



- (51) **International Patent Classification:**
C08G 59/42 (2006.01) *C08L 63/00* (2006.01)
- (21) **International Application Number:**
PCT/CN2015/074566
- (22) **International Filing Date:**
19 March 2015 (19.03.2015)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (71) **Applicants:** **ABLESTIK (SHANGHAI) LTD.** [CN/CN]; No. 332 Mei Gui South Road, (Shanghai) Pilot Free Trade Zone, Shanghai 200131 (CN). **HENKEL IP & HOLDING GMBH** [DE/DE]; Henkelstrasse 67, 40589 Duesseldorf (DE). **HENKEL HUAWEI ELECTRONICS CO. LTD.** [CN/CN]; Songtiao Exploited Area, Lianyungang, Jiangsu 222006 (CN).
- (72) **Inventors:** **YANG, Qingxu**; 2#401, 518, East Yierba Jini-an Rd, Shanghai 200131 (CN). **WANG, Yuting**; 2#301, 11#, 404, Heyan Rd, Qixia, Nanjing, Jiangsu 210000 (CN). **HE, George**; 13236 Aclare St., Cerritos, California 90703 (US). **SONG, Jin**; 2#307, Xincheng Huayuan, Suzhou, Jiangsu 215000 (CN). **QIN, Justin**; 1#, Shiji Rd, Chongchuan, Nantong, Jiangsu 226000 (CN). **JIA, Lufang**; 26, Xinhai Rd, Xinpu, Lianyungang, Jiangsu 222000 (CN). **BIN, Guanghui**; Weilaicheng, Xinpu, Lianyungang, Jiangsu 222000 (CN). **DU, Ning**; A3-1, Xinhaihuayuan, Lianyungang, Jiangsu 222000 (CN). **XIE, Guangchao**; No.8 Zhen Hua Road, Song Tiao Industrial Park, Lianyungang Exploited Area, Lianyungang, Jiangsu 222006 (CN).

(74) **Agent:** **NTD UNIVATION INTELLECTUAL PROPERTY AGENCY LTD.**; Room 1802, 18th Floor, Block A, Investment Plaza, 27 Jinrongdajie, Xicheng District, Beijing 100033 (CN).

(81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) **Title:** EPOXY MOLDING COMPOUND USING ANHYDRIDE HARDENER, MANUFACTURING PROCESS AND USE THEREOF

(57) **Abstract:** Provided is an epoxy molding compound comprising (a) an epoxy resin; (b) an anhydride hardener with specific structures; (c) a curing accelerator; (d) a filler; and optionally (e) one or more additives. By using anhydrides with specific structures as hardeners for epoxy resins, the molded products produced from the epoxy molding compounds can have Tg higher than 250°C, which can stand high working temperature, and thus can be used in high temperature applications, especially in high power electrical or electronic devices.



Epoxy molding compound using anhydride hardener, manufacturing process and use thereof

Technical Field

The present invention relates to an epoxy molding compound, particularly, relates to an epoxy molding compound using an anhydride with specific structure as hardener, and to a manufacturing process and use of the epoxy molding compound.

Background Art

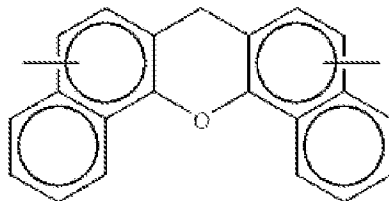
Molded epoxy resin products are widely used as component parts in electrical and electronic devices, such as transistors and integrated circuit boards, because epoxy resin has well balanced properties including molding property, electrical property, moisture resistance, heat resistance, mechanical property and adhesion to component inserted therein, etc.

Molded epoxy resin products are produced from epoxy molding compounds. A typical epoxy molding compound comprises an epoxy resin, a curing agent (hardener), a curing accelerator (catalyst), and optionally fillers and additives. An epoxy molding compound can be molded and cured to a solid shaped article in a mold at elevated temperature and for a certain time. Afterwards, the demolded article is usually post-cured at elevated temperatures to complete the curing reaction and obtain a resin article with the ultimate desired properties.

For high power electrical or electronic devices, due to the high working temperature, the molded epoxy resin products used therein should have high temperature resistance, which is associated with T_g of the products. T_g (glass transition temperature) of a conventional molded epoxy resin is usually in the range of 100°C to 180°C, but many high power electrical or electronic devices usually work under 200°C, since the higher the power is, the higher the working temperature is.

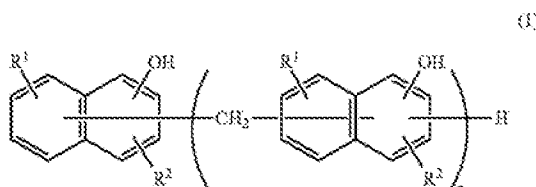
Quit a lot of works have been carried out trying to improve the heat resistance of molded epoxy resin products by selecting and designing the components of the epoxy molding compounds.

US 6207789 B1 discloses a molding composition consisting of an epoxy resin, a phenolic resin hardener and inorganic filler, wherein the phenolic resin hardener contains in the backbone chain a structure unit represented by the following formula:

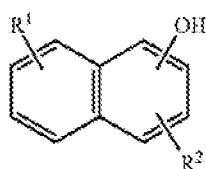


The Tg values of the cured epoxy products are no more than 145°C.

US 8394911 B2 discloses a phenol resin composition used as a curing agent for epoxy resins, wherein the phenol resin composition includes a naphthol novolac resin (a1) represented by general formula (1),



and a compound (a2) represented by general formula (2)



The cured epoxy resins using the above phenol resin composition as curing agent got a Tg around 230°C.

There is still a demand of designing and selecting the components of an epoxy molding compound to get higher Tg, preferably higher than 250°C, for the molded epoxy resin to meet the requirements of high temperature applications, especially for high power electrical or electronic devices.

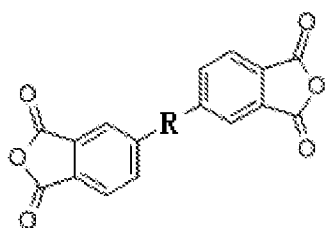
Summary of the Invention

Accordingly, the object of the present invention is to provide an epoxy molding compound, from which a molded epoxy resin having higher Tg, preferably higher than 250°C, can be obtained.

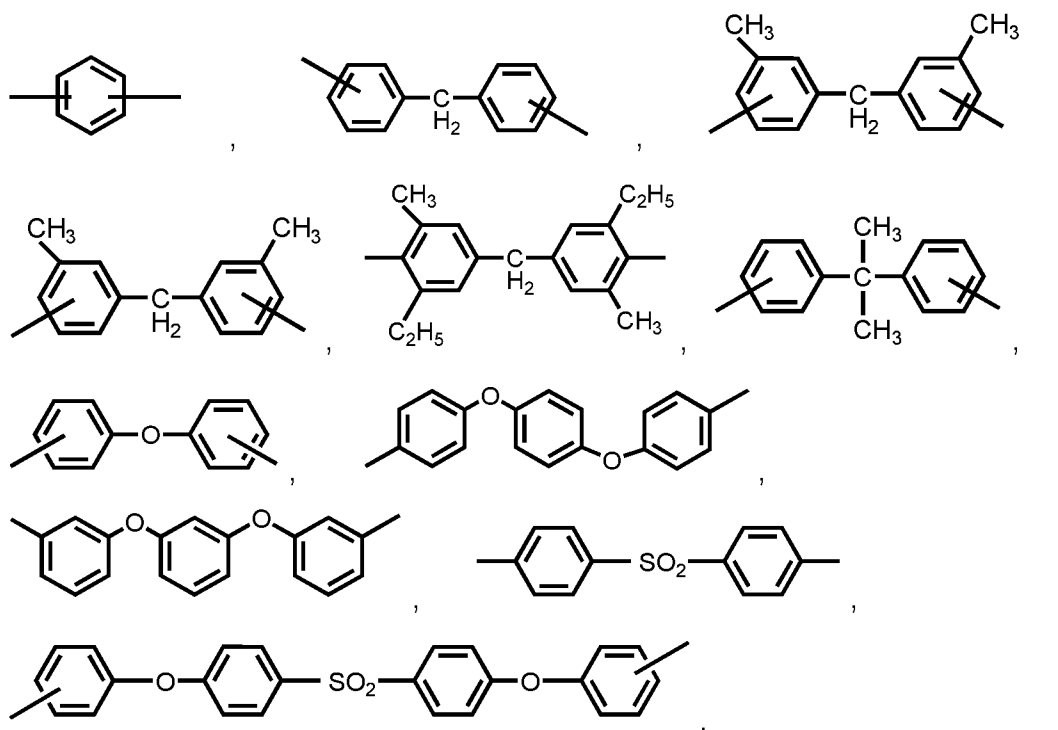
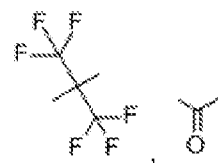
In one aspect, the present invention provides an epoxy molding compound, comprising

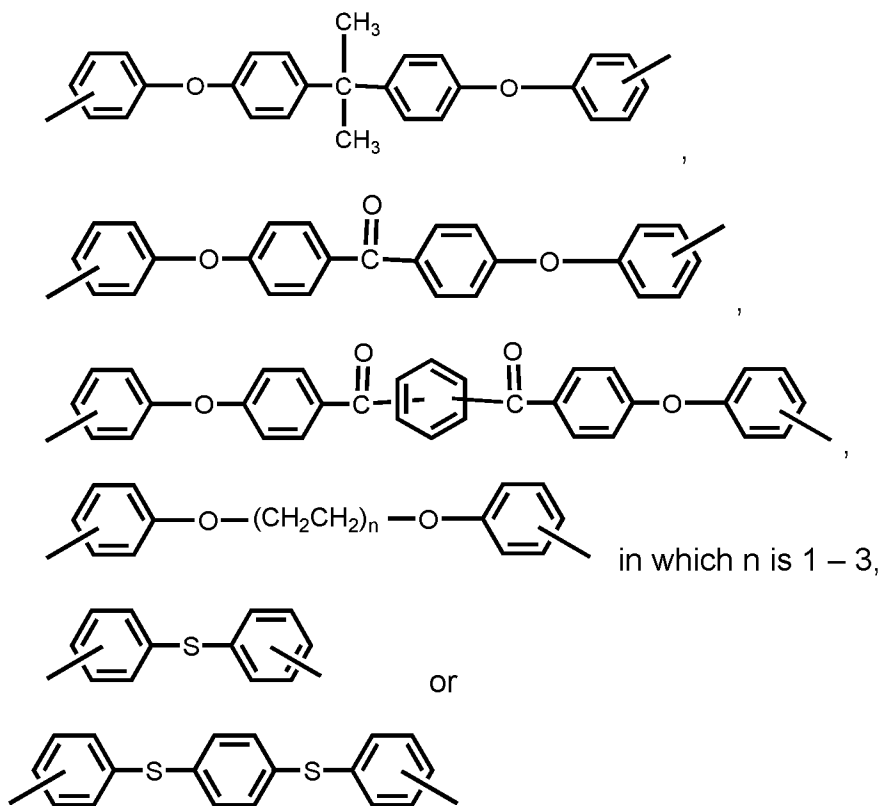
- (a) an epoxy resin;
- (b) a hardener;
- (c) a curing accelerator;
- (d) a filler; and optionally
- (e) an additives,

wherein said hardener is one or more bi-anhydride compounds represented by the following structure (1):



wherein, R represents a direct bond, -S-, -O-, -CH₂-,





In another aspect the present invention provides a process for manufacturing the epoxy molding compound of the present invention, comprising steps of:

(1) Weighing up all of the components and putting them in a high speed mixer to get a premixed powder; and

(2) Putting the premixed powder into an extruder to further mix the premixed powder and then crushing the extruded material into powder.

Yet in another aspect, the present invention provides the use of the epoxy molding compound of the present invention as transistor material, such as diode material and triode material; printed circuit board material, electronic circuit board material, adhesives, interlayer insulating materials, etc.

According to the present invention, by using anhydrides with specific structures as hardeners for epoxy resins, the molded products produced from the epoxy molding compounds can have Tg higher than 250°C, which can stand high working temperature, and thus can be used in high temperature applications, especially in high power electrical or electronic devices.

Detailed description

In the following passages the present invention is described in more detail.

Each aspect so described may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

In the context of the present invention, the terms used are to be construed in accordance with the following definitions, unless a context dictates otherwise. As used herein, the singular forms "a", "an" and "the" include both singular and plural referents unless the context clearly dictates otherwise.

The terms "comprising", "comprises" and "comprised of" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps.

The recitation of numerical end points includes all numbers and fractions subsumed within the respective ranges, as well as the recited end points. When an amount, a concentration or other values or parameters is/are expressed in form of a range, a preferable range, or a preferable upper limit value and a preferable lower limit value, it should be understood as that any ranges obtained by combining any upper limit or preferable value with any lower limit or preferable value are specifically disclosed, without considering whether the obtained ranges are clearly mentioned in the context.

All references cited in the present specification are hereby incorporated by reference in their entirety.

Unless otherwise defined, all terms used in the disclosure of the invention, including technical and scientific terms, have the meaning as commonly understood by one of the ordinary skill in the art to which this invention belongs to. By means of further guidance, term definitions are included to better appreciate the teaching of the present invention.

The present invention provides an epoxy molding compound, comprising (a) an epoxy resin; (b) an anhydride hardener; (c) a curing accelerator; (d) a filler; and optionally (e) one or more additives.

Epoxy resin (a)

As used herein, the term “epoxy resin” means a polymer containing generally two or more epoxide groups per molecule.

As the epoxy resin (a) used in the epoxy molding compound of the present invention, any epoxy resins commonly used are suitable. There are no particular limitations. Examples thereof include but not limited to bisphenol epoxy resins such as bisphenol A epoxy resins, bisphenol F epoxy resins, bisphenol S epoxy resins, and the like; biphenyl epoxy resins such as biphenyl epoxy resins, tetramethylbiphenyl epoxy resins, and the like; novolac epoxy resins such as phenol novolac epoxy resins, cresol novolac epoxy resins, bisphenol A novolac epoxy resins, epoxy compounds of condensates of phenols and phenolic hydroxyl group-containing aromatic aldehyde, biphenyl novolac epoxy resins, and the like; triphenylmethane epoxy resins; tetraphenylethane epoxy resins; dicyclopentadiene phenol addition reaction-type epoxy resins; phenolaralkyl epoxy resins; epoxy resins each having a naphthalene skeleton in its molecular structure, such as naphthol novolac epoxy resins, naphtholaralkyl epoxy resins, and the like; brominated bisphenol epoxy resins, alicyclic epoxy resins, and glycidyl ether epoxy resins. These epoxy resins may be used alone or as a mixture of two or more.

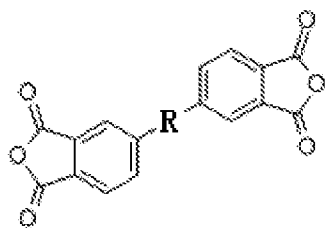
Among the above-described epoxy resins, bisphenol A epoxy resins, bisphenol F epoxy resins, bisphenol S epoxy resins, biphenyl epoxy resins, tetramethylbiphenyl epoxy resins, phenol novolac epoxy resins, cresol novolac epoxy resins, naphthol novolac epoxy resins, naphtholaralkyl epoxy resins, brominated bisphenol epoxy resins, alicyclic epoxy resins, glycidyl ether epoxy resins are preferred.

The amount of the epoxy resin (a) in the epoxy molding compound is preferably 3~20 wt.%, more preferably 3~10 wt.% based on the total weight of the epoxy molding compound.

Anhydride hardener (b)

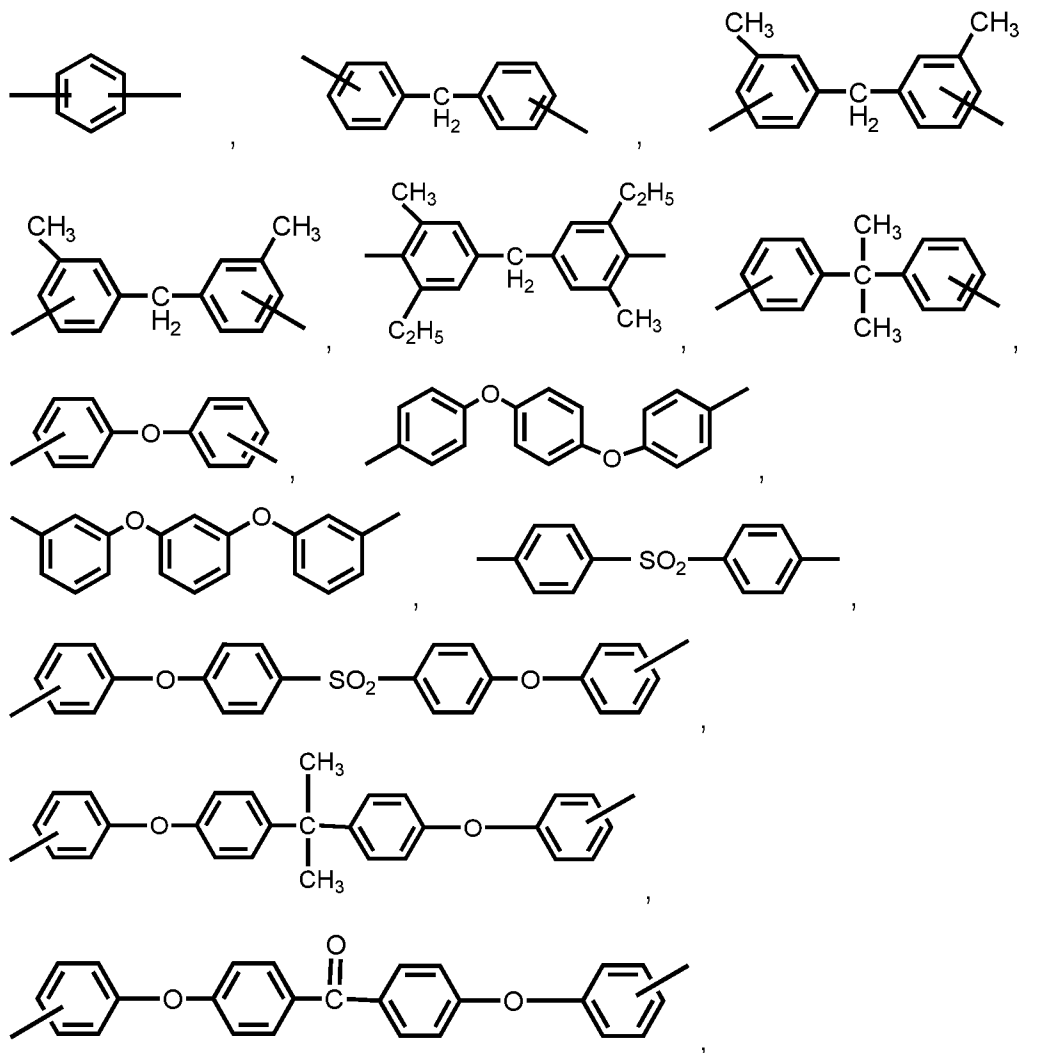
As used herein, the term “hardener” is of the same meaning as “curing agent”, which may perform different functions, such as react covalently with the functional groups of the epoxy resin to propagate the crosslinking of the resin and to get a thermoset resin.

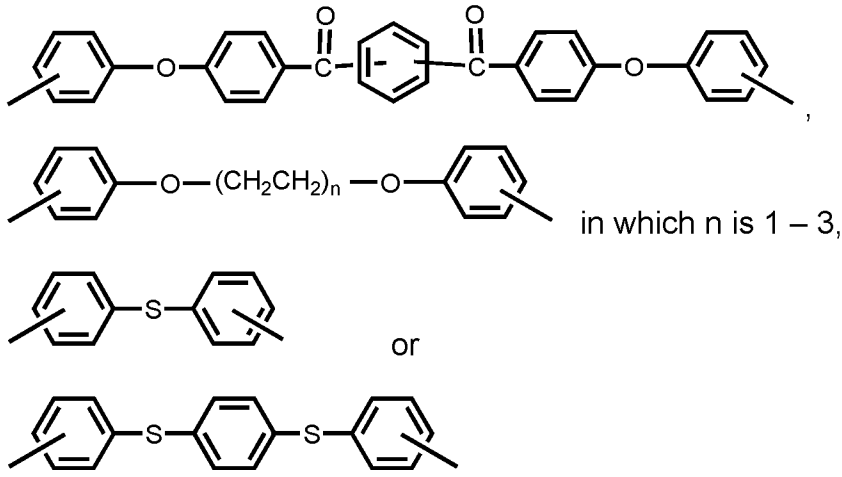
The hardener (b) used in the epoxy molding compound of the present invention is at least one bi-anhydride represented by the following structure (1):



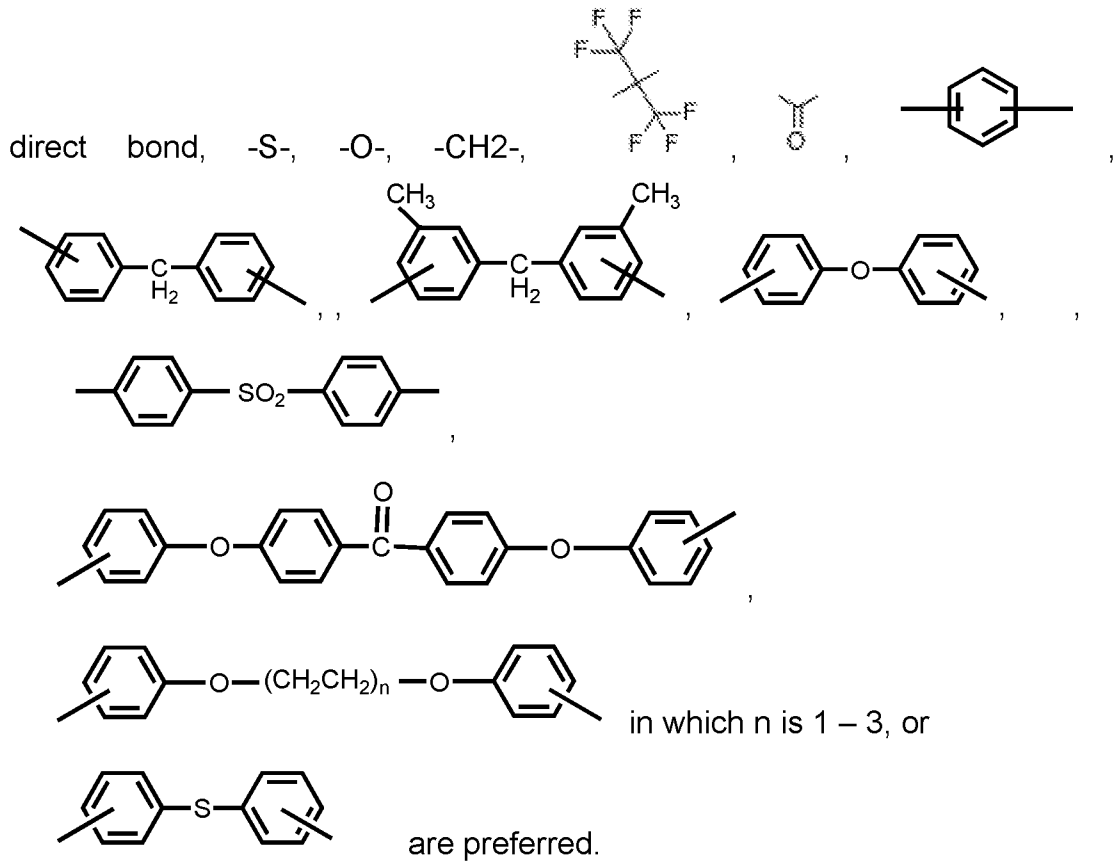
(1)



wherein, R represents a direct bond, -S-, -O-, -CH₂-, ,





Among the above-described bi-anhydride hardeners, compounds with R being



Anhydride compounds with R being -O-,  or  are specially preferred.

As hardener (b), one or more of the above-mentioned bi-anhydride hardeners

may be used, and any other conventionally known curing agent may be also used in combination.

The amount of the anhydride hardener (b) in the epoxy molding compound is preferably 3~15 wt.%, more preferably 5~12 wt.% based on the total weight of the epoxy molding compound.

Curing accelerator (c)

As used herein, the term "curing accelerator" has the same meaning as "catalyst", which catalyzes or accelerates the curing reaction between the epoxy resin and the hardener.

As the curing accelerator (c) used in the epoxy molding compound of the present invention, various compounds can be used, for example, phosphorus-based compounds, tertiary amines, imidazoles, organic acid metal salts, Lewis acids, amine complex salts, and the like. In particular, from the viewpoint of excellent curability, heat resistance, electric characteristics, and wetproof reliability, 2-ethyl-4-methylimidazole is preferred as one of the imidazoles, triphenylphosphine (TPP) is preferred as one of the phosphorus-based compounds, and 1,8-diazabicyclo-[5.4.0]-undecene (DBU) is preferred as one of the tertiary amines. Any of the above listed curing accelerators can be used alone or in a combination of two or more.

In the case when a curing accelerator (c) is used, the amount of the curing accelerator (c) in the epoxy molding compound is preferably 0.05~1 wt.%, more preferably 0.1~0.3 wt.% based on the total weight of the epoxy molding compound.

Filler (d)

A wide range of fillers may be used in the epoxy molding compound of the present invention to improve certain properties of the molded product, such as abrasion resistance, moisture resistance, thermal conductivity or electrical properties.

As filler (d) used in the epoxy molding compound of the present invention, it can be inorganic, such as silica, alumina, titania, aluminium hydroxide, silicon nitride, talc, clay, glass fiber and the like; or organic such as powdered PVC, polyamides, polyethylene, polyester or cured epoxy resins. When the amount

of the filler required is particularly high, fused silica is preferably used. Although either crushed or spherical fused silica can be used, the spherical fused silica is preferably used for increasing the amount of the fused silica mixed in and suppressing an increase in melt viscosity of the molding material. Any of the above listed fillers can be used alone or in a combination of two or more.

In the case when a filler (d) is used, the amount of filler (d) in the epoxy molding compound is preferably 60~90 wt.%, more preferably 75~85 wt.% based on the total weight of the epoxy molding compound.

Additive (e)

As used herein, the term "additive" means any compounding additives conventionally employed in molding resin compound.

If required, one or more additives (e) can be used in the epoxy molding compound of the present application. Examples of additive (e) include releasing agent such as Carnarba wax, PE wax or others; coupling agent such as gamma glycidoxytrimethoxy silane; pigment such as carbon black; stress modifier such as rubber; flame retardant such as Antimony(III) oxide; emulsifiers, and stabilizers, etc.

In the case when an additive (e) is used, the amount of additive (e) in the epoxy molding compound is preferably 0~2 wt.%, more preferably 0.5~1 wt.% based on the total weight of the epoxy molding compound.

In a preferred embodiment of the present invention, an epoxy molding compound comprises:

- (a) 3 to 20 wt.% of the epoxy resin;
 - (b) 3 to 15 wt.% of the anhydride hardener;
 - (c) 0.05 to 1 wt.% of the curing accelerator;
 - (d) 60 to 90 wt.% of the filler; and
 - (e) 0 to 2 wt.% of the one or more additives,
- wherein the weight percentages are based on the total weight of the epoxy molding compound.

In a further preferred embodiment of the present invention, an epoxy molding compound comprises:

- (a) 3 to 10 wt.% of the epoxy resin;
- (b) 5 to 12 wt.% of the hardener;
- (c) 0.1 to 0.3 wt.% of the curing accelerator;
- (d) 75 to 85 wt.% of the filler; and
- (e) 0.5 to 1 wt.% of the one or more additives.

wherein the weight percentages are based on the total weight of the epoxy molding compound.

There is no special limit for the manufacturing method of the epoxy molding compound of the present invention. In a preferred embodiment, the epoxy molding compound is manufactured by a process comprising steps of:

- (1) Weighing up all of the components (a) to (e) and putting them in a high speed mixer to get a premixed powder at 50~500rpm, preferably 200~400rpm; and
- (2) Putting the premixed powder into an extruder to mix the premixed powder at 80~120°C with the rotation speed of the paddle being 50~200 rpm and then crushing the extruded material into powder.

The epoxy molding compound of the present invention can be used as transistor material, such as diode material and triode material; printed circuit board material, electronic circuit board material, adhesives, interlayer insulating materials, etc. By using the anhydride hardeners with specific structures, the molded products produced from the epoxy molding compounds can have Tg higher than 250°C, which can stand high working temperature, and thus can be used in high temperature applications, especially in high power electrical or electronic devices.

Examples

The present invention will be illustrated in details by means of examples below. However, It is to be understood by one of ordinary skill in the art that this part is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention.

Raw materials

Tactix 742, an epoxy resin obtained from Huntsman Advanced Materials, US;
MEH-7500-3S, a multi-functional phenol resin obtained from Meiwa, Japan;
4,4'-(Hexafluoroisopropylidene)diphthalic anhydride, obtained from TCI, Japan;

3,3',4,4'-benzophenonetetracarboxylic dianhydride, obtained from TCI, Japan;
4-4'-oxydiphthalic acid anhydride, obtained from TCI, Japan;
TPP (triphenylphosphine), a curing accelerator obtained from HOKKO, Japan;
Spherical silica, FB-950 obtained from Denka, Japan;
Polyethylene, 161-P obtained from Sanyo, Japan;
Trimethoxy epoxysilane, KH-560 obtained from Chenguang chemical, China.

Test methods

The spiral flow and gel time of each of the epoxy molding compounds as well as the T_g of the molded product thereof were tested with the following test methods, respectively.

SPIRAL FLOW

In the spiral flow test the flow property of the epoxy molding compound was determined by measuring the length and weight of the resin flowing along the path of a spiral cavity. Sample for the spiral flow test was the powder sample of the epoxy molding compound. No additional preparation was required. The spiral flow test was done according to the method EMI-1-66. Test conditions were set as follows: temperature 175 °C, pressure 70km/cm² and cure time 90s.

GEL TIME

In the gel time test the gelation point of the epoxy molding compound was tested. In the test, a hot plate was heated to the temperature of 175°C. The powder sample of the epoxy molding compound was placed on the hot plate and let it stand as long as the sample was gelled, with stopwatch gelling time was measured (stopwatch was started immediately when the sample is placed on the hot plate and stopped when gelling was complete).

GLASS TRANSITION TEMPERATURE T_g

In the glass transition temperature test the T_g of the molded product was tested. In the test, the sample from the extruder was made to be a sheet by a moulding machine at a moulding temperature of 180 °C for 150s. After moulding, put the sheet into an oven at a temperature of 180°C for 6 hours. The sheet parameter is 5cm*1cm*0.4cm. T_g of the sheet was measured using DMA (Dynamic thermo-mechanical analysis), where the sample was placed in the DMA machine, the heating rate was 3°C/min, the heating was carried out until 300°C, the frequency was 5Hz and the T_g was the peak of tan δ figure.

Examples 1-3 and Comparative Example 1Preparation of Epoxy Molding Compounds**Table 1**

	<i>Comparative example 1</i>	<i>Example 1</i>	<i>Example 2</i>	<i>Example 3</i>
Tactix 742	9.23	3.99	5	5
MEH-7500-3S	5.77			
4,4'-(Hexafluoroisopropylidene)diphthalic anhydride;		11.01		
3,3',4,4'-benzophenonete tricarboxylic dianhydride			10	
4-4'-OXYDIPHTHALIC ACID ANHYDRIDE				10
Catalyst	0.15	0.15	0.15	0.15
Spherical silica	84	84	84	84
Polyethylene	0.5	0.5	0.5	0.5
Trimethoxy epoxysilane	0.35	0.35	0.35	0.35

The raw materials used for the epoxy molding compound of each of Examples 1-3 according to the present invention and Comparative Example 1 were weighed up as shown in Table 1. All the raw materials were added into a high speed mixture, and were mixed for 15 minutes at 300r/min under room temperature to get a premixed powder; The premixed powder was then put into the feeding bucket of an extruder, and was extruded at about 100°C with the rotation speed of the paddle being 120rpm; The extruded material was obtained and crushed into powder.

The obtained powdered epoxy molding compounds were tested for their spiral flow and gel time properties, and molded sheet were obtained from each of the epoxy molding compounds for Tg test.

The results of the spiral flow test, gel time test and Tg test of Examples 1-3 and Comparative Example 1 are shown in Table 2.

Table 2

	Comparative example 1	Example 1	Example 2	Examp e 3
Spiral Flow (cm)	78	65	81	85
Gel Time (s)	25	21	22	24
Tg (°C) (DMA)	184	285	267	281

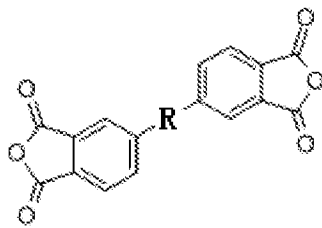
As shown in Table 2, the spiral flow values of the epoxy molding compounds of the present invention are higher than 60cm and the gel time values of the epoxy molding compounds of the present invention are over 20 s. These two properties are comparable with the corresponding values of the Comparative Example 1. While the Tg values of the moulded samples of the present invention are higher than 260°C, which is much higher than the Tg value of the comparative molded sample of the Comparative Example 1.

Although the multi-functional phenol hardener used in the Comparative Example 1 has a quite high cross density, but the Tg of the moulded sample is still not high enough to meet high power device' working temperature demand. By using the specific bi-anhydride hardeners, the molded samples produced from the epoxy molding compounds of the present invention show much higher Tg and these kind of materials can be used in the applications of high power electrical or electronic devices.

What is claimed is:

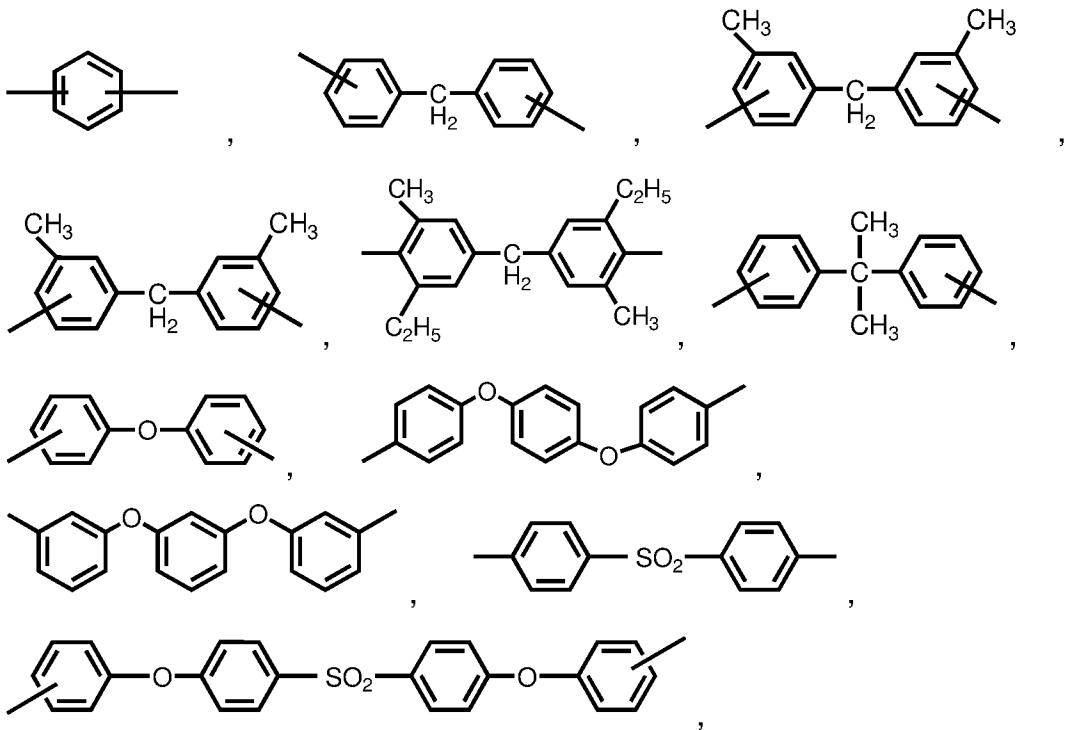
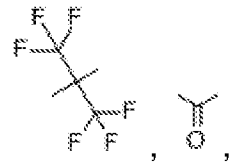
1. An epoxy molding compound, comprising
 - (a) an epoxy resin;
 - (b) a hardener;
 - (c) a curing accelerator;
 - (d) a filler; and optionally
 - (e) an additives,

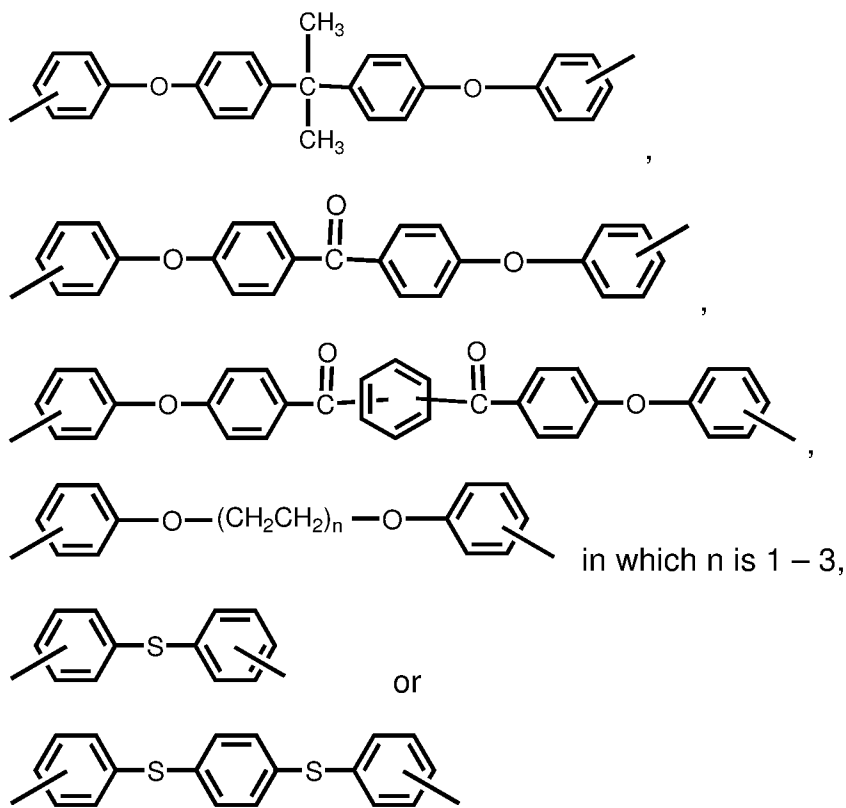
wherein said hardener is one or more bi-anhydride compounds represented by the following structure (1):



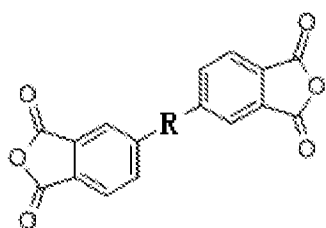
(1)

wherein, R represents a direct bond, -S-, -O-, -CH₂-,





2. An epoxy molding compound according to claim 1, wherein the epoxy resin (a) is selected from the group consisting of bisphenol A epoxy resins, bisphenol F epoxy resins, bisphenol S epoxy resins, biphenyl epoxy resins, tetramethylbiphenyl epoxy resins, phenol novolac epoxy resins, cresol novolac epoxy resins, naphthol novolac epoxy resins, naphtholaralkyl epoxy resins, brominated bisphenol epoxy resins, alicyclic epoxy resins, glycidyl ether epoxy resins, and mixtures thereof.
3. An epoxy molding compound according to claim 1, wherein the bi-anhydride hardener (b) is one or more compounds represented by the following structure (1):



(1)

wherein the weight percentages are based on the total weight of the epoxy molding compound.

9. A process for manufacturing the epoxy molding compound according to any one of claims 1 to 8, comprising steps of:
 - (1) Weighing up all of the components (a) to (e) and putting them in a high speed mixer to get a premixed powder; and
 - (2) Putting the premixed powder into an extruder to further mix the premixed powder at 80~120°C and then crushing the extruded material into powder.
10. Use of the epoxy molding compound according to any one of claims 1 to 8 as transistor material, printed circuit board material, electronic circuit board material, adhesives, and interlayer insulating materials in electrical and electronic devices.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/074566

A. CLASSIFICATION OF SUBJECT MATTER

C08G 59/42(2006.01)i; C08L 63/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G 59/-,C08L 63/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS,CNKI,DWPI,EPODOC,GOOGLE SCHOLAR:epoxy, resin,hardener,curing agent,accelerator,catalyst,filler, bianhydride,1107-00-2,2421-28-5,1823-59-2, hexafluoroisopropylidene w diphthalic w anhydride,benzophenonetetracarboxylic w dianhydride,oxydiphthalic w acid w anhydride,tg,glass w transition w temperature

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4002599 A (ORD COR) 11 January 1977 (1977-01-11) claims 1-40, description, column 2, line 33-column 4, line 35, column 5, line 14-column 6, line 15, examples	1-10
X	CN 1313872 A (BB CORP RES LT) 19 September 2001 (2001-09-19) claims 1-23, description, page 1, lines 5-11, page 8, table 7, example 2	1-10
X	JP 2001072831 A (HINETSU CHEMICAL C) 21 March 2001 (2001-03-21) claims 1-2, description, paragraphs [0004]-[0016], [0026]-[0032]	1-10
A	JP 0258527 A (UMITOMO BAKELITE C) 27 February 1990 (1990-02-27) description, page 202, right column, line 3-page 203, left column, line 20, table 1	1-10
A	JP 57119946 A (BE INDUSTRIE) 26 July 1982 (1982-07-26) claims 1-3, description, column 6, line 3-column 11, line 15	1-10
A	GB 1467275 A (EN ELECTRI) 16 March 1977 (1977-03-16) claims 1-11, description, page 1, line 27-page 2, line 28	1-10

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

05 November 2015

Date of mailing of the international search report

25 November 2015

Name and mailing address of the ISA/CN

STATE INTELLECTUAL PROPERTY OFFICE OF THE
P.R.CHINA
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088, China

Authorized officer

LIANG,Zhenfang

Facsimile No. (86-10)62019451

Telephone No. (86-10)61648409

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/074566

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6207789 B1 (ITACHI CHEMICAL CO LT) 27 March 2001 (2001-03-27) claims 1-20	1-10
<hr/>		

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2015/074566

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	4002599	A	11 January 1977	DE	2650746	A1	12 May 1977
				JP	S5286500	A	18 July 1977
				GB	1567047	A	08 May 1980

CN	1313872	A	19 September 2001	EP	1091992	A1	18 April 2001
				CN	1142960	C	24 March 2004
				WO	9967315	A1	29 December 1999
				CA	2334824	C	29 January 2008
				AU	4254999	A	10 January 2000
				DE	19828248	A1	30 December 1999
				CA	2334824	A1	29 December 1999
				AU	764356	B2	14 August 2003
				EP	1091992	B1	03 December 2003
				US	6468659	B1	22 October 2002
				AT	255611	T	15 December 2003
				ZA	200007392	A	21 June 2001
				JP	2002518567	A	25 June 2002

JP	2001072831	A	21 March 2001	JP	3637957	B2	13 April 2005

JP	0258527	A	27 February 1990	JP	H0258527	A	27 February 1990

JP	57119946	A	26 July 1982	JP	S57119946	A	26 July 1982

GB	1467275	A	16 March 1977	DK	332774	A	17 March 1975
				DE	2416594	A1	16 January 1975
				FR	2299331	A1	27 August 1976
				IT	1015232	B	10 May 1977
				DK	143400	B	17 August 1981
				AU	6775674	A	16 October 1975
				JP	S5032143	A	28 March 1975
				DK	143400	C	21 December 1981
				JP	S5850992	B2	14 November 1983
				SU	561504	A3	05 June 1977
				SE	412226	B	25 February 1980
				FR	2299331	B1	23 February 1979
				BR	7405070	D0	21 January 1975
				DE	2416594	C2	08 December 1983
				DD	112430	A5	12 April 1975
SE	7408147	L	23 December 1974				

US	6207789	B1	27 March 2001	JP	3375976	B2	10 February 2003
				KR	20010012183	A	15 February 2001
				EP	1002815	A4	22 August 2001
				EP	1002815	A1	24 May 2000
				AU	7549698	A	21 December 1998
				WO	9855523	A1	10 December 1998
				TW	452944	B	01 September 2001
