

SPECIFICATION  
RESIN COMPOSITION  
AND  
PROCESS FOR PRODUCING CURED PRODUCT  
USING THE SAME

TECHNICAL FIELD

This invention relates to a resin composition for metathesis polymerization, and a process for producing a cured product using the same. These resin composition and cured product are useful as  
5 insulating materials for electronic and electric use, molding materials for house installations such as purifier tanks, septic tanks and bathtubs, and industrial materials such as corrugated sheets and pipes.

BACKGROUND ART

10 Cycloolefins are known to undergo ring-opening polymerization in the presence of a double decomposition (metathesis) catalyst system. For example, J. Am. Chem. Soc., Vol. 82, page 2337 (1960) discloses that norbornene undergoes ring-opening polymerization in the presence of a double-decomposition catalyst  
15 system. Angew. Chem. Int. Edn., Vol. 3, page 723 (1964) discloses that cyclopentene undergoes ring-opening polymerization in the presence of a double-decomposition catalyst system [MoCl<sub>5</sub>/ Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>].

Processes for producing polymers by subjecting cycloolefins to ring-opening polymerization are also known in the art. For example, Japanese Patent Applications Laid-open (KOKAI) Nos. Sho50-130900 and Sho52-33000 disclose a process in which a double-decomposition catalyst system comprised of a halide of tungsten or molybdenum and an organoaluminum compound is used to produce a ring-opening polymerization polymer.

Meanwhile, also known are processes for producing cross-linked polymer molded products by subjecting norbornene type cycloolefins such as dicyclopentadiene (hereinafter also "DCPD") and tricyclopentadiene to bulk polymerization. For example, Japanese Patent Applications Laid-open (KOKAI) Nos. Sho58-127728 and Sho58-129013 disclose a process in which a solution A comprised of a mixture of a catalytic component of a metathesis catalyst system with DCPD and a solution B comprised of a mixture of an activator of a metathesis catalyst system with DCPD are subjected to reactive injection molding (RIM) to produce a cross-linked polymer molded product.

Japanese Patent Applications Laid-open (KOKAI) No. Sho59-51911 discloses a process in which a norbornene type cycloolefin is subjected to reactive injection molding in the presence of a double-decomposition catalyst system formed by combination of a catalytic component selected from an organoammonium salt of tungsten and that of molybdenum with an activator selected from an alkoxyalkylaluminum halide and an aryloxyaluminum halide, to produce a cross-linked polymer molded product.

Japanese Patent Applications Laid-open (KOKAI) No.

Hei3-205409 discloses a process in which a metathesis catalyst system formed by combination of a catalytic component selected from tungsten hexachloride and tungsten oxytetrachloride with an  
5 activator selected from diethylaluminum chloride and ethylaluminum dichloride are used to produce a cross-linked dicyclopentadiene polymer by reactive injection molding.

In the above double decomposition catalyst system, the catalytic component has become known to be activated by the activator to  
10 cause the norbornene type monomer to undergo ring-opening polymerization. Also, when the reactive injection molding is carried out, the solutions A and B are impact-mixed and the resultant mixture is immediately poured into a mold as it stands liquid to effect ring-opening polymerization in bulk. Cured products thus obtained  
15 are also known to have good mechanical properties, electrical properties and water resistance.

However, the organoaluminum compound used as the activator is so highly reactive as to immediately react with water or oxygen when it is present, to lose its action of catalytic activation.

20 Accordingly, when the reactive injection molding is carried out, molding materials (the solutions A and B) must be stored in a container filled with inert gas or the bulk polymerization must be effected in a space formed in the state a separation type mold is closed, in order to prevent inclusion of the water and oxygen in air as far as  
25 possible. Hence, it has been impossible to introduce the molding materials into a mold while bringing them into contact with the

atmosphere, making it difficult to produce molded products by general-purpose compression molding.

## DISCLOSURE OF THE INVENTION

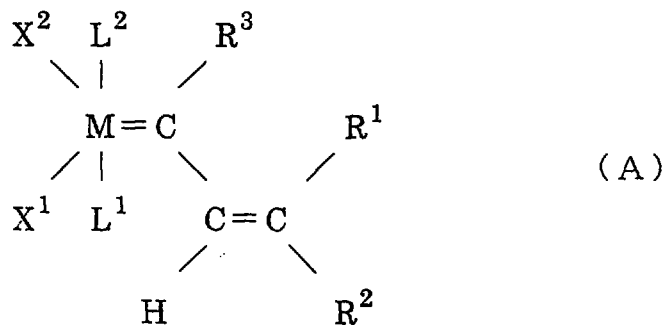
An object of the present invention is to solve the above  
5 problems and provide a resin composition suited to obtain various molded products from cycloolefin compounds in usual work environment.

The present inventors made studies on resin compositions polymerized and molded from polymerizable cycloolefin compounds  
10 in the presence of a metathesis polymerization catalyst. As the result, we have discovered that molded products having superior properties such as water resistance and tough mechanical properties and electrical properties can be obtained in usual work environment when a specific metathesis polymerization catalyst is used. Thus, we have  
15 accomplished the present invention.

More specifically, the present invention is a resin composition comprising;

(a) a metathesis-polymerizable cycloolefin compound;

(b) a metathesis polymerization catalyst represented by the  
20 following Formula (A).



wherein;

M represents a ruthenium atom or an osmium atom;

X<sup>1</sup> and X<sup>2</sup> each independently represent an anionic ligand;

L<sup>1</sup> and L<sup>2</sup> each independently represent a neutral

5 electron-donating group; and

R<sup>1</sup> and R<sup>2</sup> each independently represent an alkyl group having 1 to 18 carbon atoms, an alkenyl group having 2 to 18 carbon atoms, an alkynyl group having 2 to 18 carbon atoms, an aryl group, a carboxylate group having 1 to 18 carbon atoms, an alkoxyl group  
10 having 1 to 18 carbon atoms, an alkenyloxy group having 2 to 18 carbon atoms, an alkynyloxy group having 2 to 18 carbon atoms, an aryloxy group, an alkoxycarbonyl group having 2 to 18 carbon atoms, an alkylthio group having 1 to 18 carbon atoms, an alkylsulfonyl group having 1 to 18 carbon atoms or an alkylsulfinyl group having 1  
15 to 18 carbon atoms; and R<sup>3</sup> represents a hydrogen atom, an aryl group or an alkyl group having 1 to 18 carbon atoms; and

(c) at least one third component selected from a filler, a reinforcing material and an additive.

The above resin composition may preferably contain the  
20 component (b) in an amount of from 0.001 to 20 parts by weight based on 100 parts by weight of the component (a) and contain the component (c) in an amount of from 0.001 to 97 weight percent based on the total weight of the component (a), component (b) and component (c).

25 The present invention also provides a process for producing a cured product, comprising heating the above resin composition to

effect curing.

#### BEST MODES FOR PRACTICING THE INVENTION

The metathesis-polymerizable cycloolefin compound used as component (a) in the present invention may be any of polymerizable  
5 cycloolefins useful in metathesis polymerization. In particular, norbornene compounds such as substituted or unsubstituted norbornenes, dicyclopentadiene and dihydrodicyclopentadiene may preferably be used.

Norbornene compounds may include bicyclic norbornenes such  
10 as norbornene, methyl norbornene, dimethyl norbornene, ethyl norbornene, ethylidene norbornene, and butyl norbornene; tricyclic norbornenes such as dicyclopentadiene (cyclopentadiene dimer), dihydrodicyclopentadiene, methyldicyclopentadiene and dimethyldicyclopentadiene; tetracyclic norbornenes such as  
15 tetracyclododecene, methyltetracyclododecene and dimethylcyclotetradodecene; and penta- or more-cyclic norbornenes such as tricyclopentadiene (cyclopentadiene trimer) and tetracyclopentadiene (cyclopentadiene tetramer). Compounds having two or more norbornene groups as exemplified by  
20 norbornadiene, tetracyclododecadiene and symmetric tricyclopentadiene may also be used as polyfunctional cross-linking agents.

Of these, in view of ready availability, economical advantages and so forth, dicyclopentadiene, methyltetracyclododecene, ethylidene  
25 norbornene, tricyclopentadiene and tetracyclopentadiene are

preferred, and dicyclopentadiene is particularly preferred.

Any of these norbornene compounds may be used alone or in the form of a mixture of a plurality of compounds, and may preferably be in the form of a mixture containing 50% by weight or more of  
5 dicyclopentadiene and besides tricyclopentadiene and/or tetracyclopentadiene.

Any of cycloolefins such as cyclobutene, cyclopentene, cyclooctene, cyclooctadiene, cyclododecene, tetrahydroindene and methyltetrahydroindene (other than norbornene types) ring-opening  
10 copolymerizable with the norbornene type cycloolefins may be mixed and used as long as the object of the present invention is not damaged.

Incidentally, usual commercially available dicyclopentadienes may contain vinylnorbornene, tetrahydroindene, methylvinylnorbornene, methyltetrahydroindene, methyldicyclopentadiene,  
15 dimethyldicyclopentadiene, tricyclopentadiene or the like as an impurity. Dicyclopentadienes with various purities are commercially available. As the dicyclopentadiene used in the present invention, those having a purity usually not lower than 80% by weight, and preferably not lower than 90% by weight may be used,  
20 which may differ depending on the purpose for which polymers obtained are used.

When dicyclopentadiene is used, it may previously be subjected to heat treatment to convert part of dicyclopentadiene to a cyclopentadiene oligomer such as tricyclopentadiene or  
25 tetracyclopentadiene, or to isomerize the impurity vinylnorbornene or methylvinylnorbornene to tetrahydroindene or

methylnorbornene. The heat treatment may usually be made at 120 to 250°C for about 0.5 to 10 hours. Also, in order to prevent polymerization during the heat treatment, 1.5 to 10% by weight of an antioxidant may be added.

5 To the norbornene compound used in the present invention, the antioxidant may also optionally be added in advance. Incidentally, to usual commercially available dicyclopentadienes, an antioxidant such as 2,6-di(t-butyl)-4-methylphenol or 4-t-butylcatechol has already been added. When used, the antioxidant contained may be  
10 removed, or other antioxidant may be added anew.

Polymers formed by partial polymerization of the metathesis-polymerizable cycloolefin compound (those called semi-cured or B-stage products are also included to these) are included in the metathesis-polymerizable cycloolefin compound.

15 Where the metathesis-polymerizable cycloolefin compound and the metathesis polymerization catalyst of Formula (A) are mixed, a polymerization product, though different in degree, is formed with time, and the component (a) in the composition made up after such mixing comes to be a mixture of the metathesis-polymerizable  
20 cycloolefin compound with its polymerization product. Here, the rate of formation of such a polymerization product can appropriately be adjusted by changing conditions (quantity and type of the metathesis polymerization catalyst, temperature, time and so forth).

The component (b) used in the present invention is the  
25 metathesis polymerization catalyst represented by Formula (A) as described previously. This catalyst differs from two-part type

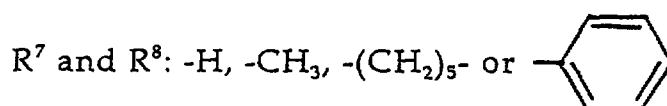
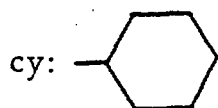
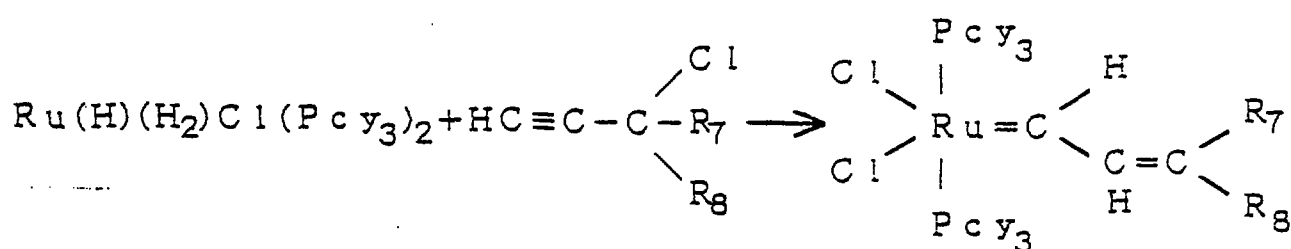
double decomposition catalysts formed of combination of a catalytic component with an activator as conventionally known. It is a catalyst capable of causing cycloolefin compounds to undergo ring-opening polymerization by metathesis reaction without losing its catalytic activity with ease because of water and oxygen in air.

The anionic ligand represented by  $X^1$  and  $X^2$  in Formula (A) refers to a group having negative electric charges when the coordination to the central metal is taken off. Such a group may include, e.g., hydrogen, a halogen,  $CF_3CO_2$ ,  $CH_3CO_2$ ,  $CFH_2CO_2$ ,  $(CH_3)_3CO$ ,  $(CF_3)_2(CH_3)CO$ ,  $(CF_3)(CH_3)_2CO$ , an alkyl group having 1 to 5 carbon atoms, an alkoxyl group having 1 to 5 carbon atoms, a phenyl group, a phenoxy group, a tosyl group, a mesyl group and a trifluoromethane sulfonate group. Particularly preferred are halogens (in particular, chlorine atoms) for the both.

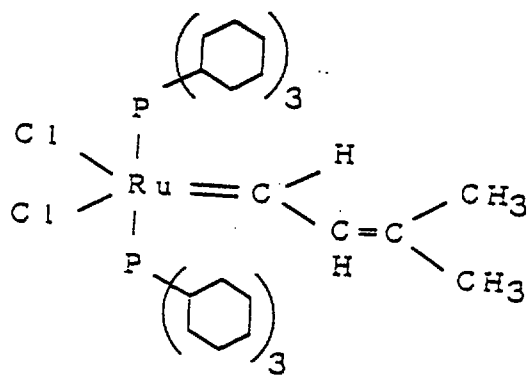
$L^1$  and  $L^2$  each independently represent a neutral electron-donating group. The neutral electron-donating group refers to a group having neutral electric charges when the coordination to the central metal is taken off. Such a group may include, e.g., a phosphine type electron-donating group represented by  $PR^4R^5R^6$  (wherein  $R^4$  represents a secondary alkyl group or a cycloalkyl group, and  $R^5$  and  $R^6$  each independently represent an aryl group, an alkyl group or a secondary alkyl group having 1 to 10 carbon atoms, or a cycloalkyl group), pyridine, p-fluoropyridine and an imidazolylidene compound. Preferred  $L^1$  and  $L^2$  are -p-(cyclohexyl)<sub>3</sub>, -p-(cyclopentyl)<sub>3</sub> or -p-(isopropyl)<sub>3</sub> groups for the both, but  $L^1$  and  $L^2$  may be electron-donating groups different from each other.  $Q^1$  and

Q<sup>2</sup> each independently represent a hydrogen atom, an alkyl group, an alkenyl group or an aromatic group. The alkyl group may be an alkyl group having 1 to 20 carbon atoms, the alkenyl group may be an alkenyl group having 2 to 20 carbon atoms, and the aromatic group  
 5 may be an aryl group. The above alkyl group, alkenyl group or aromatic group may have a substituent.

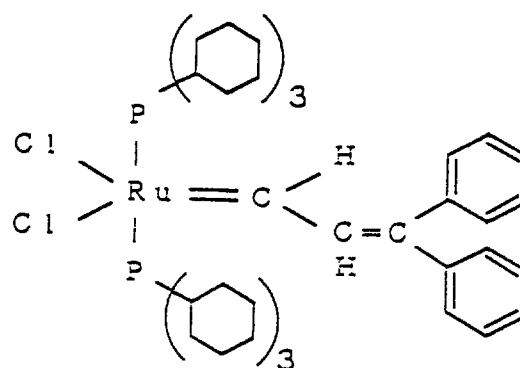
Methods for synthesizing the above compounds (catalysts) are already known in the art. For example, Organometallics Vol. 16, No. 18, page 3867 (1997) shows a method making use of propagyl chloride  
 10 (see the following scheme).



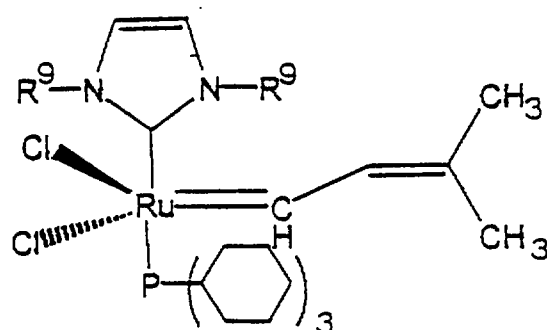
Such compounds (catalysts) may specifically include Ru carbene  
 15 catalysts such as those of the following formulas.



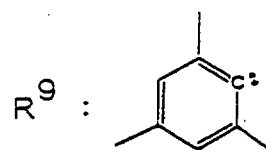
(1)



(2)



(3)



A synthesis example of the catalyst is given below.

#### Synthesis Example

5 (see the above scheme; R<sup>7</sup> and R<sup>8</sup>: methyl groups)

Cyclooctadiene ruthenium dichloride (21 mmol),  
 tricyclohexylphosphine (42 mmol), sodium hydroxide (7.2 g) and 250  
 ml of oxygen-removed sec-butanol were put into a 500 ml  
 Fisher-Porter bottle, and are heated at 90°C and hydrogen 2  
 10 atmospheric pressure. The pressure is repeatedly applied several  
 times until the hydrogen is completely absorbed, and stirring is  
 continued overnight. In the state the pressure of hydrogen is kept

applied, the reaction mixture is cooled to room temperature to obtain a yellow precipitate. With addition of 30 ml of water, the precipitate is filtered, followed by drying in a stream of hydrogen to obtain  $\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{Pcy}_3)_2$  (yield: about 80%).

5        Next, this  $\text{Ru}(\text{H})_2(\text{H}_2)_2(\text{Pcy}_3)_2$  (1.5 mmol) is dissolved in 30 ml of dichloroethane solution, and the mixture obtained is cooled to  $-30^\circ\text{C}$ .

Then, 3-chloro-3-methyl-1-butene (1.5 mmol) is added. The solution turns purplish red immediately, which is allowed to react for 15 minutes as it is. The cooling bath is taken away, and degassed  
10    methanol (20 ml) is added, whereupon purple crystals are precipitated. The particles are washed with methanol, followed by drying to obtain the Ru carbene catalyst of formula (1),  $(\text{Cl})_2(\text{Pcy}_3)_2\text{Ru}=\text{CH}-\text{CH}=\text{C}(\text{CH}_3)_2$ , (yield: 95%). (Reference: Organometallics Vol. 16, No. 18, page 3867, 1997)

15        The metathesis polymerization catalyst, i.e., the component (b) may be used in an amount of from 0.001 to 20 parts by weight, and preferably from 0.01 to 5 parts by weight, based on 100 parts by weight of the component-(a) metathesis-polymerizable cycloolefin compound and/or its polymerization product. Its use in an amount  
20    less than 0.001 part by weight may result in poor curing. Its use in an amount more than 20 parts by weight is not economical.

The resin composition of the present invention contains, in addition to the components (a) and (b), at least one third component, component (c), selected from a filler, a reinforcing material and an  
25    additive (other than the filler and reinforcing material).

Here, the filler is incorporated in order to improve mechanical

properties such as modulus of elasticity and factor of shrinkage, of the cured product to be obtained. It includes inorganic fillers and organic fillers in the form of powder or particles.

The inorganic fillers include, e.g., silica, silica sand, calcium carbonate, aluminum hydroxide, magnesium hydroxide and clay. The organic fillers include, e.g., wood flour, and polyester or polystyrene beads. The grade of its particle diameter, shape and quality level may appropriately be determined in accordance with use and physical properties of cured products. Also, the filler may be used in an amount (content) appropriately determined in accordance with use and physical properties of cured products, and may preferably be in an amount of from 1 to 2,000 parts by weight based on 100 parts by weight of the component-(a) metathesis-polymerizable cycloolefin compound and/or its polymerization product.

The reinforcing material refers to a material incorporated in order to improve mechanical properties of cured products, and typically includes fiber reinforcing materials. The fiber reinforcing materials may include inorganic reinforcing materials such as glass fibers, carbon fibers and metal fibers, aramid fibers, polyester fibers, and olefin fibers such as polyethylene or polypropylene fibers. Preferred are glass fibers, aramid fibers or carbon fibers. These reinforcing materials may be either of long fibers and short fibers. They may include rovings formed of strands drawn uniformly into a bunch, roving cloths made by weaving rovings, continuous strand mats made by molding random-coiled long fibers into mats, chopped

strands made by cutting long fibers, chopped-strand mats made by bonding chopped strands by a binder and molding into mats, surfacing mats, a three-dimensional glass mat formed of combination of a twill-woven mat or cloth with strands (available from Chori Co.,  
5 Ltd.; trade name: PARABEAM), nonwoven fabrics and preforms made by molding continuous strands or strands three-dimensionally.

As reinforcing materials having a form other than these fibers, also usable are milled glass, cut fibers, microfibers, microballoons, flaky glass powders and so forth. Any of these may be used in  
10 combination with the above fiber reinforcing material. Aspect ratios and shapes may appropriately be selected in accordance with purposes.

Any of these reinforcing materials may be used in an amount (content) of from 5 to 2,000 parts by weight based on 100 parts by  
15 weight of the component-(a) metathesis-polymerizable cycloolefin compound and/or its polymerization product.

As the component (c), in addition to the filler and reinforcing material described above, various additives may be incorporated in order to improve physical properties, external appearance and  
20 molding operability of cured products. Such additives include a modifier, a polymerization rate regulator, an anti-foaming agent, a blowing agent, a release agent, a colorant, stabilizers (an ultraviolet light absorber, a photostabilizer and an antioxidant), an adhesion-providing agent, a flame retardant, a wetting agent, a  
25 dispersant and an organic peroxide.

The modifier may include, e.g., elastomers, natural rubbers and

butadiene rubbers, and also copolymers such as styrene-butadiene copolymer (SBR), styrene-butadiene-styrene block copolymer (SBS), styrene-maleic acid copolymer and ethylene-vinyl acetate copolymer, and thermoplastic resins such as polymethyl methacrylate, polyvinyl acetate and polystyrene. Also, these copolymers and thermoplastic resins may be esterified, or their polar groups may be grafted. The modifier may also include higher fatty acids such as oleic acid and linolic acid, higher alcohols having 5 or more carbon atoms, and higher diols. These may also be mixed with any of epoxy resins, urethane resins, polyester resins, silicone resins, phenolic resins, polyimide resins, polyamide resins, polyamide-imide resins, cycloolefin polymers and derivatives of these to improve physical properties. The modifier may further include, e.g., compounds obtained by allowing an epoxy resin to react with norbornene monocarboxylic acid, compounds obtained by allowing an isocyanate compound to react with norbornene-ol, hymic acid modified polyesters, and petroleum resins.

The petroleum resins may include those produced using known C5 or C9 fractions as materials, which are purified products from ethylene plants, and may include, e.g., Quintone (trade name; available from Nippon Zeon Co., Ltd.) and a thermoplastic polynorbornene resin NORSOREX (trade name; available from Nippon Zeon Co., Ltd.). These petroleum resins may preferably have a number-average molecular weight of 1,000 or more, and more preferably be those having a functional group such as a hydroxyl group or an ester group in the resin skeleton.

It may preferably be used in an amount of from 0.5 to 500 parts by weight based on 100 parts by weight of the component (a), which depends on physical properties of the intended cured products.

The polymerization rate regulator may include phosphates such as triisopropylphosphine, triphenylphosphine, tricyclohexylphosphine and dicyclohexylphenylphosphine. It may usually be used in an amount of from 0.005 to 20 parts by weight based on 100 parts by weight of the component (a). This polymerization rate regulator is used for the purpose of controlling the serviceable life (pot life) of the resin composition. Hence, it may be used in a small quantity when the pot life may be short, and in a large quantity when it should be long.

The anti-foaming agent may include, e.g., anti-foaming agents such as silicon type oils, fluorine oils and polycarboxylic acid polymers. It may usually be used in an amount (content) of from 0.001 to 5 parts by weight based on 100 parts by weight of the component (a).

The blowing agent may include known physical-blowing agents, e.g., low-boiling hydrocarbon compounds such as pentane, propane and hexane, carbon dioxide and water vapor; and known chemical-blowing agents, e.g., azo compounds such as azobisisobutyronitrile and N,N'-dinitrosopentamethylenetetramine, and compounds capable of generating nitrogen gas upon decomposition, such as nitroso compounds.

The colorant may include inorganic pigments such as titanium dioxide, titanium black, cobalt blue and cadmium yellow, and organic

pigments such as carbon black, aniline black,  $\beta$ -naphthol, phthalocyanine, quinacridone, azo pigments, quinophthalone and Indanthrene Blue. These may each be mixed in accordance with the desired color tones. Any of these may be used in combination of two or more types. Usually, any of these pigments may be used in an amount (content) of from 0.1 to 50 parts by weight based on 100 parts by weight of the component (a).

As the stabilizers, an ultraviolet light absorber, a photostabilizer, an antioxidant and a processing stabilizer are included.

Here, the ultraviolet light absorber may include, e.g., salicylic acid type ultraviolet light absorbers such as phenyl salicylate and p-(t-butyl)phenyl salicylate, benzophenone type ultraviolet light absorbers such as 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone and 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, benzotriazole type ultraviolet light absorbers such as 2-(2'-hydroxy-5'-methyphenyl)benzotriazole, 2-[2'-hydroxy-3',5'-di(t-butyl)phenyl]benzotriazole and 2-[2'-hydroxy-3',5'-di(t-amyl)phenyl]benzotriazole, and cyanoacrylate type ultraviolet light absorbers such as 2-ethylhexyl-2-cyano-3,3'-diphenyl acrylate and ethyl-2-cyano-3,3'-diphenyl acrylate. Any of these may be used alone or in combination of two or more types. Any of these ultraviolet light absorbers may usually be used in an amount (content) of from 0.05 to 20 parts by weight based on 100 parts by weight of the

component (a), which may appropriately be determined in accordance with use environment of cured products and prescribed properties thereof.

The photostabilizer may include hindered amine type  
5 photostabilizers such as bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidiny) sebacate and a dimethyl succinate 1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine condensation product. This photostabilizer may usually be used in an amount (content) of from 0.05 to 20 parts by  
10 weight based on 100 parts by weight of the component (a).

The antioxidant may include quinones such as parabenzoquinone, toluquinone and naphthoquinone; hydroquinones such as hydroquinone, p-(t-butyl)catechol and 2,5-di-t-butylhydroquinone; phenols such as di-t-butyl  
15 paracresolhydroquinone monomethyl ether, and pyrogallol; copper salts such as copper naphthenate and copper octenoate; quaternary ammonium salts such as trimethylbenzylammonium chloride, trimethylbenzylammonium maleate and phenyltrimethylammonium chloride; oximes such as quinone dioxime and methyl ethyl ketoxime;  
20 amine hydrochlorides such as triethylamine hydrochloride and dibutylamine hydrochloride; and oils such as mineral oils, essential oils and fatty oils. The type and quantity of these antioxidants may appropriately be selected in accordance with conditions such as compatibility with fillers and intended molding operability and resin  
25 storage stability. The antioxidant may usually be used in an amount (content) of from 10 to 10,000 ppm (0.001 to 1 part by weight) based on

100 parts by weight of the component (a).

The processing stabilizer may include phosphorus type processing stabilizers such as tris(2,4-di(t-butyl)phenyl) phosphite, lactone type processing stabilizers such as

5 5,7-di(t-butyl)-3-(3,4-dimethylphenyl)-3H-benzofuran-2-one, and vitamin E type processing stabilizers such as 2,5,7,8-tetramethyl-2-(4',8',12'-trimethyltridecyl)curoman-6-ol.

The adhesion-providing agent may include silane type coupling agents. The silane type coupling agents are usually represented by

10 the formula:  $YSiX^3$  (Y is a monovalent group having a functional group and bonded to Si, and  $X^3$  is a monovalent group having a hydrolytic action and bonded to Si). The functional group in Y is exemplified by vinyl, amino, epoxy, chloro, mercapto, methacryloxy, cyano, carbamate, pyridine, sulfonyl azide, urea, styryl, chloromethyl,

15 ammonium salt and alcohol groups.  $X^3$  is exemplified by chloro, methoxy, ethoxy and methoxyethoxy. As specific examples, the silane type coupling agents may include vinyltrimethoxysilane, vinyltris(2-methoxyethoxy)silane,

γ-(2-aminoethyl)-aminopropyltrimethoxysilane,

20 γ-mercaptopropyltrimethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-methacryloxypropyltrimethoxysilane, N,N-dimethylaminophenyltriethoxysilane, mercaptoethyltriethoxysilane,

25 methacryloxyethyldimethyl-(3-trimethoxysilylpropyl)ammonium chloride, and



3-(N-styrylmethyl-2-aminoethylamino)propyltrimethoxysilane hydrochloride. Any of these may be used in the form of a mixture.

Also, as polymer type alkoxy-modified silane coupling agents, MAC-2101 and FZ-3778 (trade names; products of Nippon Unicar Co., Ltd.) are available, and these may be used alone or in combination with the above silane type coupling agents. The silane type coupling agent may usually be used in an amount (content) of from 0.001 to 5 parts by weight based on 100 parts by weight of the component (a).

The flame retardant may include, e.g., halogen type compounds such as hexabromobenzene, tetrabromobisphenol A, decabromodiphenyl oxide, tribromophenol, dibromophenylglycidyl ether, perchloropentacyclodecane and HET acid derivatives, any of which may be used alone or in combination of two or more types. A phosphoric acid compound such as tris(dichloropropyl) phosphate or tris(dibromopropyl) phosphate or a boric acid compound may also be used in combination. An auxiliary flame retardant, which may include antimony trioxide, iron oxide and aluminum hydride, may further be used in combination with the flame retardant, whereby the flame-retardant effect can be improved. The halogen type flame retardant may usually be used in an amount of from 1 to 50 parts by weight, and the auxiliary flame retardant such as antimony trioxide from 1 to 15 parts by weight, based on 100 parts by weight of the component (a). Also, hydrates such as aluminum hydroxide and magnesium hydroxide may be used as a filler aiming at flame retardation. Any of these may usually be used in an amount (content) of from 10 to 300 parts by weight based on 100 parts by

weight of the component (a).

An organic peroxide may further be added. The organic peroxide may include, e.g., known peroxides such as cumene hydroperoxide, t-butyl peroxy-2-ethylhexanate, methyl ethyl ketone peroxide, benzoyl peroxide, acetylacetone peroxide,  
5 bis-4-(t-butyl)cyclohexane dicarbonate,  
2,5-dimethyl-2,5-bis(t-butylperoxy)hexyne-3. Any of these may be used in combination of two or more types. The organic peroxide may usually be added in an amount of from 0.1 to 10 parts by weight  
10 based on 100 parts by weight of the component (a).

Besides these, in order to improved wettability between the metathesis-polymerizable cycloolefin compound and/or its polymerization product [component (a)] and the filler, a wetting agent or a dispersant (e.g., BYK series, available from BYK-CHEMIE  
15 GMBH) may also be incorporated. Also, in order to improve molding operability, a release agent such as silicon type oil or zinc stearate may be incorporated.

The resin composition of the present invention is obtained by adding and dissolving the metathesis polymerization catalyst of  
20 Formula (A) in the metathesis-polymerizable cycloolefin compound, and adding thereto at least one third component [component (c)] selected from the filler, the reinforcing material and the additive. Here, the temperature at the time the catalyst is dissolved in the cycloolefin compound and the temperature at the time the third  
25 component is added may usually be from 0 to 70°C, and preferably from room temperature to 50°C.

To cure the resin composition to obtain a molded product, heating is carried out. Heat curing may be operated by one-stage heating or two-stage heating, or by multi-stage heating. When one-stage heating is employed, temperature may usually be from 0 to 250°C, and preferably from 20 to 200°C. When two-stage heating is employed, first-stage temperature may usually be from 0 to 150°C, and preferably from 10 to 100°C, and second-stage temperature usually from 20 to 200°C, and preferably from 30 to 180°C. Also, polymerization time may appropriately be determined in accordance with the quantity of the catalyst and the polymerization temperature, and may usually be from 1 minute to 50 hours.

To obtain the molded product, any known methods may be used, as exemplified by lay-up molding such as hand lay-up or spray-up, press molding, filament winding, cast molding, centrifugal molding, vacuum or pressure bag molding, continuous molding, pultrusion, injection molding, RTM (resin transfer molding), dipping, impregnation molding and transfer molding.

The molded product (cured product) obtained can have superior mechanical properties, electrical properties and boilproofness.

The present invention will be described below by giving Examples. In Examples, "part(s)" refers to "part(s) by weight" unless particularly noted.

#### Examples 1 to 6

##### (Preparation of DCPD Resin Solution)

To 90 parts by weight of dicyclopentadiene (called "DCPD")

with a purity of about 98% by weight, 10 parts by weight of tricyclopentadiene (called "TCPD") was added to make up a DCPD resin solution.

(Making-up of Test Piece)

5           To the above DCPD resin solution, the Ru carbene catalyst represented by formula (1) was added in a room kept at 5°C, and these were stirred for 5 minutes to dissolve the catalyst completely. In the case of formulation where a filler is added, the filler was subsequently added to this resin solution to which the catalyst had been added,  
10 followed by stirring for 5 minutes by means of a stirrer. Resin solutions thus obtained (i.e., resin compositions formulated as shown in Table 3) were each poured into a casting mold assembled with two iron plates (300 mm x 300 mm x 6 mm) coated with a release agent and a spacer of 5 mm thickness. The filler and reinforcing material used  
15 were as shown in Table 1. Also, fiber-reinforced test pieces were prepared by hand lay-up molding on glass sheets. Each was left at room temperature for 1 hour, followed by heating according to predetermined curing conditions shown in Table 2, thus cured products were obtained.

Table 1

| Symbol | Filler                                                                 | Reinforcing material                                      |
|--------|------------------------------------------------------------------------|-----------------------------------------------------------|
| A      | Aluminum hydroxide (C-308, available from Sumitomo Chemical Co., Ltd.) | -                                                         |
| B      | Crystalline silica (SS-100, available from Tokai Mineral Co., Ltd.)    | -                                                         |
| C      | -                                                                      | Glass mat (MC-450N, available from NittoBoseki Co., Ltd.) |

Table 2

| Symbol | Initial curing | Post-curing    |
|--------|----------------|----------------|
| I      | 35°C, 3 hours  | 125°C, 3 hours |
| II     | 30°C, 3 hours  | 100°C, 3 hours |
| III    | 35°C, 3 hours  | 80°C, 3 hours  |

## Comparative Example 1

Into a 2-liter four-necked flask provided with a stirrer, a condenser, a nitrogen gas feed pipe and a thermometer, 380 parts of propylene glycol, 624 parts of neopentyl glycol and 747 parts of isophthalic acid were charged, and temperature was raised to 150°C in 1 hour by means of a mantle heater while nitrogen gas was slowly flowed, and the temperature was further raised to 220°C over a period of 6 hours. Temperature was kept for 5 hours at that temperature to obtain an intermediate product with an acid value of 8. After it was cooled, 539 parts of maleic anhydride was charged thereinto, and temperature was raised to 150°C in 1 hour, and the temperature was further raised to 210°C over a period of 4 hours. Keeping

temperature at that temperature, the reaction was allowed to proceed to obtain an unsaturated polyester with an acid value of 25. In this polyester, styrene monomer in which 0.01% by weight of hydroquinone was dissolved was so dissolved that the unsaturated polyester was in a concentration of 60% by weight. Subsequently, 0.5 parts by weight of a 6% by weight cobalt naphthenate solution was added as an accelerator to make up an unsaturated polyester resin solution having a viscosity of 0.4 Pa·s at 25°C and containing the accelerator.

#### 10 Comparative Examples 2 and 3

To the same DCPD resin solutions as those of Examples, diethylaluminum chloride, n-propyl alcohol and silicon tetrachloride were so added as to be in concentrations of 40 mmol/L, 52 mmol/L and 20 mmol/L, respectively, in a nitrogen-purged dry box to make up a solution A. Also, in the same manner as the solution A, tridecylammonium molybdenate was so added to the DCPD resin solution as to be in a concentration of 10 mmol/L to prepare a solution B. These solutions A and B were mixed in equal weight for each in a nitrogen-purged dry box. The mixture obtained was casted into a mold at 20°C within a pot life of 20 minutes, and thus cast products were prepared.

#### Comparative Example 4

DCPD solutions A and B were made up in the same manner as in Comparative Examples 2 and 3. Mixing and casting into a mold were carried out in a room (in air) to form a cured product.

- Evaluation on Cured Products -

Evaluation on the cured products thus obtained was made in the following way.

a. Mechanical Properties

Measured by a bending test (according to JIS K-7203).

5 Shape of test piece: 120 mm x 12 mm x 5 mm

Test speed: 5 mm/minute

Test span: 80 mm

Number of test:  $n = 5$

b. Degree of curing

10 Using TG-DTA (a thermobalance analyzer), manufacture by Shinku-Riko, Inc., temperature was raised from room temperature to 600°C at a rate of 10°C/minute, and weight loss on heating at 400°C was measured. Degree of curing of samples tested was calculated by the following expression.

15 Degree of curing (%) =

weight (g) of test piece at 400°C / weight (g) of test piece at room temperature

c. Glass Transition Temperature

20 Glass transition temperature was measured with Model DSC-7, manufactured by PE Corporation.

d. Boilproofness

Cured products having the above shape were immersed in about 95°C hot water for 300 hours, and flexural strength of the test pieces after the boiling test was measured in the same manner as the above  
25 bending test. Retention of flexural strength was calculated by the following expression.



Retention of flexural strength (%) =

(flexural strength after boiling test / flexural strength before boiling test) x 100

e. Electrical Properties

- 5        With regard to electrical properties of the cast products, their dielectric loss factors ( $\tan \delta$ ) were measured with LCR Meter HP4275A, manufactured by Japan Hewlett-Packard Co. Measured at a temperature of 25°C, a humidity of 60% and a frequency of 10 kHz.

- 10       The results of evaluation in Examples and Comparative Examples were as shown in Table 3. The resin compositions of the present invention, making use of the specific metathesis polymerization catalyst, provided cured products having a high degree of curing and whose various properties were better than those of cured products obtained by conventional metathesis
- 15       polymerization or unsaturated polyester resin cured products, even though they contained a filler and cured products were produced in air. In Table 3, MEKPO indicates methyl ethyl ketone peroxide.

Table 3

| Items                                   | (unit) | Example1 | Exempl<br>e2 | Exempl<br>e3 | Exempl<br>e4 | Exempl<br>e5 | Exempl<br>e 6 | Compara-<br>tive<br>Example 1 | Compara-<br>tive<br>Example 2 | Compara-<br>tive<br>Example 3 | Compara-<br>tive<br>Example 4 |
|-----------------------------------------|--------|----------|--------------|--------------|--------------|--------------|---------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| DCPD resin solution                     | parts  | 100      | 100          | 100          | 100          | 100          | 100           | -                             | -                             | -                             | -                             |
| Triphenylphosphine*                     |        | 0.1      | 0.1          | 0.1          | 0.1          | -            | 0.1           | -                             | -                             | -                             | -                             |
| Unsaturated polyester resin             |        | -        | -            | -            | -            | -            | -             | 100                           | -                             | -                             | -                             |
| DCPD solution A                         |        | -        | -            | -            | -            | -            | -             | -                             | 50                            | 50                            | 50                            |
| DCPD solution B                         |        | -        | -            | -            | -            | -            | -             | -                             | 50                            | 50                            | 50                            |
| Ru carbene catalyst                     |        | 0.1      | 0.1          | 0.1          | 0.1          | 0.06         | 0.1           | -                             | -                             | -                             | -                             |
| 55% MEKPO                               |        | -        | -            | -            | -            | -            | -             | 1.0                           | -                             | -                             | -                             |
| Filler, reinforcing material: (content) | parts  | -        | A (100)      | B (100)      | C (54)       | A (100)      | B (100)       | -                             | -                             | A (100)                       | -                             |
| Lay-up molding environment              | -      | air      | air          | air          | air          | air          | air           | air                           | nitrogen                      | nitrogen                      | air                           |
| Curing conditions                       | -      | I        | I            | I            | I            | II           | III           | III                           | I                             | I                             | I                             |
| Test results                            |        |          |              |              |              |              |               |                               |                               |                               |                               |
| Flexural strength                       | MPa    | 68       | 71           | 70           | 182          | 70           | 72            | 72                            | 66                            | faulty curing                 | faulty curing                 |
| Flexural modulus                        | GPa    | 2.2      | 3.1          | 3.0          | 7.2          | 3.0          | 3.1           | 2.7                           | 2.1                           |                               |                               |
| Degree of curing                        | %      | 99       | 98           | 98           | 98           | 99           | 98            | 99                            | 95                            |                               |                               |
| Glass transition temperature            | °C     | 140      | -            | -            | -            | -            | -             | 90                            | 135                           |                               |                               |
| Boilproofness                           | %      | 97       | -            | -            | -            | 98           | -             | 97                            | 95                            |                               |                               |
| Electrical properties                   | %      | 0.01     | -            | -            | -            | -            | -             | 0.9                           | 0.01                          |                               |                               |

\* : Wako Pure Chemical Industries, Ltd.

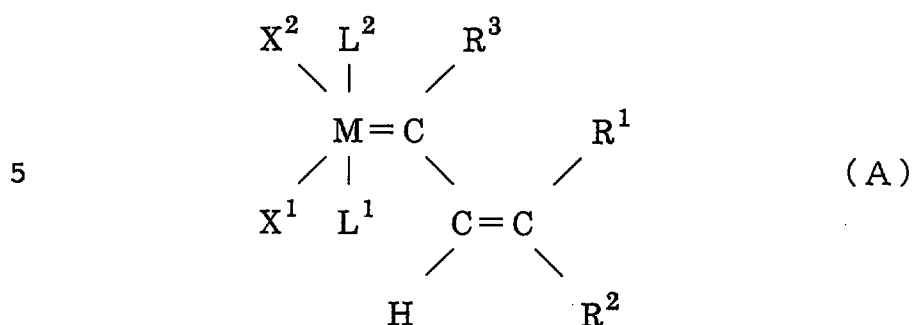
## POSSIBILITY OF INDUSTRIAL APPLICATION

As described above, the use of the resin composition of the present invention enables production of molded products from  
5 cycloolefin compounds by general-purpose molding (not only closed-mold molding but also open-mold molding of various types) in usual operation environment without preventing inclusion of water and oxygen in air.

The cured products produced by the production process of the  
10 present invention also can be utilized in uses where water resistance, tough mechanical properties, good electrical properties and so forth are required, e.g., in insulating materials for electronic and electrical use such as coils, wiring boards and semiconductors, molding materials for house installations such as purifier tanks, septic tanks,  
15 bathtubs, wall panels and pleasure boats, and industrial materials such as corrugated sheets and pipes.

## Claims

- 1           1. A resin composition comprising;
- 2           (a) a metathesis-polymerizable cycloolefin compound;
- 3           (b) a metathesis polymerization catalyst represented by the
- 4           following Formula (A).



- 6           wherein;
- 7           M represents a ruthenium atom or an osmium atom;
- 8           X<sup>1</sup> and X<sup>2</sup> each independently represent an anionic ligand;
- 9           L<sup>1</sup> and L<sup>2</sup> each independently represent a neutral
- 10          electron-donating group; and
- 11          R<sup>1</sup> and R<sup>2</sup> each independently represent an alkyl group having 1
- 12          to 18 carbon atoms, an alkenyl group having 2 to 18 carbon atoms, an
- 13          alkynyl group having 2 to 18 carbon atoms, an aryl group, a
- 14          carboxylate group having 1 to 18 carbon atoms, an alkoxy group
- 15          having 1 to 18 carbon atoms, an alkenyloxy group having 2 to 18
- 16          carbon atoms, an alkynyloxy group having 2 to 18 carbon atoms, an
- 17          aryloxy group, an alkoxycarbonyl group having 2 to 18 carbon atoms,
- 18          an alkylthio group having 1 to 18 carbon atoms, an alkylsulfonyl



19 group having 1 to 18 carbon atoms or an alkylsulfinyl group having 1  
20 to 18 carbon atoms; and R<sup>3</sup> represents a hydrogen atom, an aryl group  
21 or an alkyl group having 1 to 18 carbon atoms; and

22 (c) at least one third component selected from a filler, a  
23 reinforcing material and an additive.

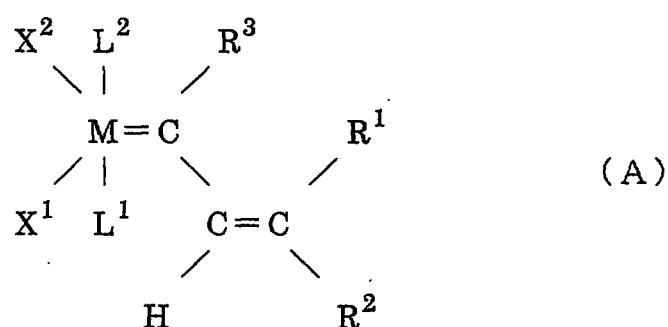
1 2. The resin composition according to claim 1, which contains  
2 the component (b) in an amount of from 0.001 to 20 parts by weight  
3 based on 100 parts by weight of the component (a), and contains the  
4 component (c) in an amount of from 0.001 to 97 weight percent based  
5 on the total weight of the component (a), component (b) and  
6 component (c).

1 3. A process for producing a cured product, comprising  
2 heating the resin composition according to claim 1 or 2 to effect  
3 curing.



## ABSTRACT

The present invention provides a resin composition comprising (a) a metathesis-polymerizable cycloolefin compound, (b) a  
 5 metathesis polymerization catalyst represented by the following Formula (A), and (c) a filler, a reinforcing material or an additive, and a process for producing a cured product, comprising heating the resin composition to effect curing.



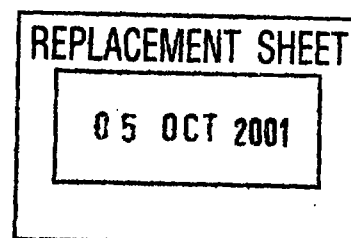
10 wherein M represents ruthenium or osmium,  $X^1$  and  $X^2$  each independently represent an anionic ligand,  $L^1$  and  $L^2$  each independently represent a neutral electron-donating group, and  $R^1$  and  $R^2$  each represent an organic group, and  $R^3$  represents hydrogen, an aryl group or an alkyl group.

100 parts by weight of the component (a).

The processing stabilizer may include phosphorus type processing stabilizers such as tris(2,4-di(t-butyl)phenyl) phosphite, lactone type processing stabilizers such as

- 5 5,7-di(t-butyl)-3-(3,4-dimethylphenyl)-3H-benzofuran-2-one, and vitamin E type processing stabilizers such as 2,5,7,8-tetramethyl-2-(4',8',12'-trimethyltridecyl)curoman-6-ol.

The adhesion-providing agent may include silane type coupling agents. The silane type coupling agents are usually represented by the formula:  $Y_nSiX^3_{(4-n)}$  (Y is a monovalent group having a functional group and bonded to Si, and  $X^3$  is a monovalent group having a hydrolytic action and bonded to Si, n is an integer of 1 to 3). The functional group in Y is exemplified by vinyl, amino, epoxy, chloro, mercapto, methacryloxy, cyano, carbamate, pyridine, sulfonyl azide, urea, styryl, chloromethyl, ammonium salt and alcohol groups.  $X^3$  is exemplified by chloro, methoxy, ethoxy and methoxyethoxy. As specific examples, the silane type coupling agents may include vinyltrimethoxysilane, vinyltris(2-methoxyethoxy)silane,  $\gamma$ -(2-aminoethyl)-aminopropyltrimethoxysilane,  $\gamma$ -mercaptopropyltrimethoxysilane,  $\gamma$ -glycidopropyltrimethoxysilane,  $\gamma$ -methacryloxypropyltrimethoxysilane, N,N-dimethylaminophenyltriethoxysilane, mercaptoethyltriethoxysilane, methacryloxyethyldimethyl-(3-trimethoxysilylpropyl)ammonium chloride, and



Evaluation on the cured products thus obtained was made in the following way.

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Measured by a bending test (according to JIS K-7203).

5 Shape of test piece: 120 mm x 12 mm x 5 mm

Test speed: 5 mm/minute

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Number of test:  $n = 5$

b. Degree of curing

10 Using TG-DTA (a thermobalance analyzer), manufacture by Shinku-Riko, Inc., temperature was raised from room temperature to 600°C at a rate of 10°C/minute, and weight loss on heating at 400°C was measured. Degree of curing of samples tested was calculated by the following expression.

15 Degree of curing (%) =  
$$\frac{\{\text{weight (g) of test piece at 400°C} / \text{weight (g) of test piece at room temperature}\}}{x 100}$$

c. Glass Transition Temperature

Glass transition temperature was measured with Model DSC-7,  
20 manufactured by PE Corporation.

d. Boilproofness

Cured products having the above shape were immersed in about 95°C hot water for 300 hours, and flexural strength of the test pieces after the boiling test was measured in the same manner as the above  
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