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(54) Title: ELECTROMAGNETIC SHIELDING ADHESIVE COMPOSITE MATERIAL

(57) Abstract: An electromagnetic shielding adhesive composite material comprising a thermoplastic binder made of an adhesive agent composition and organic synthetic fibers, having thereon electrically conductive surface-coating, dispersed in the binder, wherein the organic synthetic fibers are contained in an amount of 1 to 50 % by weight based on the weight of the thermoplastic binder.

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ELECTROMAGNETIC SHIELDING ADHESIVE COMPOSITE MATERIAL

Field

The present invention relates to an electromagnetic shielding material which prevents leakage of electromagnetic waves or prevents absorption of external electromagnetic waves from the outside, and specifically relates to an electromagnetic shielding adhesive composite material for use in electronic machinery.

Background

Electronic machinery has control digital circuits. As the electronic machinery has developed, the frequency used for the digital circuits has become equal to or higher than a gigahertz. As a result, the digital circuits themselves work as antennas, and an unintentional leak of the electromagnetic waves or reception from the outside may occur.

Emitted electromagnetic waves have bad influences on neighboring electronic machinery as noises. Therefore technologies for shielding electromagnetic waves have recently become important as the electronic machinery is reduced in size and improved in performance.

For example, parts such as gaskets are required to have electromagnetic shielding ability for a countermeasure against the bad influences by the electromagnetic waves. Japanese Patent Kokai Publication No. H11-346082, for example, describes a shielding soft packing with a structure in which an elastic resin-foam is employed as a core material, the core material is wrapped with electromagnetic shielding woven or non-woven cloth made of conductive fibers, and fixed with acrylic adhesive tape.

Other types of electromagnetic shielding gaskets include those in which elastic foaming urethane is injected in a tube made of conductive fibers, or those in which a sponge hollow tube made of nonflammable urethane is rolled by conductive woven or non-woven cloth with adhesives.

However, the conventional gaskets easily drop conductive fibers from a cut end in use. The dropped conductive fibers may short the circuits which are put inside electronic machinery, or ground them to other locations so as to cause short-circuit incidents or lowering in electromagnetic shielding ability. In addition, the dropped conductive fibers may scatter to make the inside of machinery dirty. Further, the conventional gaskets are

high in manufacturing cost and involve difficulty for reducing their thickness because they have complicated structure.

Japanese Patent Kokai Publication No. H4-7899 describes an electromagnetic shielding sheet having a structure in which a synthetic resin film is closely adhered along and filled in a curved surface of a metal-fiber mat which has been formed to a desired curved plain shape. However, the metal-fiber mat is poor in conformity to a site to be adhered due to its high rigidity, and it is difficult to shape it into a desired shape.

Japanese Patent Kokai Publication No. H11-354969 and U.S. Patent No. 4,566,990 describe electromagnetic shielding materials in which conductive fillers such as metal coated fibers and the like are dispersed in a thermoplastic resin. However, it is not considered in the publications, conforming ability nor adhering ability of the electromagnetic shielding materials themselves to a site to be adherend. Therefore, double-faced tape or adhesives have to be used when the electromagnetic shielding materials are applied to an adherend. Such procedure makes an applying step complicated. Further, presence of adhesive layers makes it difficult to reduce their thickness.

Summary

There is a need to provide an electromagnetic shielding composite material, conductive fillers contained in which are well dispersed, the material having good conforming ability and adhering ability to an adherend, and having adhesiveness.

The present invention provides an electromagnetic shielding adhesive composite material comprising a thermoplastic binder made of an adhesive agent composition and organic synthetic fibers having thereon conductive surface-coating dispersed in the binder, wherein the organic synthetic fibers are contained in an amount of 1 to 50% by weight based on the weight of the thermoplastic binder, and the objective is achieved thereby.

In the specification, the wording "adhesive" is used as in wide-ranged concept, also including the concepts of adhesion, adherence, tackiness, and pressure sensitive adhesive.

Brief Description of the Drawings

Fig. 1 is an illustrative view of an electromagnetic shielding ability measurement apparatus by KEC method.

Fig. 2 is a graph showing measurement results in electromagnetic shielding ability of the electromagnetic shielding adhesive composite material of the present invention.

Detailed Description

Thermoplastic Binder

The thermoplastic binder is a binder having good flexibility and showing adhesiveness but not limited thereto. The thermoplastic binder is usually a composition containing major amount of resins showing adhesiveness.

The adhesive resins showing adhesiveness are generally classified as rubber type, acryl type and silicone type. The rubber type adhesive agents are those made of elastomer, and tackifying agents, softening agents, anti-aging agents and the like mixed therewith. The elastomer is usually natural rubber, but SBR, SIS, polyisobutylene, butyl rubber and the like may be used. The acryl type adhesive agents are synthetic products from acrylates and the like, and a main low-Tg and soft monomer providing adhesiveness, a minor amount of high-Tg and hard comonomer providing adhesiveness and cohesiveness, and a functional group containing monomer for crosslinkage or improvement of adhesiveness are copolymerized. The silicone type adhesive agents are those made of silicone rubber and silicone resins.

The adhesive resins referred to herein include, hotmelt materials such as ethylene-vinyl acetate copolymer, polyamide, polyester, polyolefin and the like.

The adhesive agent compositions are prepared by blending conventional additives in the adhesive resins. The plural adhesive resins may be employed with blending.

Preferred adhesive agent compositions are ethylene-vinyl acetate copolymer and ethylene vinyl acetate which are hotmelt materials, or adhesive agents comprising acryl resins. When the hotmelt materials are employed as the thermoplastic binder, the adhesive composite material may be used as conductive hotmelt materials.

Being a copolymer of ethylene with vinyl acetate, the ethylene vinyl acetate varies in physical properties depending on the molar ratio thereof. When melting point is important, it is preferred to select and use the ethylene vinyl acetate having low molar ratio of vinyl acetate, even at the cost of poor fluidity on heating. The copolymer may be adjusted in viscosity by addition of polymerization initiators.

Organic Synthetic Fibers Having Conductive Surface-coating

The organic synthetic fibers having conductive surface-coating are conductive fillers included in the thermoplastic binder. The organic synthetic fibers having conductive surface-coating are organic synthetic fibers (plastic fibers) which are coated with conductive substances such as metals. The metals may be surface treated.

The organic synthetic fibers employed in the present invention have at once flexibility, and can be electrically conductive materials and/or non-electrically conductive materials. But they are different from rigid fibrous materials such as metal fibers and carbon fibers. Therefore, they are easier to be dispersed in the thermoplastic binder with shorter dispersing time, than the rigid fibrous materials. This allows dispersing volume ratio to be increased. Fluidity of the thermoplastic binder is not impeded as well, and an adhesive composite material excellent in flexibility is obtained.

Whereas the metal fibers, the carbon fibers and the like are extremely higher in rigidity of fibers by comparison with the organic synthetic fibers. Therefore, if they are incorporated in the thermoplastic binder, the matrix material is impeded in flexibility and fluidity, and the resulting adhesive composite material becomes rigid.

That is, flexibility of the both organic synthetic fibers and thermoplastic binder allows long-fibers to be dispersed largely and uniformly in the adhesive resins, and as a result, a conductive composite material which has adhesiveness and has good shaping ability and conforming ability, is provided.

The organic synthetic fibers may be made of, for example, polyester, polyolefin, polyamide, acryl, rayon and the like. The polyester is particularly preferred.

The plastic fibers preferably have a fineness of from 0.1 d to 10 d (denier). If thickness of the plastic fibers is less than 0.1 d, the resulting fibers become high in specific gravity because large amount of conductive substances are required for coating. If the thickness is more than 10 d, the resulting fibers become rigid. These situations are not preferred.

Examples of the conductive substances used for the conductive surface-coating include silver, copper, gold, aluminium, nickel, alloys thereof, and combinations thereof. Those having good conductivity are preferred. Specific examples include organic synthetic fibers coated with silver, the surface of which is optionally treated with sulfurization.

In one embodiment, silver has good electroconductivity, so it works as a good antenna when it is coated on the organic synthetic fibers, and electromagnetic waves are converted to electric currents. Electric currents which are converted from the noises of electromagnetic waves, are converted to heat with resistance of the polymer which the silver is plated to, or by the resistance of the silver itself.

If a surface of the electrically conductive material, for example, silver, coated fibers which are organic synthetic fibers having conductive surface-coating, is treated with sulfurization, resistance is improved on a surface of conductive surface-coating, and reflection of electric waves at a surface of a composite shaped article of the present invention is reduced thereby. This allows the electromagnetic wave absorbing ability to be improved, and the absorbance frequency band to be broad.

As a method for coating electrically conductive material on the organic synthetic fibers, a conventional method may be employed. Examples thereof include electroless plating, sputtering, vacuum evaporation and the like. The electroless plating method is particularly preferred from the viewpoint of mass production and homogeneity. The electrically conductive material is preferably coated in an amount of about 5 to 50% by weight based on the weight of the plastic fibers. If the coating amount is less than 5% by weight, electrical conductivity becomes insufficient. If it is more than 50% by weight, electrical conductivity does not vary, whereas specific gravity becomes large and is not preferred.

As a method for treating a silver coated surface with sulfurization, a method of dipping the silver coated fibers into an aqueous solution of sulfides such as sodium sulfide and potassium sulfide, or a method of treating with gases such as hydrogen sulfide may be used. Among these, the method of dipping into an aqueous solution of sulfides is particularly preferred because the treatment is subjected homogeneously just on the surface of the silver coated layer, and the procedure is easy. Silver sulfide is formed on a silver surface of the silver coated fibers with the sulfurization treatment.

The organic synthetic fibers having conductive surface-coating may be determined in length, and be cut uniformly to length. The fibers may be employed with their uniform length, or as a mixture of fibers having different lengths. The fibers may have a fiber length of from about 0.01mm to 100 mm, preferably 0.1mm to 30 mm.

As a wavelength of an electromagnetic wave is taken into consideration, the fiber length more preferably is several times or several fractions of the wavelength. For example, to damp effectively a frequency of 60 GHz (5 mm of wavelength), the fiber length may be any one of 15 mm, 10 mm, 5 mm, 3 mm, 0.5 mm, and the like, or the several lengths may be mixed.

Commercially available organic synthetic fibers having conductive surface-coating may be employed. Examples of those on the market include SILFIBERTM which is silver coated polyester long-staples manufactured by Mitsubishi Material K.K.

Method for Preparing Composite Material of the Present Invention

The composite material of the present invention is prepared by incorporating the organic synthetic fibers having conductive surface-coating into the thermoplastic binder as a filler. By first, the organic synthetic fibers having conductive surface-coating are cut to a predetermined length. The fibers are then mixed and dispersed uniformly in the thermoplastic binder. The amount of the fibers is 1 to 50% by weight, preferably 1 to 30% by weight, more preferably 5 to 20% by weight based on the weight of the thermoplastic binder.

If the blending amount of the organic synthetic fibers is less than 1% by weight, the composite material becomes poor in electromagnetic shielding ability. If the amount is more than 50% by weight, electromagnetic shielding ability may become saturated, it becomes difficult to process, or adhesiveness and flexibility may become poor.

Other fillers may be incorporated into the thermoplastic binder. Examples thereof include fire retardants, electromagnetic absorbing materials having high magnetic permeability (e.g., ferrite is preferred), alumina providing heat conductivity, carbon and the like.

As these fillers are mixed and dispersed, conditions have to be adjusted so that the organic synthetic fibers having conductive surface-coating are not be damaged. For example, the temperature may have to be adjusted so that the organic synthetic fibers do not alter in shape when heating is conducted. Mixing step has to finish within a period so that the conductive surface-coating does not come off.

The dispersing conditions such as viscosity may have to be adjusted suitably depending on the classes and the properties of the thermoplastic binder. When ethylene

vinyl acetate is employed as the thermoplastic binder, predetermined amount of organic synthetic fibers are mixed and dispersed in the binder which has been melted to liquid with heating at a suitable temperature, for example, 100°C.

A dispersing method may include the steps of, putting into a molten binder when the thermoplastic binder is a hotmelt material, or putting into a binder containing solution when the thermoplastic binder is solution type, and mixing compulsory during a given period. The mixing can be conducted by stirring with, for example a three roll mill, a double-screw extruder, a propeller mixer and the like.

The organic synthetic fibers having conductive surface-coating are basically buried in the thermoplastic binder which is a matrix, and independent fibers are prevented from dropping, and incidents with short circuits are also prevented. The mixed and dispersed materials may be shaped by putting them into a suitable mold, or with sheeting and cutting to desired size and form.

The electromagnetic shielding adhesive composite material of the present invention can prevent electromagnetic leakage to the outside and electromagnetic absorption from the outside, and has suitable elasticity, flexibility and adhesiveness.

Therefore, shaped articles made of the composite material of the present invention may be used as electromagnetic shielding materials or gaskets, easily conformable to adherends having complicated form such as cases of electronic machinery, further adherable without using double-faced tape nor adhesives due to adhesiveness of the thermoplastic binder.

The conformity and adhesiveness thereof may easily be improved by treating with heat. Thus, it is possible to prevent electromagnetic leakage to the outside and electromagnetic absorption from the outside, without need of supplying adhesive-functional materials such as tape after being shaped, and it is easy to reduce their thickness with keeping their functions.

In some embodiments the electromagnetic shielding adhesive composite materials and the shaped articles of the present invention involve one or more of the following advantages.

- Having flexibility and adhesiveness, and easy to process;
- Having flexibility and adhesiveness, and excellent in conformity;

- Excellent in electric shielding ability, and in spite of their simple construction, performances are comparable to the conventional materials;
- Independent fibers are prevented from dropping and incidents with short circuits are prevented because the organic synthetic fibers having conductive surface-film are basically buried in the thermoplastic binder; and
- Showing sufficient grounding ability.

Examples

The following Examples further illustrate the present invention in greater detail but are not to be construed to limit the scope thereof.

Example 1

100 parts by weight of polyethylene vinyl acetate EV210 (manufactured by Mitsui Du Pont Polychemical K.K.) which is a thermoplastic binder, and 12.5 parts by weight of silver plated polyester fibers SILFIBER (manufactured by Mitsubishi Material K.K., fineness of 2 d (denier), fiber length of 5.0 mm) which are organic synthetic fibers having conductive surface-film were provided.

100 parts by weight of polyethylene vinyl acetate EV210 pellets were filled in a double-screw extruder MIXER W 50E (manufactured by Brabender Co.) adjusted to 100°C, and melted on a rotation rate of 30 rpm. 12.5 parts by weight of the silver plated polyester fibers SILFIBER was slowly added to the melted polyethylene vinyl acetate EV210, after the entire addition, it was mixed and dispersed with heating for 5 minutes to obtain an electromagnetic shielding adhesive composite material. The resulting composite material was sheeted to have a thickness of 1 mm with a hot coater adjusted to 150°C. This sheet was cut to obtain a stick shaped gasket of 10 mm width x 15 cm length.

Example 2

To 100 parts by weight of iso-octyl acrylate (manufactured by Nippon Shokubai K.K.) was added 0.020 parts by weight of a photopolymerization initiator IRGACURE 651 (manufactured by Nippon Ciba-Geigy Co., 2,2-dimethylmethoxy-2-phenyl acetone), and was stirred in a glass container. To prevent curing hindrance by oxygen, nitrogen was bubbled for ten minutes for removing oxygen dissolved in the mixed solution.

The mixed solution was then irradiated with a low pressure mercury lamp for few minutes and partially polymerized to conduct viscosity adjustment resulting in a syrup. 12.5 parts by weight of the silver plated polyester fibers SILFIBER (manufactured by Mitsubishi Material K.K., fineness of 2 d (denier), fiber length of 5.0 mm) were added to 100 parts by weight of the resulting viscous liquid, and this was stirred uniformly with a mixer.

The mixture liquid was knife coated in a thickness of 1 mm on polyester film (50 mm in thickness) which had been subjected to release treatment. To cut off oxygen which hinders photopolymerization, polyester film was laminated on the coated liquid layer. Thereafter, UV was irradiated with a low pressure mercury lamp for about 10 minutes, and monomers in the mixture liquid were photopolymerized to prepare a sheet. This sheet was cut to obtain a stick shaped gasket of 10 mm width x 15 cm length.

Example 3

Stick shaped gaskets were prepared according to the same manner as described in Examples 1 and 2, except that 10 parts by weight of soft ferrite having high magnetic permeability (BSN-125 manufactured by Toda Kogyo K.K.) was further incorporated as a filler.

Example 4

Stick shaped gaskets were prepared according to the same manner as described in Examples 1 to 3, except that 100 parts by weight of a fire retardant B53 (aluminum hydroxide) manufactured by Nikkei Sangyo K.K. was further incorporated as a filler.

Comparative Example 1

A stick shaped gasket was prepared according to the same manner as described in Example 1, except that 5 parts by weight of stainless fibers (8 micron in diameter, 5 mm in fiber length) manufactured by Nippon Seisen K.K. were used instead of the silver plated fibers.

Comparative Example 2

A stick shaped gasket was prepared according to the same manner as described in Example 1, except that 30 parts by weight of PAN type carbon fibers of 10 micron in

diameter, 50 micron in fiber length manufactured by Nippon Graphite Fiber K.K. were used instead of the silver plated fibers.

Comparative Example 3

A stick shaped gasket was prepared according to the same manner as described in Example 1, except that 100 parts by weight of polypropylene CF1064 (manufactured by Chisso Polypro K.K.) was used as a binder instead of the polyethylene vinyl acetate.

Comparative Example 4

A stick shaped gasket was prepared according to the same manner as described in Example 1, except that 100 parts by weight of polyethylene NOVATEC LD (manufactured by Nippon Polychem K.K.) was used as a binder instead of the polyethylene vinyl acetate.

Comparative Example 5

A shielding gasket STG 1.5-10 manufactured by Takeuchi Kogyo K.K. was employed as Comparative Example 5. This gasket is composed of a tube made of conductive fibers as an electromagnetic shielding member and a foaming urethane resin inserted into the tube.

Comparative Example 6

An electromagnetic shielding tape No. 8321 manufactured by Teraoka Seiksakusho was employed as Comparative Example 6. This tape is composed of a copper film of 35 micron in thickness and an acrylic adhesive agent applied thereon.

Dispersion Evaluation of Conductive Fibers

Dispersion uniformity of conductive fibers in the thermoplastic binder was evaluated by visually inspecting the sheet materials obtained by Examples 1 to 4 and Comparative Example 1. The results are shown in Table 1.

Table 1

Example 1	Uniform
Example 2	Uniform
Example 3	Uniform
Example 4	Uniform
Comparative Example 1	Not uniform (Fibers lodged in the coater-head as coating was conducted.)

The results of Table 1 show that the metal plated polyester fibers are improved in dispersion into thermoplastic binders and in coating and processing ability, by comparison with the stainless fibers.

Electromagnetic Shielding Test

Example 1, Example 2, Comparative Example 5, and Comparative Example 6 are tested for electromagnetic shielding ability by using KEC (Kansai Denshi Kogyo Shinko Center) method. For measurement, test samples were standardized to a size of 2.5 cm x 10 cm, and an attachment which is a copper plate of suitable size for the samples having an open window of 30 cm x 30 cm, was used. Fig. 1 shows illustrative view of the measurement apparatus. The measurement apparatus includes central electrical conductor 1, external electrical conductor 2, and input/output 3. Fig. 2 shows results of the measurement.

The measurement results show that test samples of the examples have the same or more excellent performances for shielding electric field, even though their construction is more simple, than those of the comparative examples.

Adhesion Test

Sample pieces of 2.5 cm (length) x 10 cm (width) x 0.1 cm (thickness) were washed on their surface with isopropyl alcohol at an ambient temperature of from 5 to 80°C. They were pressed to a stainless plate which had been set up vertically on the ground. Evaluation was made whether they came off after released. Table 2 shows the results.

Table 2

	Whether came off
Example 1	No
Example 2	No
Example 3	No
Example 4	No
Comparative Example 2	Yes
Comparative Example 3	Yes
Comparative Example 4	Yes

The results of Table 2 show that the sample in which carbon fibers were dispersed in polyethylene vinyl acetate (Comparative Example 2), and the samples in which silver plated polyester fibers were dispersed in non-adhesive thermoplastic resins (Comparative Examples 3 and 4), do not show adhesion.

Dropping Test at Cut End

Sheet materials obtained in Examples 1 and 2 were cut with a knife to 2.5 cm (length) x 1.25 cm (width) x 0.1 cm (thickness). They were put 100 ml of ion exchanged water in a glass bottle. Ultrasonic cleaning was conducted for 30 minutes, and visual inspection was conducted whether silver fibers or particles were dropped off. As a result, no dropping was observed.

Conductivity Test

Sheet materials obtained in Examples 1 and 2 were cut with a knife to 2.5 cm (length) x 2.5 cm (width) x 0.1 cm (thickness). They were put between two SUS 304 plates. Voltage between the terminals was measured with applying 100 mA of constant current to this sample, and resistance of direct current was calculated. Table 3 shows the results.

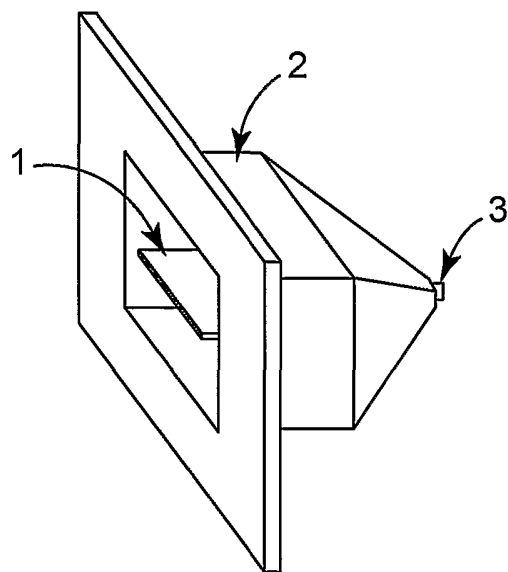
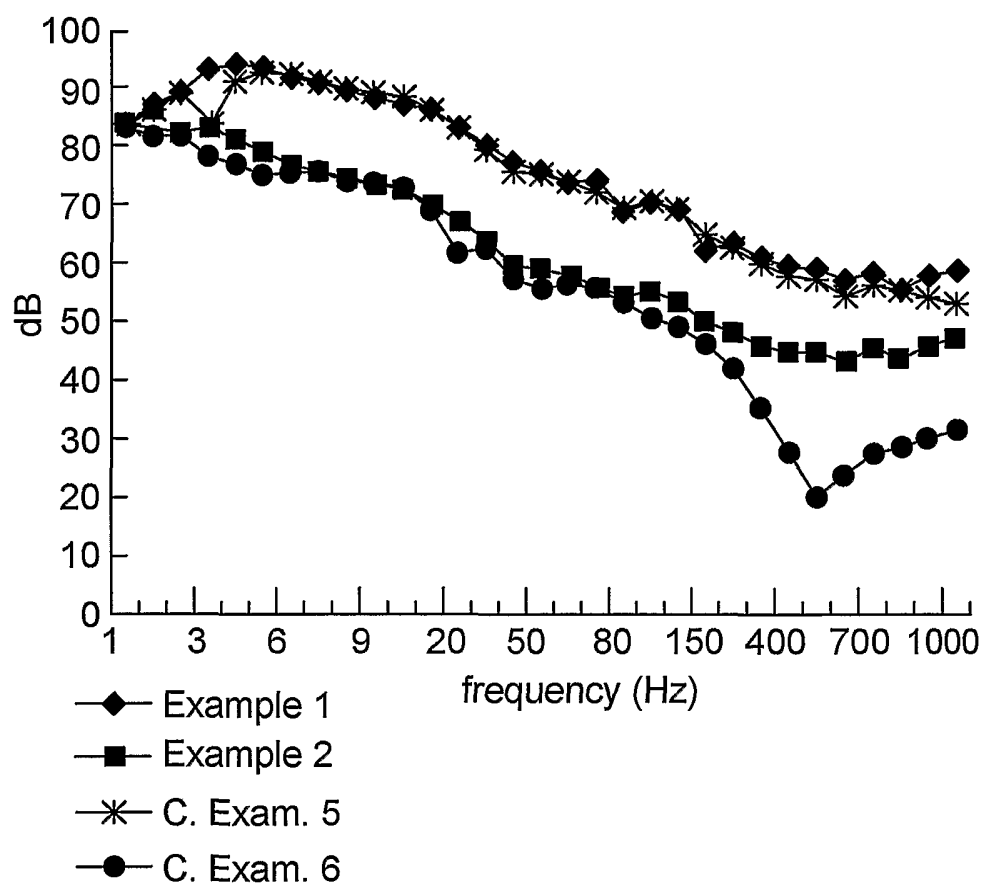
Table 3

	ohm/inch ² (6.25 cm ²)
Example 1	185
Example 2	210

Resistance values of direct current as shown in Table 3 mean that the samples of Examples 1 and 2 have sufficient grounding ability.

Claims

1. An electromagnetic-shielding composite material comprising
a thermoplastic binder made of an adhesive resin and
organic synthetic fibers dispersed in the binder,
wherein the organic synthetic fibers have an electrically conductive
surface-coating, and wherein the fibers are present in an amount of 1 to 50% by weight
based on the weight of the thermoplastic binder.
2. The electromagnetic-shielding composite material according to claim 1,
wherein the adhesive resin is a hot-melt material.
3. The electromagnetic shielding composite material according to claim 1,
wherein the adhesive resin is an acryl-resin.
4. The electromagnetic shielding composite material according to any one of
claims 1 to 3, wherein the organic synthetic fibers are polyester fibers having a fineness of
0.1 denier to 10 denier and a fiber-length of 0.1 to 30 mm.
5. The electromagnetic shielding composite material according to any one of
claims 1 to 4, wherein the electrically conductive surface-coating comprises silver.
6. An electromagnetic shielding shaped article obtained by shaping the
electromagnetic shielding composite material according to any one of claims 1 to 5.
7. A gasket obtained by shaping the electromagnetic shielding composite
material according to any one of claims 1 to 5.

*FIG. 1**FIG. 2*