its structure along lines 13—13

FIG. 14 is a plan view in perspective of a still further embodiment of a heating sheet with electrodes; and

FIG. 15 is a sectional view taken along the lines 14—14; of FIG. 14 taken along lines 15—15

EXAMPLE 1

Oil furnace black — 328 g
Acrylic acid — 72 g
Butyl acrylate — 256 g
α,β-azo-bis-isobutylnitrile (initiator) — 30 g
Methylisobutylketone — 1,000 g

The above ingredients were placed in a three neck flask and polymerized by agitating for 8 hours at 80° C in a nitrogen atmosphere. A polymerized liquid of 80 cps viscosity was obtained with a yield of 97 percent. Then a solution of cross-linking agent prepared as shown below was added to the polymerized liquid under stirring.

Epoxy resin (cross-linking agent) — 76 g
Methylisobutylketone (solvent) — 200 g
Polymerized liquid mentioned above — 1,656 g

As epoxy resin, ARALDITE (supplied from Shell Chemical Co.) of the epoxy equivalent 76 was used. The same resin was used for the cross-linking agent in all examples that follow.

Referring to FIGS. 1 and 2, the mixed solution (2) thus formed was applied onto a texture or fabric (1) made of polyester fibers (No. 3311 Tetron from Teizin Co.) wet pick up of 115 g/m^2 with a dip coating machine at the speed of 3.4 m/min. and dried with hot air at 150° C (see FIG. 2). This was further heated for 16 hours at 220° C to complete cross-linking and the aging treatment. The resulting heating sheet element (3) had an area resistance of 100Ω□ (square).

On the other hand, a comparison specimen of a heating sheet element was prepared by applying a mixed paint composed of 328 g of oil furnace black, 328 g of acrylic resin and methylisobutylketone on a texture of glass fibers, where carbon was neither polymerized nor cross-linked. The pliability and flexibility of heating sheet element (3) obtained in this example was compared with those of the above product for comparison, as shown in Table 1.

Tests were conducted by JIS L-1079 using Scott's flexing tester and by using Olsen's bending tester.

TABLE 1

	Scott's flexing tester (1 kg/1.5 cm load)	Olsen's bending tester (1 kg/1.5 cm load)
Specimen for comparison	Cut at 28 repetitions	Cut at 8 repetitions
Product of this example	Nothing wrong at 1000 repetitions	Nothing wrong at 2000 repetitions

As shown in Table 1, the heating sheet of this example proved to be superior in pliability and flexibility. Then the heating sheet was cut to appropriate dimensions, and an electroconductive paint (8) of silver was applied to the areas (4) at which electrodes were to be fixed, where ribbon wires (12) (4 mm wide, 0.2 mm thick and of electrical capacity 5A) made of 16 coaxial cables were fixed by sewing with copper threads (7) to compose electrodes for the heating sheet (6).

The electrodes were so flexible that the whole body of the heating sheet (6) was also very flexible and held good performance for a long term.

The heating sheet obtained above was covered on both sides with polyvinyl chloride sheets (5) (0.4 mm thick) (see FIGS. 1 and 2). When the interval and length of the electrodes (10) were made to be 420 mm and 900 mm, respectively, and electric current was passed at 100 V and 570 W/m^2, a temperature higher by 30° C above room temperature (20° C) was obtained on the surface of polyvinyl chloride sheet.

EXAMPLE 2

Oil furnace black — 220 g
Acrylic acid — 115 g
Acrilonitrile — 85 g
Azo-bis-isobutylnitrile — 20 g
Cyclohexanon — 680 g

The above ingredients were mixed by agitation for 6 hours while they were heated at 90° C in the same manner as in Example 1. As a result, a solution of polymerized substance having viscosity 95 cps was obtained with a yield of 98.5 percent.

Subsequently, a cross-linking agent dissolved in a solvent in the proportion as shown below was added under stirring to the solution of polymerized substance mentioned above.

Epoxy resin (cross-linking agent) — 65 g
Cyclohexane (solvent) — 170 g
Above solution of polymerized substance — 1,220 g

The mixed solution (2) thus formed was applied onto a texture (1) of polyamide fibers wet pickup of 140 g/m^2 with a dip coating machine at the rate of 1 m/min. and dried by a 150° C hot air. This was further heated for 30 hours at 200° C to complete cross-linking and aging treatment. The heating sheet element (3) obtained had an area resistance of 50Ω□ (square).

The pliability and flexibility of the heating sheet (3) obtained in this example proved excellent as seen in the following table.

TABLE 2

	Scott's flexible tester (1 kg/1.5 cm load)	Olsen's bending tester (1 kg/1.5 cm load)
Product of this example	Nothing wrong at 1000 repetitions	Nothing wrong at 2000 repetitions

A silver paint as electroconductive paint was applied to the heating sheet element (3) and a ribbon wire (12) made of thin copper wires was fixed in a zigzag line by sewing at the site with thin copper wires (7) to form an electrode as shown in FIG. 6, and a further amount of the silver paint (8') and (8'') was applied on the opposite side to cover the fixing wires (7) of the heating element as shown in FIG. 5.

Since the electrodes (4) shown in FIGS. 6 and 7 were very flexible, the heating sheet (6) of this invention was also very flexible as a whole.

The above heating sheet (6) was covered on both sides with polyvinyl chloride sheets (5) and (5') (0.4 mm thick). With the interval and the length of electrodes (4) of 420 mm and 900 mm, respectively, and the electricity of 100 V and 270 W/m^2, a temperature higher by 14° C than room temperature (20° C) was obtained on the surface of the polyvinyl chloride sheet.

EXAMPLE 3

Oil furnace black — 184 g
Vinyl acetate — 172 g
Maleic acid anhydride — 196 g
Azo-bis-isobutylnitrile — 32 g
Octyl alcohol — 12 g
Cyclohexane — 830 g

Above ingredients were agitated while being heated under the same condition as in Example 2. A solution of polymerized substance of viscosity 87 cps was obtained with a yield of 98.3 percent.

In the next step, a cross-linking agent dissolved in a solvent in a proportion described below was added to the above solution under stirring.

Epoxy resin — 85 g
Cyclohexane — 225 g
Above solution of polymerized substance — 1,394 g

The mixed solution (2) thus formed was applied onto a texture (1) made of polyester fibers with a dip coater under the same condition as in Example 1, dried and thermally treated to obtain heating sheet elements (3). The area resistance of the heating sheet elements (3) was 200Ω (square).

The pliability and flexibility of the heating sheet element (3) in this example proved to be excellent as shown in the following table.

TABLE 3

	Scott's flexing tester (1 kg/1.5 cm load)	Olsen's bending tester (1 kg/1.5 cm load)
Product of this example	Nothing wrong at 1000 repetitions	Nothing wrong at 2000 repetitions

At the opposite ends on one side of the heating sheet element was applied a silver paint (8) and two streaks of thin copper wires (7) were fixed as electrode by sewing each at an end and parallel to each other in a zigzag line. These electrodes were so flexible that the heating sheet (6) of this example was as a whole very flexible.

Meanwhile, the electrodes of (A) the heating sheet coated with silver paint equipped with electrodes formed by pasting a 0.15 mm thick copper foil thereon; (B) the heating sheet coated with silver paint equipped with electrodes formed by sewing thereon, two parallel fine copper wires in a straight line; and (C) the heating sheet coated with silver paint equipped with electrodes formed by sewing thereon fine copper wire in a zigzag form were subjected to stamping tests to determine their resistance value variations. The results are shown in Table 4.

TABLE 4

	Results of Electrode Stamping Tests After 200 Stampings	Resistance Variation Rate After 10,000 Stampings
Electrode of Heating Sheet A	Damaged	—
Electrode of Heating Sheet B	No Damage	13.7 %
Electrode of Heating Sheet C	No Damage	1.5 %

The above stamping tests were conducted as under.

The electrode portions are repeatedly stamped 20 times per minute with a stamping total load of 50 kg whole current of 100 V is passed.

$$\text{Resistance Variation Rate} = \frac{\text{Resistanc After Stampings} - \text{Resistance Before Stampings}}{\text{Resistance Before Stampings}} \times 100$$

As seen from the above results, in case of the heating sheet (A) in which the copper foil is pasted, the durability of the electrode is very poor, while in case of the heating sheet (C) in which the fine copper wire is sewn in a zigzag form, the electrode is very flexible and electrically stable.

In this example, as the fine copper wire No. 40 copper thread was used and the sewing span was 5 mm.

EXAMPLE 4

Oil furnace black — 330 g
Acrylamide — 137 g
Vinyl acetate — 163 g
Azo-bis-isobutylnitrile initiator — 35 g
Cyclohexanone — 1,500 g

Above ingredients were stirred while being heated under the same condition as in Example 2. A solution of polymerized substance of viscosity 93 cps was obtained with a yield of 98.8 percent. Subsequently, a cross-linking agent dissolved in a solvent was added to the solution of polymerized substance in the proportion described below while being stirred.

Tetrapropyl titanate (cross-linking agent) — 84 g
Cyclohexane (solvent) — 380 g
Above solution of polymerized substance — 2,139 g

The mixed solution (2) thus formed was applied onto a texture (1) made of polyamid fibers with a dip coating machine to wet pickup of 140 g/m^2 at the rate of 1 m/min., and then dried with a hot air of 150° C. Further heating was continued for 30 hours at 200° C to complete cross-linking and aging treatment. The area resistance of the heating sheet element (3) obtained was 50Ω □ (square).

The pliability and flexibility of the heating sheet produced in this example proved excellent as shown in the table below.

TABLE 5

	Scott's flexing tester (1 kg/1.5 cm load)	Nothing wrong at (1 kg/1.5 cm load)
Product of this example	Nothing wrong at 1000 repetitions	Nothing wrong at 2000 repetitions

As shown in FIG. 7 a silver paint (8) was applied onto the heating sheet element (3) at the two areas (4) and two streaks of thin copper wires (7) were fixed by sewing at each area almost in parallel to each other, and the silver paint (8) placed on areas (4) on the heating sheet. These electrodes were very flexible. The whole body of the said heating sheet (6) was covered with films (5) and (5') (0.5 mm thick) of polyvinyl chloride for insulation. The films of polyvinyl chloride was so flexible that they did not interfere with the flexibility of the heating sheet.

EXAMPLE 5

Mixture composition A
Oil furnace black — 24.0 kg
Acrylic acid — 4.4 kg
Butyl acrylate — 15.6 kg
Azo-bis-isobutylnitrile — 0.64 kg
Cyclohexanone — 110.0 kg

Cyclohexanone and then other constituents, were placed in a 200*l* reaction vessel provided with a reflux condenser and the reaction was continued for 5 hours at 90° C while nitrogen was being introduced at the rate of 10*l* per minute. When the reaction was completed, a dispersion of non-precipitative grafted carbon, of which the viscosity was 18.5 cps at 20° C and containing 28.9 percent of solid matter, was obtained.

To the 25 kg of mixed solution obtained, the solution of cross-linking agent shown as the mixture composition B was added and the whole mixture was made uniform with a stirrer. The paint had a viscosity of 12.5 cps at 20° C and contained 24.4 percent of solid matter.

Mixture composition B
Tetrapropyl titanate — 0.897 kg
Cyclohexanone — 6.36 kg

A portion of the above paint was applied onto a glass plate, dried at 150° C for an hour and heated at 225° C for 5 hours and then the volume resistibity was 0.26 ohm/cm.

The original base material used was a texture having 50 percent by volume of porosity which was prepared by weaving 75 denier multifilament polyester fibers in 110 and 98 threads per inch in the longitudinal and lateral directions, respectively. This texture was introduced to pass into a vat of cyclohexanone solvent to remove bubbles between the fibers. Subsequently the texture was introduced five times into a paint bath at the rate of 1 m per minute and then dried, taking 4 minutes at the drying temperature 150 to 160° C. The amount of solid substance attached to the texture amounted approximately to 9 g/m for a single dipping, and to 41 g/m^2 for five times of dipping.

The base material texture to which application of paint has been done was heated at 180° C in an oven for 2 hours to complete the cross-linkage. Then, this was heated for additional 8 hours in an oven at 225° C for aging. The electrical resistance of the product was 49 ohm per cm^2 and was uniform everywhere on the texture. Physical properties of the flexible heating sheet obtained were as follows:

Tensile strength	26 kg/3 cm (longitudinal) 19.5 kg/3 cm (lateral)
Tear strength (test method JIS K6772)	160 g
Bending test (Orsen)	at 1 kg load applied No change occurred at 4000 bendings
Flexing test (Scott)	at 1 kg load applied No change occurred at 2000 flexing

Electrodes were settled on the heating sheet of this invention at a distance 50 cm × 50 cm, and an ac voltage 100V was applied between them. A current of 2.0 A flew which remained constant for 500 hours and a uniform temperature between 62° to 64° C was maintained when the room temperature was 22° C. The numerical values mentioned above show satisfactory performance of the flexible heating sheet.

The heating sheet of the present invention showed excellent flexibility in the direction perpendicular to the sheet so that conductivity did not change even for bending up to 180° and no carbon was scraped off at the Gakushin-type friction strength test.

EXAMPLE 6

A mixture consisting of 60 g of oil furnace black, 11 g of acrylic acid, 39 g of butyl acrylate, 16 g of azo-bis-isobutylnitrile, and 1,100 g of cyclohexanone was treated to react for 5 hours in at about 90° C just as in Example 5 to obtain a liquid (A) of graft carbon polymer in which acrylic acid and butyl acrylate were grafted on the surface of carbon black. The product contained 28.8 percent of 18.5 cps solid. Then a mixed liquid as under was prepared and mixed by a high-speed mixer.

Graft carbon polymer liquid (A liquid) — 100 parts

Diaziridinyl-m-xylene diamine — 6 parts
Cyclohexanone — 4.5 parts

Thus obtained liquid (B) was applied to the texture uniformly in an amount of 30 g/m^2 in solid resin in a similar way as in Example 5. Then the obtained heating sheet was heat treated at 220° C for 3 hours and the integrated resistance was 128Ω . The physical properties of this heating sheet are as under which indicates excellent strength with good flexibility.

Tensile strength (JIS L–1068) — 35.2 kg/3 cm
Tear strength (JIS K–6772) — 430 g
Bending test (Orsen) at 1 kg load
No change occurred at 10,000 bending Flexing test (JIS L–1079)(Scott) at 1 kg load
No change occurred at 10,000 flexing

This heating sheet cut into a 50 cm length and 32 cm width sheet, and a high conductivity paint with silver powder therein was applied on the heating sheet at two sides in a width of 1 cm and a length of 50 cm in the lateral direction of the heat to form the electrode portions. Then the sheet was heat treated in a heating oven at 150° C for 10 minutes to make up fully the conductivity the silver electrode. The resistances of the electrodes of 50 cm length were 1.2Ω and 1.5Ω respectively. On the silver electrode, a flat ribbon of 6 mm width made of 34 copper wires each of 0.01 mm^2 cross section was placed and sewed with fine copper thread of No. 40 in a zigzag line by a sewing machine. The resistance of this heating sheet was 76.3Ω. Then the heating sheet with the electrodes was covered on both side with two sheets (0.8 mm thickness) of soft vinyl chloride prepared by mixing 50 parts of plasticizer DOP (di-2-ethylhexylphtalate) to polyvinyl chloride having average polymerization degree of 1,200, and the sheet was insulated by a hydraulic press at 150° C for 5 minutes. The resistance after the insulation treatment was 76.5Ω and showed no substantial change. This indicates a stable insulation resistance was obtained, and thus a heating unit sheet having excellent flexibility was obtained. Then the heating unit sheet was subjected to a durability test by giving the sheet an alternative current of 100V for 1 hour and stopping the current for 30 minutes and repeating this cycle in a chamber maintained at 20° C. The surface temperature of the heating unit sheet during the current passage was 70° C in average. After 2,000 times of the above current passages, the resistance of the heating unit sheet showed 75.2Ω. Thus it was confirmed that no substantial change of resistance takes place and the sheet is an electrically stable resistor.

The following examples show the modes of electrode setting on the heating sheet.

EXAMPLE 7

As shown in FIG. **10** the parts of the heating sheet (3) obtained in Example 1 which will compose electrodes were coated with a silver paint (**8**), then covered with small pieces (**13**) of copper foil (6 mm^2) at 3 cm intervals, ribbon wires (**12**) made of thin copper wires were placed upon them, as shown in FIG. **11**, and the whole was fixed by sewing with thin copper (**7**) wires to form electrodes for heating sheet.

The electrodes (**4**) of the heating sheet (**6**) of this example do not lack flexibility since the copper pieces (**13**) are fixed at intervals. Further, in this example terminals were fixed to the copper pieces (**13**) and lead wires (**9**) were connected to the terminals (**11**).

EXAMPLE 8

As shown in FIG. **10** the parts of the heating sheet element (**3**) obtained in Example 2 which will compose electrodes were coated with a silver paint (**8**) then covered with small pieces (**13**) of copper foil (4 mm^2) at 2 cm intervals, ribbon wires (**12**) were placed upon them, as shown in FIG. **11** and the whole was fixed by sewing with thin copper wires (**7**). Further, the same silver paint (**8**) was applied on the other side to cover the fixing wires on the heating sheet eleement (**3**) and the copper foils (**13**) and to reduce the contact resistance to be used as electrode (**4**) of the heating sheet (**6**).

The electrode part (**4**) of the heating sheet (**6**) of this example is flexible enough because small pieces of copper foil (**13**) are fixed at intervals.

EXAMPLE 9

The parts of the heating sheet element (**3**) obtained in Example 3 which will compose electrodes (**4**) were coated with a silver paint (**8**), then covered with small pieces (**13**) of copper foil (**13**) (5 mm^2) at 4 cm intervals and two streaks of thin copper wires (**7**) were fixed by sewing together with the copper pieces to form electrodes of the heating sheet (**6**).

Since the small pieces (**13**) of copper composing electrodes (**4**) are fixed at intervals, the heating sheet (**6**) of this example is sufficiently flexible.

EXAMPLE 10

The parts of the heating sheet element (**3**) obtained in Example 4 which will compose electrodes (4) were coated with a silver paint (**8**), then covered with small pieces (**13**) of copper foil (4 mm^2) at 5 cm intervals and three streaks of thin copper wires (**7**) were fixed by sewing together with the copper pieces and again the silver paint was applied from outside onto the fixing wires on the heating sheet and the copper pieces to reduce the contact resistance of electrodes. Thus, a heating sheet was composed.

Since the electrode parts (**4**) of the heating sheet (**6**) of this example were made of small pieces of copper foil fixed at intervals, they were very flexible.

EXAMPLE 11

The parts of the heating sheet element (**3**) obtained in Example 1 which will compose electrodes (**4**) were covered with small pieces (**13**) of copper foil (4 mm^2) at 2 cm intervals, ribbon wires (**12**) were fixed on the parts with thin copper wires, and the silver paint (**8**) was applied from outside onto the fixing wires on a heating sheet and the small pieces of copper foil to reduce the contact resistance of electrodes. Thus, a heating sheet (**6**) was composed.

Since the electrode parts of the heating sheet of this example were made of small pieces of copper foil fixed at intervals, they were sufficiently flexible.

EXAMPLE 12

The parts of the heating sheet element (**3**) obtained in Example 2 which will compose electrodes (**4**) were covered with ribbon wires which were fixed by sewing with thin copper wires (**7**) and as shown in FIG. **5**, the silver paint (**8**) was applied from inside onto the fixing wires on the heating sheet element to reduce the contact resistance of electrodes. Thus, a heating sheet was formed.

Since the electrodes of the product of this example were good in flexibility, the heating sheet of this example as a whole was very flexible.

EXAMPLE 13

The parts of the heating sheet (**3**) obtained in Example 3 which will compose electrodes (**4**) were covered with small pieces (**13**) of copper foil (3 mm^2) at 3 cm^2 intervals, ribbon wires (**12**) were placed upon the areas and they were fixed by sewing all together to form electrodes of a heating sheet.

Since the electrode parts (**4**) of the heating sheet (**6**) of this example were covered with small pieces of copper foil (**13**) fixed at intervals, they were sufficiently flexible.

EXAMPLE 14

At the parts of the heating sheet element (**3**) obtained in Example 4 which will be electrodes (**4**) were fixed by sewing four streaks of thin copper wires (**7**) in parallel to each other, where the silver paint (**8**) was applied from outside to cover the fixing wires on the heating sheet to reduce the contact resistance of electrodes. Thus, a heating sheet (**6**) was formed.

Since the electrode parts (**4**) of the product of this example were very flexible, the heating sheet of this example as a whole was sufficiently flexible.

EXAMPLE 15

At the parts of the heating sheet (**3**) obtained in Example 1 which will compose electrodes, small pieces (**13**) of copper foil were placed at 3 cm intervals, four streaks of thin copper wires (**7**) were fixed by sewing in parallel at the areas, and the silver paint (**8**) and (**8'**) was applied from both sides, as shown in FIG. **9**, to cover the fixing wires on the heating sheet element (**3**) to reduce the contact resistance of electrodes. Thus, a heating sheet (**6**) was formed.

Since the electrode parts of the heating sheet of this example were composed of small pieces of copper foil fixed at intervals, they were sufficiently flexible.

EXAMPLE 16

In FIG. 12 and FIG. 13, (21) is a heating sheet, (23) is a ribbon made by knitting fine metal wires which is sewed in a zigzag form onto the heating sheet (21). The seams (25) formed on the heating sheet (21) may be filled with a paint (26) having good electric conductivity so as to reduce the contact resistance between the conductive wire (24) and the heating sheet (21). As for the paint (26) having good electric conductivity, and that used for the portion (22) it may be prepared by dispersing powder such as silver powder dispersed in synthetic resins.

The electrode in this example is prepared by sewing the ribbon (23) of metal wires onto the portion (22) coated with paint having good conductivity in a zigzag form using the fine wire (24).

EXAMPLE 17

In FIG. 14 and FIG. 15, the heating sheet (31) schematically shown is covered on both sides by an insulating material (32) (32′) and on one side of thus obtained sheet (33) flexible insulating material (34) is laminated to form a laminated layer (35) and the sheet (33) and the laminated layer (35) are covered by a surface protecting material (36). Thin electrode plates (37), (37′) are provided on the heating sheet (31) and lead wires (38), (38′) are connected to the electrode plates.

The insulating material (32), (32′) may be a flexible thin insulating sheet made of various synthetic sheets and rubber sheet. The flexible insulating material (34) may be made of flexible urethane, foamed rubber, foamed polyethylene etc., and laminated on one side of the heating sheet (33) using a bonding agent. The surface protecting material (36) may be rubber sheet, synthetic resin sheet, synthetic resin leather, etc.

EXAMPLE 18

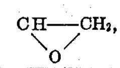
This example shows a water-proof heating unit sheet according to the present invention. In FIG. 1, the heating sheet with electrodes (4) is connected with a lead wire (15) and covered from both sides with waterproof insulating sheets (5) and (5′) and sealed by using a bonding agent having high heat-resistance or by heat fusion.

The lead wire (15) penetrates the water-proof sealer (16) closely adhering the water-proof insulating sheets (5) and (5′). The sealer (16) is positioned at the inner portion of the water-proof insulating sheets (5) and (5′). In this example, the opening for the lead wire (15) is equipped with a conventional water-proof device. As the water-proof sealer (16) is positioned at the inner portion of the water-proof insulating sheets (5) (5′), and not at the outer edge portion which is subjected impact, this sealer (16) is free from damage. And as the sealer (16) is closely fixed to the inner portion of and completely heated by (5) and (5′) there is no danger of water leakage even when the sealer (16) is damaged, due to the close adhesion of the sheets (5) and (5′).

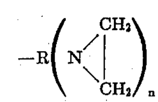
What is claimed is:

1. A waterproof heating sheet comprising a laminate of:

a. an inner layer of woven fabric composed of flexible heat-resistant synthetic fibers having a coating of an electro-conductive high molecular weight cross-linked paint composed of a graft polymer of a vinyl monomer grafted onto carbon black, wherein said vinyl monomer possesses a functional group selected from the group consisting of -OH, -COOH, $-NH_2$, =NH, -CONH,



$SONH_2$, and is cross-linked with a cross-linking agent selected from the group consisting of compounds having the formula:



wherein R is an aliphatic, aromatic or alicylic group and *n* is 2 or 4;

b. upper and lower waterproof insulating layers completely surrounding said inner layer;

c. said inner layer having spaced-apart, flexible electrodes conductively attached thereto; and

d. electrical leads connected to said electrodes, said leads extending from said insulating layer and being in sealed relationship therewith.

2. The heating sheet of claim 1 wherein the woven fabric has a porosity of 20 to 65 percent by volume and consists of synthetic fiber filaments having a melting point and thermal decomposition temperature above 250° C.

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