Abstract:

Title: POLYAMIDE COMPOSITION WITH IMPROVED CHEMICAL RESISTANCE

A heat-conditioned polyamide composition comprising polyhydric alcohol additives that is acid-resistant without adversely affecting mechanical properties of articles molded therefrom is provided.
POLYAMIDE COMPOSITION WITH IMPROVED CHEMICAL RESISTANCE

FIELD OF INVENTION

[0001] The present application relates to a polyamide having improved chemical resistance with the preservation of mechanical properties. More particularly, the present application relates to polyamide compositions comprising a polyhydric alcohol, which demonstrate excellent acid resistance after heat treatment and without adversely affecting mechanical properties. An acid-resistant polyamide, an article or part therefrom, is particularly suitable for engineering plastics that require chemical compatibility.

BACKGROUND OF THE INVENTION

[0002] The present application relates to polyamides having excellent acid resistance after heat treatment.

[0003] U.S Patent No. 4,822,373A discloses fibrous polyamide substrates, such as nylon carpet, having resistance to staining by acid colorants comprising fibrous polyamide substrate having applied thereto (a) a partially sulfonated novolak resin and (b) polymethacrylic acid, copolymers of methacrylic acid, or combinations of said polymethacrylic acid and said copolymers of methacrylic acid.

[0004] U.S Patent No. 3,673,277A relates to articles and coatings made from thermosetting plastics which are manufactured by mixing together polyamides and polycarboxylic acids, followed by heating and forming.


In many commercial applications where polyamides are used, it is desirable to have high mechanical strength, and also, high chemical resistance. Resistance from corrosive chemicals, such as acids, would be of interest in applications.

The problem of poor acid resistance of polyamide materials is solved by providing a polyamide composition comprising a polyhydric alcohol, which upon heat treatment significantly improves the acid resistance without adversely affecting the mechanical properties.

SUMMARY OF THE INVENTION

Accordingly, an object of the present application relates to a heat-conditioned polyamide composition comprising a polyamide resin and a polyhydric alcohol, wherein the polyamide composition is chemically resistant to an acid medium.

In one aspect of the present application, said polyamide composition comprises from 0.1 to 15 % by weight of polyhydric alcohol, relative to the total weight thereof.

In one aspect of the present application, said polyamide composition comprises from 0.25 to 10 % by weight of polyhydric alcohol, relative to the total weight thereof.

In one aspect of the present application, said polyamide composition comprises from 0.5 to 6 % by weight of polyhydric alcohol, relative to the total weight thereof.

In one aspect of the present application, said polyhydric alcohol is chosen from a group consisting of neo-pentyl polyhydric polyol.

In one aspect of the present application, said polyhydric alcohol is chosen from a group consisting of neo-pentyl glycol (NPG), trimethylolpropane, trimethylolethane, pentaerythritol, dipentaerythritol (DPE), tripentaerythritol and tetrapentaerythritol.

In one aspect of the present application, said polyhydric alcohol is dipentaerythritol.

In one aspect of the present application, the polyamide resin is chosen from a group consisting of Nylon 6, Nylon 6,6, Nylon 6,6/6, Nylon 6,12, Nylon 4,6, Nylon 6,10, Nylon 7,
Nylon 10, Nylon 10, 10, Nylon 12, Nylon 12, 12, Nylon 6T, Nylon 6T/6I, Nylon 6T/DT, Nylon MXD-6 and combinations thereof.

[0017] In one aspect of the present application, the polyamide resin is PA66 or PA6.

[0018] In one aspect of the present application, said polyamide composition is preserved in the presence of an acid medium.

[0019] In one aspect of the present application, said polyamide composition is preserved in the presence of an acid medium for at least 1 hour.

[0020] In one aspect of the present application, said polyamide composition is preserved in the presence of an acid medium for at least 24 hours.

[0021] In one aspect of the present application, said polyamide composition is preserved in the presence of an acid medium for at least 100 hours.

[0022] In one aspect of the present application, said polyamide composition is preserved in the presence of an acid medium for at least 250 hours.

[0023] In one aspect of the present application, said polyamide composition is preserved in the presence of an acid medium for at least 500 hours.

[0024] In one aspect of the present application, said polyamide composition is preserved in the presence of an acid medium for at least 750 hours.

[0025] In one aspect of the present application, said polyamide composition is preserved in the presence of an acid medium for at least 1000 hours.

[0026] In one aspect of the present application, the acid medium comprises an organic, an inorganic acid, and mixtures thereof.

[0027] In one aspect of the present application, the acid medium comprises an acid chosen from a group consisting of formic acid, acetic acid, propionic acid, butyric acid, hydrochloric acid, hydrofluoric acid, nitric acid, sulfuric acid, carbonic acid, and mixtures thereof.

[0028] In one aspect of the present application, the acid medium contains formic acid.
In one aspect of the present application, the acid medium contains sulfuric acid.

In one aspect of the present application, an article of manufacture, at least a portion of which is molded from said polyamide composition.

DETAILED DESCRIPTION OF THE INVENTION

Polyamides (nylons) find very many applications in today's engineered plastics and thermoplastics. The most common polyamides used in the textile and plastics industries are polycaproamide (PA6) and polyhexamethyleneadipamide (PA66). These crystalline, aliphatic polyamides are widely used in industrial applications mainly due to their high mechanical strength and rigidity. Applications include carpet and textile fibers, films, laminates, articles and molded parts.

PA66 (or N66) find "under the hood" applications in automotive industry such as radiator end tanks, covers, in-take manifolds, oil pans, and other structural parts such as ball bearing cages, electro-insulating elements, pipes, and various machine parts such as conveyor belts, hoses, etc. Most of these and many other applications require articles and parts to provide high chemical resistance and also high mechanical properties for parts durability. As an example, tubing and pipes, which come in direct contact with the corrosive environment in chemical and petrochemical industries, must be able to withstand corrosiveness, and at the same time, provide sufficient mechanical strength. However, that is not the case at present.

A common industrial problem with these polyamides is that articles and fibers made from polyamides show poor chemical resistance, especially in a corrosive acid environment. For example, a sample of PA6 dissolves in an acidic medium. The drawback of chemical attack on the polyamide is that it undoubtedly compromises the mechanical strength, further increasing its failure probability. Applications with increased failure probability for articles and parts means inferior performance, increased environmental and safety incidents, lost productivity, higher maintenance costs, and overall, an inefficient system and/or operation. A polyamide composition with improved chemical resistance with uncompromised mechanical properties is an unmet need that is satisfied by the present disclosure.
[0034] It has been unexpectedly found that the addition of a polyhydric alcohol to polyamide enhances and improves the chemical resistance after heat treatment. Further, addition of the polyhydric alcohol followed by heat treatment does not adversely affect the mechanical properties of articles and parts molded from the heat-treated polyamide.

[0035] It is possible, for example, to use a polyamide composition comprising from about 0.1 to about 15 % by weight of polyhydric alcohol, relative to the total weight of the composition. In some embodiments, the polyhydric alcohol may be present in an amount from about 0.1 to about 12 % by weight, relative to the total weight of the composition. In other embodiments, the polyhydric alcohol may be present in an amount from about 0.25 to about 10 % by weight, relative to the total weight of the composition. In some other embodiments, the polyhydric alcohol may be present in an amount from about 0.5 to about 8 % by weight, relative to the total weight of the composition. In some embodiments, the polyhydric alcohol may be present in an amount from about 0.5 to about 6 % by weight, relative to the total weight of the composition.

[0036] In some embodiments, a polyamide composition comprising a polyhydric alcohol may contain glass fiber in an amount from about 10 to about 60 % by weight, relative to the total weight of the composition. In other embodiments, a polyamide composition comprising a polyhydric alcohol may contain glass fiber in an amount from about 15 to about 50 % by weight, relative to the total weight of the composition. In some other embodiments, a polyamide composition comprising a polyhydric alcohol may contain glass fiber in an amount from about 20 to about 40 % by weight, relative to the total weight of the composition. A 35 wt% glass fiber filled polyamide composition comprising a polyhydric alcohol may be preferred.

[0037] In an exemplary embodiment of the present application, the polyamide composition further comprises additives such as lubricants, glass fillers, mineral fillers, plasticizers, pigments, dyes, antioxidants, heat stabilizers, hydrolysis stabilizers, nucleating agents, flame retardants, blowing agents and combinations thereof.

[0038] In another embodiment, the mineral fillers are selected from the group consisting of kaolin, clay, talc, and wollastonite, diatomite, titanium dioxide, mica, amorphous silica and combinations thereof.
In another embodiment, the glass fillers are selected from the group consisting of glass fiber, glass flakes, glass beads and combinations thereof.

In another embodiment, the glass fillers are hydrolysis resistant glass fibers coated with a sizing composition and organosilane coupling agents.

In another embodiment, the heat stabilizers are selected from the group consisting of hindered phenols, amine antioxidants, hindered amine light stabilizers (HALS), aryl amines, phosphorus based antioxidants, copper heat stabilizers, etc.

In one exemplary embodiment, the polyamide composition of the present application is formed by adding a polyhydric alcohol and other additives package to a polyamide resin and mixing the polyhydric alcohol, additives and polyamide resin to form an acid-resistant polyamide. Suitable equipment for blending the polyamide resin, polyhydric alcohol and other additives include a twin-screw extruder, melt kneader or batch mixer. The polyamide composition is suitable for compounding or for use as a masterbatch.

Suitable polyamide resins that may be used in the present application include any known polyamides in the art. These include aliphatic, semicrystalline, aromatic or semiaromatic nylon resins. The nylon resins are those prepared from starting materials of essentially a lactam or a diamine, and an aliphatic, semiaromatic or aromatic dicarboxylic acid. Suitable lactams include caprolactam and laurolactam. Suitable amines include tetramethylenediamine, hexamethylenediamine (HMD), 2-methylpentamethylenediamine, undecamethylenediamine, dodecamethylenediamine, 2,4-/2,4,4-trimethylhexamethylenediamine, 5-methylnonamethylenediamine, metaxylylenediamine (MXD), paraxylylenediamine and 2-Memyl-1,5-pentamethylene diamine (MPMD). Suitable dicarboxylic acids such include adipic acid, suberic acid, azelaic acid, sebacic acid, dodecanedioic acid (DDDA), terephthalic acid (TPA), isophthalic acid (IPA), 2-chloroterephthalic acid, 2-methylterephthalic acid, 5-methylisophthalic acid, 5-sodium-sulfoisophthalic acid, hexahydronephthalic acid and hexahydroisophthalic acid. In the present application, nylon homopolymers or copolymers to be derived from those starting materials are used either singly or as their mixtures.

Specific examples of polyamide resins that are suitable for the present application are polycapramide (nylon 6), polyundecanamide (nylon 11), polylauramide (nylon 12),
polyhexamethylenadipamide (nylon 66), polytetramethylenadipamide (nylon 46),
polyhexamethylenesebacamide (nylon 610), polyhexamethylenehexadecamide (nylon 612),
polyhexamethyleneterephthalamide/polycapramide copolymer (nylon 6T/6),
polyhexamethyleneterephthalamide/polydodecanamide copolymer (nylon 6T/12),
polyhexamettylenadipamide/polyhexamethyleneterephthalamide copolymer (nylon 66/6T),
polyhexamethylenadipamide/polyhexamethylenisophthalamide copolymer (nylon 66/61),
polyhexameiiiylenadlpamide/polyhexamethyleneterephthalamide/-polycapramide copolymer (nylon 66/61/6), polyhexameiiiylenadlpamide/polyhexamethyleneterephthalamide /polyhexamethylenisophthalamide copolymer (nylon 66/6T/61), polyhexamethyleneterephthalamide/-polyhexamethylenisophthalamide copolymer (nylon 6T/61), polyhexamethyleneterephthalamide/polydodecanamide/polyhexamethylenadipamide copolymer (nylon 6T/12/66), polyhexamethyleneterephthalamide/polydodecanamide/polyhexamethylenisophthalamide copolymer (nylon 6T/12/61), poly m-xylylenadipamide (nylon MXD6), as well as their mixtures and copolymers, etc.

[0045] Especially preferred are nylon resins suitable for the present application are Nylon 6, Nylon 6,6, Nylon 6,6/6, Nylon 6,12, Nylon 4,6, Nylon 6,10, Nylon 7, Nylon 10, Nylon 10, 10, Nylon 12, Nylon 12, 12, Nylon 6T, Nylon 61, Nylon DT, Nylon DI, Nylon MXD-6 and combinations or copolymers thereof. In another exemplary embodiment of the present application the polyamide resin is Nylon 6,6.

[0046] In some embodiments, the polyhydric alcohol used in the present application may include, but are not limited to, a polyalcohol with more than one hydroxyl (-OH) groups that are attached to carbon in a hydrocarbon chain. In other embodiments, the polyhydric alcohol used in the present application may be chosen from a class of neo-pentyl polyhydric polyols. The neo-pentyl polyhydric polyols may have any suitable number of hydroxyl groups. In one embodiment, the neo-pentyl polyhydric polyl used in the present application may include about 2 or 4 to about 12 or 8 hydroxyl groups. Commercially available polyols of this type are, for example, neo-pentyl glycol (NPG), trimethylolpropane, trimethylolethane, pentaerythritol,
dipentaerythritol (DPE), tripentaerythritol and tetrapentaerythritol. The preferred polyol may be
dipentaerythritol (DPE), although other polyols and mixtures thereof may be used.

[0047] In some embodiments, the polyamides of the present disclosure can be used in
applications where resistance to low-molecular weight organic and inorganic acids is required.
In other embodiments, the polyamides of the present disclosure may be preserved in the presence
of an acid. In one embodiment, the acid may be low-molecular weight, short-chain, linear acid.
In another embodiment, the acid may be from a class of common industrial acids, such as but not
limited to, formic acid, acetic acid, propionic acid, butyric acid, hydrochloric acid, hydrofluoric
acid, nitric acid, sulfuric acid, carbonic acid, etc.

[0048] In one embodiment, a heat-treated (hot air aging at 210°C) polyamide sample of the
present disclosure did not dissolve even after it has been fully immersed in formic acid at room
temperature for extended time.

[0049] Articles and parts, having the desired shape and form, may be produced by applying
conventional molding and forming techniques to the polyamides and polyamide compositions of
the present disclosure. These techniques may include injection molding, blow molding, molding
by extrusion, vacuum or compression forming and like. Therefore, the molded articles or parts
meeting the design specification could be used as engineered thermoplastic pieces in installations
and assemblies. Further, films, laminates and fibers could also be formed and suitably used in
the field of industrial materials and household goods.

[0050] In some embodiments, the polyamide composition of the present disclosure may
comprise one or more other polymers, preferably thermoplastic polymers such as polyamide,
polyester, polyolefin, or ABS.

[0051] In some embodiments, the composition according to the present disclosure may comprise
functional additives that are typically employed during the manufacture. Examples of functional
additives include, but not limited to, lubricants, chain extenders, antifoam agents, flame
retardants, plasticizers, nucleants, modifiers, colorants, catalysts, light and/or heat stabilizers,
antioxidants, antistatic agents, dyes, pigments, matting agents, molding aids and other
conventional additives.
In some embodiments, fillers and additives may be added to the polyamide via conventional means suitable for each additive. These may be added either, before, during or after the polymerization process.

In some embodiments, the polyamide composition of the present application may be heat-conditioned via conventional means, such as but not limited to, conventional oven, vacuum oven, corona treatment, flame treatment, ultrasound methods, electron-beaming, radiation methods, and other industrial methods. In other embodiments, the polyamide composition of the present application may be heat-conditioned by surrounding the polyamide composition with an environment of hot, fluid medium at desired temperature and for set time period. Any fluidic medium may be used so long as it is inert to the polyamide composition.

TEST AND ANALYTICAL METHODS

The following test methods are used for the polyamide property determinations:

ISO 527  determination of tensile strength, tensile modulus, and elongation at break,

ISO 188  Method of heat aging used for test samples

Test sample bars (e.g.: dogbones) are molded using conventional methods and from individual polyamide compositions prepared in each example.

EXAMPLES

A commercially available feedstock of PA6 is compounded with commercially available glass-fiber and used in the below examples.


The polyhydric alcohol, dipentaerythiitol or "DPE" (CioH_{22}O_{7}; Chemical Abstracts Registry Number CAS No. 126-58-9), as used herein, is purchased from Perstorp Holding AB (Sweden). The DPE product data sheet for Charmor™ DP40 is available at the Perstorp

[0059] The formic acid, as used herein, is obtained from EMD Chemicals. A typical composition of the formic acid is 90 % by weight.

[0060] The sulfuric acid, as used herein, is obtained from Sigma Aldrich. A typical composition of the sulfuric acid is 95-98 % by weight.

**Example 1** (comparative)

[0061] A test sample of conventionally heat-stabilized, 35% glass-filled PA66 base resin is heat-conditioned in the presence of air using an oven set temperature 210 °C for 500 hrs and immersed in formic acid. The test sample dissolved completely overnight showing no acid resistance.

**Example 2**

[0062] A test sample of conventionally heat-stabilized 35% glass-filled PA66, comprising a polyhydric alcohol (dipentaerythritol or DPE) in the amount 2 wt% of the total weight of the composition, is heat-conditioned in the presence of air using an oven set temperature 210 °C for 500 hrs and immersed in formic acid. The test sample did not dissolve overnight showing improved acid resistance.

**Example 3**

[0063] A test sample of 35% glass-filled PA6 resin, comprising a polyhydric alcohol (dipentaerythritol or DPE) in the amount 2 wt% of the total weight of the composition, is heat-conditioned in the presence of air using an oven set temperature 210 °C for 500 hrs and immersed in formic acid. The test sample soaked up some free acid and did not dissolve overnight showing improved acid resistance.

**Examples 4-S**

[0064] Individual test samples of conventionally heat-stabilized, 35% glass-filled PA66 base resin, are heat-conditioned as in Example 1. A control sample of the same is not heat-
conditioned and used as is. The samples are exposed to a 1:5 (w:w) sulfuric acid:water medium at room temperature. The mechanical strength of the test sample is measured at 250h, 500h, 750h and 1000h along with the starting unexposed test sample. Table 1 below gives the mechanical strength data for the test samples of these examples.

**TABLE 1**

<table>
<thead>
<tr>
<th></th>
<th>Example 4 (Control)</th>
<th>Example 5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>not heat-conditioned</td>
<td>heat-conditioned</td>
</tr>
<tr>
<td></td>
<td>Exposure time in hrs.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Unexposed</td>
<td>250</td>
</tr>
<tr>
<td>Tensile Strength @ break (MPa)</td>
<td>218.9</td>
<td>171.6</td>
</tr>
<tr>
<td>Elongation @ break (%)</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Tensile Modulus (MPa)</td>
<td>10979</td>
<td>9358</td>
</tr>
</tbody>
</table>

**Examples 6-8**

[0065] Individual test samples of conventionally heat-stabilized 35% glass-filled PA66, comprising a polyhydric alcohol (dipentaerythritol or DPE) in the amount 2 wt% of the total weight of the composition are heat-conditioned in the presence of air using an oven set temperature 210 °C for 500 hrs. A control sample of the same is not heat-conditioned and used as is. The samples are exposed to a 1:5 (w:w) sulfuric acid:water medium at room temperature. Also, individual test samples of 35% glass-filled PA6 resin, comprising a polyhydric alcohol (dipentaerythritol or DPE) in the amount 2 wt% of the total weight of the composition are heat conditioned in the presence of air using an oven set temperature 210 °C for 500 hrs and exposed to the 1:5 (w:w) sulfuric acid:water medium at room temperature. The mechanical strengths of these test samples are measured at 250h, 500h, 750h and 1000h along with the unexposed test samples.
Table 2 represents the mechanical strength comparison for not heat-conditioned and heat-conditioned PA66 test samples along with the data for each of the starting unexposed sample.

**TABLE 2**

<table>
<thead>
<tr>
<th></th>
<th>Example 6 (Control)</th>
<th>Example 7 (Control)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>not heat-conditioned</td>
<td>heat-conditioned</td>
</tr>
<tr>
<td><strong>Unexposed</strong></td>
<td>250 500 750 1000</td>
<td>250 500 750 1000</td>
</tr>
<tr>
<td>Tensile Strength @ break (MPa)</td>
<td>213.8 166.5 151.9 141.9 128.4</td>
<td>234.7 221.7 210.3 203 192.4</td>
</tr>
<tr>
<td>Elongation @ break (%)</td>
<td>3 3 2.9 3 2.9</td>
<td>2.8 3.4 3.3 3.2 3.2</td>
</tr>
<tr>
<td>Tensile Modulus (MPa)</td>
<td>12413 9641 9006 8458 7959</td>
<td>11935 11152 11255 10773 10423</td>
</tr>
</tbody>
</table>

Table 3 represents the mechanical strength comparison for not heat-conditioned and heat-conditioned 35% glass-filled PA6 + DPE test samples versus the Example 6 (Control) test samples. Table 3 also provides the mechanical strength data for each of the unexposed samples.

For the heat-conditioned test samples of Example 8 that are acid-exposed for 1000 hrs, the % Retentions of Tensile Strength at break, Elongation at break and Tensile Modulus show improvements over those of the Example 6 (Control) samples.
In addition, the present application provides articles of manufacture, at least a portion of
which is molded from a polyamide composition comprising a polyamide resin and a polyhydric
alcohol in accordance with the present application.

The present application is illustrated by the above examples. It is to be understood that
the examples are for illustration purposes only and are not used to limit the present application
thereto.

| TABLE 3 |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Example 6 (Control)             | Example 8       |
| not heat-conditioned            | 35% glass-filled PA6 + DPE, heat-conditioned |
|                                 | Exposure time in hrs. | Unexposed | Exposure time in hrs. | Unexposed |
|                                 |                   | 250 | 500 | 750 | 1000 | 250 | 500 | 750 | 1000 |
| Tensile Strength @ break (MPa)  | 213.8 | 166.5 | 151.9 | 141.9 | 128.4 | 227.2 | 194.2 | 177.4 | 163.9 | 145.7 |
| Elongation @ break (%)          | 3 | 3 | 2.9 | 3 | 2.9 | 3 | 3.5 | 3.5 | 3.3 | 3.2 |
| Tensile Modulus (MPa)           | 12413 | 9641 | 9006 | 8458 | 7959 | 13354 | 11068 | 10457 | 9658 | 9326 |
What is Claimed is:

1. A polyamide composition comprising a polyaraide resin and a polyhydric alcohol, said polyamide composition being heat-conditioned and chemically resistant to an acid medium.

2. The polyamide composition of claim 1 wherein the polyamide composition is heat-conditioned by a means selected from the group consisting of a conventional oven, vacuum oven, corona treatment, flame treatment, ultrasound method, electron-beaming, radiation method and industrial method.

3. The polyamide composition of claim 1 wherein the polyamide composition is heat-conditioned by surrounding the polyamide composition with an environment of hot, fluid medium at a selected temperature and for a selected time period.

4. The polyamide composition of claim 1 wherein the polyamide composition is heat-conditioned in the presence of air using an oven set temperature 210°C for 500 hours.

5. The polyamide composition of any of the preceding claims comprising from 0.1 to 15 % by weight of polyhydric alcohol, relative to the total weight thereof.

6. The polyamide composition of any of claims 1, 2, 3 or 4 comprising from 0.25 to 10 % by weight of polyhydric alcohol, relative to the total weight thereof.

7. The polyamide composition of any of claims 1, 2, 3 or 4 comprising from 0.5 to 6 % by weight of polyhydric alcohol, relative to the total weight thereof.
8. The polyamide composition of any of the preceding claims wherein the polyhydric alcohol comprises a neo-pentyl polyhydric polyol.

9. The polyamide composition of any of claims 1, 2, 3, 4, 5, 6, or 7 wherein the polyhydric alcohol is selected from the group consisting of neo-pentyl glycol, trimethylolpropane, trimethyloethane, pentaerythritol, dipentaerythritol, tripentaerythritol and tetrapentaerythritol.

10. The polyamide composition of any of claims 1, 2, 3, 4, 5, 6, or 7 wherein the polyhydric alcohol is dipentaerythritol.

11. The polyamide composition of any of the preceding claims wherein the polyamide resin is selected from the group consisting of: nylon 6; nylon 6,6; nylon 6,6/6; nylon 6,12; nylon 4,6; nylon 6,10; nylon 7; nylon 10; nylon 10,10; nylon 12; nylon 12,12; nylon 6T; nylon 6T/6I; nylon 6T/DT; and nylon MXD-6 and combinations thereof.

12. The polyamide composition of claim 11 wherein the polyamide resin is nylon 6 or nylon 6,6 or a combination thereof.

13. The polyamide composition of any of the preceding claims which is chemically resistant to an acid medium for at least one hour up to at least 1000 hours.

14. The polyamide composition of claim 13 wherein the acid medium comprises an organic acid, an inorganic acid, or a mixture thereof.
15. The polyamide composition of claim 13 wherein the acid medium is selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, hydrochloric acid, hydrofluoric acid, nitric acid, sulfuric acid and carbonic acid and mixtures thereof.

16. An article of manufacture comprising at least a portion molded from the polyamide composition of any of the preceding claims.

17. A method for increasing chemical resistance of a polyamide composition to an acid medium, said method comprising heat-conditioning a polyamide composition comprising a polyamide resin and a polyhydric alcohol.

18. The method of claim 17 wherein the polyamide composition is heat-conditioned by a means selected from the group consisting of a conventional oven, vacuum oven, corona treatment, flame treatment, ultrasound method, electron-beaming, radiation method and industrial method.

19. The method of claim 17 wherein the polyamide composition is heat-conditioned by surrounding the polyamide composition with an environment of hot, fluid medium at a selected temperature and for a selected time period.

20. The method of claim 17 wherein the polyamide composition is heat-conditioned in the presence of air using an oven set temperature 210°C for 500 hours.

21. The method of claims 17, 18, 19 or 20 wherein the polyamide composition comprises from 0.1 to 15 % by weight of polyhydric alcohol, relative to the total weight thereof.
22. The method of claims 17, 18, 19 or 20 wherein the polyamide composition comprises from 0.25 to 10% by weight of polyhydric alcohol, relative to the total weight thereof.

23. The method of claims 17, 18, 19 or 20 wherein the polyamide composition comprises from 0.5 to 6% by weight of polyhydric alcohol, relative to the total weight thereof.

24. The method of any of claims 17, 18, 19, 20, 21, 22 or 23 wherein the polyhydric alcohol comprises a neo-pentyl polyhydric polyol.

25. The method of any of claims 17, 18, 19, 20, 21, 22 or 23 wherein the polyhydric alcohol is selected from the group consisting of neo-pentyl glycol, trimethylolpropane, trimethyloethane, pentaerythritol, dipentaerythritol, tripentaerythritol and tetrapentaerythritol.

26. The method of any of claims 17, 18, 19, 20, 21, 22 or 23 wherein the polyhydric alcohol is dipentaerythritol.

27. The method of any of claim 17, 18, 19, 20, 21, 22, 23, 24, 25 or 26 wherein the polyamide resin is selected from the group consisting of: nylon 6; nylon 6,6; nylon 6,6/6; nylon 6,12; nylon 4,6; nylon 6,10; nylon 7; nylon 10; nylon 10,10; nylon 12; nylon 12,12; nylon 6T; nylon 6T/6I; nylon 6T/DT; and nylon MXD-6 and combinations thereof.

28. The method of claim 27 wherein the polyamide resin is nylon 6 or nylon 6,6 or a combination thereof.
29. The method of claims 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27 or 28 wherein the polyamide composition is chemically resistant to an acid medium for at least one hour up to at least 1000 hours.

30. The method of claim 29 wherein polyamide composition is chemically resistant to an acid medium comprising an organic acid, an inorganic acid, or a mixture thereof.

31. The method of claim 29 wherein polyamide composition is chemically resistant to an acid medium selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, hydrochloric acid, hydrofluoric acid, nitric acid, sulfuric acid and carbonic acid and mixtures thereof.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/053
ADD.

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)
C08K  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 practicable, search terms used)
EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<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>
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</table>

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

* Special categories of cited documents :
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "B" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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Name and mailing address of the ISA/
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Kaul-Buchberger, Eva
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<tr>
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<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
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<tbody>
<tr>
<td>US 2011028628 A1</td>
<td>03-02-2011</td>
<td>BR 112012001747 A2</td>
<td>12-04-2016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 102471530 A</td>
<td>23-05-2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2459639 A1</td>
<td>06-06-2012</td>
</tr>
<tr>
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<td></td>
<td>JP 5647244 B2</td>
<td>24-12-2014</td>
</tr>
<tr>
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<td></td>
<td>JP 2013501095 A</td>
<td>10-01-2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2011028628 A1</td>
<td>03-02-2011</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2011014556 A1</td>
<td>03-02-2011</td>
</tr>
<tr>
<td>US 2010120958 A1</td>
<td>13-05-2010</td>
<td>CN 101735629 A</td>
<td>16-06-2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2010120958 A1</td>
<td>13-05-2010</td>
</tr>
<tr>
<td>US 2014031476 A1</td>
<td>30-01-2014</td>
<td>CN 104684999 A</td>
<td>03-06-2015</td>
</tr>
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<td></td>
<td>DE 112013003661 T5</td>
<td>25-06-2015</td>
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<td>US 2014031476 A1</td>
<td>30-01-2014</td>
</tr>
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<td></td>
<td>WO 2014018738 A1</td>
<td>30-01-2014</td>
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