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(54) **APPAREIL DE CHAUFFAGE PAR CONDUCTION**

(54) **CONDUCTIVE HEATING UNIT**

(57) Disclosed are a fine conductive particle powder comprising fine hollow spherical glass or resin particles plated with a metal and having a bulk density of 0.2 to below 0.9 g/cm³, an exothermic conductive coating or paste comprising the above powder and a synthetic resin binder, a conductive heating unit having a desirably shaped solid or solid surface coated or impregnated with the above coating or paste, and a process for producing the above conductive heating unit, whereby the conductive heating unit operable at low voltages can be obtained.



TITLE: CONDUCTIVE HEATING UNIT

ABSTRACT

Disclosed are a fine conductive particle powder
5 comprising fine hollow spherical glass or resin particles
plated with a metal and having a bulk density of 0.2 to
below 0.9 g/cm³, an exothermic conductive coating or paste
comprising the above powder and a synthetic resin binder, a
conductive heating unit having a desirably shaped solid or
10 solid surface coated or impregnated with the above coating
or paste, and a process for producing the above conductive
heating unit, whereby the conductive heating unit operable
at low voltages can be obtained.

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CONDUCTIVE HEATING UNITBACKGROUND OF THE INVENTION

The present invention relates to an exothermic
5 conductive coating or paste and a conductive heating unit
having the same, and more particularly to a conductive
heating unit operable at low voltages.

Various conductive heating units each of which
comprises a conductive sheet or coating film containing a
10 fine conductive powder and a binder have previously been
known, and a fine powder of carbon black, graphite, a metal
or a metal oxide has been used as the fine conductive powder
(Japanese Patent Unexamined Publication Nos. 60-59131/1985
and 54-149758/1979).

15 Prior-art conductive heating units using carbon black
or graphite as the fine conductive powder can be used at
commercial voltages of 100 to 200 V, but can not be used at
low voltages of 1.2 to 24 V which are applied, for example,
when batteries are used as power sources, because the
20 resistance of carbon black or graphite is too high to
develop heat. For the purpose of reducing the resistance
(Ω) of a conductive heating unit to several tenths to
several hundredths that of the heating unit containing
carbon black or graphite, attention can be given to metal
25 powders.

However, the metal powders incorporated in coating
solutions, even if they are finely pulverized, precipitate

downward during storage as conductive coatings or during
solidifying procedure of liquid coating films because of
their high specific gravity. Consequently, the production
of the heating units by using the metal powders results in
5 the difficulty of obtaining uniform exothermic surfaces.
One possible solution for prevention of this precipitation
is to mix the coating with a thickener or a suspending
agent. However, such prior-art thickeners or suspending
agents can not effectively disperse the metal powders, and
10 hence only exothermic conductive coatings partially
different in resistance are obtained. For this reason, such
coatings are unsuitable for surface heaters which are
required to have uniform temperature distribution.

At present, therefore, there are utilized no surface
15 heaters operable at low voltages which are applied, for
example, when batteries are used as power sources.

SUMMARY OF THE INVENTION

It is therefore a primary object of the present
invention to provide a conductive heating unit operable at
20 low voltages.

Other objects of this invention will be apparent from
the following description.

The present inventors discovered that fine hollow resin
or glass particles plated with a metal can be uniformly
25 dispersed in an exothermic conductive coating film, thereby
obtaining a conductive heating unit operable at low
voltages.

The present invention provides a fine conductive particle powder comprising fine hollow spherical glass or resin particles plated with a metal and having a bulk density of 0.2 to below 0.9 g/cm³, an exothermic conductive coating or paste comprising the above powder and a synthetic resin binder, a conductive heating unit having a desirable shaped solid or solid surface coated or impregnated with the above coating or paste, and a process for producing the above conductive heating unit.

10 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing the resistance relative to the ratio of the resin to the conductive powder; and

Fig. 2 is a graph showing the relationship between the exothermic temperature of the present invention at 6 V and the electric resistance.

15 DESCRIPTION OF THE PREFERRED EMBODIMENT

The fine hollow spherical glass or resin particles used in the present invention include, for example, glass such as Scotch Light (registered trade mark) Glass Bubble (S60/10000 and so on, Sumitomo 3M) and resins such as polymethyl methacrylate (PMMA) and polystyrene.

As the glass, soda-lime borosilicate glass (SiO₂ 54, Al₂O₃ 14, BeO₃ 8.3, FeO₃ 0.2, Na₂O 0.5, MgO 1, CaO 22) is used, and as heat-resistant resins, polyamide resins are used.

The size of the fine hollow spherical glass or resin particles is suitably 4 to 350 μm, preferable 10 to 200 μm.

The particles having a size of less than 4 μm increase the resistance (Ω) of the surface heater too high, and the particles having a size of more than 350 μm are difficult to disperse in the coating. These particles are therefore
5 unfavorable. The thickness of the glass or resin particles can be 0.5 to 2 μm .

The metal plating on the fine hollow spherical glass or resin particles is performed by electroless plating, a combination of electroless plating and electrode plating or
10 the like. In the case of the metal plating, Pt, Au, Ag and Ni are preferably used as the metals. Other metals such as Cu and Sn are unsuitable, because they are oxidized in use of the heating unit to increase the electric resistance.

Of the metals, Ag can satisfy both of cost and
15 stability in quality.

The thickness of metallic deposits is not particularly limited, and can be selected, taking cost and dispersibility into account. The thickness is suitably about 0.03 to 0.8 μm , preferably about 0.1 to 0.3 μm . The deposits having a
20 thickness of less than 0.03 μm increase the resistance (Ω) of the surface heater too high, and the deposits having a thickness of more than 0.8 μm make it difficult to disperse the particles in the coating, which results in the rise of cost.

25 The bulk density of the fine hollow spherical metal-plated glass or resin particle powders is similar to that of the synthetic resin binders, namely 0.2 to less than 0.9

g/cm³. If the bulk density is less than 0.2 g/cm³, segregation takes place to provide insufficient strength. On the other hand, if the bulk density is 0.9 g/cm³ or more, precipitation occurs to result in deterioration in
5 dispersibility.

As the synthetic resin binders for the conductive materials, there are used thermoplastic, thermosetting and electron beam curable resins, which can be suitably selected depending on the application field of the heating unit. The
10 thermoplastic resins have a softening point of at least 15°C and a mean molecular weight of thousands to hundreds of thousands. The thermosetting resins or reactive resins have a molecular weight of not more than 200,000 in the state of coating solutions. The resins are heated after their
15 coating and drying to infinitely increase their molecular weight by reactions such as condensation and addition. There can also be used the radiation curable resins in which groups cross-linkable or polymerizable to dryness by radiation exposure are contained or introduced in the
20 molecules of thermosetting resins. Such groups include acrylic double bond groups such as a radical-polymerizable unsaturated double bond group contained in acrylic acid, methacrylic acid or their ester compounds, allylic double bond groups such as a group contained in diallyl phthalate,
25 and unsaturated bond groups such as a group contained in maleic acid or its derivatives.

Examples of such synthetic resins include polyimide

resins, polyamide resins, polyphenylene oxide resins, silicone resins, polytitanocarboasilane resins, phenol resins, epoxy resins, polyparabanic acid resins, polyurethane resins, polyester resins, polyetheretherketone
5 resins, polyphenylene sulfide resins, polyflon resins, polyolefin resins and polyvinyl chloride resins. There can be selected a resin having a softening temperature or a decomposition temperature depending on the temperature desired for the coated film.

10 The amount ratio of the synthetic resin binder to the fine hollow spherical conductive particle powder is variously selected depending on the desired heating temperature, the area of the heating surface, the kind of the fine conductive particle powder and the synthetic resin,
15 combinations thereof and the like. However, the synthetic resin is generally used in a ratio of 25 to 360 parts by weight, preferable 30 to 200 parts by weight, to 100 parts by weight of the fine conductive particle powder.

When the ratio of the synthetic resin is less than 25
20 parts by weight, the electric resistance value decreases and the temperature of the heating unit can be elevated (therefore, applicable to the heating unit having a large heating surface). However, the strength of the coated film is insufficient, and the temperature coefficient of the
25 electric resistance is reduced, thereby being liable to produce temperature unevenness. On the other hand, when the ratio of the synthetic resin is more than 360 parts by

weight, the electric current necessary for heating can not be obtained (because of the excessive resistance value), which results in unsuitableness for the practical use.

The applied voltage which can be used in the present invention is 0.5 to 200 V, and can be adjusted by varying the ratio of the synthetic resin binder to the fine conductive powder and the thickness of the film. For example, when the low voltage is applied from a battery, the amount ratio of the fine conductive powder is increased. According to the present invention, the surface temperature of the heating unit is stably heated at desired temperatures up to at most about 450°C (at an environmental temperature of -30 to 40°C) for a long time by combinations of the compounding of the coating, the thickness of the coated film, the applied voltage and the like.

The coatings mainly comprising the fine conductive particle powders and the synthetic resins are applied by various coating methods such as brushing, roller coating, spray coating, electrostatic coating, electrodeposition coating and power coating, or by immersing methods. To the coatings, other additives or auxiliary agents may be added. Examples of the additives or the auxiliary agents include diluting agents, suspending agents, dispersants, antioxidants, other pigments and other necessary additives.

As the diluting agents, there are employed solvents used for coatings, such as aliphatic hydrocarbons, aromatic petroleum naphtha, aromatic hydrocarbons (for example,

toluene and xylene), alcohols (for example, isopropyl alcohol, butanol and ethylhexyl alcohol), ether alcohols (for example, ethyl cellosolve, butyl cellosolve and ethylene glycol monoether), ethers (for example, butyl ether), acetates, acid anhydrides, ether esters (for example, ethyl cellosolve acetate), ketones (for example, methyl ethyl ketone and methyl isobutyl ketone), N-methyl-2-pyrrolidone, dimethylacetamide and tetrahydrofuran. The preferred solvent is suitable selected depending on the synthetic resin as the binder. The diluting solvent is used in an amount of 400 parts by weight or less per 100 parts by weight of the resin.

The suspending agents used as required include methyl cellulose, calcium carbonate and fine powders of modified bentonite. As the dispersants, various surface-active agents are used. Such surface-active agents include anionic surface-active agents (such as fatty acid salts and liquid fatty oil sulfate salts), cationic surface-active agents (such as aliphatic amine salts and quaternary ammonium salts), amphoteric surface-active agents and nonionic surface-active agents.

In order to achieve solidification to dryness or curing of the coatings or pastes with ease for a short time, curing agents can be added. The curing agent can be selected depending on the resin used, and there are used known curing agents such as aliphatic or aromatic amines, polyisocyanates, polyamides, amines, thiourea and acid

anhydrides.

In addition, stabilizers, plasticizers, antioxidants or the like are suitably used.

The solids formed of substrates such as plastic materials, ceramic materials, woody materials, fibers, paper and metal materials coated with electric insulators in desired shapes, or the surfaces thereof are coated with or immersed in the exothermic conductive coatings of the present invention to produce the heating units.

10 The exothermic conductive coatings of the present invention include a paste of a solid powder mixture comprising the electrically conductive spherical powder particles and a synthetic resin (epoxy resin, vinyl chloride, and etc.). The paste can be molded by extrusion or roll molding and the powder mixture can be molded by cast molding which comprises casting the mixture into an air gap of an air gap pipe. Known molding methods to produce an electrically conductive heating unit using a mixture of the electrically conductive powder and the synthetic resin can be used in the present invention.

20 For example, the substrate formed of the metal material coated with the electric insulator, the ceramic material, the plastic material, woody material or a combination thereof, to which at least two metal terminals are securely attached, is coated with the coating of the present invention to a thickness of about 0.2 to 3.5 mm (the thickness of the coated film after curing is 0.1 to 3 mm).

The shape of the substrate described above is not

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particularly limited, which may be a plane surface or a curved surface. The heating units can be formed of linear, rod-like, cylindrical, plane or other three-dimensionally curved substrates.

Although it is desirable to coat the substrate surfaces with the ceramic materials, the woody materials are sometimes usable if a desired temperature is 150°C or lower. There are also usable combined articles such as a composite comprising the woody material, the plastic material or the metal material and the ceramic material applied thereon.

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When the solid surface to be coated is large and the brushing, the roller coating or the spray coating is adopted, the coating is increased in fluidity to improve the workability. In this case, a solvent for dilution is preferably incorporated in an amount of not more than 400 parts by weight per 100 parts by weight of the conductive powder. If more solvent is incorporated, the coating is too much fluidized and it is difficult to obtain a prescribed thickness of the coated film. The use of excessive solvent is therefore unsuitable for obtaining a desired surface temperature of the coated film.

The coated film is cured, solidified to dryness or cured by electron beams (radiation) at a temperature ranging from about 70 to 350°C.

When the solidification to dryness or the curing is conducted at a temperature ranging from about 70 to 350°C for an ample time, a smooth film having a prescribed thickness can be obtained. Higher temperatures are undesirable, because foaming, flowing, cracking and deterioration in quality are liable to take place. Temperature lower than 70°C are also undesirable, because it requires a lot of time.

When the coating is applied to a thickness of about 0.2 to 3.5 mm, followed by reaction at a temperature of not more than 350°C to cure the coating, the coated film solidified to dryness and having a thickness of about 0.1 to 3.0 mm is obtained. This electric resistance heating coated film

generates high temperature as well as low temperature. It is preferred that the coating is applied to a thickness of about 0.1 to 3.0 mm. If the thickness is less than 0.1 mm, the electric resistance increases too high, the wattage per unit area decreases too low, and further the film strength is insufficient. If the thickness is more than 3.0 mm, the segregation is liable to occur by precipitation and separation of the particles, and the uniform coated film is difficult to be obtained. The electric resistance between the metal terminals on this coated film is 0.1 to 300 Ω/\square at ordinary temperature (wherein Ω/\square represents electric resistance value per square area).

If there is a fear of leak, the exothermic coated film is covered with an electric insulating film thinly so far as the strength is maintained. Too thick film results in disturbance of heat transfer.

The heating units are similarly produced by treating the fibers or the paper with the coatings or pastes of the present invention containing the fine hollow spherical metal-plated particles and the synthetic resins.

Also, the heating units having excellent surface properties can be obtained by the use of the electron beam (radiation) curable resins.

According to the exothermic conductive coatings of the present invention, the temperature of the heating units is adjustable to a desired temperature by the selection of the kind of the fine hollow spherical metal-plated particles and

the synthetic resin, the compounding ratio, the thickness of the coated film and combination thereof, and further by the selection of the heating area or the applied voltage.

The exothermic conductive coatings of the present invention have temperature self-controlling function. In particular, the thickness of the coated films is unnecessary to be precisely made uniform, and the coated films can be manually formed on the solid surfaces of a desired shape. Further, the heating units can be produced by immersing the impregnatable solid materials (such as the fibers and the paper) of a desired shape in the coatings. The heating units of the present invention can therefore be widely utilized in various fields such as an interior wall application, flooring, roofing, a furnace inner surface use, pipe inner and outer surface applications, carpets, blankets, simplified heaters, warmers, antifreezers, signal covers and pots. In particular, the heating units are excellent as heaters for room heating and hot insulation and heating parts. According to the present invention, there can be obtained the heating units having the temperature self-controlling function, arbitrarily adjustable to desired temperatures up to about 450°C and further having the uniform temperature distribution over a large heating surface to a small heating surface in various shapes and surfaces (including an uneven surface).

The present invention will be described in detail with reference to the following Examples. It is understood of

course that these are not intended to limit the scope of the invention. In the following Examples, all parts are by weight.

Example 1

5 A hollow spherical Ag-plated conductive particle powder (PM) having a bulk density of 0.6 to 0.8 g/cm³ and obtained by plating hollow spherical particles (30 to 70 μm in size) of soda-lime borosilicate glass with silver to a deposit thickness of 0.1 to 0.2 μm by electroless plating was mixed
10 with each of various synthetic resins (R) as the binders to prepare a coating. The coatings in which the R was compounded in amounts of 50, 100, 200 and 500 parts, respectively, per 100 parts of the PM were applied on 3 cm X 3 cm glass plates each having terminals attached to both
15 ends thereof to produce heating units having a film thickness of 1 mm. The electric resistance (Ω/\square) was measured for each heating unit by an ohmmeter. The results fell between two upper and lower curves showing the relationship between R/PM and Ω/\square in Fig. 1. The
20 resistance differs according to the kind of the resins. For example, when the R/PM is 2, the heating units high in resistance exhibited a resistance of 10 Ω/\square at ordinary temperature (one-pack type silicones and urethane resins) and the heating units low in resistance exhibited a
25 resistance of 3 Ω/\square (unsaturated polyester resins). The resistance of the heating units containing epoxy resins, polyamide resins, polyflon resins, polyetheretherketone

resins, polytitanocarbosilane resins, polyphenylene oxide resins and the like fell between the above resistance values. It was shown that the resistance varied depending the kind of the resin and the manufacturing condition and
5 fell between two curves shown in Fig. 1.

As apparent from these results, it is seen that the resistance (Ω/\square) increases with an increase in amount of the resin binder. This shows that the heating units generating various temperatures can be obtained by changing
10 the kind of the resin and the ration thereof.

Example 2

There were compounded 100 parts of the hollow spherical Ag-plated glass particles (having a size of 30 to 70 μm , a deposit thickness of 0.1 to 0.2 μm and a bulk density of 0.6
15 to 0.8 g/cm^3) obtained in the same manner as with Example 1 and 130 parts of one-pack type epoxy resin containing dodeceny succinic anhydride (DDSA) as the curing agent to prepare a conductive coating. The resulting coating was applied on a 10 cm x 10 cm glass substrate to a thickness of
20 2 mm, followed by curing at 100°C. The relationship between the resistance (Ω/\square) and the temperature in the surface heater thus obtained is as shown in Fig. 2. When a voltage of 6 V was applied to this heater, a surface temperature of 55°C was obtained (the room temperature was 18°C).

25 Estimated from this experiment, the temperature of the coated film having a resistance of $10\Omega/\square$ and a size of 172 cm X 172 cm can be elevated to 55°C, when a voltage of 100 V

was applied thereto.

Example 3

A coated film containing 100 parts of the hollow spherical Ag-plated glass particles (having a size of 30 to 5 70 μm , a deposit thickness of 0.1 to 0.2 μm and a bulk density of 0.6 to 0.8 g/cm^3) and 60 parts of a polyamide resin was formed on a 95% Al_2O_3 ceramic plate (20 cm X 20 cm in size and 2 cm in thickness). When a voltage of 24 V (144 W) was applied to copper terminals embedded in the coated 10 film in parallel with each other at both ends of the plate, a high temperature of 210°C was obtained (the room temperature was 20°C). When a voltage of 100 V was applied, the power was heightened from 144 W to 2,500 W, and the temperature of the coated film having a size of about 80 cm 15 X 80 cm was elevated to 210°C . Thus, the surface heater having such a large heating area as previously not considered could be obtained. In contrast, with respect to prior-art surface heaters, an SiC, Ni-Cr heater only has the maximum size of 15 cm X 30 cm whose temperature is elevated 20 to 200°C at 100 V.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An electrically conductive exothermic composition comprising electrically conductive spherical powder particles and a synthetic resin binder in an amount of 25 to 360 parts by weight per 100 parts by weight of the spherical powder particles, wherein the powder particles have a bulk density of 0.2 to below 0.9 g/cm³ and are composed of non-magnetic hollow spherical particles of glass or of a heat resistant resin having a particle size between 4 to 350 μm and being plated at a thickness of 0.03 to 0.8 μm with a metal which is stable against oxidization during use and wherein the composition produces heat when an electric voltage is applied to a heating unit produced by coating the composition on a solid substrate.

2. The composition according to claim 1, in which the synthetic resin binder is at least one resin selected from the group consisting of a silicone resin, a urethane resin, an epoxy resin, a polyamide resin, a polyester resin, a polyimide resin, a polyolefin resin, a polytetrafluoroethylene resin, a polyetheretherketone resin, a polyphenylene sulfide resin, and a polytitanocarbosilane resin.

3. The composition according to claim 1 or 2, which is a coating or paste composition and which also contains a solvent in an amount of 400 parts by weight or less per 100

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parts by weight of the synthetic resin binder.

4. The composition according to claim 1, 2, or 3, wherein the hollow spherical particles have a wall thickness of 0.5 to 2 μm .

5. The composition according to any one of claims 1 to 4, wherein the hollow spherical particles are made of soda-lime borosilicate glass.

6. The composition according to any one of claims 1 to 4, wherein the hollow spherical particles are made of polyamide.

7. The composition according to any one of claims 1 to 4, wherein the hollow spherical particles are made of polymethyl methacrylate or polystyrene.

8. The composition according to any one of claims 1 to 7, wherein the metal plated on the hollow spherical particles is Pt, Au, Ag or Ni.

9. The composition according to any one of claims 1 to 7, wherein the metal plated on the hollow spherical particles is Ag.

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10. The composition according to any one of claims 1 to 9, which further comprises an aliphatic or aromatic amine, a polyisocyanate, thiourea or an acid anhydride as a curing agent.

11. An electrically conductive exothermic heating unit operable at a voltage of from 0.5 to 200 V and obtained by applying to a surface of a solid substrate the composition according to any one of claims 1 to 10.

12. The heating unit according to claim 11, wherein the composition is applied as a coating to have a thickness of 0.1 to 3 mm after curing the coated composition.

13. The heating unit according to claim 11 or 12, wherein the substrate is made of a ceramic material.

14. A process for producing the electrically conductive heating unit according to any one of claims 10 to 12, which comprises applying to the surface of the substrate with the exothermic composition and then curing the composition at temperature of 70 to 350°C.

15. An electrically conductive exothermic heating unit, which comprises:

(A) a substrate formed of a ceramic material, a plastic material, a woody material, a metal material coated with an

electric insulator or a combination thereof;

(B) on a surface of the substrate, a coated film having a thickness of 0.1 to 3 mm and being formed by (i) coating a coating or paste composition comprising electrically conductive spherical powder particles, a synthetic resin binder in an amount of 25 to 360 parts by weight per 100 parts by weight the electrically conductive spherical powder particles and optionally a solvent in an amount of up to 400 parts by weight per 100 parts by weight of the synthetic resin binder, wherein the electrically conductive spherical powder particles are composed of hollow spherical particles of a glass or heat resistant resin having a particle size between 4 to 350 μm and being plated at a thickness of 0.03 to 0.8 μm with a metal which is stable against oxidation during use and (ii) curing the coated composition; and

(C) at least two metal terminals attached at opposite ends of the substrate,

wherein the heating unit is operable at an electric voltage of from 0.5 to 200 V and produces heat when the electric voltage is applied thereto via the metal terminals.

16. The heating unit according to claim 15, wherein the electrically conducted spherical powder particles are silver-plated hollow spherical particles of soda-lime borosilicate glass.

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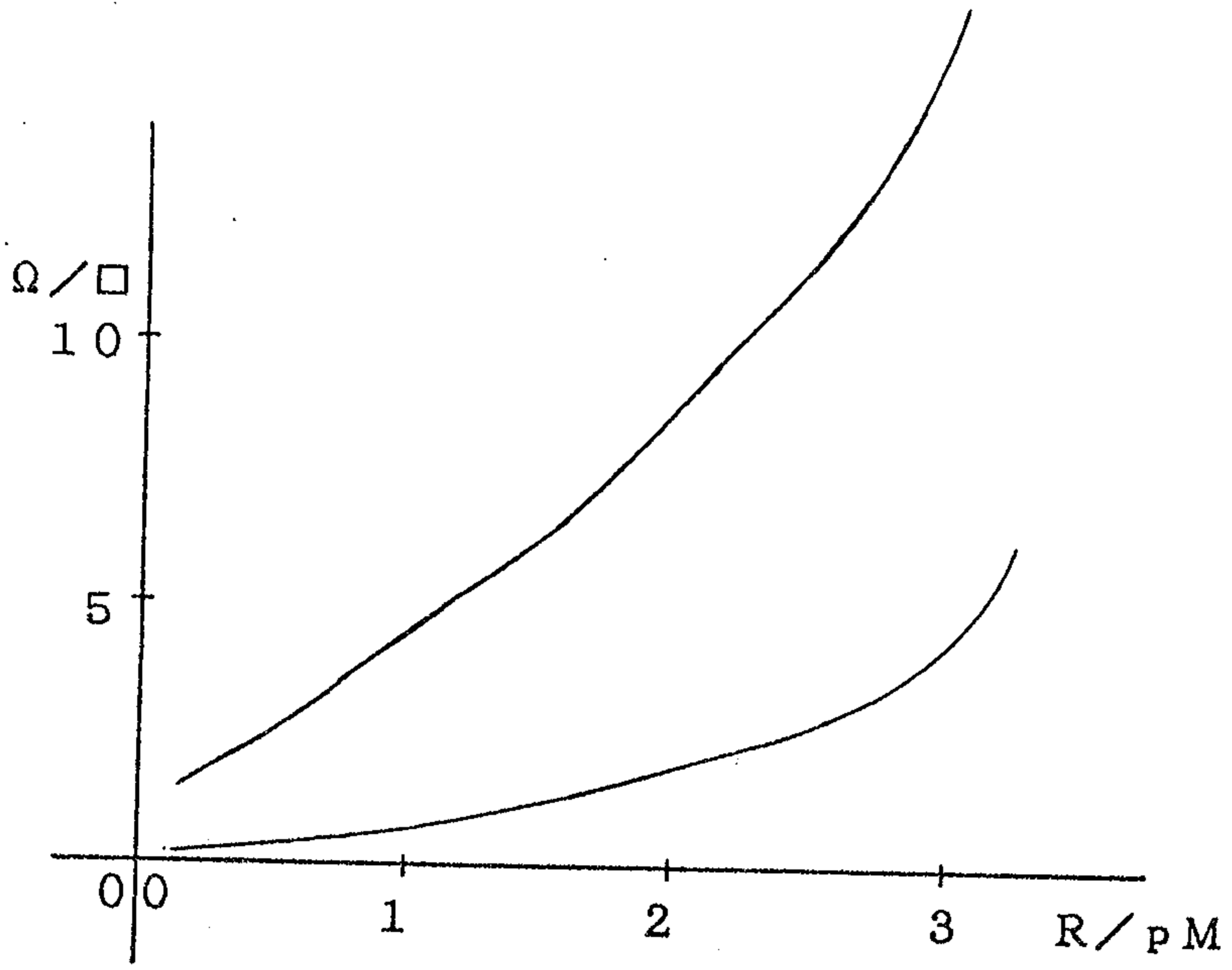
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17. The heating unit according to claim 15 or 16,
wherein the substrate is formed of a ceramic material.

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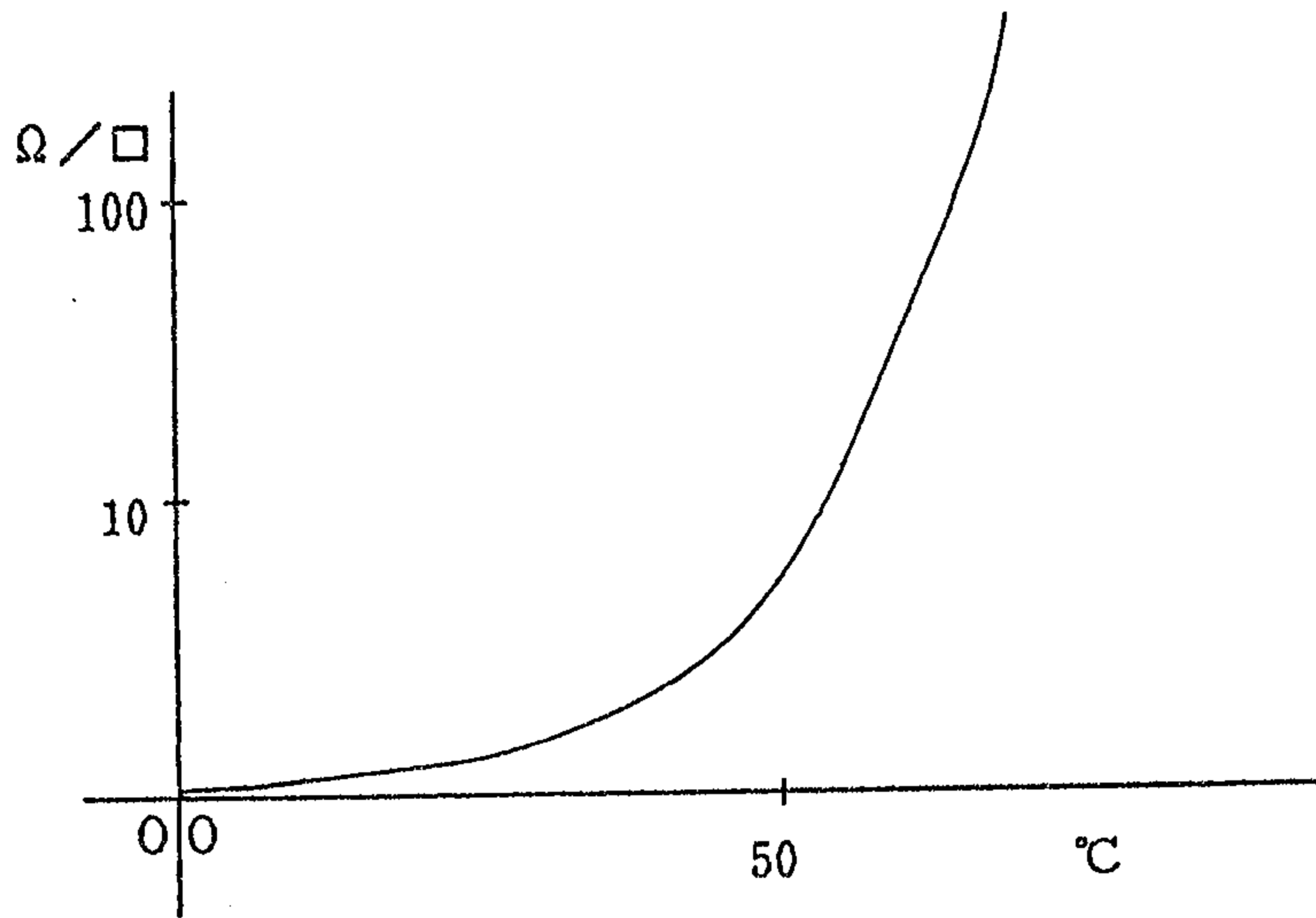
PATENT AGENTS

Fig. 1



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Fig. 2



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