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(54) **Method of coating a substrate**

(57) A method of coating a substrate comprising the steps of:

providing a substrate;

preparing an inorganic component

preparing an organic component

combining the inorganic component with the organic component prior to application of the mixture on the substrate;

applying the combined inorganic and organic components over the substrate;

exposing the combined inorganic and organic components to a predetermined temperature to cause a reaction between inorganic and organic components so as to produce a network structure of the coating on the substrate.

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Description**FIELD OF THE INVENTION**

[0001] The present invention relates to the field of abrasion-resistant coatings for coil substrates and method for producing coated coil products, in particular, but not exclusively, abrasion-resistant organic-inorganic coatings for coil substrates.

BACKGROUND OF THE INVENTION

[0002] During their production, surfaces of strip or coiled products are exposed to tortuous winding operations, elevated temperatures and corrosive environments, which can impair the performance of the coil while in use in a variety of applications. Therefore, there exists a potent rationale for applying surface treatments to strip or coil substrates principally to enhance engineering, aesthetic and environmental prowess of these products while continuing to utilise cost-effective manufacturing techniques. Surfaces treatments tend to provide improved surface-related properties such as wear, abrasion, fatigue and corrosion resistance, in addition to enhancing handleability and ease of formation of products.

[0003] Recent development work has resulted in the application of protective coating on polymer substrates. For example, polyurethane resins are now considered acceptable for coating plastic materials to impart abrasion resistance because even though the abrasion resistance of such polyurethane coatings is not as good as some siloxane-based coatings, the polyurethane coatings are less expensive.

[0004] Scratch and abrasion resistant coatings have been successfully developed and commercially exploited to protect the surface of transparent plastics from abrasion. In some techniques, an acidic dispersion of colloidal silica and hydroxylated silsesquioxane has been used in an alcohol-water medium to coat substrates such as acrylic lenses to provide an abrasion-resistant coating.

[0005] Moreover, significant research has been undertaken to improve the scratch/abrasion-resistance of ceramic substrates, such as glass, by using acidic aqueous solutions to deposit inorganic coatings

[0006] In contrast to the efforts in improving abrasion/scratch resistant coatings for ceramic or polymer-based substrates, very few coatings which can combine flexibility with hardness have been hitherto reported for metal substrates, in particular, strip products manufactured by coil coating processes. The flexibility of the coating in such applications is imperative to protect the coil from the detrimental consequences of tortuous winding operations during manufacture while the relative hardness of the coating is necessary to impart excellent abrasion or scratch resistance. Such properties have been hitherto imparted to the strip product by applying on its surface either an organic or an inorganic coating.

[0007] Ideally a coil or strip product manufactured in drawing processes requires a coating to be sufficiently flexible to withstand winding operations and have adequate abrasion resistant so as to endure a production environment in which the surface of the coil could be damaged and consequently its properties impaired to intolerant levels.

[0008] The object of this invention is to create a multi-functional coating that can be applied in a single pass utilising existing coating technology. The flexibility of the coating can be achieved by the use of organic materials while the hardness of inorganic materials can improve mechanical properties.

[0009] An object of this invention is to combine inorganic and organic components into one material to provide an organic-inorganic hybrid material. Depending on the mol fraction of the organic and inorganic mol fraction ratio and reaction conditions, the properties can be varied continuously from soft and flexible to brittle and hard materials and thus enable the 'tailoring' of certain properties to form an optimum coating.

[0010] Such multifunctional coatings described in the invention of this patent can be realised by using the *sol-gel* process, wherein inorganic material can be synthesized in organic media at temperatures at which organic compounds are thermally stable. The sol-gel process starts with a colloidal dispersion, or sol, from the hydrolysis and condensation reactions of metal alkoxides such as silicone, aluminium or titanium metal alkoxides. Through subsequent curing (chemical cross-linking, electrostatic destabilisation, solvent evaporation or some combination), the sol may be transformed into a rigid gel, which could be shaped into different forms such as films, monoliths, or fibres.

[0011] Due to the nature of the coatings (transparent, hard yet flexible), it is perceived that the ideal application is within the domestic appliance and consumer goods sector.

[0012] Hence, domestic appliance polyesters where excellent flexibility is important, and co-laminated products where excellent abrasion resistance, were selected as benchmarks. The aim is to combine the flexibility of the domestic appliance polyester with hardness.

[0013] No cross-linking agents have been hitherto known for a coil coating process, which requires moderately high temperatures but very short residence times, for example, an object temperature of 232° C with a residence time of 35 seconds.

[0014] The use of *sol-gel* coatings for coil-coating applications has previously been avoided due to their long curing times and poor flexibility caused by the build up of intrinsic coating stresses and rigidity of inorganic content. With this

development of the coatings of this invention, it has been seen that the final product combines the hardness associated with harder co-laminated products with a similar flexibility to DA polyesters.

[0015] The invention addresses the disadvantages and deficiencies of organic or inorganic protective coatings alone, and provides an abrasion-resistant flexible coating for a variety of substrates. The hybrid coating composition has one inorganic compound of hydrolysed glycidoxymethyltrialkoxysilane, an organic compound selected from the group consisting of modified diamine, and a curing agent. It is preferred that the inorganic compound is alkylsilane with an epoxy group. The composition is coated to the primed non-primed metal substrate and then thermal cured to constitute an abrasion resistant but flexible coating film. The flexibility of the hybrid coating is controlled by the molar ratio between the organic and inorganic compound.

SUMMARY OF THE INVENTION

[0016] It is an object of the invention to provide a hybrid abrasion resistant and flexible coating having excellent corrosion and mechanical properties.

[0017] It is an object of the invention to provide an abrasion resistant coating for coil products.

[0018] It is a further object of the invention to provide a fast cured hybrid durable coating which can be fabricated at moderate temperatures, much lower than the conventional high temperatures required for processing inorganic materials.

[0019] In a first aspect of the invention there is provided:

a method of coating a substrate comprising the steps of:

providing a substrate;

preparing an inorganic component

preparing an organic component

combining the inorganic component with the organic component prior to application of the mixture on the substrate;

applying the combined inorganic and organic components over the substrate;

exposing the combined inorganic and organic components to a predetermined temperature to cause a reaction between inorganic and organic components so as to produce a network structure of the coating on the substrate.

[0020] Preferably, the inorganic component is selected from a group comprising hydrolysed silanes, and preferably the organic component is selected from a group comprising modified di-amines.

[0021] Advantageously, preparing the inorganic component and the organic component includes weighing the appropriate fractions of each components.

Preferably the step of combining the inorganic and the organic components includes mechanical stirring preferably magnetic stirring of the components.

[0022] Advantageously, the step of applying the combined inorganic and organic components over the substrate is achieved by draw bar coating the components as a film having a pre-determined thickness.

[0023] In a preferred embodiment of the invention the step of preparing the inorganic component is undertaken by hydrolysing glycidoxymethyltrialkoxysilane (GPS) alone.

[0024] Preferably the step of hydrolysing GPS is undertaken in combination with other silanes.

[0025] Preferably the step of hydrolysing GPS is undertaken in combination with colloidal silica nanoparticles.

[0026] Advantageously the step of preparing the organic component includes endcapping ethanolamine to a bisphenol A diglyoxygl ether compound to produce a modified amine. This includes difunctional amine to a diglycidyl ether compound to produce a modified amine. Typical difunctional amines are ethanolamine, propylamine and ethylamine, cyclohexanamine etc. Typical difunctional diglycidyl ethers are bisphenol A diglycidyl ether.

[0027] Preferably, the molar ratio of the ethanolamine (diamine) to a bisphenol A diglyoxygl ether (diglycidyl ether) compound is from 2:1 to 2:1.6

[0028] Preferably, the molar ratio of the ethanolamine (diamine) to a bisphenol A diglyoxygl ether (diglycidyl ether) compound is 2:1.1.

[0029] Advantageously, the step of exposing the inorganic and organic components is undertaken at a predetermined temperature ranging from 80°C to 280°C, for a period typically around 30 seconds to 30 minutes, preferably hot air or current or IR lamp is used to heat the substrate.

[0030] Preferably, the step of exposing the inorganic and organic components leads to a metal peak temperature of between 160° C to 234° C.

[0031] Advantageously, method can be applied for coating a strip product.

Advantageously, method can be applied for coating a coil product.

[0032] Preferably the combined inorganic and organic components are applied using the draw bar method

DETAILED DESCRIPTION OF THE INVENTION

[0033] Embodiments of the present invention will now be described, by way of example only with reference to experiments performed as described hereunder.

[0034] The organic/inorganic hybrid coatings relating to this invention are provided for in the context of a two-pack system produced by sol-gel processing, both of which will be described hereunder with reference the drawings indicated above.

[0035] The hybrid coating are to be applied to primed or unprimed steel strips. Substrates that can have improved abrasion resistance using the above coatings in accordance with this invention include a variety of plastic substrates, including polycarbonate and acrylic, and non-plastic substrates.

[0036] In accordance with this invention, the abrasion resistant hybrid coating composition comprises an inorganic component ("Component A") and an organic component ("Component B") and each can be prepared in the following manner. Preparation of the inorganic component is undertaken by hydrolysing glycidoxylalkyltrialkoxysilane alkylalkoxysilane (GPS) alone, or in combination with other silane or colloidal silica nanoparticles.

[0037] The organic component is a modified amine prepared by endcapping ethanolamine to a bisphenol A diglyoxygl ether compound (difunctional amine to a diglycidyl ether compound) at molar ratio of 2:1.1. This includes difunctional amine to a diglycidyl ether compound to produce a modified amine. Typical difunctional amines are ethanolamine, propylamine and ethylamine, cyclohexanamine etc. Typical difunctional diglycidyl ethers are bisphenol A diglycidyl ether.

[0038] The molar ratio between the glycidoxyl group from silane and the amino group from modified amine ranges between 1:0.5 and 2:1.

[0039] The weight ratio between GPS and other silane from 1:0 to 1:1 can be used, but could preferably be extended to 1:2.

[0040] Hydrolysed silane and silane-silica solution forms component A of the formulation, while an organic component forms component B of the formulation. To prepare the hybrid coating before applying it to the substrate, the required amount of component A and component B are weighed to the desired amounts and magnetically stirred before being draw bar coated onto the substrate. In accordance with this invention the substrate may be primed or non-primed steel and should be cleaned with acetone prior to application of the coating.

[0041] The two components are mixed together just before being coated to the substrate. Once the coating is applied using the draw bar method of this invention, the coated material is placed in a chamber in which the wet film may be heated in the temperature range from 80°C to 280°C, for a period typically around 30 seconds to 30 minutes.

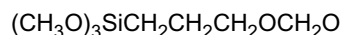
[0042] In a first experiment the composition of the hybrid 2-pack coating comprising:

- i) component A being a hydrolysed γ aminopropyltrimethoxysilane (γ APS, amino silane) sol and*
- ii) component B being a bisphenol A diglycidyl ether-ethanolamine-bisphenol A diglycidyl ether (BPADGE -EOA-BPADGE). This modified di-epoxide heated in the temperature range from 80°C to 280°C, for a period typically around 60 seconds to 30 minutes.*

[0043] In a second experiment the composition of another hybrid 2-pack coating comprising:

- i) component A being a hydrolysed γ glycidylpropyltrimethoxysilane (γ GPS, epoxy silane) solution and*
- ii) component B being ethanolamine-bisphenol A diglycidyl ether-ethanolamine (EOA-BPADGE- EOA). This is a modified di-amine heated in the temperature range from 80°C to 280°C, for a period typically around 30 seconds to 30 minutes.*

[0044] The formula below shows the structure of the glycidoxylalkyltrialkoxysilane alkylalkoxysilane molecule



[0045] In the above first and second experiment 2-pack coatings, other amines such as propylamine and other epoxies such as glycerol diglycidoxyl ether could be used to make the modified amine.

[0046] During thermal curing, a silicate network is formed by the condensation reaction of hydrolysed silane, with the network providing the desired mechanical property of the coating, in particular, the abrasion resistance. Organic component participates in the network formation by the reaction of the glycidoxyl group and amino group. The level of organic (the molar ratio between glycidoxyl group and amino group) in the composition controls the degree of flexibility of the hybrid coating.

[0047] Measurements to characterise the coating included coating thickness, Taber abrasion resistance testing and T-bend testing. The former giving an indication of the performance of the hybrid coating in an abrasive environment while the latter giving an indication of the flexibility of the hybrid coating. Coating thickness on the substrate can be

measured by permascope or borascopy techniques and was determined to lie in the range between 6-10 μm . The abrasion resistance was undertaken by Taber abrasion testing while the flexibility of the coatings was determined using the T-bend test. Abrasion resistance was measured by ECCA T16 [1999] Taber abrasion testing using CS10 Calibrase wheels and 1000g weights on the abraser arms for 250 cycles. In T-bend test, the substrate is wrapped around itself to form a "swiss-roll" configuration, the result being quoted in "T" value and represents the minimum bend radii at which point film failure (in the form of cracking or delamination) does not occur. Half T is the equivalent of one thickness of substrate.

[0048] The physical properties of the first and second experiment coatings are shown in Table 1 below. As an indication of the improvements in abrasion resistance and flexibility of the new coatings, the results are compared with abrasion resistance and flexibility T-bent tests conducted on domestic appliance polyester and co-laminated products.

Table 1. Physical Properties

	Abrasion resistance: Taber	Flexibility: T-Bend
DA Polyester	19mg	1 T
Model coating 1	0.7-0.8mg	2T
Model coating 2	a) 0.1mg b) 0.9mg	a) 4T b) 2T

[0049] The first and second experiment coatings above were tested using salt spray tests, which demonstrated that the coatings act as a good physical barrier against corrosion, but will not prevent or slow down the corrosion reaction, as corrosion inhibitors have not been included within the formulation.

[0050] The tests demonstrated that the inorganic-organic hybrid coating in accordance with the invention combines excellent abrasion resistance with an acceptable flexibility. It can be seen that by altering the mix of the inorganic-organic components, a wide range of properties can be achieved. For example, it may be possible to increase the flexibility of the coating but with a subsequent reduction in the abrasion resistance. The flexibility of the coating is quite important especially where it is applied on substrates such as coils. In particular flexibility of the coating is paramount where the substrate coils are subjected to moderate to aggressive manufacturing environments in which they are tortuously and repetitively wound before being mounted on the end product.

[0051] The invention clearly demonstrates that two series of two-pack *sol-gel* hybrid coatings can be produced which have an excellent combination of abrasion resistance, flexibility and fast curing times. Coatings can be cured at a PMT of 160°C, and more significantly, there is no impact on physical properties from over-curing. In the Taber abrasion resistance test, most novel compositions of the coatings of this invention had a mass loss of 0.1-0.9 mg per 250 cycles but coatings with a mass loss as low as 0.3 mg after 500 cycles have been produced. The flexibility is 2T (4T for the harder coatings) in T-bend test and can be better than 16J in reverse impact tests (move this above).

[0052] The use of modified amine(s) and the proportions described herein are novel in accordance with this invention. Further, the general use and preparation method of the inorganic component (hydrolysed silane) is well known to the skilled addressee in this field and will not be described herein. Traditional multi-functional amine has been used but leads to a hard and rigid coating.

[0053] It is the combination of the inorganic and organic compounds that forms a hybrid network on the surface of the substrate. The level of organic component controls the flexibility of the coating. If the organic component is taken away, the conventional sol-gel coating will be formed, which is hard and rigid and may not be useful for coating coil or strip products.

[0054] The molar ratio between the glycidoxyl group from silane and the amino group from modified amine ranges between 1:1 and 2:1. To endcap the epoxy by amine, a molar ratio between epoxy and amine group of 1:2 is used at the moment. Another ratio such as 1:1.5 could also be used. The weight ratio between GPS and other silane from 1:0 to 1:1 has been used, but could be extend to 1:2.

[0055] The new hybrid coatings have combined the hardness of a co-laminate and the flexibility of DA polyester. Further, salt spray test results have shown that hybrid coatings can act as a physical barrier and can give good corrosion protection to galvanised steel substrates.

[0056] The skilled addressee will appreciate that the coating compositions and the coating method of this invention may be equally have compositions different from that used in the above experiments. Further, it will be apparent to the person skilled in the art that variations and modifications can be made to the embodiments described herein without departing from the scope of the invention.

Claims

1. A method of coating a substrate comprising the steps of:

5 providing a substrate;
preparing an inorganic component
preparing an organic component
combining the inorganic component with the organic component prior to application of the mixture on the sub-
strate; applying the combined inorganic and organic components over the substrate;
10 exposing the combined inorganic and organic components to a predetermined temperature to cause a reaction
between inorganic and organic components so as to produce a network structure of the coating on the substrate.

2. Method as claimed in claim 1 wherein the inorganic component is selected from a group comprising hydrolysed
silanes.

3. Method as claimed in claim 1 or 2 wherein the organic component is selected from a group comprising modified di-
amines.

4. Method as claimed' in any preceding claim wherein the step of preparing the inorganic component and the organic
component includes weighing the appropriate fractions of each components.

5. Method as claimed in any preceding claim, wherein the step of combining the inorganic and the organic components
includes mechanical stirring preferably magnetic stirring of the components.

6. Method as claimed in any preceding claim wherein the step of applying the combined inorganic and organic com-
ponents over the substrate is achieved by draw bar coating the components as a film having a pre-determined
thickness.

7. Method as claimed in any preceding claim wherein the step of preparing the Inorganic component is undertaken by
hydrolysing glycidoxymethyltrialkoxysilane (GPS) alone.

8. Method as claimed in claim 7, wherein the step of hydrolysing GPS is undertaken in combination with other silanes.

9. Method as claimed in claim 7 or 8 wherein the step of hydrolysing GPS is undertaken in combination with colloidal
silica nanoparticles.

10. Method as claimed in claims 1 to 6 wherein the step of preparing the organic component includes endcapping
ethanolamine to a bisphenol A diglyoxygl ether compound to produce a modified amine.

11. Method as claimed in claim 10 wherein the molar ratio of the ethanolamine to a bisphenol A diglyoxygl ether (diglycidol
ether) compound is in the range from 2:1 to 2:1.6.

12. Method as claimed in claim 11 wherein the molar ratio of the ethanolamine to a bisphenol A diglyoxygl ether (diglycidol
ether) compound is 2:1.1.

13. Method as claimed in any preceding claim wherein the predetermined temperature is ranging from 80°C to 280°C,
for a period typically around 30 seconds to 30 minutes.), preferably hot air or current or IR lamp is used to heat the
substrate.

14. Method as claimed in any preceding claim wherein the step of exposing the inorganic and organic components
leads to a metal peak temperature of between 160 C to 234 C.

15. Method as claimed in any preceding claim wherein the combined inorganic and organic components are applied
using the draw bar method.

16. Method as claimed in any preceding claim wherein the combined inorganic and organic components are produced
using sol-gel processing.

17. Method as claimed in claims 1-16 for coating a strip product.

18. Method as claimed in claims 1-16 for coating a coil product.

5 **19.** Method as claimed in claim 17 or 18, wherein the product is mounted on an article.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 06 02 2490

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