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(54) Title: A METHOD OF PREPARING A POLYETHERIMIDE COATED SUBSTRATE

(57) Abstract: The invention relates to a method for preparing a polyetherimide coated metal substrate. According to the invention the polyetherimide coated metal substrate is prepared by mixing an aromatic dianhydride or derivative thereof and an aliphatic polyetherdiamine in a water based solution; subjecting the mixture to a first heat treatment to produce a water based solution comprising a polyetherimide intermediate; applying the water based solution comprising the polyetherimide intermediate on the metal substrate; and subjecting the substrate and the water based solution comprising the polyetherimide intermediate thereon to a second heat treatment.



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A METHOD OF PREPARING A POLYETHERIMIDE COATED SUBSTRATE

The present invention relates to a method of preparing a polyetherimide coated substrate, a polyetherimide coated substrate and the use of a polyetherimide coated substrate.

5 The invention further relates to a polyetherimide intermediate.

Uncoated metallic substrates such as steel are known to form iron oxides (rust) when in contact with water, oxygen or other strong oxidants. Further, the presence of salt, for example, in salt water, accelerates the rusting process. One method which is used to protect metallic substrates such as steel from corrosive environments is to provide such substrates with an impervious metallic coating of zinc or zinc/aluminium alloy. Such coatings are however expensive and erode over time due to the capacity of zinc and aluminium to afford cathodic protection.

Organic coatings offer a viable alternative to protect metallic substrates such as steel from environmental degradation, primarily due to their moderate cost and ease of preparation. However, many organic coatings do not provide sufficient corrosion protection and/or contain high concentrations of volatile organic compounds (VOCs) that are of environmental concern.

Due to their thermal, dielectric and mechanical properties, imide-type polymers are being investigated as alternatives to current organic coatings and metallic coatings for the protection of metallic substrates. Polyetherimides are a class of polyimide, which contain both ether and imide linkages along the polymeric backbone. Such polymers have been applied as films, adhesives, paints and moulded articles in the electronics, automotive and aerospace sectors in the past. Polyetherimides are typically obtained by polymerising an aromatic dianhydride and an aromatic diamine to form a high molecular weight polyetherimide intermediate known as polyamic acid. The polyetherimide intermediate is then shaped and subjected to a chemical or thermal treatment to produce the corresponding polyetherimide.

Polyetherimides prepared according to the above method tend to be difficult to process since they possess high glass transition temperatures (T_g) and have limited solubility due to the presence of ordered aromatic groups along the polymeric backbone. As a consequence the above reactions are typically carried out in the presence of polar organic solvents such as N-methyl pyrrolidone, N,N-dimethylacetamide or Dimethylformamide, since these solvents are capable of solubilising the aromatic diamine and/or aromatic dianhydride and the polyetherimide intermediate.

The corrosion resistance and flexibility of polyetherimides is influenced by molecular weight. For instance, a polyetherimide having an increased molecular weight (M_w) typically exhibits improved corrosion resistance and flexibility, whereas polyetherimides having lower molecular weights are less resistant and less flexible by comparison. It is known in the art that the use of organic solvents such as N-methylpyrrolidone (NMP) allows polyetherimides ($M_w = 100,000$) to be prepared and as a consequence such polyetherimides are known to offer superior corrosion resistance and flexibility relative to other protective organic coatings.

Although the use of such polar organic solvents enables high molecular weight polyetherimides to be obtained, their hazardous and toxic nature introduces environmental and safety issues related to the handling and disposal of such solvents. A further disadvantage of using polar organic solvents is that they have a tendency to form complexes with polyetherimides, which upon solvent removal can lead to coating defects through the formation of voids.

It is an object of the present invention to provide a polyetherimide coated substrate wherein the polyetherimide exhibits improved properties such as corrosion resistance, temperature resistance, coating adhesion and coating formability.

It is a further object of the present invention to provide a polyetherimide intermediate having improved solubility and processability.

It is a further object of the invention to provide a method of preparing a polyetherimide intermediate and a polyetherimide coated substrate which is more environmentally friendly and which meets the objects hereinabove.

According to a first aspect of the invention there is provided a method of preparing a polyetherimide coated metal substrate, which comprises the steps of mixing an aromatic dianhydride or derivative thereof and an aliphatic polyetherdiamine in a water based solution; subjecting the mixture to a first heat treatment to produce a water based solution comprising a polyetherimide intermediate; applying the water based solution comprising the polyetherimide intermediate on the metal substrate; and subjecting the metal substrate and the water based solution comprising the polyetherimide intermediate thereon to a second heat treatment.

The inventors observed that even though the polyetherimide intermediate was prepared in a water based solution, the corrosion resistance of the corresponding polyetherimide was comparable to that of a polyetherimide intermediate which had been prepared in an organic solvent such as NMP. As an example, polyetherimide coated steel substrates prepared according to the invention were subjected to a salt spray test (ASTM B117 standard) to investigate their corrosion resistance. After 400hrs no delamination or red rust spots were observed. The polyetherimides prepared according to the above method were found to be amorphous and exhibited improved flexibility relative to polyetherimides which comprise aromatic dianhydrides and aromatic diamines.

The first heat treatment is carried out between 60°C and 120°C to copolymerise the aromatic dianhydride or derivative thereof and the aliphatic polyetherdiamine, thereby forming the polyetherimide intermediate. The water based solution comprising the polyetherimide intermediate is then applied on the metal substrate by roller coating, dipping or spraying. The second heat treatment comprises a drying step and a curing step wherein the polyetherimide intermediate is dried between 60°C and 100°C, preferably between 60°C and 80°C in a convection oven or by using near infrared radiation (NIR). The dried polyetherimide intermediate is then cured between 180°C and 220°C and preferably between 180°C to 200°C in a convection oven or by using NIR. Curing takes place at a pressure of 20 psi or less and preferably at atmospheric pressure. The use of NIR in lieu of a convection oven enables the

drying and curing steps of the second heat treatment to be carried out in seconds rather than in minutes. Advantageously, the use of a two-step approach in the second heat treatment reduces thermal shock and stresses in the polymer upon curing, avoids the formation of solvent bubbles and avoids the entrapment of water and/or organic solvents inside the polymer chains. Another
5 advantage is that the polyetherimide intermediate can be cured at atmospheric pressure, this pressure is lower than the pressures that are typically used when preparing polyetherimides in the presence of water (>20 psi).

According to a preferred embodiment of the invention the water based solution is water. Preferably the aromatic dianhydride and/or the aliphatic polyetherdiamine are water soluble and
10 preferably the aromatic dianhydride is converted into a tetra-acid prior to the first heat treatment. Advantageously, the polyetherimide intermediate thus prepared is water soluble and polyetherimides having a molecular weight in the range of 1000 to 8000 and preferably 5000 to 8000 may be obtained. Since the polyetherimide intermediate is water soluble the use of high temperatures, e.g. above 100°C, to dry the polyetherimide intermediate once it has been
15 applied on the metal substrate are no longer required due to the absence of high boiling point solvents such as NMP; NMP has a boiling point in the range of 202°C to 204°C. Water based solutions wherein the solvent is water have the further advantage of avoiding the environmental and handling issues associated with solutions comprising organic solvents.

According to a preferred embodiment of the invention the water based solution
20 comprises an organic solvent and water, wherein the water content is 50% or above, preferably 80% or above and more preferably 90% or above. Preferably the organic solvent is water soluble and is able to solubilise the aromatic dianhydride, aliphatic polyetherdiamine and the polyetherimide intermediate. Preferably the organic solvent is N-methyl pyrrolidone, N,N-dimethylacetamide or Dimethylformamide. Advantageously the use of a water based solution
25 which comprises a solvent allows polyetherimide intermediates to be obtained which have a molecular weight of 8000 or above, whereas the presence of water in the water based solution reduces the temperature that is required to dry the polyetherimide intermediate following its application on the metal substrate. Water based solutions comprising a water content of 80% or above or 90% or above have the advantage that the environmental and handling issues
30 associated with solutions comprising organic solvents are reduced while the temperatures that are required to dry the polyetherimide intermediate are reduced relative to water based solutions which comprise lower water contents. Since polyetherimides having a molecular weight of 8000 or above may be obtained, it is possible to provide a polyetherimide coated metal substrate in which the polyetherimide coating possesses improved corrosion resistance
35 and flexibility.

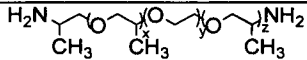
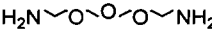
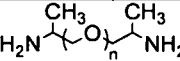
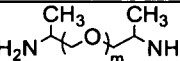
According to a preferred embodiment of the invention the polyetherimide intermediate consists of one or more water soluble aliphatic polyetherdiamines. Preferably, the water soluble aliphatic polyetherdiamine is provided in molar excess relative to the aromatic dianhydride to improve the solubility of the polyetherimide intermediate. Preferably, the molar ratio of aromatic

dianhydride to water soluble polyetherdiamine is 1:1.1 since the use of molar ratios in excess of 1:1.1 reduces the molecular weight of the polyetherimide intermediate thus produced.

Preferably, the water soluble aliphatic polyetherdiamines are soluble in a water based solution which comprises water or water and an organic solvent such as N-methyl pyrrolidone, N,N-dimethylacetamide or Dimethylformamide. Advantageously, the use of a water soluble aliphatic polyetherdiamine increases the water solubility of the polyetherimide intermediate thus produced and enables water based solutions comprising higher water contents to be used.

According to a preferred embodiment of the invention the polyetherimide intermediate comprises a water soluble aliphatic polyetherdiamine and a water insoluble aliphatic polyetherdiamine. Preferably, the aromatic dianhydride is converted into a tetra-acid and then reacted with the water insoluble aliphatic polyetherdiamine in the presence of the water based solution. Preferably, the aromatic dianhydride is provided in molar excess relative to the water insoluble aliphatic polyetherdiamine and preferably the molar ratio of aromatic dianhydride to water insoluble aliphatic polyetherdiamine is 1.1:1. The hydroxyl terminated pre-polymer thus produced is then copolymerised with the water soluble aliphatic polyetherdiamine to form the polyetherimide intermediate having improved corrosion resistance and flexibility.

According to a preferred embodiment of the invention the polyetherdiamine of polyetherimide intermediate is a Jeff amine. A Jeff amine may be defined as a polyether compound which contains at least one primary amino group attached to the terminus of a polyether backbone, wherein the polyether backbone is based either on propylene oxide (PO), ethylene oxide (EO), or mixed EO/PO. Particularly suitable Jeff amines include O,O'-Bis(2-aminopropyl) polypropylene glycol-*block*-polyethylene glycol-*block*-polypropylene glycol (J1), 4,7,10- trioxa-1,13-tridecanediamine (J2), Poly(propylene glycol) bis(2-aminopropyl ether having a molecular weight 230 (J3), Poly(propylene glycol) bis(2-aminopropyl ether having a molecular weight of 400 (J4) and 1,2-bis(2-aminoethoxyethane) (J5). The flexibility of the polyetherimide coating may be increased by selecting Jeff amines having an increased number of ether groups. The selection of Jeff amines reduces the glass transition temperature (T_g) of the polyamic acid intermediate, which enables lower temperatures to be used during the second heat treatment. Jeff amines which have been used in accordance with the invention include:

Jeff amine	Structure	Molecular weight	No of ether linkages
J1		600	~13
J2		220.31	3
J3		230	~3
J4		400	~6
J5		148.20	2

According to a preferred embodiment of the invention the aliphatic polyetherdiamine contains between 2 and 20 ether linkages, preferably between 2 and 13 ether linkages and more preferably between 2 and 6 ether linkages. Advantageously, the inventors have found that the use of aliphatic polyetherdiamines having a higher number of ether groups improved polyetherimide coating flexibility. Moreover, aliphatic polyetherdiamines having a higher number of ether groups also exhibit an improvement in polyetherimide coating adhesion since the oxygen groups act as electron donating Lewis base sites. In contrast, aliphatic polyetherdiamines which possess a lower number of ether groups exhibit a reduction in polyetherimide coating flexibility but an increase in the corrosion resistance of the polyetherimide coating. The use of aliphatic polyetherdiamines in lieu of aromatic polyetherdiamines enables polyetherimide coatings to be obtained having improved flexibility, even if the aliphatic polyetherdiamine has a low number of ether groups.

Advantageously polyetherimides comprising aromatic dianhydrides improve the corrosion resistance and the mechanical properties of the polyetherimide. Aromatic dianhydrides used in accordance with the invention include 3, 3', 4, 4'-Biphenyltetracarboxylic dianhydride (BPDA), pyrometallic dianhydride (PMDA), Benzophenone tetracarboxylic dianhydride (BPTA), 4,4'-Bisphenol A dianhydride (BPADA), 4,4' Oxydiphthalic Anhydride (ODPA) and 4, 4'-(hexafluoro-isopropylidene) diphthalic anhydride (FDA). Dianhydrides such as BPDA, BPTA and BPADA contain very rigid biphenyl structures that improve the corrosion resistance and the mechanical properties of the polyetherimide. The copolymerisation of a dianhydride such as ODPA should result in more adhesive and formable polyetherimides due to the presence of ether groups along the polymeric backbone, whereas the copolymerisation of FDA should lead to a polyetherimide exhibiting improved adhesive properties due to the presence of highly polar fluorine groups which can interact strongly with the metal substrate.

According to a preferred embodiment of the invention the polyetherimide intermediate comprises an epoxy based silane. Preferably, the epoxy based silane comprises methoxy, ethoxy, aryl, acrylic, or vinyl groups. Preferably the epoxy based silane is 3-glycidoxypropyltrimethoxysilane or aminopropyl triethoxysilane.

The polyetherimide intermediates are end-capped with epoxy based silanes by adding up to 30 mol% epoxy based silane to the water based solution comprising the polyetherimide intermediate. It was found that the flexibility of the polyetherimide coating could be improved by adding 20 mol% of epoxy based silane without sacrificing the corrosion resistance of the coating.

Flexibility was assessed by means of an Erickson cup test and a scratch test, the procedures of which are well known in the art. The results of such tests indicated that when the polyetherimide intermediate comprises an epoxy based silane in the range of 10 to 30 mol%, preferably 10 to 25 mol% and more preferably 10 to 20 mol%, the corresponding polyetherimide coating exhibits less than 10% delamination from the metal substrate.

According to a preferred embodiment of the invention the water based solution comprising the polyetherimide intermediate is provided with a metal oxide nanoparticle or a corrosion inhibitor or a halloysite or a mixture thereof. Preferably metal oxide nanoparticles such as silica, titania, magnesia, alumina or carbon nanotubes are used to improve the corrosion resistance, barrier resistance and the conductivity of the polyetherimide coating. Preferably, corrosion inhibitors such as sodium gluconate, sodium benzoate, L-Ascorbic acid, 8-hydroxy quinine, n-benzotriazole, mercaptobenzimidazol mercaptobenzothiazole or derivatives thereof are used to improve the corrosion resistance of the polyetherimide coating. Preferably halloysites are used as nanofillers or as corrosion inhibitor carriers for the controlled release of corrosion inhibitors; such halloysites comprise calcium carbonate, zeolites, barium sulphate, barium phosphate, copper ferrocyanites, carbon nanotubes and kalonites.

Metal nanoparticles including Al, Mg, Zn, Cu, Ni or alloys thereof can also be used to improve the corrosion resistance and the conductivity of the polyetherimide coating. Carbides such as TiC and nitrides such as TiN are also suitable for this purpose.

The metal oxide nanoparticles, corrosion inhibitors, halloysites or mixtures thereof are provided in the water based solution comprising the polyetherimide intermediate and mixed using conventional means that would be familiar to the person skilled in the art, i.e. sonication and/or mechanical stirring. Upon curing the water based solution comprising the polyetherimide intermediate, the metal oxide nanoparticle, corrosion inhibitor, halloysite or mixture thereof become dispersed in the polyetherimide coating that is formed.

According to a preferred embodiment of the invention the metal substrate comprises a steel strip, sheet, wire, rebar or blank. Preferably the steel is a carbon steel, a cold-rolled steel or a hot-rolled steel. Advantageously, the polyetherimide coating is able to interact strongly with the underlying steel substrate through acid-base interactions and/or hydrogen bonding, which leads to an improvement in coating adhesion. Other metal substrates on which the polyetherimide coating may be provided include aluminium, copper, nickel, tin, zinc or brass.

According to a preferred embodiment of the invention the metal substrate comprises a coating selected from the group consisting of zinc, zinc oxide, zinc and aluminium, nickel, magnesium, silane or zirconium. Preferably the metal substrate is pre-treated with zinc, zinc oxide, alloys of zinc and aluminium, magnesium or nickel to improve corrosion resistance, whereas metal substrates pre-treated with silane or zirconium exhibit improved adhesion properties since strong covalent bonds are formed between the polyetherimide and the pre-treated metal substrate surface. Polar groups of the polyetherimide are also able to hydrogen bond with hydroxyl groups of the zirconium or silane coated metal substrate surfaces.

According to a second aspect of the invention there is provided a polyetherimide coated metal substrate which comprises an aromatic dianhydride or derivative thereof and an aliphatic polyetherdiamine. It should be understood that the embodiments and the advantages thereof hereinabove similarly apply to the aromatic dianhydride or derivative thereof, the aliphatic polyetherdiamine, the polyetherimide intermediate and the polyetherimide coated metal substrate of the second aspect of the invention.

Preferably there is provided a polyetherimide coated metal substrate wherein the polyetherimide is resistant to temperatures in the range of 400°C to 500°C. Such a temperature resistance is due to the presence of a polyetherimide pentagonal link which is formed following the steps of drying and curing the polyetherimide intermediate. Advantageously, the inventors
5 found that in addition to the improved temperature resistance of the polyetherimide, an improvement in coating flexibility, coating adhesion and corrosion resistance was also observed.

According to a preferred embodiment of the invention the polyetherimide of the polyetherimide coated metal substrate comprising an aromatic dianhydride or derivative thereof
10 and an aliphatic polyetherdiamine has a dry film thickness in the range of 1-10µm, preferably in the range of 1-5µm and more preferably in the range of 1-3µm. Advantageously, both thick (<10µm) and thin polyetherimide coatings (<5µm) exhibit an improvement in corrosion resistance whereas thin coatings also improve coating performance with respect to weldability and formability. Preferably the polyetherimide of the polyetherimide coated metal substrate has
15 a coating thickness of 10µm or below since with higher thicknesses the polyetherimide may delaminate from the metal substrate.

According to a third aspect of the invention there is provided a polyetherimide intermediate in a water based solution, which polyetherimide intermediate comprises an aromatic dianhydride or derivative thereof and an aliphatic polyetherdiamine. Preferably, the
20 polyetherimide intermediate is prepared in water or in a solution comprising water and an organic solvent. It should be understood that the embodiments and the advantages thereof described hereinabove, similarly apply to the aromatic dianhydride, aliphatic polyetherdiamine and the polyetherimide intermediate of the third aspect of the invention. The method for producing the water based solution comprising the polyetherimide intermediate comprises the
25 steps of:

- a) mixing an aromatic dianhydride or derivative thereof and an aliphatic polyetherdiamine in a water based solution;
- b) subjecting the mixture to a first heat treatment to produce a water based solution comprising the polyetherimide intermediate.

30 The water based solution comprising the polyetherimide intermediate is suitable for use in the first aspect of the invention.

According to a fourth aspect of the invention the polyetherimide coated metal substrate may be used as a layer in a photovoltaic device, preferably an organic photovoltaic device, more preferably a thin film solar cell and even more preferably in a dye sensitised solar cell.
35 Preferably the polyetherimide layer functions as an electrically insulating layer which is also resistant to corrosion and temperatures in the range of 400°C to 500°C. For example, the polyetherimide coated metal substrate could be used in a dye sensitised solar cell having a reverse design, which comprises a working electrode, a counter electrode and an electrolyte disposed there between. Specifically, the polyetherimide coated metal substrate could form the
40 first two layers of the working electrode which further comprises a conductive layer on the

polyetherimide and a dye sensitised metal oxide layer on the conductive layer. Advantageously, the polyetherimide prevents the metal substrate from being corroded by the electrolyte and is able to withstand temperatures in the range of 400°C to 500°C which are typically used to sinter the metal oxide before it is sensitised with the dye.

5 The polyetherimide coated substrate is also suitable for use in the automotive industry where the polyetherimide coating will provide corrosion protection to the underlying steel substrate.

Embodiments of the present invention will now be described by way of non-limiting examples.

10 Examples 1a -1c: In a first experiment an aromatic dianhydride such as 4,4'-Biphtalic Anhydride (97%) (10 mmole, 3.032g) and de-ionised water (80ml) were charged into a 200ml one neck flask having a nitrogen inlet. To this solution was added an aliphatic water soluble polyetherdiamine such as O,O'-Bis(2-aminopropyl)polypropyleneglycol-*block*-polyethylene glycol-*block* polypropylene glycol (J1) (10 mmol, 6.0 g) thereby forming a white suspension.

15 The white suspension was stirred under N₂ at 60 °C for 4 hours until the aromatic dianhydride and J1 were solubilised. This solution was then stirred for a further 8 hours to form a water based solution (100% water) comprising a polyetherimide intermediate (TAW1). The water based solution comprising TAW1 was then roll coated on to a degreased steel substrate and dried at a temperature of 80°C for a period of 5 minutes to remove the water based solution.

20 Following this drying step, the TAW 1 coated steel substrate was cured at a temperature of 200°C for 5 minutes to form the corresponding polyetherimide. Examples 1a -1c relate to polyetherimide coated substrates wherein the polyetherimide has a dry film thickness of 2µm, 5µm and 10µm respectively.

 Example 2a: In a second experiment 10 mmol (3.032g) of 4,4'-Biphtalic Anhydride

25 (97%) and de-ionised water (80ml) were charged into a 200ml one neck flask having a nitrogen inlet. To this solution was added 10 mmol (6.0g) of O,O'-Bis(2-aminopropyl)polypropyleneglycol-*block*-polyethylene glycol-*block* polypropylene glycol (J1) to form a white suspension. The white suspension was stirred under N₂ at 60 °C for 4 hours until the aromatic dianhydride and J1 were solubilised. This solution was then stirred for a further 8

30 hours to form a water based solution (100% water) comprising a polyetherimide intermediate (TAW1). To the water based solution comprising TAW1 2mmol (0.472g) of 3-glycidoxypropyltrimethoxysilane was added and this solution was stirred for a further four hours to form a water based solution comprising polyetherimide TAW1 end-capped with 3-glycidoxypropyltrimethoxysilane (TAW1.1). The water based solution comprising TAW1.1 was

35 then roll coated on to a degreased steel substrate and dried at a temperature of 80°C for a period of 5 minutes to remove the water based solution. Following this drying step, the TAW 1.1 coated steel substrate was cured at a temperature of 200°C for 5 minutes to form the corresponding polyetherimide.

 Example 2b was prepared according to the method of Example 2a except that the

40 polyetherdiamine was provided in molar excess (11mmol) relative to the aromatic dianhydride

(10 mmol). Excess amine was used to ensure that enough amine is available for the further chain extension with epoxy based silane coupling agents.

Example 3a: In a third experiment 14 mmol (4.248g) of 4,4'-Bipthalic Anhydride (97%) and of di-ionized water (80 ml) were charged into a 200ml one neck flask having a nitrogen inlet. This solution was refluxed at 120°C for a period of 2 hours to form a tetra-acid before a water insoluble aliphatic polyetherdiamine such as 2,2'-(Ethylenedioxy)bis(ethylamine) (J5) (10mmol, 1.48g) was added. This solution was then stirred under N₂ at 60 °C 12 hrs. A water soluble polyetherdiamine such as Poly(propylene glycol) bis(2-aminopropyl ether) J3 (4 mmol, 0.92 g) was then added and this solution was stirred for a further four hours to form a water based solution (100% water) comprising a polyetherimide intermediate (TAW2). The water based solution comprising TAW2 was then roll coated on to a degreased steel substrate and dried at a temperature of 80°C for a period of 5 minutes to remove the water based solution. Following this drying step, the TAW 2 coated steel substrate was cured at a temperature of 200°C for 5 minutes to form the corresponding polyetherimide.

Example 3b was prepared according to the method of Example 3a except that the polyetherimide intermediate was dried at 100°C prior to the step of curing the polyetherimide intermediate TAW2.

Comparative example C1 relates to a polyetherimide coated steel substrate wherein the polyetherimide consists of BPDA and 4,4'-(1,3-Phenylenedioxy)dianiline (M1). The polyetherimide of C1 was prepared in 100% organic solvent.

Comparative examples C2-C3 also relate to polyetherimide coated steel substrates. The polyetherimide coating of C2 consists of BPDA, M1, m-phenylenediamine (MPA) and diminobenzoic acid (DABA) whereas the polyetherimide coating of C6 consists of BPDA, M1, MPA and 3,5-diaminophenol. C1-C3 were all prepared in NMP.

The polyetherimide coated substrates were then subjected to a number of tests to assess the corrosion resistance, flexibility and adhesion of the polyetherimide coatings. It is remarked that in previous experiments the assignment of classification category (excellent, good, bad coating performance) was erroneous. The results of the abovementioned tests are shown in Table 1, where a stricter interpretation of excellent, good and bad coating performance has been used.

The thermal stability of the polyetherimide coatings was assessed by thermogravimetric analysis using a Perkin Elmer pyris diamond DMA. Polyetherimide coatings were heated at a rate of 10 °C/min over a temperature range of 25°C to 600°C. Using the same apparatus it was also possible to determine the temperature for 10% weight loss which is a measure of polymer stability. It was found that the polyetherimide coating of Examples 1a, 1b, and 1c exhibited a 10% weight loss at a temperature of 480°C. However, after considering the water loss of imidisation the actual temperature at which 10% weight loss occurs is 410°C.

The Salt spray test (ASTM B117 standard) is used to measure the corrosion resistance of coated and uncoated metallic specimens, when exposed to a salt spray at elevated temperature. Polyetherimide coated steel substrates were placed in an enclosed chamber at 35

°C and exposed to a continuous indirect spray (fogging) of 5% salt solution (pH 6.5 to 7.2), which falls-out on to the coated steel substrate at a rate of 1.0 to 2.0 ml/80cm²/hour. The fogging of 5% salt solution is at the specified rate and the fog collection rate is determined by placing a minimum of two 80 sq. cm. funnels inserted into measuring cylinders graduated in ml.

5 inside the chamber. This climate is maintained under constant steady state conditions. The samples are placed at a 15-30 degree angle from vertical. The test duration is variable. The sample size is 76 x 127 x 0.8 mm, are cleaned, weighed, and placed in the chamber in the proximity of the collector funnels. After exposure the panels are critically observed for blisters, red rust spots and delaminations.

10 Polyetherimide coated steel substrates were deemed to have excellent corrosion resistance if 10% or less of the substrate surface was covered by red rust and/or blisters. Polyetherimide coated steel substrates were deemed to have good corrosion resistance if 11 - 15% of the substrate surface was covered by red rust and/or blisters. Polyetherimide coated steel substrates were deemed to have bad corrosion resistance if greater than 15% of the substrate surface is covered by red rust and/or blisters.

15 Coating flexibility was analysed using an Erichsen cupping test (ISO 20482), which is a ductility test that is typically employed to evaluate the ability of metallic sheets and strips to undergo plastic deformation in stretch forming. Cups were made using 5KN pressure. If no cracks are observed during the Erichsen cupping test then the flexibility of the coating is excellent. If one or more cracks are observed then the flexibility of the coating is bad.

20 Adhesion was evaluated by a scratch tape test (ASTM D 3359), which is a method for assessing the adhesion of coating films to metallic substrates by applying and removing pressure sensitive tape over cuts made in the film. If 5% or less of the coating was removed by the adhesive tape then the adhesion of the coating to the steel substrate is excellent. If 6-15 % of the coating was removed by the adhesive tape then coating adhesion is good, and if the adhesive tape removed greater than 15% of the coating then coating adhesion was bad.

Example	Flexibility	Adhesion	Corrosion resistance	10% wt loss (°C)	Mw	Tg °C
1a	*	**	**	<u>410</u>	1230	65
1b	*	**	***	<u>410</u>	1230	65
1c	*	**	***	<u>410</u>	1230	65
2a	***	***	***	<u>430</u>	2230	90
2b	***	***	***	<u>430</u>	2230	95
3a	*	**	***	<u>380</u>	3800	120
3b	*	*	**	<u>380</u>	3800	120
C1	*	**	**	<u>560</u>	100000	230
C2	***	***	**	<u>515</u>	59000	195
C3	***	***	*	<u>358</u>	209939	204

30 Table 1: Overview of corrosion resistance, flexibility and adhesion properties of polyetherimide coatings on steel substrates, wherein *** is excellent, ** is good, * is bad coating performance.

CLAIMS

1. A method of preparing a polyetherimide coated metal substrate which comprises the steps of:
 - a) Mixing an aromatic dianhydride or derivative thereof and an aliphatic polyetherdiamine in a water based solution;
 - b) subjecting the mixture to a first heat treatment to produce a water based solution comprising a polyetherimide intermediate;
 - c) applying the water based solution comprising the polyetherimide intermediate on the metal substrate;
 - d) subjecting the metal substrate and the water based solution comprising the polyetherimide intermediate thereon to a second heat treatment.
2. A method of preparing a polyetherimide coated metal substrate according to claim 1 wherein the water based solution is water.
3. A method of preparing a polyetherimide coated metal substrate according to claim 1 or claim 2 wherein the water based solution applied on the substrate comprises an organic solvent and water, wherein the water content is 50% or above, preferably 80% or above and more preferably 90% or above.
4. A method of preparing a polyetherimide coated metal substrate according to any one of the preceding claims wherein the polyetherimide intermediate consists of one or more water soluble aliphatic polyetherdiamines.
5. A method of preparing a polyetherimide coated metal substrate according to any one of the preceding claims wherein the polyetherimide intermediate comprises a water soluble polyetherdiamine and a water insoluble polyetherdiamine.
6. A method of preparing a polyetherimide coated metal substrate according to any one of the preceding claims wherein the polyetherdiamine of the polyetherimide intermediate is a polyether compound which contains at least one primary amino group attached to the terminus of a polyether backbone, wherein the polyether backbone is based either on propylene oxide (PO), ethylene oxide (EO), or mixed EO/PO.
7. A method of preparing a polyetherimide coated metal substrate according to any one of the preceding claims wherein the aliphatic polyetherdiamine contains between 2 and 20 ether linkages, preferably between 2 and 13 ether linkages and more preferably between 2 and 6 ether linkages.

8. A method of preparing a polyetherimide coated metal substrate according to any one of the preceding claims wherein the polyetherimide intermediate comprises an epoxy based silane.
- 5 9. A method of preparing a polyetherimide coated metal substrate according to any one of the preceding claims wherein the water based solution comprising the polyetherimide intermediate is provided with a metal oxide nanoparticle or a corrosion inhibitor or a halloysite or a mixture thereof.
- 10 10. A method of preparing a polyetherimide coated metal substrate according to any one of the preceding claims wherein the substrate comprises a steel strip, sheet, wire, rebar or blank
- 15 11. A method of preparing a polyetherimide coated metal substrate according to any one of the preceding claims wherein the substrate comprises a coating selected from the group consisting of zinc, zinc oxide, zinc and aluminium, nickel, magnesium, silane or zirconium.
- 20 12. A polyetherimide coated metal substrate produced according to the method of any one of claims 1-11 wherein the polyetherimide comprises an aromatic dianhydride or derivative thereof and an aliphatic polyetherdiamine.
- 25 13. A polyetherimide coated metal substrate according to claim 12 wherein the dry film thickness of the polyetherimide is in the range of 1-10 μ m, preferably in the range of 1-5 μ m and more preferably in the range of 1-3 μ m.
- 30 14. Use of the polyetherimide coated metal substrate according to any one of claims 12-13 as an electrically insulating layer in a photovoltaic device, preferably and organic photovoltaic device and more preferably in a dye sensitised solar cell.
- 35 15. Method of producing a water based solution comprising a polyetherimide intermediate for use in the method according to any one of claims 1-11 comprising the steps of:
- c) Mixing an aromatic dianhydride or derivative thereof and an aliphatic polyetherdiamine in a water based solution;
- d) subjecting the mixture to a first heat treatment to produce a water based solution comprising the polyetherimide intermediate.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/002810

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G73/10 C09D179/08 B05D3/02 B05D7/14 B05D7/16 H04M3/523 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) C08G C09D B05D 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) EPO-Internal, WPI Data, CHEM ABS Data																	
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>EP 2 070 987 A1 (MITSUBISHI GAS CHEMICAL CO [JP]) 17 June 2009 (2009-06-17) claim 1; example 1 -----</td> <td style="text-align: center; vertical-align: top;">1-12,15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>EP 0 015 720 A1 (M & T CHEMICALS INC [US]) 17 September 1980 (1980-09-17) page 28, line 20 - page 29, line 2; claim 1 -----</td> <td style="text-align: center; vertical-align: top;">12,14</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>JP 2004 162033 A (JSR CORP) 10 June 2004 (2004-06-10) paragraph [0034]; claim 1 -----</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>JP 2006 052268 A (SHIMIZU KK; OSAKA PREFECTURE) 23 February 2006 (2006-02-23) abstract; paragraph [0149]; claim 1 -----</td> <td style="text-align: center; vertical-align: top;">12,13</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	EP 2 070 987 A1 (MITSUBISHI GAS CHEMICAL CO [JP]) 17 June 2009 (2009-06-17) claim 1; example 1 -----	1-12,15	X	EP 0 015 720 A1 (M & T CHEMICALS INC [US]) 17 September 1980 (1980-09-17) page 28, line 20 - page 29, line 2; claim 1 -----	12,14	X	JP 2004 162033 A (JSR CORP) 10 June 2004 (2004-06-10) paragraph [0034]; claim 1 -----	1	X	JP 2006 052268 A (SHIMIZU KK; OSAKA PREFECTURE) 23 February 2006 (2006-02-23) abstract; paragraph [0149]; claim 1 -----	12,13
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Date of the actual completion of the international search 21 October 2011	Date of mailing of the international search report 31/10/2011																
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Glanddier, Anne																

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/002810

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2070987	A1	17-06-2009	CN 101541888 A 23-09-2009
			WO 2008041723 A1 10-04-2008
			KR 20090078786 A 20-07-2009
			US 2010029893 A1 04-02-2010

EP 0015720	A1	17-09-1980	CA 1163742 A1 13-03-1984
			DE 3065230 D1 17-11-1983
			IL 59344 A 15-06-1983
			JP 1511310 C 09-08-1989
			JP 55144026 A 10-11-1980
			JP 63058169 B 15-11-1988

JP 2004162033	A	10-06-2004	NONE

JP 2006052268	A	23-02-2006	NONE
