LOW-HALOGEN UNDERFILL, PREPARATION METHOD AND USE THEREOF

TECHNICAL FIELD

The invention relates to the field of adhesives, in particular to a low-halogen underfill, preparation method and use thereof.

BACKGROUND OF THE INVENTION

Since the beginning of the new century, with the continuous technical innovation of electronic industry, electronic products are developing toward the direction of intelligence, miniaturization, light weight, high performance and safety. Many advanced electronic packaging technologies and packaging modes have emerged to adapt to this trend. Among them, flip-chip packaging technology has become one of the most important packaging technologies in the field of advanced electronic devices and high-density packaging due to its advantages of high packaging density, short interconnection paths, low inductance, good reliability and reworkability. Liquid epoxy underfill is a key material for flip-chip packaging technology, it fills the gap between the chip and the substrate through the principle of capillary flow, and its main function is to protect the bond pads and the chip from the influence of harmful operating environment including moisture and ionic contaminants and radiation, and improve the thermal shock resistance and mechanical shock resistance of the packaged devices, thereby increasing the service life of the devices. As the packaging density is getting higher and higher, the bond pads are becoming more and more dense in flip-chip technology. In order to improve the production efficiency and the reliability of the packaged devices, the epoxy underfill is required to have good fluidity, heat resistance, and low coefficient of thermal expansion and low halogen content.

The development of high-performance epoxy underfill for flip-chip packaging has become a research hotspot in the field of microelectronic packaging technology. However, most of the epoxy underfills in the prior art usually are added with glycidyl ether type reactive epoxy diluents in order to reduce the viscosity, but these diluents generally have higher halogen content, and a small amount of addition may lead to excessive halogen content. In addition, halogen materials have significant environmental hazards. On the one hand, the inherent toxicity of halogen-containing organic substances poses a threat to the environment and human health. On

the other hand, these electronic parts cannot be recycled and reused, and during the process of combustion treatment and heating, the harmful substances such as dioxins, etc., may be released and remain in the environment for many years, or even accumulate in an organism for a life-long time and cannot be excreted, seriously threatening the health of the human body, the environment, and the next generation.

In addition, in order to improve the toughness of the underfill after curing, most of the added toughenners are rubber-like materials, which will not only increase the viscosity of the underfill but also reduce the glass-transition temperature, and they are difficult to meet the higher and higher performance requirements for the packaging materials in the electronics industry.

BRIEF DESCRIPTION OF THE INVENTION

In view of this, the present invention provides a low-halogen underfill, wherein the low-halogen underfill has low halogen content, thereby making the packaged parts more environment-friendly.

In order to achieve the purpose of the present invention, the present invention provides the following technical solutions:

In one aspect, the present invention provides a low-halogen underfill, wherein the components of the underfill comprise silica-modified epoxy resin, or comprise silica-modified epoxy resin and acrylic monomer; the halogen content of the underfill is not more than 100ppm. The halogen content in the underfill provided by the present invention is far lower than the requirements of the standard (IEC61249-2-21) guided by the International Electrotechnical Commission: the content of bromine and chlorine are respectively less than 900ppm, and the sum of the bromine and chlorine content is less than 1500ppm. The underfill according to the present invention may meet the requirements of low halogen, it may realize localization, and has good cost performance and broad market prospects.

In a specific embodiment according to the present invention, the halogen content of the underfill is not more than 80 ppm. For example, the halogen content of the underfill is 78 ppm, 76 ppm, etc.

In a specific embodiment according to the present invention, the halogen content of the underfill is not more than 40 ppm; for example, the halogen content of the underfill is 32 ppm.

More preferably the halogen content of the underfill is not more than 30 ppm; for example, the halogen content of the underfill is 30 ppm, 27 ppm, etc. Most preferably the halogen content of the underfill is not more than 25 ppm.

In a specific embodiment according to the present invention, the viscosity of the underfill is 200-900 mPa•s; preferably the viscosity of the underfill is 200-400 mPa•s.

In a specific embodiment according to the present invention, the thermal expansion coefficient of the underfill is 30-70 μm/m℃. Preferably the thermal expansion coefficient of the underfill is 30-60 μm/m℃. Further preferably the thermal expansion coefficient of the underfill is 30-50 μm/m℃. More preferably the thermal expansion coefficient of the underfill is 30-40 μm/m℃.

In a specific embodiment according to the present invention, in terms of weight percentage, the silica-modified epoxy resin is 20%-45% of the total weight of the underfill; preferably the silica-modified epoxy resin is 20%-40% of the total weight of the underfill; further preferably the silica-modified epoxy resin is 20%-35% of the total weight of the underfill; more preferably the silica-modified epoxy resin is 25%-35% of the total weight of the underfill.

The silica-modified epoxy resin applies a special preparation process, wherein the content of nanosilica is as high as 40% and the viscosity is low, and the curing shrinkage and thermal expansion coefficient may be reduced without significantly increasing the viscosity of the underfill.

In a specific embodiment according to the present invention, the silica-modified epoxy resin is NANOPOX-E601 (Evonik, Germany).

In a specific embodiment according to the present invention, in terms of weight percentage, the content of the acrylic monomer is 10%-25% of the total weight of the underfill. Preferably the content of the acrylic monomer is 10%-20% of the total weight of the underfill. Further preferably the content of the acrylic monomer is 12%-17% of the total weight of the underfill.

In a specific embodiment according to the present invention, the acrylic monomer is any one or more selected from the group consisting of: methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobornyl acrylate, lauryl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, methacrylic acid, diethylene glycol diacrylate, hexanediol diacrylate, ethoxylated trimethylolpropane triacrylate, trimethylolpropane triacrylate, pentaerythritol

triacrylate, CYCLOMER M100 (Daicel, Japan), PLACCEL FM1D (Daicel, Japan), and TTA-15 (Tetra, Jiangsu).

When the acrylic monomer selected in this application is used in combination with epoxy resin and silica-modified epoxy resin, it may not only significantly reduce the viscosity of the underfill and improve the fluidity, but also the acrylic monomer has the advantage of low halogen content as compared to glycidyl ether epoxy resin diluents.

In a specific embodiment according to the present invention, the components of the underfill further comprise a toughener. For example, the toughener is ALBIDUR® EP 5340 A (Evonik, Germany), and/or MX553 (KANEKA, Japan).

The toughener according to the application is a core-shell structure rubber particle modified alicyclic epoxy resin; when this toughener is used in combination with silica-modified epoxy resin, epoxy resin, and acrylic monomer, it not only still has a lower viscosity in the case of high content, but also has no obvious effect on the glass-transition temperature of the cured product, as compared with the direct addition of the traditional rubber toughener.

In a specific embodiment according to the present invention, the components of the underfill further comprise epoxy resin. Exemplarily, the epoxy resin is any one or more selected from the group consisting of: electronic grade low-halogen bisphenol A epoxy resin, bisphenol F epoxy resin, and alicyclic epoxy resin.

For example, the bisphenol A epoxy resin is NPEL-127E (Nanya, Taiwan) or 328 (Huayi, Shanghai); the bisphenol F epoxy resin is EPIKOTE 862 (Shell, Holland), EPIKOTE 983U (Shell, Holland) or NPEL-170 (Nanya, Taiwan); the alicyclic epoxy resin is CELLOXIDE 2021P (Daicel, Japan), CELLOXIDE 8000 (Daicel, Japan), TTA-26 (Tetra, Jiangsu) or TTA 28 (Tetra, Jiangsu) etc. The epoxy resin selected in this application not only has the characteristics of low halogen content, but also the underfill prepared by combination of this epoxy resin and the acrylic monomer obtains excellent overall performance due to its heat resistance, modulus, viscosity, and thermal expansion coefficient being a better balance point. In addition, choosing a combination of different types of epoxy resins may more effectively combine the advantages of various types of epoxy resins, thereby making an underfill with more excellent performance.

In a specific embodiment according to the present invention, the components of the underfill further comprise a curing agent, and/or a filler, and/or an accelerator, and/or an initiator,

and/or a polymerization inhibitor, and/or a coupling agent, and/or a defoamer, and/or a wetting and dispersing agent, and/or a pigment.

In a specific embodiment according to the present invention, the curing agent is an anhydride type curing agent. For example, any one or more selected from the group consisting of: methyltetrahydrophthalic anhydride, methylhexahydrophthalic anhydride, and 4-methylhexahydrophthalic anhydride. The curing agent selected in this embodiment has the advantages of low viscosity, fast curing speed at medium temperature, and excellent electrical properties of the cured product; and it may be used in combination with epoxy resin, acrylic monomer, and the like.

In a specific embodiment according to the present invention, the filler is spherical silica micro-powder and/or hollow glass microspheres with maximum particle size of 10 μm; preferably the maximum particle size is 5 μm; more preferably the maximum particle size is 3 μm. In this application, inorganic fillers are used, and they may be used in combination with epoxy resin and acrylic monomer to effectively reduce the curing shrinkage rate and thermal expansion coefficient of the underfill.

In a specific embodiment according to the present invention, the filler is spherical silica micro-powder, which is used by mixing fillers with different particle sizes, and the combination of spherical inorganic fillers with different particle sizes may reduce the influence on viscosity and effectively reduce the sedimentation of the filler.

In a specific embodiment according to the present invention, the accelerator is at least one selected from the group consisting of: 2-methylimidazole, 2-ethyl-4-methylimidazole, 1-benzyl-2-ethylimidazole, 2-undecylimidazole, 2-phenylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, and 1-cyanoethyl-2-undecylimidazole.

In a specific embodiment according to the present invention, the initiator is at least one selected from the group consisting of: dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, tert-butyl peroxyacetate, tert-butyl peroxybenzoate, tert-butyl peroxy-2-ethylhexanoate, and tert-butyl peroxypivalate.

In a specific embodiment according to the present invention, the polymerization inhibitor is at least one selected from the group consisting of: hydroquinone, tert-butylcatechol, phenol, and

p-benzoquinone.

In a specific embodiment according to the present invention, the coupling agent is at least one selected from the group consisting of: γ-(2,3-epoxypropoxy)propyltrimethoxysilane and β-(3,4-epoxycyclohexylethyl)trimethoxysilane.

In a specific embodiment according to the present invention, the defoamer is at least one selected from the group consisting of: BYK-A530 (BYK, Germany), BYK-555 (BYK, Germany), BYK-320 (BYK, Germany), BYK-323 (BYK, Germany), and ACP-0001 (Dow Coring, USA).

In a specific embodiment according to the present invention, the wetting and dispersing agent is at least one selected from the group consisting of: BYK-W9010 (BYK, Germany), BYK-W940 (BYK, Germany), BYK-W980 (BYK, Germany), BYK-W969 (BYK, Germany), Dispers 610 (Evonik, Germany), Dispers 630 (Evonik, Germany), and Dispers 652 (Evonik, Germany).

In this embodiment, the combination of the wetting and dispersing agent and the filler may effectively improve the effect of filler dispersion, reduce the agglomeration and sedimentation of the filler, and increase the fluidity of the system. If there is no additional filler, the wetting and dispersing agent may not be added.

In a specific embodiment according to the present invention, the pigment is at least one selected from the group consisting of: high-pigment carbon black, aniline black, iron oxide black, and low-halogen black color paste (Poly one, USA).

In a specific embodiment according to the present invention, in parts by weight, the raw materials of the underfill comprise: 0-20 parts of epoxy resin, 20-45 parts of silica-modified epoxy resin, 25-40 parts of curing agent, 10-25 parts of acrylic monomer, 0-10 parts of toughener, 0-20 parts of filler, 1-5 parts of accelerator, 1-5 parts of initiator, 0.1-1 part of polymerization inhibitor, 0.1-1.5 parts of coupling agent, 0.1-1 part of defoamer, 0-1 part of wetting and dispersing agent, and 0.2-0.5 part of pigment.

In a specific embodiment according to the present invention, in parts by weight, the underfill comprises: 5-15 parts of epoxy resin, 25-40 parts of silica-modified epoxy resin, 30-40 parts of curing agent, 12-20 parts of acrylic monomer, 5-10 parts of toughener, 5-15 parts of filler, 1-4 parts of accelerator, 2-4 parts of initiator, 0.3-0.8 part of polymerization inhibitor, 0.5-1 part

of coupling agent, 0.3-0.7 part of defoamer, 0.2-0.8 part of wetting and dispersing agent, and 0.2-0.4 part of pigment.

In another aspect, the present invention provides a preparation method of the low-halogen underfill, which comprises weighing out each of the components and mixing them under vacuum conditions.

In a specific embodiment of the present application, the preparation method of the low-halogen underfill comprises the following steps:

weighing 0-20 parts of epoxy resin, 20-45 parts of silica-modified epoxy resin, 10-25 parts of acrylic monomer, 0-10 parts of toughener, 0-20 parts of filler, 1-5 parts of accelerator, 0.1-1 part of polymerization inhibitor, 0.1-1.5 parts of coupling agent, 0.1-1 part of defoamer, 0-1 part of wetting and dispersing agent, and 0.2-0.5 part of pigment; putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 10-30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 25-40 parts of curing agent and 1-5 parts of initiator, keeping the vacuum and mixing at -0.1MPa for 10-30min; thereby obtaining the low-halogen underfill.

In still another aspect, the present invention provides use of the above low-halogen underfill in the field of chip-level microelectronic packaging.

In still another aspect, the present invention provides use of silica-modified epoxy resin and/or acrylic monomer in low-halogen underfill.

Exemplarily, the present invention has at least one of the following advantages:

The low-halogen underfill provided by the invention has the advantages of low viscosity, low halogen content, good mechanical properties, good heat resistance, low thermal expansion coefficient, etc., and it has a wider application prospect.

DETAILED DESCRIPTION OF THE INVENTION

The technical solutions of the present invention will be clearly and completely described below in conjunction with the examples according to the present invention. Obviously, the described examples are only a part of the examples of the present invention, rather than all the examples. Based on the examples according to the present invention, all of the other examples obtained by those skilled in the art without putting in creative work shall fall within the

protection scope of the present invention.

Example 1

Accurately weighing 100 parts of electronic grade bisphenol F epoxy resin EPIKOTE 862 (Shell, Holland), 240 parts of nanosilica-modified epoxy resin NANOPOX-E601 (Evonik, Germany), 150 parts of trimethylolpropane triacrylate, 100 parts of methacrylic monomer PLACCEL FM1D (Daicel, Japan), 40 parts of 2-ethyl-4-methylimidazole, 8 parts of coupling agent β-(3,4-epoxycyclohexylethyl)trimethoxysilane, 5 parts of defoamer BYK-555 (BYK, Germany), 5 parts of high-pigment carbon black, 2 parts of polymerization inhibitor hydroquinone; putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 320 parts of curing agent methylhexahydrophthalic anhydride and 30 parts of initiator tert-butyl peroxybenzoate, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Example 2

Accurately weighing 450 parts of nanosilica-modified epoxy resin NANOPOX-E601 (Evonik, Germany), 135 parts of methacrylic monomer CYCLOMER M100 (Daicel, Japan), 30 parts of 1-cyanoethyl-2-methylimidazole, 8 parts of coupling agent γ-(2,3-epoxypropoxy)propyltrimethoxysilane, 5 parts of defoamer BYK-A320 (BYK, Germany), 3 parts of high-pigment carbon black, 2 parts of polymerization inhibitor tert-butylcatechol; putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 340 parts of curing agent methyltetrahydrophthalic anhydride and 25 parts of initiator tert-butyl peroxy-2-ethylhexanoate, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Example 3

Accurately weighing 70 parts of electronic grade bisphenol A epoxy resin 328 (Huayi, Shanghai), 80 parts of alicyclic epoxy resin TTA28 (Tetra, Jiangsu), 200 parts of

nanosilica-modified epoxy resin NANOPOX-E601 (Evonik, Germany), 70 parts of toughener ALBIDUR®EP 5340 A (Evonik, Germany), 30 parts of lauryl methacrylate, 70 parts of methacrylic monomer PLACCEL FM1D (Daicel, Japan), 30 parts of 1-cyanoethyl-2-ethyl-4-methylimidazole, 8 parts of coupling agent β-(3,4-epoxycyclohexylethyl)trimethoxysilane, 5 parts of defoamer BYK-A530 (BYK, Germany), 5 parts of low-halogen black color paste (Poly one, USA), 2 parts of polymerization inhibitor p-benzoquinone, 50 parts of spherical silica micro-powder with maximum particle size of 5μm, 30 parts of spherical silica micro-powder with maximum particle size of 3μm, 5 parts of wetting and dispersing agent BYK-W9010 (BYK, Germany); putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 320 parts of curing agent methylhexahydrophthalic anhydride and 25 parts of initiator dibenzoyl peroxide, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Example 4

Accurately weighing 50 parts of alicyclic epoxy resin CELLOXIDE 8000 (Daicel, Japan), 260 parts of nanosilica-modified epoxy resin NANOPOX-E601 (Evonik, Germany), 60 parts of toughener MX553 (KANEKA, Japan), 40 parts of methacrylic monomer TTA-15 (Tetra, Jiangsu), 100 parts of ethoxylated trimethylolpropane triacrylate, 40 parts of 2-methylimidazole, 8 parts of coupling agent β-(3,4-epoxycyclohexylethyl)trimethoxysilane, 4 parts of defoamer ACP-0001 (Dow Coring, USA), 5 parts of low-halogen black color paste (Poly one, USA), 2 parts of polymerization inhibitor hydroquinone, 75 parts of spherical silica micro-powder with maximum particle size of 5μm, 40 parts of spherical silica micro-powder with maximum particle size of 3μm, 4 parts of wetting and dispersing agent Dispers 630 (Evonik, Germany); putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 282 parts of curing agent methyltetrahydrophthalic anhydride and 30 parts of initiator dilauroyl peroxide, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Example 5

Accurately weighing 60 parts of alicyclic epoxy resin CELLOXIDE 2021P (Daicel, Japan), 280 parts of nanosilica-modified epoxy resin NANOPOX-E601 (Evonik, Germany), 50 parts of toughener MX553 (KANEKA, Japan), 90 parts of methacrylic monomer CYCLOMER M100 (Daicel, Japan), 40 parts of isobornyl acrylate, 30 parts of 1-cyanoethyl-2-methylimidazole, 8 parts of coupling agent β-(3,4-epoxycyclohexylethyl)trimethoxysilane, 5 parts of defoamer BYK-A530 (BYK, Germany), 5 parts of high-pigment carbon black, 2 parts of polymerization inhibitor hydroquinone, 60 parts of spherical silica micro-powder with maximum particle size 10μm, 30 parts of spherical silica micro-powder with maximum particle size of 5μm, 5 parts of wetting and dispersing agent BYK-W940 (BYK, Germany); putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 305 parts of curing agent methylhexahydrophthalic anhydride and 30 parts of initiator dibenzoyl peroxide, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Example 6

Accurately weighing 400 parts of nanosilica-modified epoxy resin NANOPOX-E601 (Evonik, Germany), 60 parts of toughener ALBIDUR®EP 5340 A (Evonik, Germany), 40 parts of butyl methacrylate, 80 parts of trimethylol propane triacrylate, 30 parts of 2-ethyl-4-methylimidazole, 8 parts of coupling agent γ-(2,3-epoxypropoxy)propyltrimethoxysilane, 5 parts of defoamer BYK-A555 (BYK, Germany), 5 parts of high-pigment carbon black, 2 parts of polymerization inhibitor hydroquinone; putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 340 parts of curing agent 4-methylhexahydrophthalic anhydride and 30 parts of initiator tert-butyl peroxybenzoate, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Example 7

Accurately weighing 50 parts of bisphenol F epoxy resin NPEL-170 (Nanya, Taiwan), 250

parts of nanosilica-modified epoxy resin NANOPOX-E601 (Evonik, Germany), 100 parts of toughener MX553 (KANEKA, Japan), 120 parts of ethyl methacrylate, 80 parts of pentaerythritol triacrylate, 30 parts of 1-benzyl-2-ethylimidazole, 8 parts of coupling agent β-(3,4-epoxycyclohexylethyl) trimethoxysilane, 5 parts of defoamer BYK-A530 (BYK, Germany), 5 parts of iron oxide black, 2 parts of polymerization inhibitor hydroquinone; putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 320 parts of curing agent methyltetrahydrophthalic anhydride and 30 parts of initiator tert-butyl peroxybenzoate, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Example 8

Accurately weighing 65 parts of alicyclic epoxy resin TTA 28 (Tetra, Jiangsu), 350 parts of nanosilica-modified epoxy resin NANOPOX-E601 (Evonik, Germany), 100 parts of ethoxylated trimethylolpropane triacrylate, 70 parts of methacrylic monomer CYCLOMER M100 (Daicel, Japan), 30 parts of 1-cyanoethyl-2-methylimidazole, 8 parts of coupling agent β-(3,4-epoxycyclohexylethyl)trimethoxysilane, 5 parts of defoamer BYK-A320 (BYK, Germany), 5 parts of low-halogen black color paste (Poly one, USA), 2 parts of polymerization inhibitor hydroquinone; putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 335 parts of curing agent methylhexahydrophthalic anhydride and 30 parts of initiator dibenzoyl peroxide, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Example 9

Accurately weighing 120 parts of alicyclic epoxy resin CELLOXIDE 2021 (Daicel, Japan), 80 parts of bisphenol F epoxy resin NPEL-170 (Nanya, Taiwan), 200 parts of nanosilica-modified epoxy resin NANOPOX-E601 (Evonik, Germany), 30 parts of methacrylic acid monomer TTA-15 (Tetra, Jiangsu), 70 parts of trimethylolpropane triacrylate, 20 parts of 1-benzyl-2-ethylimidazole, 8 parts of coupling agent

γ-(2,3-epoxypropoxy)propyltrimethoxysilane, 5 parts of defoamer BYK-A530 (BYK, Germany), 5 parts of high-pigment carbon black, 2 parts of polymerization inhibitor hydroquinone, 70 parts of spherical silica micro-powder with maximum particle size of 5μm, 45 parts of spherical silica micro-powder with maximum particle size of 3μm, 5 parts of wetting and dispersing agent BYK-W940 (BYK, Germany); putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 320 parts of curing agent 4-methylhexahydrophthalic anhydride and 20 parts of initiator tert-butyl peroxybenzoate, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Comparative Example 1

Accurately weighing 205 parts of bisphenol F epoxy resin NPEL-170 (Nanya, Taiwan), 82 parts of alicyclic epoxy resin CELLOXIDE 2021P (Daicel, Japan), 110 parts of poly(propylene glycol) diglycidyl ether (diluent), 8 parts of liquid carboxyl-terminated butadiene-acrylonitrile rubber (toughener), 40 parts of 1-cyanoethyl-2-methylimidazole, 8 parts of coupling agent β-(3,4-epoxycyclohexylethyl)trimethoxysilane, 5 parts of defoamer BYK-A320 (BYK, Germany), 5 parts of high-pigment carbon black, 60 parts of spherical silica micro-powder with maximum particle size of 10 μm, 40 parts of spherical silica micro-powder with maximum particle size of 5 μm, 5 parts of wetting and dispersing agent Dispers 610 (Evonik, Germany); putting them into a planetary mixer, keeping the vacuum and mixing at -0.1MPa for 30min; after grinding the obtained liquid mixture in a three-roller machine, transferring it into the planetary mixer again; adding 432 parts of curing agent methylhexahydrophthalic anhydride, keeping the vacuum and mixing at -0.1MPa for 30min; then said underfill is obtained.

Experimental Test 1: Halogen Content Test

The samples obtained in the above Examples 1-9 are tested for chlorine and bromine content, by using an X fluorescence spectrometer according to the EN 14582:2007 test standard.

Experimental Test 2: Viscosity Test

The samples obtained in the above Examples 1-9 are tested for viscosity at room

temperature, by using a rotational viscometer.

Experimental Test 3: Glass Transition Temperature Test

The samples obtained in the above Examples 1-9 are tested for glass-transition temperature, according to the ASTM D696-79 test standard.

Experimental Test 4: Storage Modulus Test

The samples obtained in the above Examples 1-9 are tested for storage modulus, by using a dynamic mechanical analyzer.

Experimental Test 5: Thermal Expansion Coefficient Test

The samples obtained in the above Examples 1-9 are tested for thermal expansion coefficient, according to the ASTM D696-79 standard test.

The results of the above experimental tests are shown in Table 1 below.

Table 1: Test Results of Examples 1-9

	Viscosity after mixing (mPa·s)	Halogen (chlorine) content (ppm)	Curing temperature (°C)	Curing time (min)	Glass transition temperature (°C)	Storage modulus at room temperature (MPa)	Coefficient of linear thermal expansion (μm/m°C)
Example 1	215	88	150	8	85	2240	58
Example 2	452	32	150	8	183	2710	43
Example 3	520	78	150	8	148	2680	51
Example 4	395	25	150	8	162	2960	32
Example 5	372	27	150	8	165	2790	37
Example 6	484	30	150	8	168	2660	45
Example 7	248	76	150	8	121	2810	60
Example 8	275	25	150	8	160	2860	48

Example 9	570	92	150	8	179	2910	42
Comparative Example 1	965	1080	150	8	114	2720	64

As shown in Table 1, compared with Comparative Example 1, the underfills prepared in Examples 1-9 of this application have the following characteristics: ①the halogen content is not more than 100ppm, and even the halogen content may be reduced to 25ppm; ②the viscosity is lower such that the underfill have better fluidity; ③the glass-transition temperature is higher, the change range of the glass-transition temperature is larger, and the glass-transition temperature may be adjusted by adjusting the content of epoxy resin and acrylic monomer; ④the coefficient of thermal expansion is lower. Moreover, in the actual application process, the desired viscosity, glass-transition temperature, and thermal expansion coefficient of the underfill may be obtained by adjusting the types and contents of epoxy resin and acrylic monomers as required.

The above descriptions are only the preferred examples of the present invention and are not intended to limit the present invention. Any modification, equivalent replacement, etc. made within the spirit and principle of the present invention shall be encompassed in the protection scope of the present invention.

CLAIMS

1. A low-halogen underfill, wherein the components of the underfill ~~comprise silica-modified epoxy resin, or~~ comprise silica-modified epoxy resin and acrylic monomer; ~~the halogen content of the underfill is not more than 100 ppm; preferably~~ the halogen content of the underfill is not more than 80 ppm; more preferably the halogen content of the underfill is not more than 40 ppm; the content of the silica-modified epoxy resin is 20%-45% of the total weight of the underfill; the content of the acrylic monomer is 12%-17% of the total weight of the underfill.

2. The low-halogen underfill according to claim 1, wherein in terms of weight percentage, ~~the content of the silica-modified epoxy resin is 20%-45% of the total weight of the underfill; preferably~~ the silica-modified epoxy resin is 20%-40% of the total weight of the underfill; further preferably the silica-modified epoxy resin is 20%-35% of the total weight of the underfill; more preferably the silica-modified epoxy resin is 25%-35% of the total weight of the underfill.

~~3. The low-halogen underfill according to claim 1 or 2, wherein in terms of weight percentage, the content of the acrylic monomer is 10%-25% of the total weight of the underfill; preferably the content of the acrylic monomer is 10%-20% of the total weight of the underfill; further preferably the content of the acrylic monomer is 12%-17% of the total weight of the underfill.~~

~~4~~3. The low-halogen underfill according to ~~any one of~~ claim~~s~~ 1 or ~~3~~2, wherein the acrylic monomer is any one or more selected from the group consisting of: methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobornyl acrylate, lauryl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, methacrylic acid, diethylene glycol diacrylate, hexanediol diacrylate, ethoxylated trimethylolpropane triacrylate, trimethylolpropane triacrylate~~,~~ and pentaerythritol triacrylate~~, CYCLOMER M100, PLACCEL FM1D, and TTA 15~~.

~~5~~4. The low-halogen underfill according to any one of claims 1-~~4~~3, wherein the components of the underfill further comprise a toughener.

~~6. The low-halogen underfill according to claim 5, wherein the toughener is ALBIDUR EP 5340 A, and/or MX553.~~

~~7~~5. The low-halogen underfill according to any one of claims 1-~~6~~4, wherein the components

of the underfill further comprise epoxy resin.

~~8~~6. The low-halogen underfill according to any one of claims ~~7~~1-5, wherein the epoxy resin is any one or more selected from the group consisting of: bisphenol A epoxy resin, bisphenol F epoxy resin, and alicyclic epoxy resin.

~~9~~7. The low-halogen underfill according to any one of claims 1-~~8~~6, wherein the components of the underfill further comprise a curing agent, and/or a filler, and/or an accelerator, and/or an initiator, and/or a polymerization inhibitor, and/or a coupling agent, and/or a defoamer, and/or a wetting and dispersing agent, and/or a pigment.

~~10~~8. The low-halogen underfill according to claim ~~9~~7, wherein in parts by weight, the underfill comprises the following components: 0-20 parts of epoxy resin, 20-45 parts of silica-modified epoxy resin, 25-35 parts of curing agent, 10-25 parts of acrylic monomer, 0-10 parts of toughener, 0-20 parts of filler, 1-5 parts of accelerator, 1-5 parts of initiator, 0.1-1 part of polymerization inhibitor, 0.1-1.5 parts of coupling agent, 0.1-1 part of defoamer, 0-1 part of wetting and dispersing agent, and 0.2-0.5 part of pigment.

~~11~~9. A preparation method of the low-halogen underfill according to any one of claims 1-~~10~~8, wherein it comprises weighing out each of the components and mixing them under vacuum conditions.

~~12~~10. Use of the low-halogen underfill according to any one of claims 1-~~10~~ 8 ~~and/or the low-halogen underfill prepared by claim 11~~ in the field of chip-level microelectronic packaging.

~~13. Use of the silica-modified epoxy resin and/or acrylic monomer in low-halogen underfill.~~