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(54) **Title:** TOUGHENED THERMOPLASTIC NYLON COMPOSITIONS

(57) **Abstract**

A toughened nylon composition comprising about 95 - 60 wt.% polyamide and about 5 - 40 wt.% functionalised elastomeric polymer characterized by additionally comprising at least one low molecular weight composition containing a single functional moiety, such as phthalic anhydride, that is at least as reactive with the amine groups as is the functional moiety of the functionalised elastomeric polymer.

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Title: **Toughened Thermoplastic Nylon Compositions**

Technical Field

This invention relates to engineering thermoplastics comprising principally polyamides and elastomeric polymers containing functional groups reactive with the amine groups of the polyamides. By introduction of monofunctional low molecular weight compounds containing functional groups that similarly react with the amine groups of the polyamides, such as phthalic anhydride, the impact strength of the blends are significantly improved.

Background of the Invention

Polyamide engineering thermoplastics have long been known for their excellent toughness, flexibility, abrasion resistance and relatively high impact strength. Molded or extruded polyamide compositions have found application in appliances, consumer products, electrics, machine components, automotive parts, gears, and like uses.

Accordingly there is much in the literature relating to toughened thermoplastic nylon compositions. Early work addressed improving the compatibility of polyamides with other polymers. For example US-A-3,724,289 addresses compatibilization of resinous synthetic polymers, such as polyamides, with other normally incompatible polymers, particularly rubbery copolymers, to achieve particular utility as high impact molding resins of improved thermal rigidity. The rubbery copolymers are described to contain free carboxylic acid groups. GB 998,439 addresses compatibilizing blends of polyamides and olefin copolymers by incorporating acid groups with the olefin copolymers, either by direct copolymerization or by graft copolymerization. It was noted that as a result of this

compatibilization procedure the resulting compositions exhibited remarkable toughness as measured by such tests as the Izod impact test.

Subsequent work addressed selections of similarly functionalized polymers that could improve the toughness and impact strength even further. For example US-A-4,174,358 addresses toughened multi-phase thermoplastic compositions comprising a polyamide matrix resin and at least one other phase containing a branched or straight chain polymer having a tensile modulus less than 20,000 p.s.i. and being adhered to the polyamide. An extensive listing of the low tensile modulus polymers is given and as well an extensive listing in groups B, C, D, and E of monomers that can provide adhering sites in the dispersed phase. Polymers containing the adherent sites are said to be prepared by standard copolymerization or by a graft reaction. Optimal properties are said to be obtainable by both of polymer modifier selection and by processing conditions in more recent work, e.g., WO 91/07467. In this document use of polyolefin blends with ethylene-propylene rubber containing adhering sites such as maleic anhydride and use of viscosity matching and/or level of adhering site incorporation is said to have beneficial effects on phase morphology such as to optimize impact properties at room temperature without adversely affecting the ductile-brittle transition point.

There is additionally published literature addressing the inclusion in various polyamide blends of low molecular weight, polyfunctional coupling agents to improve various properties. EP-A-0 010 938 addresses polyamide resins having improved impact strength prepared by melt-blending a) polyamide resin, b) a hydroxyl-functional elastomer and c) a succinic functional coupling agent. The coupling agent contains two or more succinic groups per molecule and

is believed to react with both the amine ends of the polyamide and the hydroxyl groups of the elastomer. EP-A-0 295 103 addresses a thermoplastic resin composition comprising a polyamide resin, a polyphenylene ether , a rubber-like material, and a mutual compatibilizer being reactive or compatible with the polyphenylene ether and reactive with the polyamine. GB-A-2 207 139 addresses molding materials of thermoplastically-processable polyamide alloys which contain both an elastomeric polymer as impact-resistance-modifier and a polyfunctional epoxide or glycidal ether compound. The polyfunctional compound is said to increase the molecular weight by connecting the polyamide macromolecules and thus are to be used in small amounts to avoid increasing viscosity.

Polyamide resins are also being addressed outside the field of engineering thermoplastics for blending to achieve other uses. For example EP-A-0 140 372 describes a polyamide-rubber blended composition prepared by blending an acrylonitrile-butadiene copolymer rubber containing an epoxy group, an epichlorohydrin rubber, a polyamide resin and a carboxylic acid having a functional group being present in a prescribed amount relative to the total amount of rubbers present. The carboxylic acid compound may be such as adipic acid or phthalic acid, a polyvalent carboxylic acid such as trimellitic acid, or an acid anhydride such as maleic anhydride or phthalic anhydride. It is shown that if the carboxylic acid was not present in the specified minimum amount the polyamide was cross-linked by the epoxy nitrile rubber so as to be nearly impossible of thermoplastic shaping.

As illustrated in the developments addressed in the background art above there continues to be a need to provide economic means of optimizing the impact properties of polyamide engineering thermoplastics without adversely

increasing the viscosity properties or decreasing the potential for thermoplastic shaping.

Invention Disclosure

It has been surprisingly found that by introduction during melt processing into polyamide engineering thermoplastics, containing as impact modifiers elastomeric polymers having functional groups reactive with the amine groups of the polyamides, of monofunctional low molecular weight compounds with functional groups that similarly react with the amine groups of the polyamides, the impact strength of the blends are significantly improved. The resulting blend of the invention is a toughened nylon engineering thermoplastic composition comprising 95 - 60 wt.% polyamide and 5 - 40 wt.% functionalised elastomeric polymer characterized by additionally comprising at least one low molecular weight composition containing a single functional moiety that is at least as reactive with the amine groups as is the functional moiety of the functionalised elastomeric polymer. The invention also includes the process for improving the toughness of such nylon compositions comprising the step of simultaneously melt blending the polyamide, the functionalised elastomeric polymer, and the at least one low molecular weight composition. And, accordingly, the invention includes a process for improving the compatibilization of primary amine-terminated polyamide in polymer blends characterized by comprising the step of providing during the melt-processing reaction of the polyamide with a reactive polymer selected to improve compatibility in the polymer blend, the at least one low molecular weight composition .

Best Mode and Examples of the Invention

The polyamides of the invention include any of those known in the art to be susceptible of extrusion or molding as engineering thermoplastics and that contain $-NH_2$ functionality, typically at the chain ends. Representative polyamides and methods of preparing them are well-known in the art and appear in each of the background art references. Suitable polyamides include polyhexamethylene adipamide (polyamide 6,6), polycaprolactam (polyamide 6), polyhexamethylene azelamide (polyamide 6,9), polyhexamethylene sebacamide (polyamide 6,10), polyhexamethylene dodecanoamide (polyamide 6,12), polyhexamethylene isophthalamide (polyamide 6IA), polyhexamethylene terephthalamide (polyamide 6,T), polytetramethylene adipamide (nylon 6,6), polyhexamethylene tere-co-isophthalamide (polyamide 6TA/I), polypropiolactam (polyamide 3), polypyrolidone (polyamide 4), poly(ω-enanthamide) (polyamide 7), polycapryllactam (polyamide 8), poly(ω-undecaneamide) (polyamide 11), polylauryllactam (polyamide 12) and poly(metaxylene diamine-adipic acid) (MXD6) mixtures thereof. Polyamides of monomers of any of the foregoing polyamide polymers will also be useful in the invention so long as the terminal primary amine group is present in a significant portion of the polyamide polymers present. Similarly polyamide resins prepared by block and/or graft copolymerization of these comonomers with other monomers will clearly be useful in accordance with the invention where useful independently as engineering thermoplastics. Typically polyamide 6,6, polyamide 6 or polyamide 12 will be used.

The polyamide component of the engineering thermoplastic blends of the invention is typically 60 to 95 wt.% of the total polymer weight (excluding fillers, additives, non-polymeric modifiers, etc.), preferably 70 to 90 wt.%, and most preferably 77 to 90 wt.%.

The functionalised elastomeric polymer of the invention will include any polymer useful for the impact toughening of engineering thermoplastic compositions based on polyamide resins. More particularly it will be those both having a tensile modulus of less than 150 mPa and containing functional groups reactive with the primary amine groups of the polyamides, excluding however the nitrile rubbers based on acrylonitrile and copolymers therewith. The low tensile modulus dispersed phase polymers of US-A-4,174,358 will be suitable as the functionalised elastomeric polymer of the invention, the disclosure thereof is incorporated by reference for purposes of U.S. patent practice. The functionalised elastomeric polymer is preferably 10-30 wt.%, most preferably 10-23 wt.% of total polymer weight.

Particularly suitable in accordance with this invention are the ethylene-alpha-olefin elastomers which are defined to include copolymers of ethylene and C_3-C_{20} alpha-olefins, optionally with one or more non-conjugated diolefins. The preferred alpha-olefins are typically C_3 - C_6 alphaolefins and the most preferred are propylene, butene-1 and hexene-1. The non-conjugated dienes are any of those known in the art to be capable of Ziegler-Natta coordination polymerization with the alpha-olefins, particularly ethylidene-norbornene, 1,4-hexadiene, or dicylopentadiene. Such polymers are well-known as are their methods of preparation, for relatively recent reviews of general methods for preparing EPM and ,or EPDM rubber, including catalysts, monomers, reaction conditions, etc., reference may be made to "Elastomers, Synthetic (Ethylene-Propylene)", by E. L. Borg in Encyclopedia of Chemical Technology, 3d. Ed., V.8 pp. 492-500 (Kirk-Othmer) and "Ethylene-Propylene Elastomers", by G. VerStrate in Encyclopedia of Polymer Science and Engineering, 2d. Ed., V. 6 pp. 522-564 (J. Wiley & Sons, 1986).

Styrene-based polymers suitable as the functionalised elastomeric polymer of the invention, 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. C_3 to C_{18} alphaolefins or lower alkenes. The conjugated dienes including isoprene, butadiene, 2,3-dimethylbutadiene, 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 napthalene, but are preferably monovinyl monoaromatic compounds, such as styrene or alkylated styrenes substituted at the alpha-carbon atoms of the styrene, such as alphamethylstyrene, or at ring carbons, such as o-,m-, p-methylstyrene, ethylstyrene, propylstyrene, isopropylstyrene, butylstyrene, isobutylstyrene, tert-butylstyrene (e.g., p-tertbutylstyrene). Also included are vinylxylenes, methyl-ethyl styrenes, and ethylvinylstyrenes. Alpha-olefins 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 5 mole %, of other copolymerizable monomers such as vinyl pyridines, vinyl lactams, methacrylates, vinyl chloride, vinylidene chloride, vinyl acetate, vinyl stearate, and the like. Preferred examples include butadiene rubber and random polymers of butadiene and styrene (styrene-butadiene rubber).

The elastomeric polymers having functional groups reactive with the primary amine groups of the polyamides are prepared based on the above by either of copolymerizing or graft copolymerizing of ethylenically unsaturated electrophilic groups reactive with primary amines, as is well-known in the art. Both methods of preparation are exemplified in US-A-3,724,289, GB 998,439 and US-A-4,174,358. Both U.S. patents are incorporated by reference for purposes of U.S. patent practice. Appropriate functional groups are addressed and described in these documents.

The graft addition of ethylenically unsaturated electrophilic groups reactive with primary amines and thus suitable in this invention, e.g. the dicarboxylic moiety of maleic anhydride, is preferred and is conveniently accomplished by heating a blend of the thermoplastic polymer 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 , 3 962 265, 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 for purposes of U.S. patent practice. 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 carboxyl 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 for purposes of U.S. patent practice. 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 description 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 pendant unsaturation is known in the art. US Patents 3 330 794, 3 448 174 and 3 551 518 describe the use of epoxidising agents, such as perbenzoic acid, to directly oxidise unsaturation in ethylene-containing elastomeric compounds to attain incorporated epoxy, or oxirane, groupings. These disclosures are incorporated by reference for purposes of U.S. patent practice.

The low molecular weight functional compound of the invention is any chemical compound having a molecular weight not greater than about 1200 and containing a single functional moiety that is at least as reactive with the amine groups of the polyamides as are the functional groups of the functionalised elastomeric polymer of the invention. The molecular weight is low enough so that if the non-

reactive portion is incompatible with the polyamide it will not independently form a dispersed phase of such significance to decrease the overall properties of the invention blends. Thus preferably the molecular weight will not be greater than 600. The single reactive moiety requirement effectively precludes any cross-linking or coupling reactions between different polyamide chains, or portions thereof, or with other reactive components or modifiers in the final engineering thermoplastic blends. Included within the class of reactive moeties that should not be present in addition to the single reactive moiety are the carbon-carbon double or triple bonds, such as ethylenic unsaturation, because of their reactive potential with the primary amine of the polyamides. However aromatic unsaturation can be tolerated in the low molecular weight functional compound as such is not sufficiently reactive to lead to the avoided cross-linking or coupling reactions.

The reactivity of the low molecular weight functional compound of the invention should be comparable to or greater than that of the functional group of the functionalised elastomeric polymer in order to achieve a preferred competitive reaction with the amines of the polyamides over that with the functionalised elastomeric polymer. The low molecular weight also contributes to the reactivity with the polyamides due to the greater mobility of the low molecular weight compounds to that of the generally much longer-chain or greater-molecular-weight elastomeric modifiers. Though not intended as a limitation on the invention as described, it is believed that the more highly reactive low molecular weight compound, compared to the functionalised elastomeric modifier, will react much more quickly in melt processing with the available amine sites in the polyamides. In particular , it is believed that the lower molecular weight polyamide chains that are generally present will preferentially react with the low

molecular weight functional compound of the invention and will thus become unavailable for reaction with the functionalised elastomer. As a result the reaction product of the functionalised elastomer with the polyamide will more predominantly be with the longer chain polyamides. This polyamide-elastomer graft polymer thus has optimal compatibilization features for the polyamide-elastomer blend in that the chain-entanglement weight of the polyamide portion of the graft polymer will be achieved and exceeded to a greater extent than that before achieved. The observed improvements in impact properties are likely a result of the improved compatibilty of the final blends prepared in accordance with the invention.

Suitable examples of appropriate functional moieties for the low molecular weight compound include dicarboxylic acids/anhydrides, epoxides, and aldehydes, etc. Pthalic anhydride, succinic anhydride, ethylene oxide, propylene oxide, and acetic anhydride are particularly suitable compounds. In addition both oligomers and low molecular weight polymers containing the same functional groupings as the above compounds will also be suitable in accordance with the invention.

A particularly suitable low molecular weight compound in accordance with the invention are the succinimized elastomeric homopolymer of isobutylene ("PIBSA") or ethylene-alphaolefin copolymers ("EPSA") having the low molecular weight characteristics as described. Both the low molecular weight polyisobutylene and ethylene-alpha-olefin copolymers are well known articles of commerce manufactured in accordance with known methods, as are their modification with maleic acid/anhydride to form PIBSA and EPSA.

The low molecular weight compound is used in any amount so as to be effective for the improvement of the toughness of the polymer blend. This improvement is measured by property testing, such as the impact testing exemplified in this description. As little as 2 mmole/100 gr of Polyamide of the low molecular weight compound can exhibit noticeable improvement. Typically the amount used will be that between 0.5 and 15 mmole/100 gr of Polyamide, and preferably from 3 to 12 mmole/100 gr.

In addition to the principal components of the invention blends additional additives, fillers, dyes, pigments, heat stabilizers, antioxidants, nucleating agents, lubricants, plasticizers, antistatic agents, flame retardants, and other modifying polymers may be incorporated in known amounts to achieve specific embodiments that are considered to be within the scope of the invention claimed. So long as a weight ratio of polyamide to elastomeric modifier is maintained between 19 and 1.5 and the low molecular compound is used in the effective amounts for those ratios the benefits of the invention will be observable.

In particular, use of the invention concept will permit improved graft polymers in any of the prior art where it has been sought to graft polyamides containing terminal primary amine groups with other reactive polymers, or reactive coupling agents. As noted above the resulting graft polymers from polyamides not masked by the low molecular weight functional compound used in accordance with the invention will preferentially contain the higher molecular weight polyamides and will accordingly contribute a greater degree of cohesion in the final polymer blend prepared.

Typical industrial applications of the invention will be apparent. Engineering thermoplastic polyamide compositions having improved toughness or impact strength will find increasing use in the automotive industry, even becoming of greater use in such impact-critical applications as bumpers. The traditional industrial applications of such engineering thermoplastic compositions will also benefit from the improved polyamide compositions of the invention.

The following examples are presented to illustrate the foregoing discussion. All parts, proportions and percentages are by weight unless otherwise indicated. Although the examples may be directed to certain embodiments of the present invention, they are not to be viewed as limiting the invention in any specific respect.

Examples

The following examples demonstrate the improved impact strength of polyamide blends prepared in accordance with the invention. The polyamide used was Capron 8200®, a polyamide 6 ("PA6") available from Allied International, Belgium. The impact modifier elastomeric polymer having reactive functional groups was a maleated ethylene-propylene rubber ("EPMA") available as EXXELOR ® 1803 (MFR 31dg/min.(10kg./200°C.), 0.7 wt.% MAnh) through EXXON CHEMICAL INTERNATIONAL MARKETING, B.V./S.A., Belgium. Phthalic anhydride obtained from Merck Co., Belgium was used as the low molecular weight compound of the invention.

The Nylon 6 was dried at 80 °C for 3 hours under vacuum before extrusion. All samples of polymer blends were dry blended prior to melt-processing and then prepared under the following conditions. Melt-processing was conducted in a twin screw Werner-Pfleiderer Extruder

operated at 240 °C at a screw speed of 100 rpm. The average residence time was about 1 minute.

Injection molding for impact testing was conducted at a mold temperature of 70 °C, polymer melt temperature of 250 °C. Notched Izod impact tests were conducted in accordance with ISO 180/1A after mold samples had been dried 11 hours under vacuum at 120°C.

Table 1

Ref. No.	PA 6 (gr)	EPMA (gr)	Pht.Anh. (gr)
1	100	0	0
2	100	0	0.45
3	80	20	0
4	80	20	0.46
5	80	20	0.52
6	80	20	0.78
7	70	30	0
8	70	30	0.72

Table 2 shows the results of notched Izod testing of the samples prepared above.

Table 2

	Notched Izod Impact Strength (kJ/M2)				
Ref. No.	**- 22 °C**	**- 10 °C**	**4 °C**	**18 °C**	**35 °C**
1	6.5	-	-	6.5	5.6
2	3.5	-	-	5.5	5.8
3	41	56	40	32	27
4	56	60	48	40	33
5	59	61	46	37	31
6	24	26	57	62	65
7	54	26	33	31	28
8	72	76	76	75	67

The addition of phthalic anhydride alone (2) did not significantly change the properties of the PA6 (1). At 20 % EPMA, the addition of EPMA (3) improved the impact properties with peak improvement at -10°C and the addition of the Phthalic Anhydride ((4), (5)) significantly improved impact strength over (3) at low (- 20°C) and ambient temperatures with peak improvement at the lowest temperatures. Ref. (6) showed that a decrease in properties occurs at low temperatures when too much low molecular weight compound is provided. When Phthalic Anhydride is added at 30 % EPMA ((8) compared with (7)), a significant improvement is observed at all temperatures.

Although the invention has been described with respect to particular materials, means and embodiments it is to be

understood that the invention is not limited to the particulars disclosed and extends to all equivalents within the scope of the appended claims.

The following is claimed:

Claims:

1. A toughened nylon engineering thermoplastic composition comprising 95 - 60 wt.% polyamide and 5 - 40 wt.% functionalised elastomeric polymer, excluding those based on nitrile rubber, characterized by additionally comprising at least one low molecular weight composition containing a single functional moiety that is at least as reactive with the amine groups as is the functional moiety of the functionalised elastomeric polymer.

2. The composition of claim 1 wherein said low molecular weight composition has a molecular weight less than 1200.

3. The composition of claim 2 wherein said low molecular weight composition is one or more selected from the group consisting of phthalic anhydride, succinic anhydride, acetic anhydride, ethylene oxide, PIBSA and EPSA.

4. The composition of claim 1 wherein said functionalised elastomeric polymer is one based upon one or more selected from the group consisting of ethylene-alpha-olefin polymers, ethylene-alpha-olefin-diolefin polymers, at least partially hydrogenated styrene block copolymers, random polymers containing styrene and butadiene, and butadiene rubber.

5. The composition of claim 4 wherein said functionalised elastomeric polymer is one modified with a dicarboxylic acid moiety.

6. A process for improving the compatibilization of amine-terminated polyamide in polymer blends characterized by comprising the step of providing during the melt-processing reaction of the polyamide with at least one reactive polymer, excluding those based on nitrile rubber, selected to improve compatibility in the polymer blend, at least one low molecular weight composition containing a single functional moiety that is at least as reactive with the amine groups as is the functional moiety of the reactive polymer.

7. The process of claim 6 wherein said polymer blend comprises 95 - 60 wt.% polyamide and 5 - 40 wt.% functionalised elastomeric polymer as the at least one reactive polymer.

8. The process of claim 7 wherein said functionalised elastomeric polymer is one based upon one or more selected from the group consisting of ethylene-alpha-olefin polymers, ethylene-alpha-olefin-diolefin polymers, at least partially hydrogenated styrene block copolymers, random polymers containing styrene and butadiene, and butadiene rubber.

9. The process of claim 8 wherein said functionalised elastomeric polymer is one modified with a dicarboxylic acid moiety.

10. The process of claim 9 wherein said low molecular weight composition has a molecular weight less than 1200.

11. The process of claim 10 wherein said low molecular weight composition is one or more selected from the group consisting of phthalic anhydride, succinic anhydride, acetic anhydride, ethylene oxide, PIBSA and EPSA.

INTERNATIONAL SEARCH REPORT

Intern al Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08L77/00 C08K5/09 C08K5/15 C08L51/00 //(C08L77/00, 51:00),(C08L77/00,51:04),(C08L77/00,51:06)

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 5 C08L C08K

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.
A	EP,A,0 010 938 (MONSANTO) 14 May 1980 cited in the application	
A	EP,A,0 140 372 (TOYODA GOSEI) 8 May 1985 cited in the application	
A	FR,A,2 024 787 (UNION CARBIDE CANADA) 4 September 1970	
A	EP,A,0 469 542 (SUMITOMO) 5 February 1992	

☐ 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	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Leroy, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. al Application No
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		CA-A-	1223997	07-07-87
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