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(21) International Application Number: PCT/US99/30198 (22) International Filing Date: 17 December 1999 (17.12.99) (30) Priority Data: 09/243,330 3 February 1999 (03.02.99) US (71) Applicant: GENERAL ELECTRIC COMPANY [US/US]; 1 River Road, Schenectady, NY 12345 (US). (72) Inventors: TALIBUDDIN, Sapna, Halim; 6227 Chesapeake Drive, Mount Vernon, IN 47620 (US). SASTRI, Vinod, R.; 6428 Antoinette Drive, Evansville, IN 47715 (US). MERCX, Franciscus; Fabriekstraat 6, NL-4611 HH Bergen op Zoom (NL). CHERET, Estelle; Esdoorn Iaan 28, B-2940 Stabroek (BE). GALLUCCI, Robert, Russell; 1109 Tanglewood Drive, Mount Vernon, IN 47620 (US). (74) Agents: WINTER, Catherine, J. et al.; General Electric Company, 3135 Easton Turnpike W3C, Fairfield, CT 06431 (US).		(81) Designated States: JP, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: POLYESTER MOLDING COMPOSITION (57) Abstract A thermoplastic glass filled resin composition having improved hydrolysis resistance and reduced warp comprising a resin blend consisting essentially of an alkylene aryl polyester, a cross-shell ASA (alkylacrylate-styrene-acrylonitrile interpolymer) and an effective amount of at least one difunctional epoxy compound, said at least one difunctional epoxy compound having at least one cyclohexane ring moiety and having two terminal epoxy functional groups, wherein at least one of the two terminal epoxy functional groups is a substituent on the at least one cyclohexane ring moiety; and an effective amount of a catalyst compound and from 0-5% of a carbodiimide.		

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POLYESTER MOLDING COMPOSITION

FIELD OF THE INVENTION

The invention relates to a molding composition comprising a glass filled polyester resin including an impact modifier and stabilizers.

BACKGROUND OF THE INVENTION

For thermoplastic polyester resins, the fibrous glass enhances the mechanical properties and heat distortion of the resin. However, glass filled crystalline resin blends are often more difficult to mold. The crystalline resin also has poor melt strength and high shrinkage upon cooling. Orientation of glass fibers and differential shrinkage between the glass and resin makes it difficult to obtain good dimensional tolerances. Fiber glass filled parts usually have a higher degree of warp than seen in unfilled resin compositions. Typically, glass reinforced blends also have a rough surface.

Unfortunately, the addition of glass fibers can substantially lower the Izod impact strengths of the fiber reinforced compositions, and, also, substantially reduce the biaxial impact (instrumented impact) energies of such compositions.

In order to achieve improved properties in the glass filled blends, especially impact strength, impact modifiers have been added to poly(alkylene terephthalates) including rubbers of polybutadiene, butadiene-styrene copolymers, butadiene-acrylonitrile styrene copolymers, ethylene-propylene rubbers, polyisobutene and polyisoprene, alkyl acrylate acrylate rubbers and acrylate styrene acrylonitrile rubbers. Acrylic based rubbers are preferred for many applications involving exposure to light because of their resistance to yellowing.

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Blends of thermoplastic polyesters with acrylic rubbers have been described in the art. Japanese 1978 publication, 53-129246 to relates to a polycarbonate and saturated polyester A and B components with the ASA (C) component comprising component (I) of at least one monomer such as
5 styrene grafted on component (II) which is an elastomer based on the cross-linking copolymerization of a mixture of an acrylic ester and a cyclic monomeric compound of triallyl cyanurate and triallyl isocyanurate.

U.S. patent 4,096,202 to Franham et. al. describes modifiers based on acrylic rubbers for improving impact strength without significantly increasing
10 melt viscosity for poly(alkylene terephthalates). The impact modifier is a multi-phase composite interpolymer comprising a cross linked acrylic first stage which also contains graftlinking monomer and a final rigid thermoplastic phase. The crosslinking monomers include poly acrylic and poly methacrylic esters of polyols such as butylene diacrylate and
15 dimethacrylate, trimethylol propane trimethacrylate, and the like; di- and trivinyl benzene, vinyl acrylate and methacrylate, and the like. Among effective graftlinking monomers, which are polyethylenically unsaturated monomers, are allyl group-containing monomers of allyl esters of ethyleneically unsaturated acids such as allyl acrylate, allyl methacrylate,
20 diallyl maleate, diallyl fumarate, diallyl itaconate, allyl acid maleate, allyl acid fumarate, and allyl acid itaconate. The resulting multi-phase composite interpolymer is known in the art as an ASA polymer.

United States Patent 5,219,915 to McKee et al. relates to glass fiber-reinforced thermoplastic molding materials based on polyesters and graft
25 polymers. The thermoplastic molding materials based on a mixture of polybutylene terephthalate and polyethylene terephthalate as essential components, graft polymers having acrylate rubbers as the grafting base, copolymers of vinylaromatic monomers and acrylonitrile or methacrylonitrile

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and glass fibers. As set forth, the compositions of both Examples also contained the following additives (in each case in % by weight, based on the total weight of A+B): 1.5% by weight of carbon black, 0.1% by weight of talc, 0.8% by weight of pentaerythritol stearate.

5 United States Patent 4,148,956 to Breitenfellner relates to thermoplastic molding compositions of linear polyesters and styrene/acrylonitrile modified by alpha-methylstyrene and/or acrylates. Disclosed are "inert additives of all types, for example fillers such as talc, calcium carbonate, barium sulphate, SiO₂, kaolin, micromica, wollastonite and metal powders, and reinforcing
10 fillers, such as glass fibers and glass beads, inorganic or organic pigments, optical brighteners, delustering agents, processing auxiliaries, such as lubricants, mould release agents and agents which promote crystallization, flameproofing agents, nucleating agents and stabilizers, such as phosphorus-organic compounds, for example triphenyl phosphite, can be added during
15 working up of the polyester melt or even prior to the polycondensation reaction or during mixing of the polyesters with modified styrene/acrylonitrile."

 United States Patent 5,733,959 to Heitz, et. al. relates to thermoplastic molding compositions comprise from 20 to 99% by weight of a polyester, up
20 to 90% by weight of which may be replaced by a polycarbonate or a polyamide, from 0.1 to 7% by weight of a specific sterically hindered aliphatic carbodiimide. The compositions may contain impact modifiers which are generally copolymers, preferably built up from at least two of the following monomers: ethylene, propylene, butadiene, isobutene, isoprene, chloroprene,
25 vinyl acetate, styrene, acrylonitrile and (meth)acrylates having from 1 to 18 carbon atoms in the alcohol component.

 United States Patent 5,596,049 to Gallucci et. al. describes the stabilization of polyesters using epoxy compounds in combination with a

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catalyst. The disclosed polyester composition comprises a linear polyester resin, a difunctional epoxy compound and a catalyst. The difunctional epoxy compound has two terminal epoxy functionalities. Examples of preferred difunctional epoxy compounds are 3,4-epoxycyclohexyl-3,4-

5 epoxycyclohexylcarboxylate, bis(3,4-epoxycyclohexylmethyl) adipate, vinylcyclohexene di-epoxide, and the like. Especially preferred is 3,4-epoxycyclohexyl-3,4 epoxycyclohexylcarboxylate.

United States Patent 4,894,416 to Gallucci relates to low gloss thermoplastic blends with good physical properties consisting of a blend of
10 ASA and a gloss-reducing amount of a glycidyl (meth)acrylate copolymer.

The compositions of the prior art still suffer from limitations with respect to impact, modulus and retention of mechanical properties and melt viscosity under hydrolytic conditions and from poor dimensional stability and warp. Accordingly, there is a need for glass reinforced polyester resin
15 compositions which exhibit consistent and uniform properties together with enhanced properties of improved hydrolysis resistance and reduced warp.

The prior art focus is to add various ingredients to enhance the properties of the polyester material. However, with this approach, it is often difficult to fully achieve the desired improvement in properties. For example
20 fiber glass improves stiffness and heat distortion temperature but harms impact and dimensional stability. The addition of one ingredient may improve one property but result in the degradation of another desirable property. As a result, a combination of various ingredients are added which further complicates the production of a consistent product due to the
25 interactions of the various ingredients with one another.

SUMMARY OF THE INVENTION

We have found that modification of a polyester/ASA resin with difunctional epoxides and catalysts, such as salts of aliphatic carboxylic acids,

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provide a composition which possesses good hydrolytic stability, reduced warp and good melt viscosity stability. Further, preferred polyester compositions possess high melt viscosity and ease of processability as well as good mechanical properties. The compositions of the present invention
5 unexpectedly exhibit reduced warp over compositions employing no epoxide.

In accordance with the present invention, there is provided a thermoplastic glass filled resin composition having improved hydrolysis resistance and reduced warp properties comprising of a resin blend
10 consisting essentially of an alkylene aryl polyester, a core-shell or graft ASA (alkylacrylate-styrene-acrylonitrile interpolymers) and an effective amount of at least one difunctional epoxy compound. The difunctional epoxy compound includes at least one cyclohexane ring moiety and has two terminal epoxy functional groups. At least one of the two terminal epoxy
15 functional groups is a substituent on the at least one cyclohexane ring moiety. An effective amount of a catalyst compound is utilized. The composition may further contain a carbodiimide stabilizer to improve said performance.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 Type I illustrates the USCAR III hydrolysis test procedure.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In accordance with the principles of the present invention,
20 compositions comprising linear polyesters, difunctional epoxides and salts of aliphatic carboxylic acids provide a composition which possesses both improved hydrolytic stability and retention of melt viscosity stability. Further, preferred polyester compositions possess high melt viscosity and reduced warp. The compositions of the present invention unexpectedly
25 exhibit improved results over compositions without epoxides.

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The preferred difunctional polyepoxy compound is 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate. The preferred catalysts are salts of an aliphatic or aromatic carboxylic acids. The most preferred catalysts are Group IA (alkaline) metal carboxylates .

5 The epoxy component is at least one difunctional epoxy compound. By difunctional epoxy compound is meant a compound having two terminal epoxy functionalities. Preferably the compound will contain only carbon, hydrogen and oxygen. The compound will preferably have a molecular weight of below about 1000 to facilitate blending with the polyester resin.

10 Preferred difunctional epoxy compounds will have at least one of the epoxide groups on a cyclohexane ring. Examples of preferred difunctional epoxy compounds are 3,4-epoxycyclohexyl-3,4-epoxycyclohexylcarboxylate, bis(3,4-epoxycyclohexylmethyl) adipate, vinylcyclohexene di-epoxide, , epoxy cyclohexane adducts of carboxylic acids and the like. Especially preferred is
15 3,4-epoxycyclohexyl-3,4 epoxycyclohexylcarboxylate.

The difunctional epoxide compounds can be made by techniques well known to those skilled in the art. For example, the corresponding alpha, beta-dihydroxy compounds can be dehydrated to produce the epoxide groups, or the correspondingly unsaturated compounds can be epoxidized by treatment
20 with a peracid, such as peracetic acid, in well-known techniques. The compounds are also commercially available.

The difunctional epoxy compound may be employed in any effective amount, but preferably small amounts are use, e.g., at a range of about 0.1 to about 5 percent by weight. However, a particularly preferred range is from
25 about 0.1 to about 3.5 percent by weight. A more preferred range is from about 0.5 to about 2 percent by weight. Within this particularly preferred range it has been found advantageous to employ in certain compositions from

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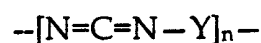
about 1 to about 2.0 percent by weight of the difunctional polyepoxy compound. All percentages are based on the total weight of the blend.

Another component of the present invention consists of the catalyst compound. Preferred catalysts are salts free from direct carbon-phosphorous bonds and containing at least one of alkali metal cations and alkaline earth metal cations and halide anions. It is apparent that this class contains a large number of compounds. They include alkali metal halides, alkali metal carboxylates, and alkali metal carbonates.

Illustrative compounds within this class are lithium fluoride, lithium iodide, potassium bromide, potassium iodide, sodium acetate, sodium benzoate, sodium caproate, sodium stearate, and potassium oleate.

The catalyst component can be present in the composition of the present invention in any effective amount. Preferably the catalyst is present in an amount ranging from about 0.001 to about 1 weight percent, more preferably from about 0.03 to about 0.1 weight percent based on the total weight of the resin composition.

Carbodiimides can also be used in combination with the epoxides and catalyst of the present invention to improve hydrolysis resistance. Both monomeric and polymeric carbodiimides can be used although polymeric carbodiimides may be preferred due to the potential for lower plate out. Carbodiimides of the following structure may be used:

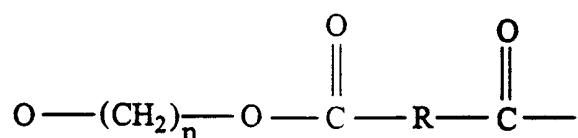


Where Y is an aromatic, aliphatic or alkyl substituted aromatic radical of from 2 to 20 carbon atoms. Generally $n = 1-50$. Y = alkyl substituted aryl groups are most preferred. The combination of epoxide with carbodiimide gives surprisingly better color and extends the effectiveness of the more expensive carbodiimide. Overall lower levels of carbodiimide in the blends may reduce the potential generation of unwanted isocyanates by reaction of

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carbodiimide with water. The epoxy carbodiimide combination reduces carbodiimide loading while retaining good hydrolysis resistance with improved color over the epoxide alone. Carbodiimide loadings of 0.01 to 5.0% are preferred.

- 5 The term alkylene aryl polyester refers to crystalline thermoplastic polyesters such as polyesters derived from an aliphatic or cycloaliphatic diols, or mixtures thereof, containing from 2 to about 10 carbon atoms and at least one aromatic dicarboxylic acid. Preferred polyesters are derived from an aliphatic diol and an aromatic dicarboxylic acid having repeating units of the
- 10 following general formula:



wherein n is an integer of from 2 to 6. R is a C₆-C₂₀ aryl radical comprising a decarboxylated residue derived from an aromatic dicarboxylic acid.

- 15 Examples of aromatic dicarboxylic acids represented by the decarboxylated residue R are isophthalic or terephthalic acid, 1,2-di(p-carboxyphenyl)ethane, 4,4'-dicarboxydiphenyl ether, 4,4' bisbenzoic acid and mixtures thereof. All of these acids contain at least one aromatic nucleus. Acids containing fused rings can also be present, such as in 1,4- 1,5- or 2,6-
- 20 naphthalenedicarboxylic acids. The preferred dicarboxylic acids are terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid or mixtures thereof.

- The most preferred polyesters are poly(ethylene terephthalate) ("PET"), and poly(1,4-butylene terephthalate), ("PBT"), poly(ethylene naphthanoate)
- 25 ("PEN"), poly(butylene naphthanoate), ("PBN") poly(propylene terephthalate) ("PPT") and poly(cyclohexane dimethanol terephthalate), (PCT).

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Also contemplated herein are the above polyesters with minor amounts, e.g., from about 0.5 to about 5 percent by weight, of units derived from aliphatic acid and/or aliphatic polyols to form copolyesters. The aliphatic polyols include glycols, such as poly(ethylene glycol). Such
5 polyesters can be made following the teachings of, for example, U.S. Pat. Nos. 2,465,319 and 3,047,539.

The preferred poly(1,4-butylene terephthalate) resin used in this invention is one obtained by polymerizing a glycol component at least 70 mol %, preferably at least 80 mol %, of which consists of tetramethylene glycol and
10 an acid component at least 70 mol %, preferably at least 80 mol %, of which consists of terephthalic acid, or polyester-forming derivatives therefore.

The polyesters used herein have an intrinsic viscosity of from about 0.4 to about 2.0 dl/gas measured in a 60:40 phenol/tetrachloroethane mixture or similar solvent at 23°-30° C. VALOX Registered TM 315 polyester is
15 particularly suitable for this invention having an intrinsic viscosity of 1.1 to 1.4 dl/g.

Blends of polyesters may also be employed in the composition. As indicated earlier, preferred polyester blends are made from poly(ethylene terephthalate) and poly(1,4-butylene terephthalate).

20 The term core-shell ASA (alkylacrylate-styrene-acrylonitrile interpolymers) refers to a thermoplastic resin which comprises a styrene-acrylonitrile matrix in which is dispersed an acrylate elastomer phase as impact modifier. ASA is a multi-phase composite interpolymers comprising about 25 to 95 weight percent of a first elastomeric phase and about 75 to 5
25 weight percent of a final rigid thermoplastic phase.

The first phase or stage is polymerized from about 75 to 99.8 weight percent C₂ to C₁₀, preferably a C₄-C₆, most preferably a C₄ alky (meth) acrylate resulting in an acrylic rubber core having a T_g below about 10° C and

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crosslinked with 0.1 to 5 weight percent crosslinking monomer and further containing 0.1 to 5 percent by weight graftlinking monomer. The preferred alkyl acrylate is butyl acrylate. The crosslinking monomer is a polyethylenically unsaturated monomer having a plurality of addition
5 polymerizable reactive groups all of which polymerize at substantially the same rate of reaction. Suitable crosslinking monomers include poly acrylic and poly methacrylic esters of polyols such as butylene diacrylate and dimethacrylate, trimethylol propane trimethacrylate, and the like; di- and trivinyl benzene, vinyl acrylate and methacrylate, and the like. The preferred
10 crosslinking monomer is butylene diacrylate. The graftlinking monomer is a polyethylenically unsaturated monomer having a plurality of addition polymerizable reactive groups, at least one of which polymerizing at substantially different rate of polymerization from at least one other of said reactive groups. The function of the graftlinking monomer is to provide a
15 residual level of unsaturation in the elastomeric phase, particularly in the latter stages of polymerization and, consequently, at or near the surface of the elastomer particles. When the rigid thermoplastic phase is subsequently polymerized at the surface of the elastomer, the residual unsaturated addition polymerizable reactive group contributed by the graftlinking monomer
20 participates in the subsequent reaction so that at least a portion of the rigid phase is chemically attached to surface of the elastomer.

The final phase or stage monomer system can be comprised of C₁ to C₁₆ methacrylate, styrene, acrylonitrile, alkyl acrylates, allyl methacrylate, diallyl methacrylate, and the like, as long as the over T_g is at least 20 degrees C.
25 Preferably the final stage monomer system is at least 50 weight percent C₁ to C₄ alkyl methacrylate. It is further preferred that the final stage polymer be free of units which tend to degrade poly(alkylene terephthalates), for example acid, hydroxyl amino, and amine groups. One or more intermediate phases

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are optional, for example a middle stage polymerized from about 75 to 100 percent by weight styrene.

Advantageous ASA resins which are commercially available comprise a crosslinked (meth)acrylate elastomer, a crosslinked styrene-acrylonitrile copolymer and a substantially linear styrene-acrylonitrile copolymer. 5 Methylated styrenes such as alpha-methylstyrene or vinyltoluene may be used in place of all or part of the styrene, and it is understood that when styrene is mentioned hereinafter, these methylated styrenes are encompassed. The preferred resins of the ASA type are composed of core-shell impact 10 modifiers in a styrene-acrylonitrile (SAN) matrix. The (meth)acrylate elastomer core portion of these resins may be composed of alkyl, or arylalkyl esters of acrylic or methacrylic acids. Preferably the alkyl (meth)acrylate alkyl is C₂ to C₁₀ with the butyl C₄ being most preferred, i.e. the core comprises a poly butylacrylate rubber. The core shell portion of the resin may 15 be prepared by a two-step process in which the (meth)acrylate elastomer core (which is often slightly crosslinked with polyfunctional vinyl compounds) is covered with a thermoplastic shell of polymethyl methacrylate, polystyrene, styrene-acrylonitrile copolymer, or similar vinyl polymers or copolymers.

The compositions may or may not have a comonomer to graft the core 20 shell structure together. These ASA resins may be made for instance by the process of U.S. Pat. No. 3,944,631 (Mar. 1976). The most preferred resins of this group comprise about 15 to about 90% of an uncrosslinked matrix of acrylonitrile-styrene copolymer polymerized and partly grafted on a core-shell impact modifier, typically about 5 to 50% of a crosslinked (meth)acrylate 25 elastomer core with about 15 to about 35% of a crosslinked styrene-acrylonitrile copolymer shell. The crosslinking monomer may be typically a diacrylate of a diol. The shell and core are believed to be linked by having

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interpenetrating molecular networks, and the term interpolymer is applied to such products having such networks.

Other ASA resins which may be advantageously used in the composition of the invention are the types disclosed in U.S. Pat. Nos.
5 3,655,824, 3,830,878, 3,991,009, 4,433,102, 4,442,263, 4,096,202 and, 4,409,363, all of which are incorporated herein by reference thereto. These ASA resins have in common the use of the three monomers, namely acrylate ester, styrene (or alpha-methylstyrene), and acrylonitrile, to make a thermoplastic with good impact, heat distortion and weathering characteristics. They differ principally
10 in the method of manufacture and in the detailed structure of the essential rubbery phase and the interphases if any. As a class the ASA resins have relatively similar blending properties in view of their outer continuous phase of acrylonitrile-styrene copolymer.

The polyester/ASA/glass resin blend preferably consists essentially of
15 the polyester, ASA, fiber glass, cyclohexyl difunctional epoxide and catalyst. The blends comprises about 20 to 80, most preferably 30 to 70 pbw polyester per part of resin blend.

The present molding compositions are reinforced or stiffened by the inclusion of a fibrous glass, preferably glass fibers, in amounts ranging from
20 about 3 to 50 pbw of the total composition, preferably from about 7 to about 45 pbw, more preferably from about 10 to about 30 pbw.

The glass fiber or filamentous glass employed as reinforcement in the present compositions, preferably comprise lime-aluminum borosilicate glass that is relatively soda-free. The filaments are made by standard processes,
25 e.g., by steam or air blowing, flame blowing and mechanical pulling. For compositions ultimately to be employed for electrical uses, it is preferred to use fibrous glass filaments comprised of borosilicate glass that is relatively soda-free. This is known as "E" glass. The filaments are made by standard

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processes, e.g., by steam or air blowing, flame blowing and mechanical pulling.

The preferred filaments for plastic reinforcement are made by mechanical pulling. The filament diameters range from about 3 to 30 microns
5 . The filament diameters preferably range from about 10-15 microns. Use of equivalent non-round fiber cross section is also possible.

The length of the glass filaments and whether or not they are bundled into fibers and the fibers bundled in turn into yarns, ropes or rovings, or woven into mats and the like are also not critical to the invention. In
10 preparing the molding compositions of the present invention, it is convenient to use filamentous glass in the form of chopped strands of from about one-eighth to about 2 inches long. In articles molded from the compositions, on the other hand, even shorter lengths will be encountered because, during compounding, considerable fragmentation will occur. This is desirable,
15 however, because the best properties are exhibited by thermoplastic injection molded articles in which the filament lengths lie between about 0.000005" and 0.125 (1/8 ").

The most preferable resin blend optionally includes from 1.0 to about 30, more preferably from 3 to 10 pbw of vinyl aromatic-vinyl cyanide
20 copolymer. The preferred SAN composition comprises 15 to 40, more preferably 30-40, percent by weight AN with the remainder styrene, para-methystyrene, alpha- methyl styrene. The vinyl cyanide compound includes acrylonitrile (AN) and substituted vinyl cyanides such a methacrylonitrile. Preferably the copolymer is a styrene-acrylonitrile copolymer (SAN). The
25 preferred SAN is copolymer with the vinyl cyanide being present from about 20 to about 40 pbw based on total weight of the SAN. In the resin portion of the composition, it is desirable to have from about 5 to about 30, and

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preferable from about 10 to about 20 pbw free SAN based on the total composition.

The composition of the present invention may include additional components which do not interfere with the previously mentioned desirable
5 properties but enhance other favorable properties.

Flame-retardant additives may be present in an amount sufficient to reduce the flammability of the polyester resin, preferably to a UL94 V-0 rating. The amount will vary with the nature of the resin and with the efficiency of the additive. In general, however, the amount of additive will be
10 from 2 to 20 percent by weight based on the weight of resin. A preferred range will be from about 5 to 15 percent.

Typically halogenated aromatic flame-retardants include tetrabromobisphenol A polycarbonate oligomer, polybromophenyl ether, brominated polystyrene, brominated BPA polyepoxide, brominated imides,
15 brominated polycarbonate, poly (haloaryl acrylate), poly (haloaryl methacrylate), or mixtures thereof.

Examples of other suitable flame retardants are brominated polystyrenes such as polydibromostyrene and polytribromostyrene, decabromobiphenyl ethane, tetrabromobiphenyl, brominated alpha , omega -
20 alkylene-bis-phthalimides, e.g. N,N'-ethylene-bis-tetrabromophthalimide, oligomeric brominated carbonates, especially carbonates derived from tetrabromobisphenol A, which, if desired, are end-capped with phenoxy radicals, or with brominated phenoxy radicals, or brominated epoxy resins. Other aromatic carbonate flame retardants are set forth in U.S. Patent
25 4,636,544 to Hepp.

The flame retardants are typically used with a synergist, particularly inorganic antimony compounds. Such compounds are widely available or can be made in known ways. Typical, inorganic synergist compounds include

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Sb₂O₅; SbS₃; and the like. Especially preferred is antimony trioxide (Sb₂O₃). Synergists such as antimony oxides, are typically used at about 0.5 to 15, and more preferably from 1 to 6 percent by weight based on the weight percent of resin in the final composition.

5 Also, the final composition may contain polytetrafluoroethylene (PTFE) type resins or copolymers used to reduce dripping in flame retardant thermoplastics.

 The blend may also contain colorants, mold releases, lubricants, antioxidants, UV stabilizers and other similar additives to enhance
10 performance.

 The blends of this invention can be processed by various techniques including injection molding, blow molding, extrusion into sheet, film or profiles, compression molding, etc. They can also be formed into a variety of articles for use in, for example; electrical connectors, electrical devices,
15 computers, building and construction, outdoor equipment, trucks and automobiles. Illustrative of the various molded articles are connectors, outdoor electrical enclosures and cabinets, structural parts in outdoor lighting applications, telecom enclosure housings, industrial power plugs. Important applications are automotive exterior parts such as door handles and luggage
20 racks.

EXAMPLES

 The following examples illustrate the present invention, but are not meant to be limitations to the scope thereof.

 The components of the formulations presented in Tables 1-3 were tumble blended and then extruded on a 2.5" 30:1 L/D HPM single-screw
25 extruder equipped with a vacuum vented, double-wave screw. A processing profile of 490-510°F from feed-zone to die-head was employed. The compositions were dried at 250°F for 4 hours and then injection molded into

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test specimens on an 85 ton Van Dorn molding machine with a barrel set temperature of 500-510°F, 150°F mold temperature, 12 s injection time, 14-18 s hold time and 100 psi back pressure. Tensile bars of Type I and Type V, Izod bars and 4.0" diameter disks, all of 0.125" thickness were employed for
5 tensile, unnotched Izod impact and instrumented impact tests, respectively, while 4.0" diameter, edge gated disks of 0.062" thickness were used for as-molded warp tests.

For the warp test, the following procedure was followed: Each as-molded 0.062" thick edge gated disk was placed on a flat surface with
10 knockout pin side facing upwards. The greatest warpage was determined by pushing down along the circumference of the disk at several points and measuring the maximum displacement from the surface to the bottom of the disk at each point. For each blend, five disks were tested as described above, the readings averaged and reported in mm.

15 Examples 1-2: As-Molded Warp and USCAR III Hydrolysis Testing

Type I tensile bars and instrumented impact discs were aged according to the USCAR III hydrolysis test procedure, as illustrated in Fig. 1.

Test parts were exposed to 60 temperature/humidity cycles. After each exposure, samples were held under ambient conditions prior to testing.
20 Tensile and instrumented impact tests were conducted as per ASTM D638 and ASTM D3763 procedures, respectively. Sample compositions and test results are presented in Table 1.

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Table 1

Example		A*	1	B*	2
5	Polyester ^a	54.77	53.22	46.51	44.96
	ASA High Rubber Graft	12.39	12.39	11.52	11.52
	(54% SAN; 46% butyl acrylate)				
	SAN (66% Styrene; 34% Acrylonitrile)	12.39	12.39	11.52	11.52
	Pentaerythritol tetrastearate	0.30	0.30	0.30	0.30
10	Irganox 1076	0.15	0.15	0.15	0.15
	Glass Fiber	20	20	30	30
	Epoxide ERL 4221	0	1.50	0	1.50
	Sodium Stearate	0	0.05	0	0.05
	As-Molded Warp (mm)	18.8	13.2	17.2	14.2
USCAR III HYDRO-AGING Tensile Strength (psi)					
Cycle					
15	0	12490	13820	15220	15750
	10	12410	12960	14270	14600
	20	11940	13270	14480	15030
	40	11810	12910	11860	14250
	60	9872	12740	9923	14450
20	Tensile Elongation at Break (%)				
	Cycle				
	0	3.4	2.9	2.7	2.5
	10	3.0	2.5	2.1	2.2
	20	2.8	2.5	1.9	2.0
25	40	2.3	2.6	1.3	2.1
	60	1.5	2.2	0.9	1.9
Instrumented Impact: Total Energy (ft-lbf)					
Cycle					
30	0	7.3	6.4	7.4	7.3
	20	4.7	6.1	4.4	6.4
	40	2.6	5.8	3.3	6.5
	60	1.9	6.1	2.6	5.6

* = Comparative Example

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* = Poly(1,4-butylene terephthalate), "VALOX", 6500 poise@ 250 oC; General Electric Company.

ERL4221 is 3,4 -epoxycyclohexylmethyl-3,4-epoxy cyclohexane carboxylate from Union Carbide Co.

5 Irganox 1076 is a hindered phenol ester antioxidant from the Ciba Geigy Co.

Table 1 clearly shows that the epoxide modified samples (Examples 1 and 2) exhibit significantly lower as-molded warp and superior tensile and impact properties on hydro-aging over the corresponding unmodified PBT/ ASA blends (Comparative examples A and B). Improved properties are especially evident after 40 & 60 cycles of aging.

Examples 3-8: Pressurized Steam Aging

Sample pellets, Izod bars and type V tensile bars were aged by suspending these above water in a pressure steam sterilizer, Model No. 25X, Wisconsin Aluminum Foundry Company, at 100% relative humidity, 110°C temperature and 0.5 kg/cm² pressure. After each exposure, samples were held under ambient conditions prior to testing. Tensile and unnotched Izod impact tests were conducted as per ASTM D638 and ASTM D256 procedures, respectively. Melt viscosity was measured on a Tinius Olsen model UE-4-78 rheometer at 250°C, using a 5000 g weight and a 0.0825" diameter orifice. Sample compositions and test results are presented in Tables 2-3.

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Table 2

Example	C*	3	4	5
Polyester ^a	57.55	57.30	56.30	55.10
ASA High Rubber Graft	15.00	15.00	15.00	15.00
5 (54% SAN; 46% butyl acrylate)				
SAN/66% Styrene; 34% Acrylonitrile	7.00	7.00	7.00	7.00
Glass Fiber	20.00	20.00	20.00	20.00
Pentaerythritol tetrastearate	0.30	0.30	0.30	0.30
Irganox 1076	0.15	0.15	0.15	0.15
10 Sodium Stearate	0	0.05	0.05	0.05
Epoxide ERL 4221	0	0.20	1.20	2.40
<u>PRESSURIZED STEAM AGING</u>		<u>Melt Viscosity (poise@ 250 oC)</u>		
Dry Pellets	14752	15997	22738	16708
Aged 3 Days	2701	4251	14886	15369
15 Aged 6 Days	660	1016	8465	15848
Aged 11 Days	161	186	2202	13953
<u>Unnotched Izod Impact (ft-lb/in)</u>				
As-molded	11.8	13.3	13.1	12.7
Aged 3 Days	6.2	6.5	7.6	6.2
20 Aged 6 Days	2.1	3.5	7	5.3
Aged 11 Days	0.85	1.2	6.1	4.6
<u>Tensile Strength (Kpsi)</u>				
As-molded	13.3	13.6	13.4	13.7
Aged 3 Days	11.7	12.2	11.6	11.1
25 Aged 6 Days	7.92	9.56	11.5	10.3
Aged 11 Days	4.06	5	11.1	9.5

* = Comparative Example

^a = Poly(1,4-butylene terephthalate), "VALOX", 6500 poise@ 250 °C; General Electric Company.

30 Table 2 demonstrates the effect of epoxide-modified PBT/ ASA compositions.. Examples 3-5 clearly show higher initial melt viscosity, as-molded impact and tensile properties and excellent melt viscosity and mechanical property retention on hydro-aging relative to the unmodified

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PBT/ASA sample (Comparative Example C), particularly at epoxide loadings greater than 0.2 parts per hundred.

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Table 3

Example	4	D	6	7	8
Polyester ^a	56.30	56.35	56.30	56.30	56.30
ASA High Rubber Graft	15.00	15.00	15.00	15.00	15.00
5 (54% SAN; 46% butyl acrylate)					
SAN(66% Styrene; 34% Acrylonitrile)	7.00	7.00	7.00	7.00	7.00
Glass Fiber	20.00	20.00	20.00	20.00	20.00
Pentaerythritol tetrastearate	0.30	0.30	0.30	0.30	0.30
Irganox 1076	0.15	0.15	0.15	0.15	0.15
10 Sodium Stearate	0.05	0	0.05	0.05	0.05
Epoxy ERL 4221	1.20	0	0.36	0.60	0.84
Carbodiimide STABAXOL I	0	1.20	0.84	0.60	0.36
<u>Pellet Color (Visual Inspection)</u>	Yellow	White	White	White	White
<u>PRESSURIZED STEAM AGING</u>					
15 <u>Melt Viscosity (poise @ 250 oC)</u>					
Dry Pellets	22738	16312	16267	18056	19177
Aged 3 Days	14886	15299	10780	12222	11809
Aged 6 Days	8465	13689	6912	7820	6698
Aged 11 Days	2202	11131	2054	2399	1910
20 <u>Unnotched Izod Impact (ft-lb/in)</u>					
As-molded	13.1	12.2	13.1	13.2	13.5
Aged 3 Days	7.6	8.1	7.7	7.6	7.5
Aged 6 Days	7	7	6.9	6.8	7
Aged 11 Days	6.1	6	5.5	5.8	6
25 <u>Tensile Strength (Kpsi)</u>					
As-molded	13.4	13.8	13.8	13.5	13.3
Aged 3 Days	11.6	12.4	12.3	12	11.6
Aged 6 Days	11.5	11.7	11.9	11.4	11.6
Aged 11 Days	11.1	10.8	11.3	11.1	11

- 30 ^a = Poly(1,4-butylene terephthalate), "VALOX", 6500 poise General Electric Company.
 Stabaxol I is 2,2',6,6'-tetrakisopropyl diphenyl carbodiimide from Wyrrough & Loser Co.

Table 3 depicts the effect of various mixtures of epoxide and carbodiimide on melt viscosity and mechanical properties of as-prepared and

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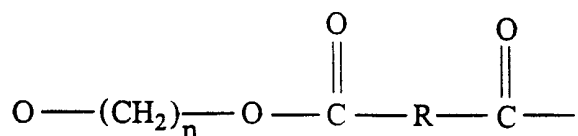
hydro-aged PBT/ASA compositions. Note that Example 4 is carried forward from Table 2 for purposes of comparison. For the Examples of Table 4 the total level of stabilizer, i.e. sum of epoxide and carbodiimide loadings, is the same at 1.2 parts per hundred. Surprisingly, all combinations of epoxide and carbodiimide provide equivalent melt stability, impact and tensile property retention on aging, indicating equivalent reactivity of epoxide and carbodiimide functionalities. Even more surprising is the improvement in pellet color on using any combination of epoxide and carbodiimide relative to epoxide alone.

Thus, Examples 1-8 clearly show that addition of epoxide, carbodiimide or mixtures to a polyester/ASA composition through extrusion provides superior as-molded mechanical performance and superior melt stability and mechanical property retention in hot humid environments relative to the unmodified polyester/ASA compositions. Furthermore, the epoxide significantly improves warp properties of the polyester/ASA composition. Combinations of epoxide and carbodiimide provide improved color relative to epoxide alone.

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CLAIMS

1. A thermoplastic resin composition having enhanced hydrolysis resistance and reduced warp comprising fiber glass and a resin blend consisting essentially of an alkylene aryl polyester, a core-shell ASA (alkylacrylate-styrene-acrylonitrile interpolymer) and an effective amount of
 5 at least one difunctional epoxy compound, said at least one difunctional epoxy compound having at least one cyclohexane ring moiety and having two terminal epoxy functional groups, wherein at least one of the two terminal epoxy functional groups is a substituent on at least one cyclohexane ring moiety; and an effective amount of a catalyst compound.
- 10 2. A thermoplastic resin composition according to claim 1 wherein at least one difunctional epoxy compound is selected from the group consisting of bis(3,4-epoxycyclohexylmethyl) adipate; vinylcyclohexene diepoxide; 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate and mixtures of any of the foregoing.
- 15 3. A thermoplastic resin composition according to claim 2 wherein the said resin blend comprises about 20 to 80 pbw polyester per part of resin blend.
4. A thermoplastic resin composition according to claim 3 including fibrous glass in an amount from about 3 to 50 pbw of the total composition.
- 20 5. A thermoplastic resin composition according to claim 4 wherein said wherein said difunctional epoxy compound comprises 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate.
6. A thermoplastic resin composition according to claim 4 having repeating units of the following general formula:



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wherein n is an integer of from 2 to 6 and R is a C₆-C₂₀ aryl radical comprising a decarboxylated residue derived from an aromatic dicarboxylic acid.

7. A thermoplastic resin composition according to claim 6 polyesters
5 are poly(ethylene terephthalate) and poly(1,4-butylene terephthalate).

8. A thermoplastic resin composition according to claim 4 wherein said ASA resin is a resin having a styrene-acrylonitrile matrix and a core-shell impact modifier of which the shell is styrene-acrylonitrile copolymer and the core is a crosslinked butyl (meth)acrylate rubber

10 9. A thermoplastic resin composition according to claim 4 wherein said ASA resin comprises about 15 to about 90% of an uncrosslinked matrix of acrylonitrile-styrene copolymer polymerized and partly grafted on a core-shell impact modifier which comprises about 5 to 50% of a crosslinked (meth)acrylate elastomer core and about 15 to about 35% of a crosslinked
15 styrene-acrylonitrile copolymer shell.

10. A thermoplastic resin composition according to claim 4 blend includes from 1 to about 30 pbw of non-alkyl substituted vinyl aromatic-vinyl cyanide copolymer.

11. A thermoplastic resin composition according to claim 10 blend
20 includes from about 3 to 10 pbw of non-alkyl substituted vinyl aromatic-vinyl cyanide copolymer.

12. A thermoplastic resin composition according to claim 10 wherein said ASA comprises a multi-phase composite interpolymer comprising about 25 to 95 weight percent of a first elastomeric phase polymerized from a
25 monomer system comprising about 75 to 99.8% by weight C₁ to C₆ alkyl acrylate, 0.1 to 5% by weight crosslinking member, 0.1 to 5% by weight graftlinking monomer, said crosslinking monomer being a polyethylenically unsaturated monomer having a plurality of addition polymerizable reactive

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groups all of which polymerize at substantially the same rate of reaction, and said graftlinking monomer being a polyethylenically unsaturated monomer having a plurality of addition polymerizable reactive groups, at least one of which polymerizes at a substantially different rate of polymerization from at least one other of said reactive groups; and about 75 to 5 weight percent of a final, rigid thermoplastic phase polymerized in the presence of said elastomer.

13. A composition as defined in claim 1 wherein said catalyst compound is selected from the group consisting of alkaline metal halides, carboxylates, carbonates and bicarbonates and mixtures thereof.

10 14. A composition as defined in claim 13 wherein said catalyst component comprises alkaline metal salts of an alkyl or aromatic carboxylic acid.

15 15. A composition as defined in claim 1 wherein said difunctional epoxy compound is present in an amount ranging from about 0.1 to about 5.0 weight percent based on the total weight of the composition.

16. A composition as defined in claim 15 wherein said difunctional epoxy compound is present in an amount ranging from about 1 to about 2.0 weight percent based on the total weight of the composition.

20 17. A composition as defined in claim 1 wherein said catalyst compound is present in an amount ranging from about 0.001 to about 1 weight percent based on the total weight of the composition.

18. A composition of claim 1 further comprising 0.01-5.0% of a carbodiimide.

25 19. A method for improving the heat distortion properties and hydrolytic stability of a thermoplastic composition of claim 1 comprising compounding:

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(a) comprising glass and a resin blend consisting essentially of an alkylene aryl polyester, a core-shell ASA (alkylacrylate-styrene-acrylonitrile interpolymer);

(b) from 0.1 percent by weight to 5 percent by weight of at least one
5 difunctional epoxy compound, said at least one difunctional epoxy compound having at least one cyclohexane ring moiety and having two terminal epoxy functional groups, wherein at least one of the two terminal epoxy functional groups is a substituent on the at least one cyclohexane ring moiety and wherein the amount of difunctional epoxy compound is based on the
10 combined weights of the linear polyester resin and difunctional epoxy compound; and

(c) from 0.001 percent by weight to 1 percent by weight of a catalyst, wherein the amount of catalyst is based on the total weight of the resin composition.

15 (d) 0 - 5.0% of a carbodiimide

20. A method as defined in claim 19 wherein said polyester resin comprises units of an aliphatic diol, a cycloaliphatic diol or a mixture of such diols and an aromatic diacid.

21. A method as defined in claim 19 wherein said polyester resin is
20 selected from the group consisting of poly(1,4-butylene terephthalate), a poly(1,4-cyclohexanedimethanol terephthalate), a poly(ethylene terephthalate), a polypropylene terephthalate and blends of any of the foregoing.

22. A method as defined in claim 21 wherein said polyester resin has an
25 intrinsic viscosity of at least about 0.4 deciliters per gram when measured in a 60:40 mixture of phenol and trichloroethane at 25 degree C.

23. A method as defined in claim 20 wherein said at least one difunctional epoxy compound is selected from the group consisting of bis(3,4-

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epoxycyclohexylmethyl)adipate; vinylcyclohexene diepoxide; 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate and mixtures of any of the foregoing.

24. A method as defined in claim 19 wherein said catalyst compound is
5 selected from the group consisting of alkaline metal halides, carboxylates, carbonates and bicarbonates and mixtures thereof.

25. A composition of claim 18 wherein the carbodiimide is an alkyl substituted aryl carbodiimide.

26. A composition of claim 18 wherein the carbodiimide is 0.2-2.0%
10 and the epoxide is 0.1-5.0% of the composition.

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FIG.1A

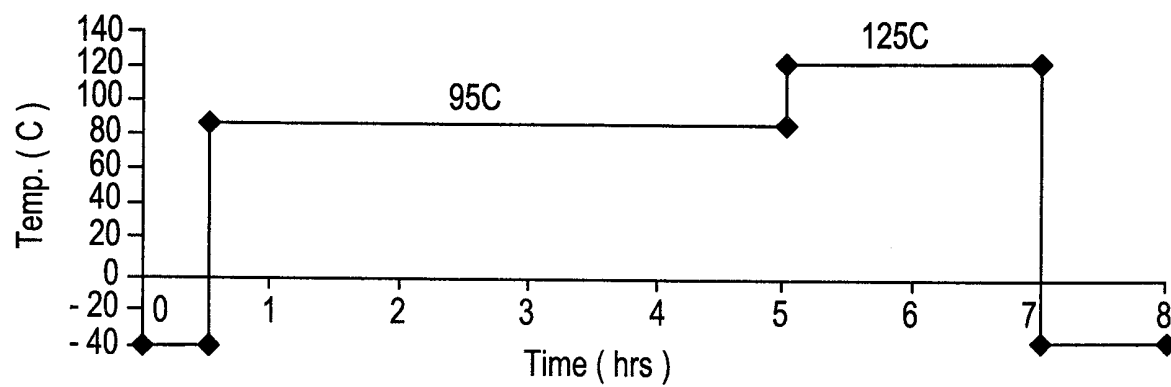
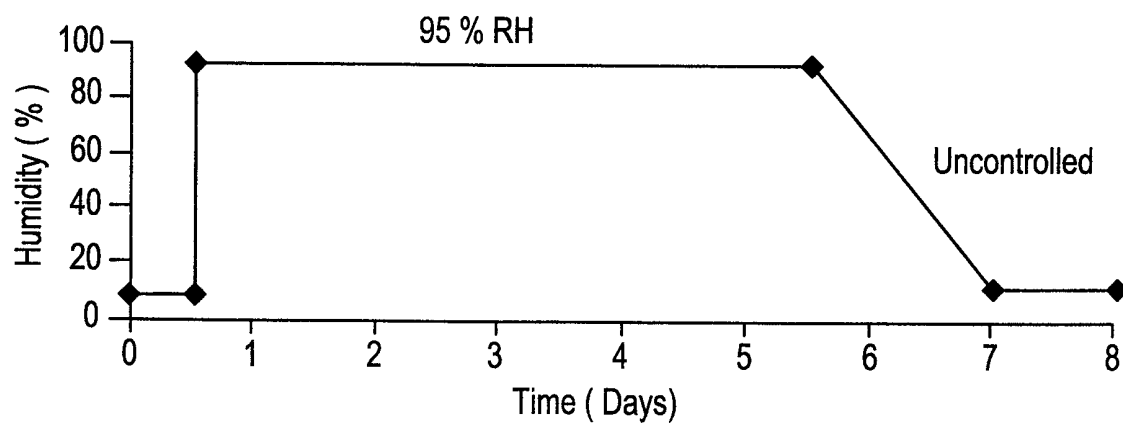


FIG.1B



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/30198

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L67/02 ///((C08L67/02,51:04),(C08L67/02,51:04,63:00),
(C08L67/02,51:04,25:12),(C08L67/02,51:04,25:12,63:00))

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)

IPC 7 C08L

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 310 977 A (BASF AG) 12 April 1989 (1989-04-12) claim 1; example 11	1-8,10, 11, 13-17, 19-24
Y	US 5 596 049 A (GALLUCCI ROBERT R ET AL) 21 January 1997 (1997-01-21) cited in the application claims 1-9,12-18,30,36 column 1, line 14 - line 19 column 6, line 35 -column 7, line 49 -/--	1-8,10, 11, 13-17, 19-24

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

2 May 2000

Date of mailing of the international search report

22/05/2000

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INTERNATIONAL SEARCH REPORT

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PCT/US 99/30198

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 386 546 A (GEN ELECTRIC) 12 September 1990 (1990-09-12) claim 1; examples 2,3 -----	1-3,5-7, 15,16, 19-23
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