## Title: Amino Containing Graft Polymers

**Abstract**

Graft polymers containing reactive amine functionality are prepared by: a) providing a thermoplastic polymer containing at least one electrophilic functionality sufficient to react with primary amine groups; and b) melt reacting with a chemical compound comprising a one primary amine and one secondary amine, the secondary amine having reactivity approximately equal to or less than the primary amine. By utilization of the selected diamine containing chemical compounds, crosslink formation is essentially avoided. Use of the graft polymer as modifier and compatibilizer of polymer compositions is described.
FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<table>
<thead>
<tr>
<th>Code</th>
<th>Country</th>
<th>Code</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>Austria</td>
<td>FI</td>
<td>Finland</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>FR</td>
<td>France</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GB</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GN</td>
<td>Guinea</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>GR</td>
<td>Greece</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>HU</td>
<td>Hungary</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>IE</td>
<td>Ireland</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>IT</td>
<td>Italy</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>JP</td>
<td>Japan</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>KP</td>
<td>Democratic People’s Republic</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>LR</td>
<td>Liechtenstein</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>LI</td>
<td>Liechtenstein</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td>LK</td>
<td>Sri Lanka</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LU</td>
<td>Luxembourg</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>MC</td>
<td>Montenegro</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>MN</td>
<td>Mongolia</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>GB</td>
<td>United Kingdom</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>GN</td>
<td>Guinea</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>GR</td>
<td>Greece</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>HU</td>
<td>Hungary</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>IE</td>
<td>Ireland</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>IT</td>
<td>Italy</td>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>JP</td>
<td>Japan</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>KP</td>
<td>Democratic People’s Republic</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>LL</td>
<td>Lichtenstein</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>LU</td>
<td>Luxembourg</td>
<td>SU</td>
<td>Soviet Union</td>
</tr>
<tr>
<td>MC</td>
<td>Montenegro</td>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>MG</td>
<td>Madagascar</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>US</td>
<td>United States of America</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

BAD ORIGINAL
Amino Containing Graft Polymers

This invention is related to graft polymers of use inter alia as modifiers and compatibilising agents, and to a method for their manufacture. In particular it relates to functional polymers grafted with certain directive amino compounds that permit facile graft reaction in polymer melt processing.

Technical Field

Engineering thermoplastics such as polyamides, polycarbonates, polyesters have excellent physical properties such as strength, impact resistance and stiffness but it is often desirable to blend or alloy these with other thermoplastics such as polyolefins to improve their toughness or to reduce their overall cost. However, the components of such blends are seldom compatible; it is thus common practice to include a compatibilizer which functions to improve the adhesion between the incompatible components and/or to modify the surface tension at phase boundaries. Alternatively, a modifier may be blended with the engineering thermoplastic, such a modifier comprising typically, a polyolefin carrying groupings compatible or reactive with the engineering thermoplastic and thus enhancing interphase adhesion.

Additionally it is well known that certain nitrogen-containing polymer compounds find significant usage as modifiers for lubricating oil compositions, and that certain of such polymer compounds are of such molecular weight characteristics that reaction by or during melt-processing is a possible if not preferable, method of preparation.

There is thus a requirement to provide functional groups on a wide range of polymers, which functional groups can provide to, or by subsequent reaction, attach
to the polymer compatibilising or modifying moieties. This has commonly been attempted by grafting or copolymerizing active groupings into the polymers. For example, polyolefins are commonly maleinised, that is reacted with maleic acid or maleic anhydride to provide such active groups.

Such a maleinised polyolefin may then be blended with, for example, a polyamide to provide enhanced adhesion by interaction of the maleic acid or anhydride groups with free-amino functions of the polyamide. Further, it has been early suggested, e.g. US Patent 3 862 265, that grafted functionalities, such as those providing the dicarboxylic functionality of maleic anhydride, can be subsequently reacted in the extruder or later with other modifying materials in order to change the properties of the grafted polymer. The present invention is based on the concept of attaching at least one of a specified class of diamine-containing chemical compounds to a functionalised polymer to facilitate the attachment of active groups or functionalised polymers thereto, or to provide additional useful functionality for the graft polymer itself.

Background Information

US Patent 4 895 897 describes impact modifiers for polycarbonates comprising the reaction product of an ethylene elastomer having at least one reactive polar group, typically a hydroxy, epoxy, amine, carboxy or carboxylic-anhydride group, with an oxazoline functionalized polystyrene. The mode of interaction of the amine polar group and the oxazoline group is not stated but it appears that a cross-linking chain containing at least one nitrogen atom is formed between the ethylene elastomer and the polystyrene.
US Patent 4 742 116 describes a thermoplastic moulding compound based on a rubber-modified copolymer in admixture with ethylene-propylene copolymer (EP) or ethylene-propylene-diene terpolymer (EDPM) rubber: the rubber modified copolymer is derived from styrene or alpha-methyl styrene and maleic anhydride, an acrylate or acrylonitrile and is bonded to functionalised EP or EPDM rubber carrying hydroxyl, amide or amine groups. There is no specific description of the use of amino groups in such bonding or of how these could be introduced into the EP or EPDM rubber. The compositions are said to be superior to conventional styrene-maleic and copolymer compositions as regards impact resistance, UV resistance and stability.

US Patent 4 749 505 describes lubricating oil compositions prepared by melt processing, optionally including the incorporation of maleic anhydride, of ethylene-propylene rubber. The optional maleic functionality may be further neutralized with any of a number of primary amine containing components including polyamines such as alkylene polyamines, piperadines, and piperazines, etc. Neutralization in the melt is suggested but only solution neutralization with N-aminopropyl morpholine is specifically illustrated.

US Patent 4 670 173 describes oil soluble reaction products of acylated reaction products, polyamines and monofunctional acids. The acylated reaction products (D) are described as being made by reacting (A) hydrogenated block copolymers and (B) alpha-beta-olefinically unsaturated reagents in the presence of (C) free radical initiators. It is said that this product can be further reacted with (E) a primary amine containing compound containing only one primary amino group. The (E) compounds are said to be broadly represented by the formula R-NH₂, where R may be hydrogen, an alkyl, a cycloalkyl, an aromatic, combinations thereof, and may
further contain secondary or tertiary amines and/or other heteroatoms of oxygen, nitrogen and sulphur. Some thirty-one (31) exemplary primary amine-containing compounds are listed with the primary-secondary amine compounds N-methyl-1,3-propanediamine, N-(2-aminoethyl) piperazine, 1-aminoethylpiperadine and 1-ethyl-3-amino- piperadine being included in addition to the "preferred" and "highly preferred" primary-tertiary amine compounds N-(3-propyl)morpholine and N-ethyl-N-methyl-1,3-propane- diamine being highlighted. Example 10 describes the extruder reaction of a primary-tertiary amine with the acylated reaction product. The resulting compositions are said to be useful as dispersant viscosity modifiers.

US Patent 4 520 171 describes light stabilisers for lubricating oils derived by reaction of maleic anhydride or maleic acid modified olefin polymers with 4-amino2,2,6, 6-tetramethyl piperidine or N-oxygen derivatives thereof.

Similar light stabilisers are described in EP 303281-A. Due to bond strain, the pKb of the secondary amino grouping of the piperidine group is about 2.9 which is significantly lower than that of a primary amino group or of most secondary amino groups.

Further, it has been reported in the literature that the use of amino piperidines, specifically 4-(amino- methyl)piperidine, for reaction with a maleated polypropylene, leads to negligible change in melt index compound of the initial polypropylene, despite screw extrusion at 220°C in the presence of free radical initiators. It is thus apparent to one skilled in the art that substantial chain extension due to cross-link formation has occurred. See Japan. Kokai Tokkyo Koho JP 58 120 408.

The melt reaction of previously known diamine compounds with a functionalised polymer has lead to cross-links or crosslinking and thus to chain-extension,
gelling or undesirable hardening, as well as loss of reactive capability. We have found that, surprisingly, it is possible to avoid such cross-link formation by using a diamine comprising one primary and one secondary amino group having reactivity approximately equal to or less than that of primary amine. Such diamines may, in fact include other more hindered (and thus less reactive) secondary amino groups, for example at intermediate positions in the linking chain.

**Summary of the invention**

The present invention is a graft polymer, comprising a thermoplastic polymer modified with one or more amine containing compounds reacted with the said polymer via one amino group and having a second amino group available for subsequent reaction. More particularly, the graft polymer comprises specific amine containing compounds particularly suitable for effective grafting under melt processing conditions without significant cross-link formation.

**Description of the invention**

Such a graft polymer will commonly be produced by reacting (1) an initial thermoplastic polymer containing functional groups reactive with amines and (2) an amino compound having one primary amino group and one secondary amino group whereby the primary amino group reacts preferentially with said functional groups. The preferential reaction of the primary amino group to leave the secondary amino group unreacted may be determined by selecting the secondary amino group so that it has a reactivity approximately equal to or less than the primary amino group. This reactivity may be determined by thermodynamic criteria, notably by the $pK_b$ values of the primary and secondary amino groups but also by reaction kinetics, which may be influenced by steric
hindrance of the secondary amine and the solubility of the amino compound in the thermoplastic polymer under the reaction conditions.

In general, the $pK_B$ of the secondary amino group should be less than 7 to provide adequate reactivity but should preferably be 3.0 or greater, when the primary amine is linked to an aliphatic carbon. If the primary amine is attached directly to an aromatic ring, optionally containing other substantiates, the $pK_B$ of the secondary amine group should be about 0.4 less than that of the primary amino group, or greater. In both cases, the phrase "approximately equal to" is being used to indicate that the $pK_B$ of the secondary amine preferably should not be less than 0.4, more preferably, not less than 0.2, the $pK_B$ of the primary amine. The solubility of the amino compound under thermoplastic melt conditions is determined empirically in accordance with the well known melt processing conditions particular to the thermoplastic polymer being grafted.

(a) The Diamine Containing Compound

Such an amino compound may be a diamine, i.e. with only the two amino groupings specified above, or may contain further substantially unreactive amino groups, for example, in intermediate positions between the reactive primary and secondary amino groups. The amino compound may thus be represented by the formula $\text{NH}_2-R-NHR^1$ where $R$ is an organic group and $R^1$ is a further organic group which may optionally be joined to the group $R$ to form a nitrogen-containing heterocyclic ring. Organic group as used herein means essentially hydrocarbon, but optionally containing one or more heteroatoms selected from the group consisting of C, N, or S wherein the number of such heteroatoms does not exceed the number of carbon atoms.
The group \( R \) may thus, for example, be a divalent alkylene group having 1 to 12 carbon atoms, preferably 1-6 carbon atoms, e.g. ethylene or propylene, optionally with the heteroatoms replacing one or more carbon atoms, or a divalent aryl group having 6-12 carbon atoms, such as phenylene e.g. 2-phenylene or 4-phenylene. When \( R \) and \( R^1 \) with the intervening nitrogen form a ring, this may contain 4-7 carbon atoms optionally with heteroatoms, e.g. a piperazine ring is equally suitable in this invention.

The group \( R \) may be an aliphatic group, e.g. an alkyl group having 1-6 carbon atoms, which may be substituted with one or more heteroatom containing groups e.g. 2-hydroxyethyl; an aralkyl group with 6-12 carbon atoms, e.g. benzyl; or an aryl group with 6 to 12 carbon atoms e.g. phenyl.

Typical diamines for use in accordance with the invention include the following:
- N-methylethyldiamine
- N-ethylethyldiamine
- N-phenylethyldiamine
- N-methyl-1,3-propyldiamine
- N-phenyl-1,2-phenyldiamine
- N-phenyl-1,4-phenyldiamine
- 1-(2-aminoethyl)piperazine
- N-(2-aminoethyl)aminoethanol

For each of these, the \( \text{pK}_b \) value for the secondary amine is as described above. This list is only exemplary and other primary and secondary amino-containing compositions in accordance with this invention are equally suitable.

(b) The functionalised polymer

The amine-reactive functional groups on the initial functional group-containing thermoplastic polymer to be reacted with the amino compound will in
general be electrophilic groups such as carboxyl, esterified carboxyl, acid chloride, acid anhydride, aldehyde, ketone, silane, epoxy or halogen groups. Anhydride groups are particularly useful in that they react with primary amino groups to form stable cyclic imido groupings while forming less stable amide groups with secondary amines. The latter amide groups can be displaced by a more thermodynamically preferred reaction with primary amino groups thus promoting selective binding of principally the primary amino groups.

The initial functional group-containing polymer may, for example, be based on a polyolefin such as those formed from one or more \( C_2-C_{20} \) alpha-olefins, optionally containing copolymerizable non-conjugated diolefins and/or vinyl monomers. Such polyolefins may be crystalline, partially crystalline or amorphous. Thus polypropylene, polyethylene, ethylene-propylene copolymers, EP rubber, EPDM rubber and polymers of any of these monomers with one more higher alphaolefins, e.g., 1-butene, 1-hexene, 1-octene, etc., are suitable polyolefins. Additionally included are the polyethylene copolymer resins comprising one or more copolymerisable vinyl esters, acids, epoxies, etc. Throughout the specification, the term "copolymer" is used in its ASTM accepted definition of a polymer formed from two or more types of monomers.

As used in the specification and claims, the term "polypropylene" includes homopolymers of propylene as well as reactor copolymers of polypropylene (RCPP) which can contain about 1 to about 20 wt% ethylene or an alpha olefin comonomer of 4 to 20 carbon atoms. The polypropylene can be isotactic, syndiotactic or atactic polypropylene. The RCPP can be either a random or block copolymer. The density of the PP or RCPP can be about 0.8 to about 0.9 g/cc. Polypropylene containing copolymerized non-conjugated diolefins will also be particularly useful.
High density polyethylene (HDPE), useful as a polyolefin resin, has a density of about 0.941 to about 0.965 g/cc. High density polyethylene is an established product of commerce and its manufacture and general properties are well known to the art.

Polyethylene copolymer resins which can optionally be used in the compositions of this invention include polybutylene, LDPE, VLDPE and LLDPE as well as copolymers of ethylene with unsaturated esters of lower carboxylic acids. The term "polybutylene" generally refers to thermoplastic resins of both poly (1-butene) homopolymer and the copolymer with, for example, ethylene, propylene, pentene-1, etc. Polybutylene is manufactured via a stereo-specific Ziegler-Natta polymerization of monomer(s). Commercially useful products are of high molecular weight and isotacticity. A variety of commercial grades of both homopolymer and ethylene copolymer are available with melt indices that range from about 0.3 to about 20 g/10 min.

The term "low density polyethylene" or "LDPE" as used in the specification and claims mean both low and medium density polyethylene having densities of about 0.91 to about 0.94 g/cc. The terms include linear polyethylene as well as copolymers of ethylene which are thermoplastic resins.

Linear low density polyethylene (LLDPE) is a relatively new class of low density polyethylene characterised by little, if any, long chain branching, in contrast to conventional LDPE. The processes for producing LLDPE are well known in the art and commercial grades of this polyolefin resin are available. Generally, it is produced in gas-phase fluidized bed reactors or liquidphase solution process reactors; the former process can be carried out at pressures of about 100 to 300 psi and temperatures as low as 100°C.
Polyethylene copolymers suitable as the polyolefin resins of this invention include copolymers of ethylene with unsaturated esters of lower carboxylic acids as well as the carboxylic acids per se. In particular, copolymers of ethylene with vinylacetate or alkyl acrylates for example methyl acrylate and ethyl acrylate can be employed. These ethylene copolymers typically comprise about 60 to about 98 wt. % ethylene, preferably about 70 to 95 wt. % ethylene, more preferably about 75 to about 90 wt. % ethylene. The expression "ethylene copolymer resin" as used in the specification and claims means, generally, copolymers of ethylene with unsaturated esters of lower (C₃-C₄) monocarboxylic acids and the acids themselves; e.g., acrylic acid, vinyl esters or alkyl acrylates. It is also meant to include both "EVA" and "EVOH", which refer to ethylene-vinylacetate copolymers, and their hydrolyzed counterpart ethylene-vinyl alcohols. Illustrative of the acrylates which can be utilised are methyl acrylate and ethyl acrylate and glycidyl methacrylate. Examples of such polyethylene copolymers include ethylene-acrylic acid, ethylene-methylacrylate, ethylene-methyl acrylate-acrylic acid, ethylene-methacrylic acid, etc. Similarly, those having acid groups only partially neutralized with metal cations to form those products known as ionomers will be suitable herein.

Particularly suitable in accordance with this invention are the ethylene-alpha-olefin elastomers which are defined to include copolymers of ethylene and C₃-C₂₀ alpha-olefins, optionally with one or more non-conjugated diolefins. Such polymers are well-known as are their methods of preparation, see earlier identified US Patents 4 895 897 and 4 749 505, which are incorporated herein by reference.
Additionally, elastomeric butyl rubber and halogenated butyl rubber are suitable as the initial thermoplastic polymer when containing, or modified to contain, functional groups reactive with primary amino groups. Butyl rubber and halogenated butyl rubber are well known articles of commerce and any such polymer product, suitably functionalized, will be effective in accordance with the invention. These polymers are based upon cationic polymerization of isobutylene, optionally with one or more monomers copolymerizable therewith, all as is well known. Included for the purpose of this invention within the term elastomeric butyl rubber is the class of compositions making up polyisobutylene rubber, which strictly speaking is not butyl rubber, but is instead an elastomeric homopolymer of isobutylene. Polyisobutylene rubber is also a well known article of commerce manufactured in accordance with known methods. Its use in lubricating oils, when modified with succinic acid/anhydride groups, optionally aminated, is particularly well suited for this invention.

The electrophilic groups are provided most preferably by ethylenically-unsaturated electrophilic group-containing compounds which are either copolymerized during the preparation of the thermoplastic polymers or are grafted onto a previously prepared polymer.

Copolymerization including the compound providing the electrophilic groups will be possible when all the monomers of the polymers are polymerizable by either conventional free radical catalysis or Ziegler coordination catalysis. Copolymerizable monomers incorporated by free-radical catalysis include such comonomers as alkyl acrylates, vinyl esters, acrylic acids, methacrylic acid, glycidyl methacrylate and the like. Such thermoplastic polymers are known in the art as is their method of preparation. Illustrative of this knowledge is US Patent 4 017 557 which is incorporated by reference.
Thus copolymerizable monomers permitting the incorporation of these reactive electrophilic groups into the polyolefins will be useful in accordance with this invention. Such compounds, methods of both preparation and incorporation with polyolefins are also well known. Descriptions for Ziegler copolymerization are to be found, inter alia, in US Patents 3 492 227, 3 761 458, 3 796 687, 4 017 669, 4 139 417, 4 423 196 and 4 987 200, the disclosures of which, including compounds and processes, are incorporated by reference. These patents teach the preparation of polyolefins, particularly ethylene random terpolymers, tetrapolymers, etc., from alphaolefins, non-conjugated dienes and unsaturated functional monomers by direct Ziegler-Natta polymerization of the monomers, usually in solvent, utilizing catalyst systems composed of trivalent, and higher, vanadium compounds, organoaluminium compounds and, for some, halogenated reactivator compounds. These polymerization reactions are run in the absence of moisture in an inert atmosphere and in a preferred temperature range of 0° to 65°C. Both continuous and batch reactions are taught.

Included within the term copolymerization, for the purpose of this invention, are those chain terminating reactions wherein the appropriate functional groups are added to a forming thermoplastic polymer and simultaneously terminate the polymerization reaction. Such reactions are sometimes termed end-capping reactions and are generally known. In particular, the carbonation of polymers prepared by anionic polymerization through the introduction of gaseous CO₂ into the "living" polymerization reaction and termination of that reaction will be suitable for this invention. Description appears in the art, see for example the teachings of U.S. Patent 4,950,721, which is incorporated herein by reference.
End-capping of polyolefins prepared by Ziegler-Natta copolymerization is known, in particular effective use of hydroxy compounds can be made in accordance with the disclosure contained in published European Patent Publication O 366 412, based on U.S. Application Ser. No. 264,484, which references disclosure contained in European Patent Publication O 234 114, based on U.S. Application Ser. No. 813,848, which is incorporated here by reference. By utilization of chain terminating functional group-containing compounds, the graft copolymers prepared by subsequent reaction with the amine compounds of the invention are end-grafted with those amino-compounds.

The graft addition of ethylenically unsaturated electrophilic group containing compounds suitable in this invention, e.g. maleic anhydride, is conveniently accomplished by heating a blend of the polyolefin and the unsaturated electrophilic group-containing compounds within a range of about 150-400°C, often in presence of free-radical initiators such as organic peroxides. Methods of preparing these graft polymers are well known in the art as is illustrated in US Patents 4 017 557 (above), 3 862 265, 3 884 882, 4 160 739, 4 161 452, 4 144 181, 4 506 056 and 4 749 505, the disclosures of which are incorporated herein by reference. The use of heat and/or physical shearing, optionally with the free-radical initiators, in such equipment as extruders or masticators to accomplish the free-radical grafting of ethylenically-unsaturated electrophilic group-containing compounds, all as known in the art, will be particularly useful in accordance with this invention.

The graft addition to polyolefins of carboxylic acid group-containing monomers, and epoxy group-containing monomers, is also known. Description appears in, inter alia, US Patents 3 862 265, 4 026 967, 4 068 057, 4 388 202 and 4 749 505, the disclosures of which are
incorporated by reference. As is noted, these grafting methods parallel those useful for the grafting of maleic anhydride described more fully above. Epoxy group-containing compounds effective in such grafting reactions are represented by such as glycidyl acrylate, glycidyl methacrylate, and the like. One or more electrophilic groups useful in accordance with this invention are thus readily incorporated in the functionalised polymers of this invention by use of knowledge in the art.

Though the descriptions herein with respect to the incorporation of electrophilic groups are directed to conventional copolymerization and grafting methods, it will be apparent to those in the art that any additional methods for such incorporation will be effective to achieve the objectives of this invention. For example, the preparation of epoxy group-containing polymeric compounds by the direct epoxidation of polymers containing either backbone or pendent unsaturation is known in the art. US Patents 3 330 794, 3 448 174 and 3 551 518 describe the use of epoxidizing agents, such as perbenzoic acid, to directly oxidize unsaturation in ethylene-containing elastomeric compounds to attain incorporated epoxy, or oxirane, groupings. These disclosures are incorporated by reference.

The amount of electrophilic group-containing compound incorporated in the functionalized polymer will be that sufficient to provide at least one site reactive with the primary amino group containing compound, that is monomers containing electrophilic groups should make up at least about 0.01 wt. % of the functional group-containing thermoplastic polymer component. Most typically, the electrophilic group-containing monomer will make up from 0.01 to 15 wt. %, preferably 0.05 to 5.0 wt. %. The amount of functional moieties present whether contributed by functional group-containing monomers, or by direct functionalization, will thus be that equivalent to this level of monomer incorporation.
Other functionalised polymers include any that can be similarly grafted or otherwise contain the described electrophilic groups, particularly, for example, maleic acid, maleic anhydride, acrylic acid, methacrylic acid, or epoxy groups, for example styrene-based polymers and copolymers.

Styrene-based polymers suitable for graft incorporation of one or more electrophilic group-containing compounds and well known in the art include those which may be described as hydrogenated or partially hydrogenated homopolymers, and random, tapered, or block polymers (copolymers, including terpolymers, tetrapolymers, etc.) of conjugated dienes and/or monovinyl aromatic compounds with, optionally, alpha-olefins or lower alkenes, e.g. C₃ to C₁₈ alphaolefins or lower alkenes. The conjugated dienes include isoprene, butadiene, 2,3-dimethyl-butadiene, piperylene and/or mixtures thereof, such as isoprene and butadiene. The monovinyl aromatic compounds include any of the following or mixtures thereof, vinyl di- or polyaromatic compounds e.g., vinyl naphthalene, but are preferably monovinyl monoaromatic compounds, such as styrene or alkylated styrenes substituted at the alpha-carbon atoms of the styrene, such as alpha-methylstyrene, or at ring carbons, such as o-, m-, p-methylstyrene, ethylstyrene, propylstyrene, isopropylstyrene, butylstyrene, isobutylstyrene, tertbutylstyrene (e.g., p-tertbutylstyrene). Also included arevinylxylenes, methylethyl styrenes, and ethylvinylstyrenes. Alphaolefins and lower alkenes optionally included in these random, tapered and block copolymers preferably include ethylene, propylene, butene, ethylene-propylene copolymers, isobutylene, and polymers and copolymers thereof. As is also known in the art, these random, tapered and block copolymers may include relatively small amounts, that is less than about ± mole %, of other copolymerizable monomers such as vinyl pyridines, vinyl
lactams, methacrylates, vinyl chloride, vinylidene chloride, vinyl acetate, vinyl stearate, and the like. Specific examples include random polymers of butadiene and/or isoprene and polymers of isoprene and/or butadiene and styrene. Typical block copolymers include polystyrene-polyisoprene, polystyrene-polybutadiene, polystyrene-polyethylene, polystyrene-ethylene propylene copolymer, polyvinyl-cyclohexane-hydrogenated polyisoprene, and polyvinyl cyclohexane-hydrogenated polybutadiene. Tapered polymers include those of the foregoing monomers prepared by methods known in the art.

Suitable styrene-based polymers having incorporated electrophilic functionality in accordance with the invention include those comprising styrene and maleic anhydride, optionally containing copolymerizable monomers as disclosed in the previously mentioned US Patent 4 742 116. The compositions and methods of preparation disclosed therein are incorporated by reference.

(c) **Description of reaction processes**

A most important feature of this invention is the ease of conducting the reaction process largely in accordance with melt processing reaction conditions well-known by those skilled in the art. Thus the reaction of the functionalised initial polymer with the amino compound is preferably effected by melt reaction. The reaction temperature will commonly be in the range of 100\(^\circ\) to 350\(^\circ\), more preferably from 170\(^\circ\) to 280\(^\circ\). Such a reaction may readily be accomplished in a mixing device such as a Brabender or Banbury mixer or an extruder, e.g. a single or double screw extruder. The reaction time may be a few seconds (e.g. 30 seconds) to a few minutes, or even longer in optimizing reaction efficiency and possible reaction temperature side-effects such as molecular weight degradation of the thermoplastic polymer. The
amine should be present in an amount equal to or exceeding the amount of functionally available reactive sites. Amine functionality may be assayed by solvent titration and residual groups such as anhydride may be assayed by I.R.

(d) Description of uses

As indicated above, the amino-modified polymers according to the invention may be used directly as compatibilizers or modifiers for thermoplastic polymer compositions. For example, US Patent 4 742 116 suggests the use of nitrogen-grafted EP or EPDM as an effective modifier for styrene-maleic anhydride copolymers. Similarly, published European Patent Application EP-A-0 321 293 discloses the use of functionalized EP or EPDM, wherein the incorporated functionality may be amino, as an effective impact modifier for polybutylene terephthalate moulding compositions. US Patent 4 895 897 discloses the use of an intermediate functionalized elastomer, including amine functionalized elastomer, reacted with oxazoline functionalized polystyrene, to prepare graft polymers effective for modifying the impact properties of aromatic polycarbonate compositions (polycarbonate).

Thus, in accordance with this invention, graft polymers are provided that can be used as modifiers or compatibilisers with any thermoplastic polymer having molecular interaction with either of the polymer backbone of the graft polymer or the grafted amine functionality. Thus blends of the graft polymer of the invention with one, two or more other polymers, particularly engineering thermoplastics or in lubricating oil compositions, will be possible.

The amine functionalised polymer according to the invention may be reacted or blended with a second polymer
by melt reaction, for example in a Brabender mixer or an extruder. This may be conducted in the same reactor as the neutralization reaction, or subsequently, in another melt reactor. The reaction time and temperature will depend on the polymers present. This reaction may be carried out in a separate subsequent step or may be effected in situ in a melt of the polymer or polymers to be compatibilized. Thus, for example, amino functionalised polypropylene (amino-PP) may be melt reacted/blended with a blend of styrene-maleic acid polymer in polypropylene.

Similarly, polypropylene blends containing other polymer systems, especially engineering thermoplastics that are reactive with, or otherwise compatible with, the aminated polypropylene, can be prepared having improved overall blend compatibility between the polypropylene, other polymer, and aminated polypropylene. Similar blends of (1) unmodified polymer with (2) aminated, functionalized polymers, either equivalent thereto in the sense of being derived from the same polymer or its family and (3) another polymer rendered at least partially miscible or compatible with (2) by presence of the amine functionality, will now be possible in accordance with the teachings of this invention. Specifically, as shown in the cited prior art, the use of EP rubber with polyester engineering plastics (e.g., polybutylene terephthalate, polycarbonate, etc.) or SMA based thermoplastics or the use of other ethylene-based copolymer resins, can be enhanced by inclusion of the aminated ethylene-based polymers and copolymers of this invention.

Also, amino-polyolefins in accordance with this invention, may be utilized to compatibilize otherwise incompatible polymer blends of polyolefins and halogenated polymers, such as PVC, PVDC, PVDF, Chlorinated-Nitrile Rubber, halobutyl rubber and the like; such blends may be useful for example for improving the
surface properties of PP articles. Aminated-PE may be advantageously used as a tie layer in multilayers films where it can promote adhesion between two polymer layers otherwise incompatible, such as PE and PVDC. For those skilled in the art, it will be apparent that the broad applicability of aminated-polyolefins will be useful to improve overall properties of polymer mixes, and thus has potential for recycling of mixed plastics, particularly those containing a significant portion of polyolefins.

For lubricating oil compositions, oil soluble polymers selected from the group consisting of ethylene-alpha-olefin elastomer, polyisobutylene rubber, and styrene-based polymers will be particularly suitable when functionalized to contain the necessary electrophilic functionality and reacted with the amino compound of this invention. Thus the oil soluble polymers prepared in accordance with the disclosure herein will be useful in lubricating oil compositions. More particularly, those polymers having a number average molecular weight from about 500 to about 10,000, preferably 800 to about 3,000 will have utility in detergent and dispersant applications. Those having a number average molecular weight from about 10,000 to about 1,000,000, preferably 20,000 to 400,000, will have multifunctional utility as viscosity index improvers, as well as dispersants. Methods of preparation and further description of such lubricating oil compositions are well known, as is exemplified by US Patents 4 749 505, 4 670 173 and 4 520 171.

It will additionally be apparent to those knowledgeable in the art that conventional additives can be utilized in conventional amounts when added according to the knowledge in the art. Such additives, amounts and conditions are illustrated in the patents incorporated by reference.
Examples
The following conditions were observed in preparing
the examples presented which are intended to illustrate
the invention and to present the preferred embodiments as
currently known.

Injection Moulding Conditions
Apparatus: Boy (Family Mould)
Conditions:
- Temperature of barrel: 250°C
- Mould T*: 60°C
- Holding Pressure: 30-40 bar/20 sec.
- Cooling time: 15 sec.

Mechanical properties
Flexural Modulus:
- Crosshead speed: 1.71 mm/min.
- Span: 64 mm
- Sample dimensions:
  - depth: 4 mm
  - width: 10 mm
  - length: 80 mm

Tensile strength:
- Crosshead speed: 20 mm/min.
- Sample dimensions:
  - width: 10 mm
  - thickness: 3.2 mm

Notched Izod Impact Strength:
- Sample dimensions:
  - width: 3.2 mm
  - thickness: 15 mm
  - length: 63 mm

All properties tested at 21°C, 50% humidity, dry as
moulded.

Materials used in the examples
MAPP Maleic Anhydride - grafted - Polypropylene
- Trade Name: Exxelor PO 1015 from Exxon Chemical Co.
- MFR: 88 g/10 min (at 230°C, 2.16 kg)
- Anhydride content: 4 mmole/100 g

MAEP Maleic Anhydride - grafted - Ethylene Propylene Rubber
- Trade Name: Exxelor VA 1820 from Exxon Chemical Co.
- MFR: 2.5 g/10 min (at 230°C, 2.16 kg)
- Anhydride content: 3.5 mmole/100 g
- Ethylene content in EPR: 77 %
MAEP2 Maleic Anhydride - grafted - Ethylene, Propylene Rubber
Trade Name: Exxelor VA 1803 from Exxon Chemical Co.
MFR: 3 g/10 min (at 230°C, 2.16 kg)
Anhydride content: 7 mmole/100 g
Ethylene content in EPR: 50 %

AMP 1-Amino-1-Methy lamino-n-Propane from Aldrich Chemicals
Cas#: 6291-64-5
Purity: 98 %

SMA1 Styrene-Maleic Anhydride Copolymer
Trade Name: Dylark 232 from Arco Chemical
Styrene content: approx. 93 %
Mw: approx. 80000 g/mole

SMA2 Styrene-Maleic Anhydride Copolymer
Trade Name: Dylark 332 from Arco Chemical
Styrene content: approx. 86 %
Mw: approx. 80000 g/mole

SMA4 Styrene-Maleic Anhydride Copolymer
Trade Name: 19.091.79 from Janssen Chimica
Styrene content: approx. 75 %
Mw: approx. 1900 g/mole

PP1 Polypropylene
Trade Name: VB40 from Neste
MFR: 4 g/10 min (230°C, 2.16 kg)

EP Ethylene-Propylene Rubber
Trade Name: Vistalon 805 from Exxon Chemical Co.
MFR: 3 g/10 min (230°C, 2.16 kg)
Ethylene content: 77 %

Example: Production of Amino-PP in Extruder

Extrusion conditions:
Welding Engineer Twin Screw Extruder
Temperature: 174 to 222°C
Screw speed: 250 RPM
N₂ stripping: 0.7 kg/h
Vacuum on vent barrel: 700 mbar

Feeding conditions:
MAPP: - kg/h
AMP: 1.25 ml/min
Amino-PP analysis:

MFR : 76 g/10 min (230°C, 2.16 kg)
Amine Content (by HCL Titration) : 3.2 mmole/100 g

In this Example 1, an aminated polypropylene was prepared by neutralization of maleated polypropylene with an amino compound in accordance with the invention in a melt processing reaction. There was negligible decrease in melt flow rate between the initial maleated polypropylene and the final aminated polypropylene. The final amine content showed almost equivalent reaction of amine groups with available anhydride sites. There was essentially no cross-linking or chain extension.

Example 2:
Production of Amino-PP (amPP2) in Brabender mixer

Mixing conditions:
Brabender mixer
Temperature : 180°C
Screw speed : 60 RPM

Feeding conditions:
50 g MAPP mixed for 3 min
0.29 g AMP added to the melt
Sample recovered after 6 additional min of mixing

amPP2 Analysis:
No residual anhydride (by IR)
Amine Content (by HCL Titration) : 2.9 mmole/100 g

In this Example 2, the reaction of Example 1 was repeated in a Brabender mixer. No significant cross-linking or chain extension was observed. By Infrared Analysis it was shown that no anhydride functionality remained unreacted.
Example 3: Production of Amino-EP (amEP1), in extruder

Extrusion conditions: As example 1

Feeding conditions:

MAEPI: 7 kg/h
AMP: 0.823 ml/min

amEP1 analysis:

MFR: 1.5 g/10 min (230°C, 2.16 kg)
Amine content (by HCL Titration): 2 mmole/100 g

In this Example 3, an aminated ethylene-propylene copolymer was prepared utilizing a commercially available maleated ethylene-propylene rubber under melt processing conditions utilizing a twin screw extruder as in Example 1. Negligible decrease in MFR was observed while a substantial portion of anhydride sites were neutralized.

Example 4: Production of Amino-EP (amEP2), in extruder

Extrusion conditions: As example 1

Feeding conditions:

MAEP2: 7 kg/h
AMP: 1.92 ml/min

amEP2 analysis:

MFR: 2.4 g/10 min (230°C, 2.16 kg)
Amine content (by HCL Titration): 4 mmole/100 g

In this Example 4, the preparation, as in Example 1, was repeated using a different commercially available maleated ethylene-propylene rubber. Similar results were obtained.

Blends prepared in a Brabender Mixer, at 240°C and 60 RPM.

<table>
<thead>
<tr>
<th>SMA1 wt %</th>
<th>EP wt %</th>
<th>amEP1 wt %</th>
<th>amEP2 wt %</th>
<th>Size (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Note: Size is diameter of dispersed EP in SMA matrix as observed by SEM on microtomed surface.

In this Example 5, the aminated ethylene-propylene copolymer prepared in Examples 3 and 4 were melt blended with a commercially available styrene-maleic anhydride copolymer and compared for resulting blend microstructure with an equivalent ethylene-propylene copolymer blend with the same styrene-maleic anhydride copolymer. The decreased dispersed phase particle size showed improved compatibility and resulting improvement in dispersion. The decrease in particle size should be commensurate with improved impact strength.

Example 6 : Use of Amino-PP in SMA/PP blends

Blends prepared in a Brabender Mixer, at 240°C and 60 RPM.

<table>
<thead>
<tr>
<th>SMA4 wt %</th>
<th>PP1 wt %</th>
<th>amPP2 wt %</th>
<th>Size (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>80</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>20</td>
<td>75</td>
<td>5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Note: Size is diameter of dispersed SMA in PP matrix observed by SEM on microtomed surface.
In this Example 6A, the aminated polypropylene prepared in Example 2 was blended with a commercially available styrenemaleic anhydride copolymer and commercially available polypropylene. This was compared against a similar blend not containing the aminated polypropylene. Microstructural analysis of the two blends showed significantly decreased dispersed phase particle size and significantly improved dispersion of the styrene-maleic anhydride copolymer in the polypropylene when aminated polypropylene is added.

This Example 6B was repeated using the aminated polypropylene prepared in Example 1. The melt processing reaction was conducted in a Brabender extruder at 250°C with 110 RPM. To polypropylene, as in Example 6, was added the aminated polypropylene and a different commercially available styrenemaleic anhydride copolymer ("SMA2"). The resulting blend contained 67 wt% polypropylene, 4.8 wt% aminated polypropylene and 28.2 wt% SMA2.

The following mechanical properties were measured under standard conditions.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>100 wt% PP</th>
<th>100 wt% SMA2</th>
<th>65 wt% Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>33</td>
<td>53</td>
<td>38</td>
</tr>
<tr>
<td>Secant Fluxural Modulus (GPa)</td>
<td>1.2</td>
<td>3.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Notched Izod Impact (kJ/m2)</td>
<td>3.1</td>
<td>2.4</td>
<td>3.6</td>
</tr>
</tbody>
</table>

The resulting polypropylene blend according to the invention showed intermediate properties for tensile strength and secant flexural modulus, improved over neat polypropylene, and impact properties unexpectedly improved over both of the neat polypropylene and the SMA2. Increased utility of the polypropylene blends according
to this invention can be expected as a consequence of generally good correlation between improved secant flexural modulus and heat distortion temperatures, and as well the concurrent improvement in impact strength.


Blends 1-3 obtained on a Leistritz Twin Screw Extruder.
All components dry-blended,
Feed rate : 15 kg/h,
Screw speed : 150 RPM,
Temperature : 200 to 260°C.

Blends 4-5 obtained on a Brabender Single Screw Extruder.
All components dry-blended,
Feed rate : 3 kg/h,
Screw speed : 110 RPM,
Temperature : 240°C

All blends 1-5 injection-moulded on a Boy Injection Moulding machine under conditions recommended by SMA producer. SMA1 was injection-moulded as received for comparison under the same conditions.

Injection-moulded samples were tested under the listed ASTM standards.

<table>
<thead>
<tr>
<th></th>
<th>SMA1 wt %</th>
<th>EP wt %</th>
<th>amEP1 wt %</th>
<th>amEP2 wt %</th>
<th>Dy MPA</th>
<th>Ef GPA</th>
<th>Iz kJ/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend 1</td>
<td>83</td>
<td>0</td>
<td>0</td>
<td>17</td>
<td>40</td>
<td>2.3</td>
<td>9.4</td>
</tr>
<tr>
<td>Blend 2</td>
<td>83</td>
<td>0</td>
<td>17</td>
<td>0</td>
<td>41</td>
<td>2.3</td>
<td>6.2</td>
</tr>
<tr>
<td>Blend 3</td>
<td>83</td>
<td>8.5</td>
<td>0</td>
<td>8.5</td>
<td>41</td>
<td>2.3</td>
<td>9.4</td>
</tr>
<tr>
<td>Blend 4</td>
<td>90</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>45</td>
<td>2.4</td>
<td>6.8</td>
</tr>
<tr>
<td>Blend 5</td>
<td>80</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>41</td>
<td>2</td>
<td>19</td>
</tr>
<tr>
<td>Reference</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>53</td>
<td>3</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Dy is maximum tensile strength
Ef is secant flexural modulus
Iz is room temperature (20-25°C) notched Izod impact strength
In this Example 7, aminated ethylene-propylene copolymer rubber was blended with both of the styrene-maleic anhydride copolymer of Example 5 and a blend of that copolymer with an unmodified, commercially available ethylene-propylene copolymer rubber. Both resulting blends containing the aminated ethylene-propylene copolymer rubber of this invention showed significantly improved impact properties at room temperature. It was noted that Blend 1 and Blend 3 utilizing an aminated EP copolymer rubber of lower ethylene content and higher amine content provided greater improvement, and that Blend 5 showed that a small increase in the aminated EP copolymer led to a significant increase in impact strength. It is believed that the lesser degree of crystallization of the modified EP copolymer rubber of Blends 1, 3, 4 and 5 was a significant factor in the noted improvement.

Various changes and modifications in the products and process of this invention can be made without departing from the spirit and scope thereof. The various embodiments which have been disclosed herein were for the purpose of further illustrating the invention but were not intended to limit it.
CLAIMS:
1. A graft polymer that is the reaction product of (1) a thermoplastic polymer containing electrophilic functionality sufficient to react with primary amino groups and (2) a chemical compound comprising one primary amine and one secondary amine, the secondary amine having reactivity approximately equal to or less than the primary amine, wherein said thermoplastic polymer is based upon at least one member of the group consisting of polypropylene, polyethylene, ethylene-propylene copolymer, polyethylene copolymer, ethylene-alpha-olefin elastomer and butyl rubber.

2. A graft polymer as claimed in claim 1 wherein said reaction product is obtained via melt processing reaction without significant cross-link formation.

3. A polymeric product as claimed in claim 1 wherein the said secondary amino group has a pK_b of 3.0 or greater.

4. A polymeric product as claimed in claim 1 in which the thermoplastic polymer is a functional group containing polyolefin.

5. A graft polymer as claimed in claim 4 wherein said polyolefin is based upon polypropylene, polyethylene, copolymer of ethylene and propylene, or ethylene copolymer resin.

6. A graft polymer as claimed in claim 4 wherein said polyolefin is based upon ethylene-alpha-olefin elastomer or polyisobutylene rubber.
7. A process for the preparation of a polymer containing a graft reactive amino group comprising the steps of:
   (a) providing a thermoplastic polymer containing at least one electrophilic functionality sufficient to react with primary amino groups, wherein said thermoplastic polymer is based upon at least one member of the group consisting of: polypropylene, polyethylene, ethylene-propylene copolymers, polyethylene copolymer, ethylene-alpha-olefin elastomer and butyl rubber;
   (b) and melt reacting with a chemical compound comprising one primary amine and one secondary amine, the secondary amine having reactivity approximately equal to or less than the primary amine.

8. The process according to claim 7 wherein the said secondary amino group has a pKₐ of 3.0 or greater.

9. The process according to claim 7 wherein said thermoplastic polymer is a functional group containing polyolefin.

10. The process according to claim 9 wherein said polyolefin is one based upon polypropylene, polyethylene, copolymer of ethylene and propylene, ethylene copolymer resin.

11. The process according to claim 9 wherein said polyolefin is based upon an ethylene-alpha olefin elastomer.
12. The use as a modifier or compatibilizer for thermoplastic polymer compositions of a graft polymer that is the reaction product of (1) a thermoplastic polymer containing electrophilic functionality sufficient to react with primary amino groups and (2) a chemical compound comprising one primary amine and one secondary amine, the secondary amine having reactivity approximately equal to or less than the primary amine.

13. The use according to claim 12, wherein said polymer composition comprises at least one engineering thermoplastic selected from the group consisting of polyester engineering resins, aromatic polycarbonate compositions, polyvinyl chloride, and polyvinylidene chloride.

14. The use according to claim 12 wherein said thermoplastic polymer is a functional group containing polyolefin.

15. The use according to claim 14, wherein said polyolefin is based on polypropylene, polyethylene, copolymer of ethylene and propylene or ethylene copolymer resin.

16. The use according to claim 14, wherein said polyolefin is based upon ethylene-alpha olefin elastomer.

17. The use according to claim 12, wherein said thermoplastic polymer is based upon halogenated butyl rubber or chlorinated nitrile rubber.
18. The use, according to Claim 12, wherein said thermoplastic polymer is based upon styrene-based polymers.

19. The use in lubricating oil compositions of the graft polymer according to Claim 6.
INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08F8/32

II. FIELDS SEARCHED

Minimum Documentation Searched?

Classification System Classification Symbols

Int.Cl. 5 C08F

Documentation Searched other than Minimum Documentation to the extent that such documents are included in the Fields Searched?

III. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>EP,A,0 400 866 (EXXON CHEMICAL PATENTS INC.) 5 December 1990 see the whole document</td>
<td>1-19</td>
</tr>
<tr>
<td>X</td>
<td>GB,A,2 080 313 (INSTITUT FRANCAIS DU PETROLE) 3 February 1982 see the whole document</td>
<td>1-19</td>
</tr>
<tr>
<td>A</td>
<td>FR,A,2 234 319 (EXXON RESEARCH AND ENGINEERING CO.) 17 January 1975 see claims 1-14</td>
<td>1</td>
</tr>
<tr>
<td>A</td>
<td>EP,A,0 331 306 (ICI AUSTRALIA OPERATIONS PROPRIETARY LTD.) 6 September 1989 see claims 1-10</td>
<td>1</td>
</tr>
</tbody>
</table>

* 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 document but published on or after the international filing date

“F” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another invention 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

“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 of other such documents, such combination being obvious to a person skilled in the art.

“&” document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 04 NOVEMBER 1992

Date of Mailing of this International Search Report 7. 11. 92

International Searching Authority EUROPEAN PATENT OFFICE

Signature of Authorized Officer PERMENTIER W.A.
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>EP, A, 0 234 114 (EXXON RESEARCH AND ENGINEERING CO.) 2 September 1987 cited in the application see claims 1-41</td>
<td>1</td>
</tr>
<tr>
<td>A</td>
<td>DE, A, 2 165 330 (UNION CARBIDE CORP.) 5 July 1973 see claims 1-12</td>
<td>1</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU-A- 5598990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA-A- 2015061</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BE-A- 889483</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA-A- 1157647</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE-A, CA- 3126404</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE-A- 3153653</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP-C- 1615599</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP-B- 2037958</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP-A- 57040591</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL-A- 8103228</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US-A- 4375974</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA-A- 1023092</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE-A- 2429819</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB-A- 1457328</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP-A- 50037886</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU-A- 2993289</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB-A- 2216128</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU-B- 600696</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU-A- 6849587</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO-A- 8703603</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US-A- 5030695</td>
</tr>
<tr>
<td>DE-A-2165330</td>
<td>05-07-73</td>
<td>None</td>
</tr>
</tbody>
</table>

For more details about this annex: see Official Journal of the European Patent Office, No. 12/82