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(54) Titre : REVETEMENTS CONDUCTEURS TRES RESISTANTS A L'USURE, PROCEDE PERMETTANT DE LES PRODUIRE ET LEUR UTILISATION

(54) Title: CONDUCTIVE COATINGS WHICH ARE HIGHLY RESISTANT TO ABRASION, METHOD FOR THE PRODUCTION AND USE THEREOF

(57) Abrégé/Abstract:
The invention relates to coatings on moulded bodies, said coatings being conductive and highly resistant to abrasion, comprising at least one conductive layer and at least one layer which is highly resistant to abrasion. The invention also relates to a method for the production and use thereof.

Abstract

The invention relates to coatings on moulded bodies, said coatings being conductive and highly resistant to abrasion, comprising at least one conductive layer and at least one layer which is highly resistant to abrasion. The invention also relates to a method for the production and use thereof.

30771-214

Conductive coatings which are highly resistant to abrasion, method for the production and use thereof

The invention relates to conductive, highly abrasion-resistant coatings on shaped bodies, which coatings comprise at least one conductive layer and at least one highly abrasion-resistant layer, and also to a process for producing them and to their use.

Conductive coatings based on polyethylenedioxythiophene (PEDT) are already used in a broad range of applications, for example for antistatic treatment of photographic films. Numerous methods for producing such conductive coatings have been described. In principle, either the PEDT mixed with a binder is applied or a multilayer structure is chosen; the latter has the advantage that the binder and the PEDT do not have to be compatible (miscible).

WO 96/05606 describes conductive and scratch-resistant multilayer structures for coating picture tubes. Scratch-resistant layers, for example silicon dioxide obtained by hydrolysis and condensation of tetraethyl orthosilicate, are applied to a conductive PEDT layer. Here, the layer thickness is limited to 50 – 250 nm. An alternative method described is to produce scratch-resistant layers comprising inorganic/organic hybrid materials, which can be applied in a thickness of 10 µm and more to the conductive layer. These hybrid materials are based on trialkoxysilanes of the formula $R'\text{-}Si(OR)_3$, where R' is a polymerizable group. However, the multilayer structures described in WO 96/05606 have a number of significant disadvantages:

- As a result of the application of one of the scratch-resistant layers described, no appreciable conductivity is then measurable at the surface of the multilayer structure.

- Although good scratch resistance has been found (measured by determination of the pencil hardness), the abrasion resistance of the coatings is low.

- High curing temperatures, 160°C in the examples.

Antistatic multilayer structures in which the uppermost (scratch-resistant) layer, too, has to have a certain conductivity or multilayer structures having glass-like abrasion resistance can thus not be produced. Furthermore, curing temperatures of 160°C cannot be employed for coating most plastics (softening).

Conductive coatings for transparent substrates, e.g. plastics or glass, have to retain their optical properties unimpaired under mechanical stress and must therefore have a high abrasion resistance. WO 98/25274 describes mixtures which give firmly adhering, conductive coatings having improved scratch resistance and transmission of visible light. These mixtures comprise a binder based on polyfunctional organo-sil(ox)anes and a conductive organic polymer, as are known from WO 98/25274 and EP-A 0 947 520. The binders described comprise heterometals such as boron or aluminum and have a particularly good abrasion resistance.

In EP-A 0 947 520, it is stated that these binders are sensitive to the addition of water, so that, for example, the processing time of these mixtures is significantly reduced by the addition of PEDT in the customary commercial form (Baytron®P, about 1.3% strength dispersion of PEDT and polystyrenesulfonate in water). Furthermore, the addition of PEDT to the binder often leads to a decrease in the abrasion resistance, and even in the case of highly abrasion-resistant coatings this decrease is clearly noticeable.

The present invention provides conductive surfaces which have a highly abrasion-resistant coating and in whose production the above-mentioned disadvantages are avoided.

In one aspect of the invention, there is provided a conductive and highly abrasion-resistant coating, comprising: (a) a first layer comprising an electrically conductive polymer; and (b) a second layer comprising a highly abrasion-resistant layer of a polyfunctional organosiloxane comprising a cyclic carbosiloxane, wherein the coating is on a substrate of a multi-layer structure.

In a further aspect of the invention, there is provided a process for making a conductive and highly abrasion-resistant coating, comprising a conductive and highly abrasion-resistant coating, comprising: (i) a first layer comprising an electrically conductive polymer, and (ii) a second layer comprising an applied highly abrasion-resistant layer of a polyfunctional organosiloxane comprising a cyclic carbosiloxane, wherein the coating is on a substrate of a multilayer structure, and wherein the process comprises: (a) applying the first layer in a first stage on the substrate; and (b) subsequently applying the second layer in a second stage.

It has now surprisingly been found that a multilayer structure comprising at least one conductive layer and at least one highly abrasion-resistant layer on a substrate (shaped body) has a measurable electrical conductivity on the surface of a shaped body even though the uppermost, highly abrasion-resistant layer is a good electrical insulator.

The present invention accordingly provides a conductive and highly abrasion-resistant multilayer coating on a substrate, characterized in that an electrically conductive polymer is applied in a first layer and a highly abrasion-resistant layer of polyfunctional organosil(ox)anes is applied in a second layer.

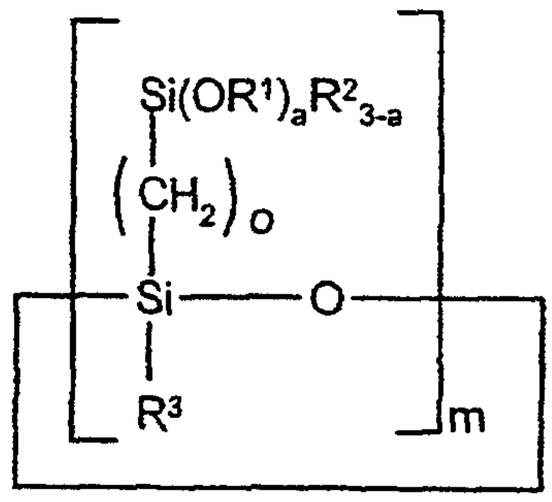
The shaped bodies coated according to the invention have a measurable electrical conductivity at the surface, even though the highly abrasion-resistant layer is a good insulator. The abrasion resistance of the multilayer structure of the invention (according to the Taber Abraser test) is similar to that of glass and curing can advantageously be carried out at temperatures below 160°C.

The present invention further provides a process for producing conductive and highly abrasion-resistant coatings, in which a conductive layer is applied by wet chemical methods in a first step and a highly abrasion-resistant layer is subsequently applied by wet chemical methods in a second step.

Highly abrasion-resistant coatings for the purposes of the invention are ones which after scratching in the Taber Abraser test (determined in accordance with ASTM D 1044, 1000 cycles, 500 g loading per wheel, CS-10-F stones) display light scattering on the scratch trace (determined in accordance with ASTM D 1003) of less than 20%, preferably less than 10%, particularly preferably less than 5%. In comparison, commercial Makrolon®, for example, displays light scattering of more than 30% on the scratch trace after only 100 cycles in the Taber Abraser test. Glass displays light scattering of about 1-3% after 1000 cycles in the Taber Abraser test.

For the purposes of the invention, polyfunctional organosil(ox)ane are linear, branched or cyclic monomeric organosil(ox)anes which have at least two silicon atoms bearing hydrolyzable and/or condensation-crosslinking groups, with each of the silicon atoms being joined to one another via a linking structural unit having at least one carbon atom. Examples of polyfunctional organosil(ox)anes may be found, for example, in EP-A 0 947 520. The preparation of aluminum- and boron-containing sol-gel condensates from which coatings having particularly high abrasion resistance can be obtained is also described there.

Highly abrasion-resistant coatings are preferably produced using sol-gel materials based on cyclic carbosiloxanes of the formula (I),



(I)

where

m = 3 to 6, preferably m = 3 or 4,

o = 2 to 10, preferably o = 2

and

a = 1 to 3,

R^1 = C_1-C_6-alkyl, C_6-C_{14}-aryl, preferably R^1 = methyl, ethyl, isopropyl, and R^1 may also be hydrogen when a = 1, and

R^2 = C_1-C_6-alkyl, C_6-C_{14}-aryl, preferably R^2= methyl and

R^3 = C_1-C_6-alkyl, C_6-C_{14}-aryl,

preferably R^3 = methyl, ethyl and particularly preferably R^3 = methyl,

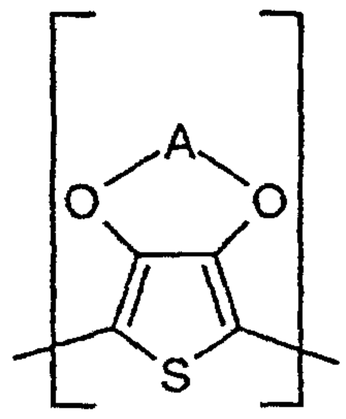
which display not only high mechanical strength but also good weathering stability.

As stated in WO 98/52992 and US-A 6,005,131, the cyclic carbosiloxanes are cocondensed with tetraalkoxysilanes, organotrialkoxysilanes and/or nanosize

particles; as shown in EP-A 0 947 520, the presence of aluminum alkoxides or boron alkoxides has a favorable effect on the abrasion resistance of the coatings produced from the condensates.

Conductive coatings have, for the purposes of the invention, a surface resistance of from 0.1 to 10^{12} Ω/□.

As conductive layer, preference is given to using polythiophene preparations as are described in DE-A 42 11 459, EP-A 339 340 and EP-A 440 957. They comprise polythiophene salts of the polythiophene^{m+} An^{m-}(≙ polyanion) type, where the polythiophene cation polythiophene^{m+} comprises positively charged units of the formula (II),



(II)

where

A is an unsubstituted C_1-C_4-alkylene radical or a C_1-C_4-alkylene radical substituted by C_1-C_{20}-alkyl, -CH_2-OH or C_6-C_{14}-aryl groups. The number of units in the polythiophene cation can be from 5 to 100.

Examples of polyanions which can be used according to the invention are the anions of polymeric carboxylic acids such as polyacrylic acids, polymethacrylic acids, polymaleic acids, and also anions of polymeric sulfonic acids such as polystyrene-sulfonic acids and polyvinylsulfonic acids. These polycarboxylic acids and polysulfonic acids can also be copolymers of vinylcarboxylic acids and vinylsulfonic acids with other polymerizable monomers such as acrylic esters and styrene.

The mean molecular weight M_w of the polymeric acids from which the polyanions used according to the invention are derived is from 1,000 to 2,000,000, preferably

from 2,000 to 500,000. The polymeric acids or their alkali metal salts are commercially available or can be prepared by known methods, as are described, for example, in Houben-Weyl: "Methoden der organischen Chemie", Vol. E20 "Makromolekulare Stoffe", Part 2, p. 1141 ff.

In the multilayer structure produced according to the invention, a distinction has to be made between the conductivity of the PEDT-containing layer as such and the conductivity of the uppermost, highly abrasion-resistant coating. Since the latter is an electrical insulator, the conductivity of the total layer structure is naturally smaller than that of the underlying PEDT layer(s).

The simplest layer structure produced according to the invention comprises the substrate, a PEDT-containing layer and a highly abrasion-resistant covering layer.

In one embodiment of the present invention, conductive and abrasion-resistant surfaces on shaped bodies are obtained by firstly applying a PEDT-containing layer to the substrate and, if appropriate, vaporizing volatile constituents such as solvents. With or without further curing, the highly abrasion-resistant layer is then applied and finally cured thermally or by irradiation.

In a further embodiment of the present invention, the surface of the substrate is treated chemically with an adhesion promoter or physically (plasma, corona) prior to application of the conductive layer in order to achieve improved adhesion. This is of particular impotence in the case of plastics, but may also be necessary in the case of, for example, glass. Moreover, it is also possible to mix the adhesion promoter into the PEDT-containing solution, thus avoiding an additional coating step.

Furthermore, it is possible to provide the wet-chemically produced multilayer structure of the invention with a final inorganic layer, for example of SiO_2, TiO_2 or Al_2O_3, deposited from the gas phase. The wear resistance can be increased further or the antireflective action can be improved in this way.

The application of the conductive and highly abrasion-resistant layer can be carried out by all customary techniques, e.g. spin coating, spraying, dipping, casting, doctor blade coating or brushing.

As substrates which can be provided with the multilayer structure of the invention, mention may be made of metals, ceramics, wood, glass and plastics such as polycarbonate.

The surfaces provided with a conductive and highly abrasion-resistant coating which are prepared according to the invention are used, for example, as low-radiation VDU screens (electrical resistance of the PEDT layer less than 1000 Ω/□) or as antistatic and abrasion-resistant plastics, e.g. in the form of films, extruded or injection-molded shaped bodies. Polycarbonate in particular can be protected against mechanical damage and electrostatic charging in this way.

Examples

All percentages are by weight and based on the total amount of all components used.

To produce the conductive layer ("CPP 105"), use was made of a mixture comprising 42.92% of Baytron® P, 2.58% of N-methyl-2-pyrrolidone, 0.86% of Silquest® A 187 and 53.64% of isopropanol. Baytron® P (Bayer AG, Leverkusen) is an approximately 1.3% strength dispersion of polyethylenedioxythiophene and polystyrenesulfonate in water.

Production of the scratch-resistant layer I from sol-gel solution I

The scratch-resistant layer I was produced from the sol-gel solution I comprising 6.8% of *cyclo*-$\{SiOCH_3[(CH_2)_2Si(CH_3)_2OH]\}_4$, 32.1% of tetraethyl orthosilicate, 9.6% of aluminum 2-butoxide, 5.1% of ethyl acetoacetate, 12.6% of 0.1 N aqueous p-toluenesulfonic acid solution, 32.8% of 1-methoxy-2-propanol and 1% of Tinuvin® 384; the method of production is described in EP-A 0 947 520.

Cyclo-$\{SiOCH_3[(CH_2)_2Si(CH_3)_2OH]\}_4$ was prepared as described in US-A 5,880,305.

Production of the scratch-resistant coating II from sol-gel solution II

The scratch-resistant coating II was produced from the sol-gel solution II which had been prepared as follows: a mixture of 12.7% of *cyclo*-$\{SiOCH_3[(CH_2)_2Si(CH_3)(OEt)_2]\}_4$ oligomer, 26.6% of tetraethyl orthosilicate and 33.3% of 1-methoxy-2-propanol was hydrolyzed with 7.0% of 0.1 N aqueous p-toluenesulfonic acid solution while stirring; after a reaction time of 120 minutes, complexed aluminum tributoxide (prepared by mixing 7.9% of aluminum tri-sec-butoxide in 2.6% of 1-methoxy-2-propanol with 4.2% of ethyl acetoacetate while stirring at 0°C) was then added at 5°C and, after stirring for a further 5 minutes, 4.8% of 0.1 N aqueous p-toluenesulfonic acid solution, 0.1% of Tegoglide® 410 and 0.9%

of Tinuvin® 384 were added. After warming to room temperature, the reaction mixture was finally stirred for another 90 minutes and was then ready to process.

Cyclo-$\{SiOCH_3[(CH_2)_2Si(CH_3)(OEt)_2]\}_4$ oligomer was prepared as described in WO 98/52992.

The various layers were applied by means of spin coating, with the maximum rotational speed (in rpm) and the hold time at maximum rotational speed (in sec) being indicated in each case.

The determination of the pencil hardness was carried out in accordance with ASTM 3363, and the wear resistance was checked by means of the Taber Abraser test (ASTM D 1044; 1000 cycles, 500 g per wheel, CS-10-F stones) and subsequent determination of the light scattering (ASTM D 1003).

The surface resistance was determined by means of a commercial measuring instrument (ITT, model MX52S) and conductive silver strips in a square arrangement (length of the strips = spacing of the strips).

Example 1: Coating of glass with scratch-resistant coating I

The mixture CPP 105 was firstly applied to six 7.5 x 7.5 cm glass plates by means of spin coating and was cured at 130°C for one hour. To obtain a double coating, the process was repeated. A 2 mm wide strip of conductive silver was then applied on two opposite sides over the entire length and was cured at 160°C for 30 minutes. After cooling, the electrical resistance was measured.

The above-described sol-gel mixture I was then applied, likewise by spin coating (500 rpm, 20 sec); curing was carried out at 130°C for one hour. After cooling, both the surface resistance of the total layer structure and the electrical resistance of the conductive layer as such were determined. The abrasion resistance was measured by determination of the pencil hardness.

The precise application conditions for spin coating, the measured electrical resistances and the results of the pencil hardness test are summarized in Table 1.

Table 1

Specimen No.	Application conditions for conductive layer CPP 105	Surface resistance [kΩ/□]		Pencil hardness
		CPP 105	Scratch-resistant coating I	
1	400 rpm, 20 sec	2.8	133	> 9 H
2	2 x 400 rpm, 20 sec	1.3	270	7 H
3	600 rpm 20, sec	3.6	not determined	> 9 H
4	2 x 600 rpm, 20 sec	1.8	48	> 9 H
5	1000 rpm 20, sec	120	not determined	> 9 H
6	2 x 100 rpm, 20 sec	7.0	53	> 9 H

Example 2: Coating of Makrolon® with scratch-resistant coating I (with intermediate curing of the conductive layer)

To improve the adhesion, a 10 x 10 cm Makrolon® plate was firstly coated with 3-aminopropyltrimethoxysilane by spin coating (2000 rpm, 20 sec) and treated thermally at 80°C for one hour. The PEDT-containing mixture CPP 105 was then applied (1000 rpm, 20 sec) and subsequently cured at 130°C for 1 hour. After cooling to room temperature, the scratch-resistant coating I was finally applied (500 rpm, 20 sec), and this was then cured for one hour at 80°C and one hour at 130°C.

Measurement of the electrical resistances gave a value of 1.4×10^4 Ω/□ for the conductive layer and 10^8 Ω/□ on the surface of the scratch-resistant coating I.

Example 3: Coating of Makrolon® with scratch-resistant coating I (without intermediate curing of the conductive layer)

To improve the adhesion, six 10 x 10 cm Makrolon® plates were firstly coated with 3-aminopropyltrimethoxysilane by spin coating (2000 rpm, 20 sec) and treated thermally at 80°C for one hour. The PEDT-containing mixture CPP 105 was then applied and, after air drying for 10 minutes at room temperature, the scratch-resistant coating I was applied and was then cured for one hour at 80°C and one hour at 130°C. The application conditions for the PEDT-containing layer and the scratch-resistant finish I were varied and are summarized in Table 2; this table likewise shows the results of the Taber Abraser test by determination of light scattering.

Table 2:

Specimen No.	Application conditions for CPP 105	Application conditions for scratch-resistant finish I	Light scattering*)	Surface resistance [Ω/□]
7	2000 rpm, 20 sec	400 rpm, 20 sec	4.8 (0.7)	8.0×10^8
8	2000 rpm, 20 sec	500 rpm, 20 sec	4.8 (0.8)	6.0×10^8
9	1000 rpm, 20 sec	400 rpm, 20 sec	4.7 (0.7)	2.0×10^9
10	1000 rpm, 20 sec	500 rpm, 20 sec	5.3 (0.6)	1.3×10^9
11	500 rpm, 20 sec	400 rpm, 20 sec	4.4 (0.8)	1.6×10^9
12	500 rpm, 20 sec	500 rpm, 20 sec	4.6 (0.7)	1.0×10^9

*) Light scattering by the scratch-resistant coating after Taber Abraser test (initial values in brackets)

Example 4: Coating of glass with scratch-resistant coating II

The mixture CPP 105 was firstly applied to four 10 x 10 cm glass plates by means of spin coating and was cured at 130°C for one hour. To obtain a double or triple coating, the process was repeated. The surface resistance of the layer applied in this way was subsequently determined.

The above-described sol-gel mixture II was then applied by spin coating (500 rpm, 20 sec); it was cured at 130°C for one hour. After cooling, the pencil hardness and the optical transmission of the multilayer structures obtained were determined. The results are summarized in Table 3.

Table 3:

Specimen No.	Application conditions for the conductive layer CPP 105 scratch-resistant layer II	Surface resistance [Ω/□] CPP 105	Pencil hardness	Trans-mission in the range from 400 to 700 nm
1	500 rpm, 20 sec 800 rpm, 20 sec	5100	> 7 H	> 84%
2	500 rpm, 20 sec 400 rpm, 20 sec	5100	> 7 H	> 86%
3	2 x 500 rpm 20, sec 400 rpm, 20 sec	1900	> 7 H	> 68%
4	3 x 500 rpm 20, sec 400 rpm, 20 sec	900	> 7 H	> 51%

Comparative example 1:

A mixture of 10 mol% of phenyltrimethoxysilane, 65 mol% of 3-glycidoxypropyl-trimethoxysilane, 5 mol% of 3-aminopropyltriethoxysilane and 20 mol% of aluminum tributoxide was prepared as described in WO 96/05606. For this purpose, 40 g of aluminum tributoxide were dissolved in 48 g of isopropanol and reacted with 21 g of ethyl acetoacetate. This mixture was then added to a mixture of 16 g of phenyltrimethoxysilane, 120 g of 3-glycidoxypropyltrimethoxysilane and 9 g of 3-aminopropyltriethoxysilane. The mixture was then diluted with 100 g of isopropanol and 100 g of diacetone alcohol, and water was added while cooling in ice; after the addition was complete, the reaction mixture was finally stirred for

another 2 hours at room temperature. To improve the adhesion, a 10 x 10 cm Makrolon® plate was firstly coated with 3-aminopropyltrimethoxysilane by spin coating (2000 rpm, 20 sec) and treated thermally at 80°C for one hour. The above-described reaction mixture was then applied, likewise by spin coating (300 rpm, 20 sec), and was treated thermally at 130°C for one hour.

In the Taber Abraser test (1000 cycles), a very low abrasion resistance was found; the scratch trace displayed light scattering of more than 38%.

CLAIMS:

1. A conductive and highly abrasion-resistant coating, comprising:

(a) a first layer comprising an electrically conductive polymer; and

(b) a second layer comprising a highly abrasion-resistant layer of a polyfunctional organosiloxane comprising a cyclic carbosiloxane,

wherein the coating is on a substrate of a multi-layer structure.

2. The coating of claim 1, wherein the substrate is a moulding and the coating further comprises polyethylene dioxythiophene.

3. The coating of claim 1 or 2, wherein the highly abrasion-resistant layer is produced from the cyclic carbosiloxane.

4. The coating of any one of claims 1 to 3, wherein the coating exhibits less than 20% scattered light on the scratch mark in the Taber abraser scratch test.

5. The coating of claim 4, wherein the coating exhibits less than 10% scattered light on the scratch mark.

6. The coating of claim 5, wherein the coating exhibits less than 5% scattered light on the scratch mark.

7. The coating of any one of claims 1 to 6, wherein the coating exhibits a surface resistance of 0.1 to 10^{12} $\Omega/9$.

8. Use of the coating of any one of claims 1 to 7 for producing a low-radiation screen or an antistatic plastic material.

9. Use of the coating of any one of claims 1 to 7 for producing a film, an extruded part or an injection moulding.

10. A process for making a conductive and highly abrasion-resistant coating, comprising a conductive and highly abrasion-resistant coating, comprising:

(i) a first layer comprising an electrically conductive polymer, and

(ii) a second layer comprising an applied highly abrasion-resistant layer of a polyfunctional organosiloxane comprising a cyclic carbosiloxane, wherein the coating is on a substrate of a multilayer structure, and wherein the process comprises:

(a) applying the first layer in a first stage on the substrate; and

(b) subsequently applying the second layer in a second stage.

11. The process of claim 10, wherein a polyethylene dioxythiophene-containing layer is applied to the substrate in step (a) and any highly volatile constituents comprising solvents, are optionally evaporated.

12. The process of claim 10 or 11, wherein the highly abrasion-resistant coating is applied in step (b) and is cured by heat or irradiation.

13. The process of claim 10 or 11, further comprising thermal curing at a temperature lower than 160°C.

30771-214

14. The process of any one of claims 10 to 13, wherein prior to step (a), the surface of the substrate is chemically or physically treated.

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