



(11) **EP 2 063 024 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
21.09.2011 Bulletin 2011/38

(51) Int Cl.:
D21H 13/50 ^(2006.01) **D21H 17/67** ^(2006.01)
D21H 21/54 ^(2006.01) **H05B 3/36** ^(2006.01)

(21) Application number: **07022709.5**

(22) Date of filing: **22.11.2007**

(54) **Nano carbon crystal material and method of manufacturing electrothermal board by using the same**

Nano-Kohlenstoff-Kristallmaterial und Verfahren zur Herstellung einer elektrothermischen Platte damit
Matériau de nanocristaux de carbone et procédé pour la fabrication d'une carte électrothermique avec celui-ci

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE
SI SK TR**

(43) Date of publication of application:
27.05.2009 Bulletin 2009/22

(73) Proprietors:
• **Pan, Ching-Ling**
Taipei County 242 (TW)
• **Wu, Yung-Shun**
Taipei County 241 (TW)

(72) Inventors:
• **Pan, Ching-Ling**
Taipei County 242 (TW)
• **Wu, Yung-Shun**
Taipei County 241 (TW)

(74) Representative: **Dossmann, Gérard**
Casalonga & Partners
Bayerstrasse 71-73
80335 München (DE)

(56) References cited:
WO-A-02/19771 WO-A-2007/106122

EP 2 063 024 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to a nano carbon crystal material and a method of manufacturing electrothermal board using the same, and more particularly to a crystal material and a method of manufacturing a facial heating body by using the crystal material.

[0002] Carbon fiber is a high performance material with excellent electrical and thermal conductivity, and its cost becomes increasingly lower, and thus extensive applications are developed in the areas of our daily life. However, most of the present carbon fiber electrothermal boards for preserving temperature and keeping warm have the following issues:

1. Since an improper carbon fiber is selected, the texture is loose and soft, and the paper pulp is mixed to form coagulated lumps. As a result, the temperature rise and heat dissipation at the surface of the pressed complex product are uneven, and deformations or burned spots will occur easily.

2. Since a gap formed between the carbon fiber and the conducting band causes a poor contact, an electric arc will be produced easily after an electric connection, so that the carbon fiber paper and the board connected to an electrode may be scraped due to the result of punctures.

3. The carbon fiber material leaks a large quantity of current in a salt mist or wet working environment, and thus its use jeopardizes the safety of our lives.

[0003] The aforementioned issues affect the extensive use of carbon fiber electrothermal boards in our daily life.

[0004] It is a primary object of the invention to provide a nano carbon crystal material and a method of manufacturing an electrothermal board by using the nano carbon crystal material to overcome the shortcomings of the prior art, such as the temperature rise and heat dissipating at the surface of the carbon fiber electrothermal board are uneven, the carbon fiber and the conducting band have a poor contact, the insulation is poor, and the working life is short.

[0005] The carbon crystal is described briefly here. Under certain conditions, carbon is a very good semiconductor material. Theoretically, each monomer has an anode and a cathode no matter how many particles is cut and divided from carbon. In fact, most carbon particles do not have these features. In special manufacturing methods (such as the ball milling, softening, purification and extraction processes conducted at high temperature and high pressure) by a modified carbon material for extracting pure large mesh carbon crystals, and a large quantity of carbon crystals perform Brownian motion under the effect of electric fields to rub and oscillate with each other to produce a large quantity of heat, so as to convert electric energy into heat energy.

[0006] The nano carbon crystal material consists of acrylonitrile-based carbon fibers, occupying 70~80% of the total weight of the nano carbon crystal material; nano carbon fibers, occupying 1~5% of the total weight of the nano carbon crystal material; and carbon crystals, occupying 15~29% of the total weight of the nano carbon crystal material. The acrylonitrile-based carbon fiber is composed of acrylonitrile-based carbon fibers having a number of thousand-filaments of 10~15K, a diameter of 1~5 μ m, and a length of 2~4mm and 4.5-6mm respectively, and formed according to the ratio of 0.5~2: 1 by weight; and the diameter of the nano carbon fiber is 50~200nm; and the number of meshes of the carbon crystal mesh is 400~1000 meshes.

[0007] A method of manufacturing an electrothermal board by using the above-mentioned nano carbon crystal material includes the steps of:

1. preparing a nano carbon crystal heat-generating paper;

a. setting a ratio of the weight of the nano carbon crystal material and the weight of the paper pulp for making paper to be 1: 9~19, and mixing the nano carbon crystal material into the paper pulp for making paper, and then adding water solution into a dispersant to form a mixed carbon fiber pulp, wherein the consuming quantity of the dispersant is equal to 0.5~5% of the weight of the nano carbon crystal material;

b. adding the mixed carbon fiber pulp into a high-speed isotropic machine containing a water soluble adhesive solution and blended at a speed of 800~2000 rpm for 1~2 hours, so that the degree of beating of the pulp falls within a range of 35°~55°SR;

c. using a paper making machine having a 50-mesh paper marking net to control the paper marking machine at a speed of 10~15m/min for processing the processed carbon fiber mixed pulp, and then compressing the carbon fibers on a piece of woolen cloth, and drying and shaping the carbon fibers by a baking bobbin;

2. preparing a glass fiber cloth prepreg: applying the mixed paint onto the surface of a fiber cloth with over 25×16

transverse and longitudinal glass fibers, wherein the mixed paint has a proportion of phenolic resin, epoxy resin and acetone mixture equal to 1~5: 4~8: 1 by weight to obtain a glass fiber cloth prepreg with a thickness of 0.1~0.3mm;

3. preparing a nano carbon crystal electrothermal board;

d. placing six layers of 50-gram Kraft paper on an iron tray first, and then placing a leveling iron plate with a thickness of 1~3mm, and finally coating a mold release agent on the iron plate;

e. coating a layer of a high pressure resisting polyethylene film of 0.01~0.05mm thick on the iron plate, and placing a piece of decoration paper on the high pressure resisting polyethylene film;

f. laying 3~5 layers of fiber cloth prepreps on the decoration paper, and then putting a piece of nano carbon crystal paper, and putting a copper foil wrapped with tin foil separately on both sides as conducting electrode;

g. laying 3~5 layers of fiber cloth prepreps on the nano carbon crystal paper;

h. laying a layer of the high pressure resisting polyethylene film of 0.01~0.05mm thick on the fiber cloth prepreg, and coating a mold release agent thereon, and then laying a leveling iron plate of 1~3mm thick on the high pressure resisting polyethylene film, and then laying 6 layers of 50-gram Kraft paper on the iron plate;

i. securing the flat copper meshed conducting wire with the copper electrode as conducting anode and cathode, and leading them parallelly from the backside of the glass fiber cloth prepreg; and

j. putting the semi-finished product on a thermal press machine, and preheating it up to 80°C, and turning on the thermal press machine to pressurize up to 200 tons and increase the temperature up to 100°C, and keep the constant temperature and pressure for 8~9 minutes, and then increase the temperature to 120°C, and keep the constant temperature and pressure for 8~9 minutes, and then increase the temperature to 140°C, and keep the constant temperature and pressure for 8~9 minutes and then lower the temperature to 55°C while keeping the pressure constant, and then reduce the pressure and temperature to room temperature, and finally open the mold to get the nano carbon crystal electrothermal board.

[0008] In addition, the dispersant is composed of sodium alginate, methyl cellulose, polyacrylamine or any combination of the above. The paper pulp for making paper is a wood cellulose pulp. The water soluble adhesive is composed of polyaniline, polyvinyl alcohol, water soluble phenolic resin or any combination of the above. The mold release agent is a polyurethane mold release agent.

[0009] Carbon crystals are used for lattice vibrations to generate heat, and acrylonitrile-based carbon fiber materials with different aspect ratios form the connecting wires of the lattices. Adding nano carbon fibers not only reduces the occurrence of electrostatic dissipations and sparks, and also guarantees the heat dissipation of the lattices that are contacted with each other or separated with a distance equal to several atomic diameters, and the nano carbon crystal material is constituted of a three-dimensional network with transversal and longitudinal intersections of points, lines and planes for moving carriers in this network along the direction towards a low electric potential. As to the microscopic view, nano carbon crystals are partially disordered, but as to the macroscopic view, nano carbon crystals are totally ordered. Carbon crystals can form an even facial heat-generating surface, and thus the surface of an electrothermal board made of a nano carbon crystal material comes with even temperature rise and heat dissipation.

[0010] Therefore, the present invention an electrothermal board made of a nano carbon crystal material, and the electrothermal board is a whole facial heat dissipating board whose conductor is a facial heat-generating surface formed by carbon fibers with a three-dimensional network which is partially disordered, totally ordered, and cut into different lengths. The electrothermal board can produce far infrared rays of 8~10μm, and a long time of use provides a health care effect to users. In addition, electrothermal boards are rigid, safe and highly insulated, and usually come with a puncture voltage of 10000V, a long life that will not break or fall off after a continuous use of over 30000 hours, and moisture-proof and waterproof features, and thus the electrothermal boards are suitable for the application of keeping warm at home, heating a bathing pool, drying clothes, offices, meeting rooms or hotels.

[0011] Further, the electrothermal board manufactured by the method of the present invention features the advantages of having an even stable heat generating performance, a quick temperature rise, an excellent insulating function, and a long working life, and thus such electrothermal board is suitable for mass production to satisfy production requirements and our daily needs, and the manufacturing method is simple, easy and convenient to operate.

FIG. 1 is a schematic view of a distribution of temperature detection points in accordance with Embodiment 10 of

the present invention;

FIG. 2 is a curve of a room air temperature that varies with time;

FIG. 3 is a curve of an average temperature of a carbon crystal electrothermal board that varies with time; and

FIG. 4 is a curve of the quantity of heat at the surface of a carbon crystal electrothermal board that varies with time.

[0012] To make it easier for our examiner to understand the objective of the invention, its structure, innovative features, and performance, we use the following preferred embodiments together with the attached drawings for the detailed description of the invention.

[0013] Embodiment 1: The nano carbon crystal material is composed of acrylonitrile-based carbon fibers occupying 70~80% of the total weight, nano carbon fibers occupying 1~5% of the total weight, and carbon crystals occupying 15~29% of the total weight, wherein the acrylonitrile-based carbon fibers have a number of thousand-filaments of 10~15K, a diameter of 1~5 μ m, and lengths of 2~4mm and 4.5~6mm respectively, and a weight ratio of 0.5~2: 1. In addition, the diameter of the nano carbon fibers is 50~200nm, and the number of carbon crystal meshes is equal to 400~1000 meshes.

[0014] The processing method is carried out according to the following reactions:

1. Mix the acrylonitrile-based carbon fibers occupying 70~80% of the total weight, the nano carbon fiber occupying 1~5% of the total weight, and the carbon crystals occupying 15~29% of the total weight;

2. Add the mixture into a clean container that contains an acetone solution with a mass concentration of 10~30%, and blend the mixtures at a speed of 300~600 rpm, and dip and soften the mixture for one hour;

3. The blended solution goes through an ultrasonic cleaning for 0.5-2 hours (for removing impurities and keep the surface clean and free of glues);

4. The cleaned solution is heated until the acetone is vaporized completely to obtain the nano carbon crystal material.

[0015] Embodiment 2: The difference between this embodiment and Embodiment 1 is that the nano carbon crystal material is composed of acrylonitrile-based carbon fibers occupying 72~78% of the total weight, nano carbon fibers occupying 2~4% of the total weight, and carbon crystals occupying 18~25% of the total weight, and the rest is the same as Embodiment 1.

[0016] Embodiment 3: The difference between this embodiment and Embodiment 1 is that nano carbon crystal material is composed of acrylonitrile-based carbon fibers occupying 75% of the total weight, nano carbon fibers occupying 3% of the total weight, and carbon crystals occupying 20% of the total weight, and the rest is the same as Embodiment 1.

[0017] Embodiment 4: The difference between this embodiment and Embodiment 1 is that the diameter of acrylonitrile-based carbon fibers is 2~4 μ m, and the rest is the same as Embodiment 1.

[0018] Embodiment 5: The difference between this embodiment and Embodiment 1 is that the diameter of acrylonitrile-based carbon fibers is 3 μ m, and the rest is the same as Embodiment 1.

[0019] Embodiment 6: The difference between this embodiment and Embodiment 1 is that the diameter of nano carbon fibers is 80~150nm, and the rest is the same as Embodiment 1.

[0020] Embodiment 7: The difference between this embodiment and Embodiment 1 is that the diameter of nano carbon fibers is 100nm, and the rest is the same as Embodiment 1.

[0021] Embodiment 8: The difference between this embodiment and Embodiment 1 is that the carbon crystal mesh is 600~900 meshes, and the rest is the same as Embodiment 1.

[0022] Embodiment 9: The difference between this embodiment and Embodiment 1 is that the carbon crystal mesh is 800 meshes, and the rest is the same as Embodiment 1.

[0023] Embodiment 10: The method of manufacturing an electrothermal board by using the nano carbon crystal material produced by Embodiment 1 comprises the following steps:

1. Prepare a nano carbon crystal heat-generating paper:

a. The ratio of the weight of the nano carbon crystal material and the weight of the paper pulp for making paper is 1: 9~19. Mix the nano carbon crystal material into the paper pulp for making paper, and then add water solution into a dispersant to form a mixed carbon fiber pulp, and the consuming quantity of the dispersant is equal to 0.5~5% of the weight of the nano carbon crystal material. The dispersant is composed of sodium alginate, methyl cellulose, polyacrylamine or any combination of the above, and the paper pulp for making paper

is a wood cellulose pulp.

b. Add the carbon fiber mixed pulp into a high-speed isotropic machine that contains a water soluble adhesive solution, and blend the pulp at a speed of 800~2000 rpm for 1~2 hours until the degree of beating of the pulp is in the range of 35°~55°SR. The water soluble adhesive is composed of polyaniline, polyvinyl alcohol, water soluble phenolic resin or any combination of the above.

c. The processed carbon fiber mixed pulp goes through a paper making machine having a 50-mesh paper marking net to control the paper marking machine at a speed of 10~15m/min, and then the carbon fibers are compressed on a piece of woolen cloth, dried and shaped by a baking bobbin, cut by a cutting equipment, tested by bulk module measuring device, and finally the carbon crystal content of a large roll of nano carbon crystal heat-generating paper is selected to meet the product requirements of the paper, and the paper is cut into a shape according to the product requirement.

2. Prepare the glass fiber cloth prepreg: Apply the mixed paint onto the surface of a fiber cloth with over 25x16 transverse and longitudinal glass fibers, and the mixed paint has a proportion of phenolic resin, epoxy resin and acetone mixture equal to 1~5: 4~8: 1 by weight to obtain a glass fiber cloth prepreg with a thickness of 0.1~0.3mm, and the phenolic resin is a phenolic resin 1411, and the epoxy resin is an epoxy resin E44.

3. Prepare the nano carbon crystal electrothermal board:

d. Place six layers of 50-gram Kraft paper on an iron tray first, and then place a leveling iron plate with a thickness of 1~3mm, and finally coat a mold release agent on the iron plate. The mold release agent is a polyurethane mold release agent.

e. Coat a layer of a high pressure resisting polyethylene film of 0.01~0.05mm thick on the iron plate, and place a piece of decoration paper on the high pressure resisting polyethylene film.

f. Lay 3~5 layers of fiber cloth prepreps on the decoration paper, and then put a piece of nano carbon crystal paper, and put a copper foil wrapped with tin foil separately on both sides as conducting electrodes, wherein the copper foil has a width of 10~15mm, and a thickness of 0.6mm, and then use an edge knurling machine to press both sides to form meshes (and the purpose of the pressed marks it to keep the tin foil, copper foil and carbon crystal paper in full contact).

g. Lay 3~5 layers of fiber cloth prepreps on the nano carbon crystal paper.

h. Lay a layer of the high pressure resisting polyethylene film of 0.01~0.05mm thick on the fiber cloth prepreg, and coat a mold release agent thereon, wherein the mold release agent is a polyurethane mold release agent, and then lay a leveling iron plate of 1~3mm thick on the high pressure resisting polyethylene film, and then lay 6 layers of 50-gram Kraft paper on the iron plate. i. Secure the flat copper meshed conducting wire with the copper electrode as conducting anode and cathode, and lead them parallelly from the backside of the glass fiber cloth prepreg.

j. Put the semi-finished product on a thermal press machine, and preheat it up to 80°C, and turn on the thermal press machine to pressurize up to 200 tons and increase the temperature up to 100°C, and keep the constant temperature and pressure for 8~9 minutes, and then increase the temperature to 120°C, and keep the constant temperature and pressure for 8~9 minutes, and then increase the temperature to 140°C, and keep the constant temperature and pressure for 8~9 minutes and then lower the temperature to 55°C while keeping the pressure constant, and then reduce the pressure and temperature to room temperature. Finally, open the mold to get the nano carbon crystal electrothermal board.

[0024] In this embodiment, the heat-generating paper has a basis weight of 30~70g/m², a thickness of 60~80μm; both upper and lower layers of the Kraft paper provide a pressure reducing and buffering effect; if the dispersant is a mixture, the different dispersants can be mixed according to any proportion; if the water soluble adhesive is a mixture, different water soluble adhesives can be mixed according to any proportion; the phenolic resin in the fixed paint is a curing agent; the epoxy resin is an adhesive, and the acetone solution is a thinner.

[0025] The experiments below demonstrate the effect of the aforementioned embodiments of the invention:

[0026] The experiments were conducted in a temperature controlled chamber with international standard, and the

chamber has no heat source inside out and provides an almost 100% heat insulating effect, and the net dimensions of the interior of the chamber include: a floor of $(3.93 \pm 0.2\text{m}) \times (3.93 \pm 0.2\text{m})$, a height of $2.8 \pm 0.2\text{m}$, 16 pieces of nano carbon crystal electrothermal boards of $(600\text{mm} \times 900\text{mm})$ on the floor of the chamber 16, and all nano carbon crystal electrothermal boards are connected in series.

[0027] Testing Condition: The nano carbon crystal electrothermal board is placed horizontally in the standard chamber, and the edge of the electrothermal board is kept 0.3m from the wall and set at the middle.

[0028] Testing Apparatuses: Thermal couple for measuring temperature, galvanometer, temperature indicating meter, voltmeter, ammeter, anemometer, humidity meter, and watt-hour meter.

[0029] In any selected electrothermal board, eight temperature detection points are set on the surface of the selected electrothermal board as shown in FIG. 1, and set in the standard chamber without cold or hot sources such as air conditioners, and close to absolutely insulating. If the room temperature is at 12.5°C , the nano carbon crystal electrothermal board is electrically conducted to continue measuring the temperature. From the measuring results listed in Table 1 (that shows the measurements of temperature at each measuring point of the electrothermal board while the temperature is rising and Table 2 (that shows that temperature of each measuring point of the electrothermal board after the temperature is stable, regardless of the condition of a temperature rise as shown in Table 1 or a stable process as shown in Table 2, the temperature of each measuring point of the electrothermal board is uniform, and close to an isothermal field, and each measuring time and the average difference between the maximum temperature and minimum temperature fall within a range of $0.5 \sim 2.5^\circ\text{C}$.

Table 1

Temperature ($^\circ\text{C}$) Time (hr)	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7	Point 8
10	13.20	13.34	13.40	13.50	13.27	13.84	13.56	13.89
30	13.94	14.17	15.65	15.45	16.01	15.88	16.05	15.34
50	16.36	17.77	18.02	17.32	18.10	18.13	16.67	17.85
70	17.22	18.17	17.39	19.33	19.02	17.37	18.29	18.63
90	21.74	23.27	24.09	25.17	21.29	23.34	24.18	22.31
110	24.38	25.36	26.22	24.19	26.32	27.01	26.89	24.59
130	28.69	28.83	28.90	30.11	31.31	29.61	30.42	31.04
150	33.23	33.91	33.29	34.37	35.11	34.74	35.26	34.29
180	36.12	36.37	36.22	37.09	37.82	36.32	37.19	38.10
200	37.89	38.09	39.24	39.73	40.05	39.28	39.21	40.13
220	38.89	39.02	40.56	40.28	42.35	42.79	39.37	39.37
240	41.28	42.37	39.98	39.74	42.13	42.29	41.29	39.86
280	41.69	42.10	40.06	39.89	42.07	42.19	41.37	39.88
300	42.22	42.02	39.88	39.90	42.08	42.10	41.35	39.70

Table 2

Temperature (°C) Time (hr)	Point 1	Point 2	Point 3	Point 4	Point 5	Point 6	Point 7	Point 8
1	41.28	42.37	39.98	39.74	42.13	42.29	41.29	39.66
2	41.69	42.10	40.06	39.89	42.07	42.19	41.37	39.88
3	42.22	42.02	39.88	39.90	42.08	42.10	41.35	39.70
4	42.28	42.27	39.78	39.94	42.23	42.19	41.39	39.76
5	42.19	42.19	40.06	39.89	42.17	42.29	41.27	39.58
6	42.02	42.01	39.78	39.80	42.08	42.20	41.15	39.60

[0030] In the standard chamber at a room temperature of 12.5°C as shown in Fig. 2, after the nano carbon crystal electrothermal board is electrically conducted, the average surface temperature of 16 pieces of electrothermal board varies with time, and it shows that the average surface temperature of the electrically conducted board rises rapidly, and the average surface temperature of the 16 boards reaches an appropriate temperature 36°C within 4.4minutes for the construction requirements on ground.

[0031] In an electrically conducted electrothermal board as shown in FIG. 3, the room air temperature in the chamber varies with time, and it shows that the nano carbon crystal electrothermal board can dissipate heat into air rapidly, so that it only takes 23.2 minutes for the room temperature to rise quickly to the standard temperature of 18°C.

[0032] After the electrothermal board is electrically conducted as shown in FIG. 4, the curve of the average heating generating quantity of the 16 pieces of boards varying with time indicates that the quantity of generated heat of the electrically conducted electrothermal board increases rapidly. After 4.3 minutes, the quantity of generated heat reaches its maximum, and remains unchanged thereafter.

[0033] Embodiment 11: The difference between this embodiment and Embodiment 10 is that the ratio of the weight of the nano carbon crystal material and the weight of the paper pulp for making paper is 1: 12~17, and the rest is the same as Embodiment 10.

[0034] Embodiment 12: The difference between this embodiment and Embodiment 10 is that the ratio of the weight of the nano carbon crystal material and the weight of paper pulp for making paper is 1: 15, and the rest is the same as Embodiment 10.

[0035] Embodiment 13: The difference between this embodiment and Embodiment 10 is that the proportion of the weight of the phenolic resin, the weight of the epoxy resin and the weight of the acetone is 3: 6: 1, and the rest is the same as Embodiment 10.

Claims

1. A nano carbon crystal material, comprising:

acrylonitrile-based carbon fibers, occupying 70~80% of the total weight of the nano carbon crystal material;
nano carbon fibers, occupying 1~5% of the total weight of the nano carbon crystal material; and
carbon crystals, occupying 15~29% of the total weight of the nano carbon crystal material.

2. The nano carbon crystal material of claim 1, **characterized in that** the nano carbon crystal material is composed of acrylonitrile-based carbon fibers occupying 72~78% of the total weight, nano carbon fibers occupying 2~4% of the total weight, and carbon crystals occupying 18~25% of the total weight.

3. The nano carbon crystal material of claim 1 or 2, wherein the acrylonitrile-based carbon fiber is composed of acrylonitrile-based carbon fibers having a number of thousand-filaments of 10~15K, a diameter of 1~5 μm , and a

length of 2~4mm and 4.5~6mm respectively, and formed according to the ratio of 0.5~2: 1 by weight; and the diameter of the nano carbon fiber is 50~200nm; and the number of meshes of the carbon crystal mesh is 400~1000 meshes.

- 5 4. A method of manufacturing an electrothermal board by using the nano carbon crystal material as recited in claim 1, comprising the steps of:

1. preparing a nano carbon crystal heat-generating paper;

- 10 a. setting a ratio of the weight of the nano carbon crystal material and the weight of the paper pulp for making paper to be 1: 9~19, and mixing the nano carbon crystal material into the paper pulp for making paper, and then adding water solution into a dispersant to form a mixed carbon fiber pulp, wherein the consuming quantity of the dispersant is equal to 0.5~5% of the weight of the nano carbon crystal material;
- 15 b. adding the mixed carbon fiber pulp into a high-speed isotropic machine containing a water soluble adhesive solution and blended at a speed of 800~2000 rpm for 1~2 hours, so that the degree of beating of the pulp falls within a range of 3 5 °~55 °SR;
- c. using a paper making machine having a 50-mesh paper marking net to control the paper marking machine at a speed of 10~15m/min for processing the processed carbon fiber mixed pulp, and then compressing the carbon fibers on a piece of woolen cloth, and drying and shaping the carbon fibers by a baking bobbin;

2. preparing a glass fiber cloth prepreg: applying the mixed paint onto the surface of a fiber cloth with over 25×16 transverse and longitudinal glass fibers, wherein the mixed paint has a proportion of phenolic resin, epoxy resin and acetone mixture equal to 1~5: 4~8: 1 by weight to obtain a glass fiber cloth prepreg with a thickness of 0.1~0.3mm;

25 3. preparing a nano carbon crystal electrothermal board;

- d. placing six layers of 50-gram Kraft paper on an iron tray first, and then placing a leveling iron plate with a thickness of 1~3mm, and finally coating a mold release agent on the iron plate;
- 30 e. coating a layer of a high pressure resisting polyethylene film of 0.01~0.05mm thick on the iron plate, and placing a piece of decoration paper on the high pressure resisting polyethylene film;
- f. laying 3~5 layers of fiber cloth prepreps on the decoration paper, and then putting a piece of nano carbon crystal paper, and putting a copper foil wrapped with tin foil separately on both sides as conducting electrode;
- 35 g. laying 3~5 layers of fiber cloth prepreps on the nano carbon crystal paper;
- h. laying a layer of the high pressure resisting polyethylene film of 0.01~0.05mm thick on the fiber cloth prepreg, and coating a mold release agent thereon, and then laying a leveling iron plate of 1~3mm thick on the high pressure resisting polyethylene film, and then laying 6 layers of 50-gram Kraft paper on the iron plate;
- i. securing the flat copper meshed conducting wire with the copper electrode as conducting anode and cathode, and leading them parallelly from the backside of the glass fiber cloth prepreg; and
- 40 j. putting the semi-finished product on a thermal press machine, and preheating it up to 80°C, and turning on the thermal press machine to pressurize up to 200 tons and increase the temperature up to 100°C, and keep the constant temperature and pressure for 8~9 minutes, and then increase the temperature to 120°C, and keep the constant temperature and pressure for 8~9 minutes, and then increase the temperature to 140°C, and keep the constant temperature and pressure for 8~9 minutes and then lower the temperature to 55°C while keeping the pressure constant, and then reduce the pressure and temperature to room temperature, and finally open the mold to get the nano carbon crystal electrothermal board.

- 50 5. The method of manufacturing an electrothermal board by using a nano carbon crystal material as recited in claim 4, wherein the dispersant is composed of sodium alginate, methyl cellulose, polyacrylamine or any combination of the above.

6. The method of manufacturing an electrothermal board by using a nano carbon crystal material as recited in claim 4, wherein the paper pulp for making paper is a wood cellulose pulp.

- 55 7. The method of manufacturing an electrothermal board by using a nano carbon crystal material as recited in claim 4, wherein the water soluble adhesive is composed of polyaniline, polyvinyl alcohol, water soluble phenolic resin or any combination of the above.

8. The method of manufacturing an electrothermal board by using a nano carbon crystal material as recited in claim 4, wherein the phenolic resin is a phenolic resin 1411, and the epoxy resin is an epoxy resin E44.
9. The method of manufacturing an electrothermal board by using a nano carbon crystal material as recited in claim 4, wherein the copper foil has a width of 10~15mm and a thickness of 0.6mm, and the copper foil is pressed by an edge knurling machine to form meshes on both edges of the copper foil.
10. The method of manufacturing an electrothermal board by using a nano carbon crystal material as recited in claim 4, wherein the mold release agent is a polyurethane mold release agent.

Patentansprüche

1. Nano-Kohlenstoffkristallmaterial, umfassend:

acrylnitrilbasierte Kohlefasern, die 70~80% des Gesamtgewichts des Nano-Kohlenstoffkristallmaterials ausmachen;
 Nanokohlenstofffasern, die 1~5% des Gesamtgewichts des Nano-Kohlenstoffkristallmaterials ausmachen; und
 Kohlenstoffkristalle, die 15~29% des Gesamtgewichts des Nano-Kohlenstoffkristallmaterials ausmachen.

2. Nano-Kohlenstoffkristallmaterial nach Anspruch 1, **dadurch gekennzeichnet, dass** sich das Nano-Kohlenstoffkristallmaterial aus acrylnitrilbasierten Kohlefasern, die 72~78% des Gesamtgewichts ausmachen, Nanokohlenstofffasern, die 2~4% des Gesamtgewichts ausmachen, und Kohlenstoffkristallen, die 18~25% des Gesamtgewichts ausmachen, zusammensetzt.

3. Nano-Kohlenstoffkristallmaterial nach Anspruch 1 oder 2, wobei sich die acrylnitrilbasierte Kohlefaser aus acrylnitrilbasierten Kohlefasern mit einer Filamentzahl von 10.000~15.000, einem Durchmesser von 1~5 μm und einer Länge von 2~4 mm bzw. 4,5~6 mm zusammensetzt und in einem Gewichtsverhältnis von 0,5~2:1 gebildet ist; und wobei der Durchmesser der Nanokohlenstofffaser 50~200 nm beträgt; und die Maschenzahl des Kohlenstoffkristallnetzes 400~1000 Maschen beträgt.

4. Verfahren zur Herstellung einer elektrothermischen Platte unter Verwendung des Nano-Kohlenstoffkristallmaterials nach Anspruch 1, mit den folgenden Schritten:

1. Herstellen eines wärmeerzeugenden Papiers aus Nanokohlenstoffkristall;

- a. Einstellen eines Verhältnisses des Gewichts des Nanokohlenstoff-Kristallmaterials und des Gewichts des Papierbreis zur Herstellung des Papiers auf 1:9~19, und Mischen des Nanokohlenstoffmaterials in den Papierbrei, um Papier herzustellen, und dann Zugabe einer Wasserlösung zu einem Dispergiermittel, um einen gemischten Kohlefaserbrei zu bilden, wobei die Verbrauchsmenge des Dispergiermittels gleich 0,5~5% des Gewichts des Nano-Kohlenstoffkristallmaterials ist;
- b. Einleiten des gemischten Kohlefaserbreis in eine isotrope Hochgeschwindigkeitsmaschine, die eine wasserlösliche Klebstofflösung enthält, und Mischen mit einer Drehzahl von 800~2000 UpM für 1-2 Stunden, so dass der Mahlgrad des Faserbreis in einen Bereich von 35°~55° SR fällt;
- c. Verwenden einer Papierherstellungsmaschine mit einem 50 mesh-Papiermarkierungsnetz, um die Papiermarkierungsmaschine mit einer Geschwindigkeit von 10~15 m/min zur Verarbeitung des aufbereiteten gemischten Kohlefaserbreis zu steuern, und dann Komprimieren der Kohlefasern auf einem Stück Wollstoff sowie Trocknen und Formen der Kohlefasern mit einer Heizspule;

2. Herstellen eines Prepregs aus Glasfasergewebe: Aufbringen der gemischten Farbe auf die Oberfläche eines Glasfasergewebes mit über 25x16 quer- und längsgerichteten Glasfasern, wobei die gemischte Farbe eine Mischung von Phenolharz, Epoxidharz und Aceton in einem Gewichtsverhältnis von 1~5:4~8:1 enthält, um ein Prepreg aus Glasfasergewebe mit einer Dicke von 0,1~0,3 mm zu erhalten;

3. Herstellen einer elektrothermischen Platte aus Nanokohlenstoffkristall;

- d. zuerst Auflegen von sechs Lagen 50 Gramm-Kraftpapier auf ein Eisenblech und dann Auflegen einer egalisierenden Eisenplatte mit einer Dicke von 1~3 mm und schließlich Auftragen eines Formtrennmittels auf die Eisenplatte;

e. Auftragen einer Schicht einer hochdruckbeständigen Polyethylenfolie mit einer Dicke von 0,01~0,05 mm auf die Eisenplatte und Auflegen eines Stücks Dekorationspapier auf die hochdruckbeständige Polyethylenfolie;

f. Auflegen von 3~5 Lagen Prepregs aus Glasfasergewebe auf das Dekorationspapier und dann Auflegen eines Stücks Nanokohlenstoffkristallpapier und einer mit Stanniolfolie umwickelten Kupferfolie getrennt voneinander auf beide Seiten als leitende Elektrode;

g. Auflegen von 3~5 Lagen Prepregs aus Glasfasergewebe auf das Nanokohlenstoffkristallpapier;

h. Auflegen einer Schicht der hochdruckbeständigen Polyethylenfolie mit einer Dicke von 0,01~0,05 mm auf das Prepreg aus Glasfasergewebe und Auftragen eines Formtrennmittels, und dann Auflegen einer egalisierenden Eisenplatte mit einer Dicke von 1~3 mm auf die hochdruckbeständige Polyethylenfolie und dann Auflegen von 6 Lagen 50 Gramm-Kraftpapier auf die Eisenplatte;

i. Befestigen des flachen leitenden Kupferdrahtgitters mit der Kupferelektrode als leitender Anode und Kathode und Herausführen derselben parallel zueinander aus der Rückseite des Prepregs aus Glasfasergewebe; und

j. Auflegen des halbfertigen Produkts auf eine Heißpressmaschine und Vorheizen derselben bis auf 80°C, und dann Einschalten der Heißpressmaschine, um einen Druck von bis zu 200 Tonnen aufzubringen und die Temperatur bis auf 100°C zu erhöhen, und Beibehalten von Temperatur und Druck für 8~9 Minuten, und dann Erhöhen der Temperatur auf 120°C und Beibehalten von Temperatur und Druck für 8~9 Minuten, und dann Erhöhen der Temperatur auf 140°C und Beibehalten von Temperatur und Druck für 8~9 Minuten, und dann Absenken der Temperatur auf 55°C unter Beibehaltung des Drucks, und dann Absenken von Druck und Temperatur auf Raumtemperatur, und schließlich Öffnen der Form, um die elektrothermische Platte aus Nanokohlenstoffkristall zu erhalten.

5. Verfahren zur Herstellung einer elektrothermischen Platte unter Verwendung eines Nano-Kohlenstoffkristallmaterials nach Anspruch 4, wobei sich das Dispergiermittel aus Natriumalginat, Methylcellulose, Polyacrylamid oder einer Kombination der obigen zusammensetzt.

6. Verfahren zur Herstellung einer elektrothermischen Platte unter Verwendung eines Nano-Kohlenstoffkristallmaterials nach Anspruch 4, wobei der Papierbrei zur Herstellung von Papier ein Holzzellstoffbrei ist.

7. Verfahren zur Herstellung einer elektrothermischen Platte unter Verwendung eines Nano-Kohlenstoffkristallmaterials nach Anspruch 4, wobei sich der wasserlösliche Klebstoff aus Polyanilin, Polyvinylalkohol, wasserlöslichem Phenolharz oder einer Kombination der obigen zusammensetzt.

8. Verfahren zur Herstellung einer elektrothermischen Platte unter Verwendung eines Nano-Kohlenstoffkristallmaterials nach Anspruch 4, wobei das Phenolharz ein Phenolharz 1411 ist und das Epoxidharz ein Epoxidharz E44 ist.

9. Verfahren zur Herstellung einer elektrothermischen Platte unter Verwendung eines Nano-Kohlenstoffkristallmaterials nach Anspruch 4, wobei die Kupferfolie eine Breite von 10~15 mm und eine Dicke von 0,6 mm hat und die Kupferfolie mit einer Rändelmaschine gepresst wird, um an beiden Rändern der Kupferfolie Maschen zu bilden.

10. Verfahren zur Herstellung einer elektrothermischen Platte unter Verwendung eines Nano-Kohlenstoffkristallmaterials nach Anspruch 4, wobei das Formtrennmittel ein Formtrennmittel auf Polyurethanbasis ist.

Revendications

1. Matériau à cristaux de nanocarbone, comprenant :

- des fibres de carbone à base d'acrylonitrile, constituant de 70 à 80 % du poids total du matériau à cristaux de nanocarbone,
- des fibres de nanocarbone, constituant de 1 à 5 % du poids total du matériau à cristaux de nanocarbone,
- et des cristaux de carbone, constituant de 15 à 29 % du poids total du matériau à cristaux de nanocarbone,

2. Matériau à cristaux de nanocarbone, conforme à la revendication 1, **caractérisé en ce que** ce matériau à cristaux de nanocarbone comprend des fibres de carbone à base d'acrylonitrile, constituant de 72 à 78 % de son poids total, des fibres de nanocarbone, constituant de 2 à 4 % de son poids total, et des cristaux de carbone, constituant de 18 à 25 % de son poids total.

3. Matériau à cristaux de nanocarbone, conforme à la revendication 1 ou 2, dans lequel

- les fibres de carbone à base d'acrylonitrile sont des fibres de carbone à base d'acrylonitrile qui présentent un nombre de milliers de filaments de 10 à 15, un diamètre de 1 à 5 μm , et une longueur de 2 à 4 mm ou de 4,5 à 6 mm, valeurs réparties suivant un rapport pondéral de 0,5/1 à 2/1 ;
- le diamètre des fibres de nanocarbone vaut de 50 à 200 nm ;
- et les cristaux de carbone ont une granulométrie de 400 à 1000 mesh.

4. Procédé de fabrication d'un panneau électrothermique à l'aide d'un matériau à cristaux de nanocarbone conforme à la revendication 1, lequel procédé comporte les étapes suivantes :

1) préparation d'un papier thermo-générateur à cristaux de nanocarbone

a) mélanger le matériau à cristaux de nanocarbone à de la pâte à papier pour fabrication de papier, en un rapport de 1/9 à 1/19 du poids du matériau à cristaux de nanocarbone au poids de la pâte à papier pour fabrication de papier, et ajouter une solution aqueuse dans un agent dispersant, pour obtenir une pâte mêlée de fibres de carbone, la quantité consommée de dispersant représentant de 0,5 à 5 % du poids du matériau à cristaux de nanocarbone ;

b) verser cette pâte mêlée de fibres de carbone dans une machine isotrope à haute vitesse contenant une solution d'un adhésif hydrosoluble et brasser le tout à une vitesse de 800 à 2000 t/min pendant 1 à 2 heures, de manière à ce que le degré de raffinage de la pâte se situe dans la gamme de 35 à 55 °SR ;

c) utiliser une machine de fabrication de papier, munie d'un filet de marquage de papier de 50 mesh pour régler la machine de marquage de papier à une vitesse de 10 à 15 m/min pour traiter la pâte mêlée de fibres de carbone et traitée, puis presser les fibres de carbone sur un morceau d'étoffe de laine, et faire sécher ces fibres de carbone et les mettre en forme à l'aide d'une bobine de cuisson ;

2) préparation d'un pré-imprégné de tissu de fibres de verre appliquer, sur la surface d'un tissu de fibres de plus de 25 x 16 fibres de verre transversales et longitudinales, un enduit qui est un mélange de résine phénolique, de résine époxy et d'acétone en proportions pondérales de 1-5/4-8/1, de manière à obtenir un pré-imprégné de tissu de fibres de verre, épais de 0,1 à 0,3 mm ;

3) préparation d'un panneau électrothermique à cristaux de nanocarbone

d) placer six couches de papier Kraft de 50 grammes sur un premier plateau en fer, puis placer une plaque de nivelage en fer, épaisse de 1 à 3 mm, et ensuite enduire cette plaque de fer d'un agent de démoulage ;

e) revêtir cette plaque de fer d'une couche de film de polyéthylène résistant aux pressions élevées et épais de 0,01 à 0,05 mm, et placer un morceau de papier décoratif sur ce film de polyéthylène résistant aux pressions élevées ;

f) placer sur le papier décoratif 3 à 5 couches de pré-imprégné de tissu de fibres, puis un morceau de papier à cristaux de nanocarbone, et placer séparément, sur les deux côtés, une mince feuille de cuivre enveloppée dans une mince feuille d'étain, en guise d'électrode conductrice ;

g) placer sur le papier à cristaux de nanocarbone 3 à 5 couches de pré-imprégné de tissu de fibres ;

h) placer sur le pré-imprégné de tissu de fibres une couche de film de polyéthylène résistant aux pressions élevées et épais de 0,01 à 0,05 mm, et l'enduire d'un agent de démoulage, puis placer sur ce film de polyéthylène résistant aux pressions élevées une plaque de nivelage en fer, épaisse de 1 à 3 mm, et placer ensuite sur cette plaque de fer six couches de papier Kraft de 50 grammes ;

i) assujettir aux électrodes en cuivre des conducteurs plats en cuivre ajouré de mailles, en guise de conducteurs d'anode et de cathode, et les disposer parallèlement depuis le côté arrière du pré-imprégné de tissu de fibres de verre ;

j) et placer ce produit semi-fini sur une machine de pressage à chaud, pré-chauffer le tout à 80 °C, puis mettre en marche la machine de pressage à chaud de manière à atteindre une pression de 200 tonnes et à porter la température à 100 °C, maintenir la température et la pression constantes pendant 8 à 9 minutes, augmenter ensuite la température jusqu'à 120 °C, maintenir la température et la pression constantes pendant 8 à 9 minutes, augmenter ensuite la température jusqu'à 140 °C, maintenir la température et la pression constantes pendant 8 à 9 minutes, puis abaisser la température jusqu'à 55 °C tout en maintenant la pression constante, puis réduire la pression et laisser la température baisser jusqu'à la température ambiante, et enfin ouvrir le moule pour obtenir le panneau électrothermique à cristaux de nanocarbone.

5. Procédé de fabrication d'un panneau électrothermique à l'aide d'un matériau à cristaux de nanocarbone, conforme

EP 2 063 024 B1

à la revendication 4, dans lequel l'agent dispersant est constitué d'alginate de sodium, de méthyl-cellulose, de polyacrylamine ou d'une combinaison de ceux-ci.

- 5 **6.** Procédé de fabrication d'un panneau électrothermique à l'aide d'un matériau à cristaux de nanocarbone, conforme à la revendication 4, dans lequel la pâte à papier pour fabrication de papier est une pâte de cellulose de bois.
- 10 **7.** Procédé de fabrication d'un panneau électrothermique à l'aide d'un matériau à cristaux de nanocarbone, conforme à la revendication 4, dans lequel l'adhésif hydrosoluble est constitué de polyaniline, de poly(alcool vinylique), d'une résine phénolique hydrosoluble, ou d'une combinaison de ceux-ci.
- 15 **8.** Procédé de fabrication d'un panneau électrothermique à l'aide d'un matériau à cristaux de nanocarbone, conforme à la revendication 4, dans lequel la résine phénolique est de la résine phénolique 1411 et la résine époxy est de la résine époxy E44.
- 20 **9.** Procédé de fabrication d'un panneau électrothermique à l'aide d'un matériau à cristaux de nanocarbone, conforme à la revendication 4, dans lequel la mince feuille de cuivre est large de 10 à 15 mm et épaisse de 0,6 mm, et cette mince feuille de cuivre a subi un pressage effectué à l'aide d'une machine permettant le molettage des bords, de manière à ce que soient formées des mailles sur les deux bords de la mince feuille de cuivre.
- 25 **10.** Procédé de fabrication d'un panneau électrothermique à l'aide d'un matériau à cristaux de nanocarbone, conforme à la revendication 4, dans lequel l'agent de démoulage est un agent de démoulage à base de polyuréthane.

25

30

35

40

45

50

55

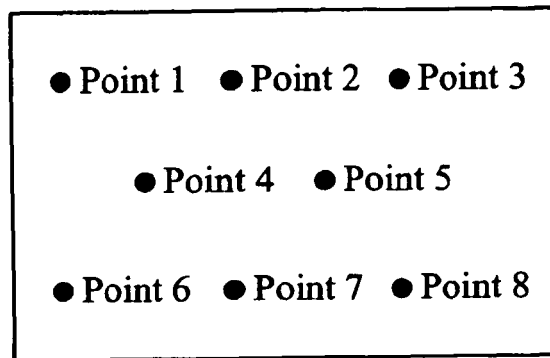


FIG.1

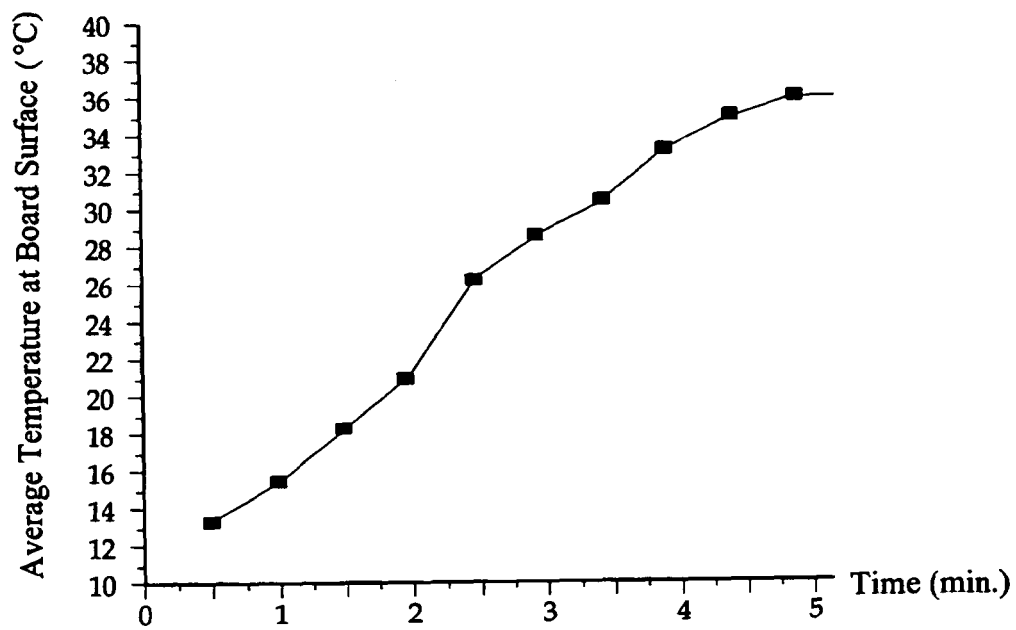


FIG.2

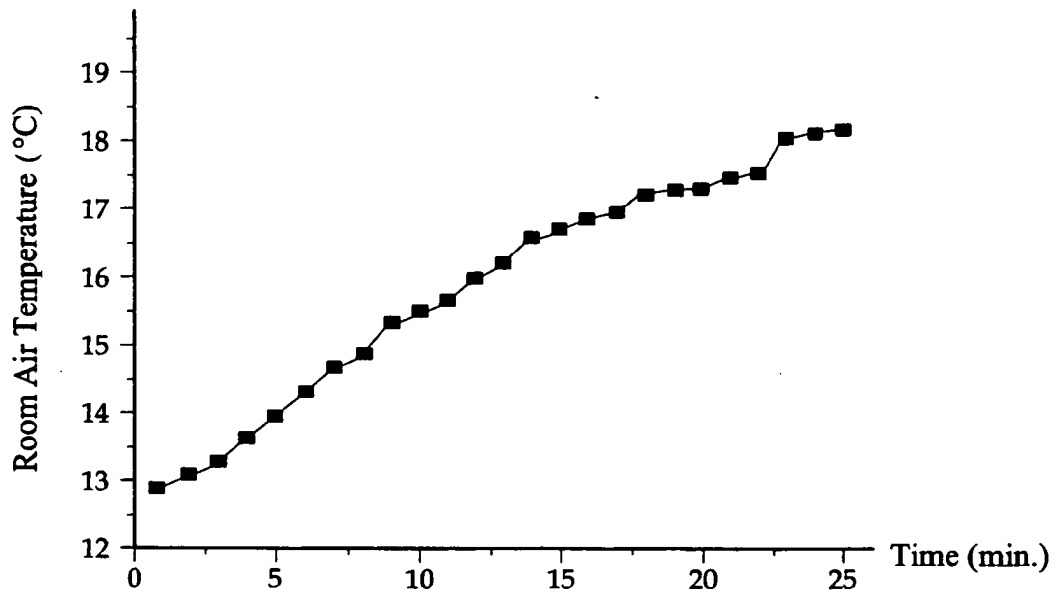


FIG.3

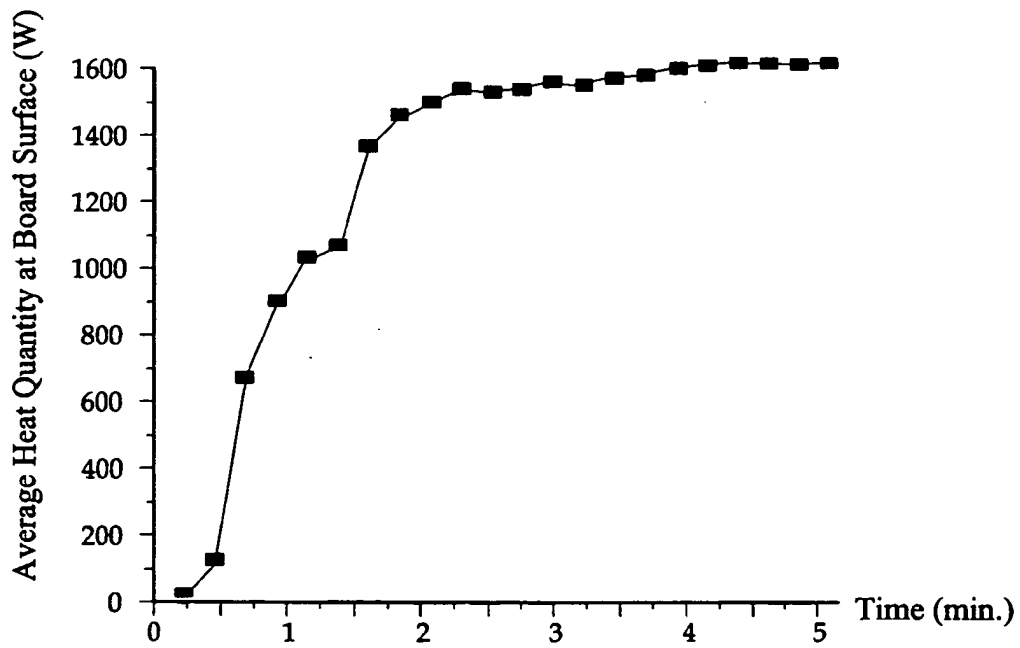


FIG.4