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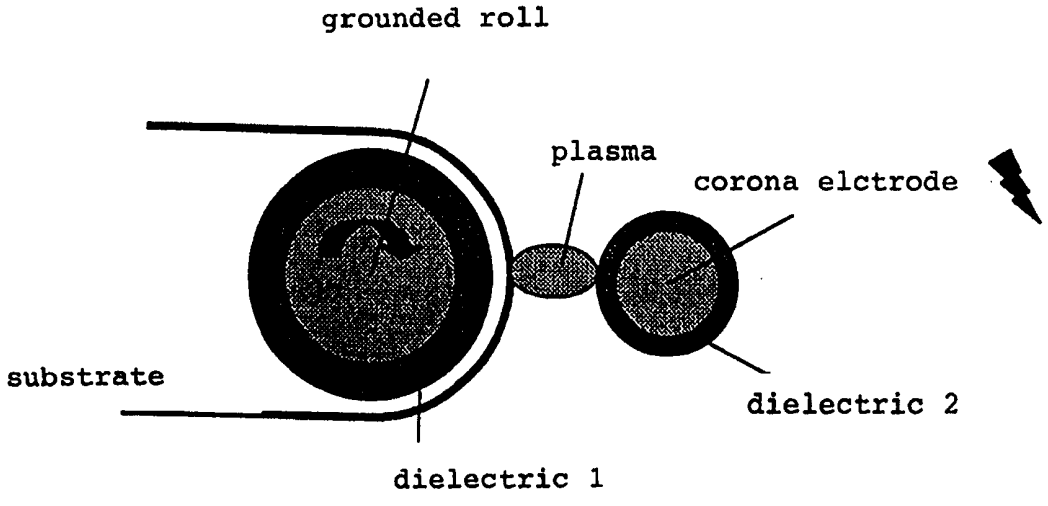
(54) Title: METHOD FOR APPLYING A COATING TO A SUBSTRATE



(57) Abstract

The invention relates to a method for applying a coating to a substrate, wherein a substrate is introduced into an atmosphere which contains a chemically reactive compound and water, and subsequently, using a corona discharge, on the substrate a coating is formed from the reactive compound.

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Title: Method for applying a coating to a substrate.

This invention relates to the application of a coating to various substrates, including the application of barrier layers to plastics.

The provision of coatings on all kinds of substrates, as on plastic film or on articles formed from plastic, on metals, or on other materials, is an important tool for improving the (surface) properties of such substrates. To be considered here are, for instance, improving the wear and/or scratch resistance of plastics, the corrosion resistance of metals, and especially improving the barrier properties of plastics, as in polyester bottles or polyester or polyolefin films. Particularly the last-mentioned application is of great commercial and technical importance, since the greater part of plastics have moderate to poor barrier properties in respect of oxygen and CO_2. This means that such plastics are less suitable for use as packing material for oxygen- and CO_2-sensitive materials and foods.

Plastic materials that have sufficient barrier properties are, for instance, PVDC, and laminates of non-barrier plastics and other plastics, such as EVOH and the like, or metals, such as aluminum, which have a good barrier function. The use of this kind of systems, however, meets with other objections, for instance from an environmental point of view. On the one hand, chlorine containing plastics are less desirable specifically in garbage incineration, while, on the other hand, multilayer systems possess disadvantages from the viewpoint of reuse.

Accordingly, there is a need for a system enabling a coating to be applied to a plastic or any other substrate, which coating imparts to the substrate additional useful properties. The present invention now provides for this need.

The invention relates, in a first variant, to a method for applying a coating to at least one surface of a substrate, wherein the substrate is introduced into an

atmosphere which contains at least one chemically reactive compound and water, and subsequently, using a corona discharge, on the surface of the substrate a coating is formed from the reactive compound.

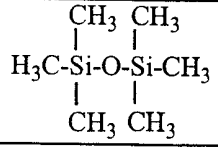
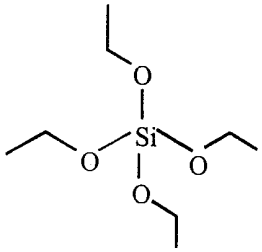
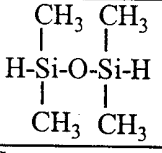
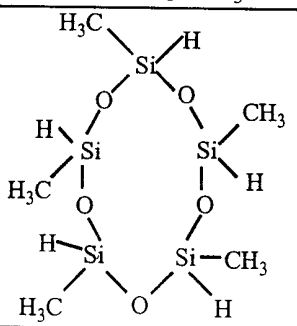
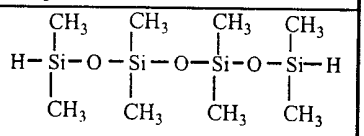
Surprisingly, it has been found to be possible to form a coating by activating a suitable chemically reactive compound using a corona discharge, in the presence of water, to form a coating on the surface with good properties. Suitable reactive compounds include inter alia silicon-containing compounds which can be brought into the gas phase, such as silanes and siloxanes.

It has been found that for obtaining good properties in respect of the permeability to vapor and/or gas, the presence of water is essential. In case an anhydrous gas phase is used in the corona treatment, the coating obtained is not sufficiently vapor/gas inhibiting. As soon as water is present in the gas phase, however, the permeability of the coating is found to be greatly reduced.

Preferably, the amount of water is more than 0.1% by volume, based on the volume of the gas phase, while the balance consists of inert gas and the chemically reactive compound. More preferably, the amount of water is at least 0.5% by volume, the upper limit being formed by the saturation vapor pressure. Obviously, it is dependent on the temperature, but will not exceed 5% by volume.

Suitable as chemically reactive compound are *inter alia* the compounds given in Table 1.

Table 1: *Examples of reactive components for forming a coating on a substrate using the reactive corona technique.*

name	abbreviation	structure
Hexamethyl-disiloxane	HMDSO	
Tetraethoxy-silane	TEOS	
1,1,3,3-Tetra-methyldisiloxane	TMDSO	
2,4,6,8,10-Penta-methylcyclo-pentasiloxane	-	
1,1,3,3,5,5,7,7-Octamethyl-tetrasiloxane	-	

The choice of the compound depends on various factors. Primarily, the desired properties of the coating are of importance. What substrate the coating is to be applied to also plays a role.

Suitable substrates are especially metals and plastics. As has already been indicated, the invention can be advantageously used for imparting barrier properties to plastics that do not inherently possess these properties. Examples include polyester bottles and polypropylene films.

These materials are often used for packing beverages and foods. It is then of importance that no oxygen can reach them, or that no CO_2 can escape. By applying a coating in the manner described hereinabove, a single-layer plastic having a coating thereon that does not give any adverse effects upon subsequent processing and/or reuse is obtained in a simple manner.

The coating is applied by contacting the surface with a gas phase in which at least one chemically reactive compound and water are present. The gas phase further contains inert gas, such as nitrogen, or noble gas, including argon.

Subsequently, in the presence of this gas phase, a corona treatment is carried out. Corona treatments are known per se, for instance for promoting adhesion of inks and glues to plastics.

A corona treatment consists in subjecting the surface to a corona discharge for a limited time (1 second to a few minutes). A corona discharge is a stable electrical discharge between two electrodes in a gas having a pressure of more than 0.2 bar (typically 0.8 to 1.0 bar). The discharge is maintained with an AC high voltage (voltage: 5 to 30 kV, frequency: 15 to 30 kHz). One or both of the electrodes is/are coated with a dielectric. A schematic representation of a set-up for corona treatment is given in Fig. 1.

The pressure at which the treatment occurs is preferably at least 0.2 bar, more particularly at least 1 bar.

Finally, the invention further relates to a substrate having at least one surface provided with a coating in the manner described hereinabove.

The invention will presently be elucidated in and by a few examples.

In an experimental set-up, flat films were provided with a coating produced with the reactive corona process.

Two different substrate films were used, viz. a PET film, 12 μm thick, biaxially stretched, without further specifications, and a PP film, V47 PED 10 (Hoechst), 10 μm thick, stretched.

Different combinations of electrodes and dielectrics (see Fig. 1) were used. These combinations are listed in Table 2.

Table 2: *Overview of the different combinations of electrodes and dielectrics for the reactive corona.*

#	grounded roll	dielectric 1	corona electrode	dielectric 2	distance
1	metal, 100 mm Ø	rubber, 2.3 mm	metal, 12.8 mm Ø	-	2-3 mm
2	metal, 100 mm Ø	rubber, 2.3 mm	metal, 50 mm Ø	-	1.7 mm spacer
3	metal, 100 mm Ø	rubber, 2.3 mm	metal, 50 mm Ø	rubber, 2 mm	1.7 mm spacer
4	metal, 100 mm Ø	rubber, 2.3 mm	metal balls, 29.7 mm Ø	glass tube, 1.8 mm	2-3 mm
5	'aquadag' 121 mm Ø	ceramic, 10.1 mm	metal balls, 29.7 mm Ø	glass tube, 1.8 mm	1 mm spacer

In configuration 5 the grounded roll is formed by a ceramic tube internally provided with a layer of 'aquadag', i.e. an electrically conductive graphite coating. In configurations 4 and 5 the corona electrode consists of a glass tube filled with metal balls as conducting electrode.

The gas atmosphere in which the reactive component is introduced, and in which the corona discharge is induced, has an influence on the nature of the coating formed on the substrate. Table 3 gives an overview of the

different gas compositions using which the substrate films were provided with a coating.

Table 3: *Examples of the composition of the gas atmosphere in which the reactive component is included.*

	Composition
1	Nitrogen (dry), 0.9(a), 0.5(b), 0.2(c) bar
2	Nitrogen (wet, 0.9 bar)

Coatings were applied to substrate films, under variation of the following conditions: electrode configuration, partial pressure of the reactive component, the composition and total pressure of the gas atmosphere, the power of the corona discharge, and the duration of the treatment. Subsequently, the oxygen-permeability of the films with coating was measured. The gas permeability of a film is expressed in cm^3/m^2 dag.bar. By way of example, Table 4 shows, by way of example, some results of the permeability of the PP film with coatings applied under different conditions. Summarized in the table are: the reactive component with the partial pressure, the gas atmosphere (see Table 3), the electrode configuration (see Table 2), the corona power, the treatment time, and the measured permeability to oxygen for different samples per condition. In these experiments, a film having a surface of about 0.05 m^2 was provided with a coating. In the experiments underlying the results of Table 4, the time duration of the corona treatment was varied. The permeability of the films with coating is compared with the permeability of the PP film without a coating (PP v).

Table 4: *Permeability to oxygen of PP films with a coating applied by the reactive corona technique.*

exp.	reactive component	gas	config.	P[W]	t[min]	permeability [cm^3/m^2 dag.bar]
PPv	-	-	-	-	-	3100
PP 76	TEOS, 1 mbar	2	3	75	5	2400 2400
PP 75	TEOS, 1 mbar	2	3	75	10	60 60 70
PP 80	TEOS, 1 mbar	2	3	75	20	20 160 60 70

It is clear that the coating applied reduces the permeability of the film considerably. Measurements on the thickness of some of the coatings produced show that the thickness of the coating is in the order of magnitude of 0.1 to 1 μm.

In Table 5 some other results of the experiments are summarized. In these measurements, use was made of two types of gas atmosphere, viz. wet (2.3 vol.% water) nitrogen (2) and dry nitrogen. The coating was applied to a PP film and the reactive component is TEOS (partial pressure 1 mbar). The permeability of the films with coating is compared with the permeability of the PP film without a coating (PP v). It appears from the table that a wet nitrogen atmosphere results in a coating having a considerably lower permeability to oxygen than does a dry nitrogen atmosphere. It further appears from the table that the reproducibility of the treatment is reasonably good.

Table 5: *Permeability to oxygen of PP films with a coating applied by the reactive corona technique*

exp.	reactive component	gas	config.	P[W]	t[min]	permeability [cm^3/m^2 dag.bar]
PPv	-	-	-	-	-	3100
PP 80	TEOS, 1 mbar	2	3	75	20	20 160 60 70
PP 81	TEOS, 1 mbar	2	3	75	20	70
PP 87	TEOS, 1 mbar	1a	3	75	20	850
PP 88	TEOS, 1 mbar	1a	3	75	20	2300 1800

Finally, Table 6 shows the permeability to oxygen of the PP film and the PET film with a coating applied using the reactive corona technique. The permeability of the films with coating is compared with the permeability of the corresponding films without coating (PET v and PP v, respectively).

Table 6: *Permeability to oxygen of PP film and PET film with a coating applied by the reactive corona technique.*

exp.	reactive component	gas	config.	P[W]	t[min]	permeability [cm^3/m^2 dag.bar]
PET v	-	-	-	-	-	103 70
PET 91	TEOS, 1 mbar	2	3	75	20	40 9 8 6
PPv	-	-	-	-	-	3100
PP 80	TEOS, 1 mbar	2	3	75	20	20 160 60 70

Again, there is a clear decrease of the oxygen permeability as a result of the application of a coating using the reactive corona technique.

CLAIMS

1. A method for applying a coating to at least one surface of a substrate, wherein said substrate is introduced into an atmosphere which contains at least one chemically reactive compound and water, and subsequently, using a corona discharge, on the surface of the substrate a coating is formed from said reactive compound.

2. A method according to claim 1, wherein said coating has an inhibiting effect on the permeability to vapor and/or gas.

3. A method according to claim 1 or 2, wherein said coating has an inhibiting effect on the permeability to water vapor, CO_2 and/or oxygen.

4. A method according to claim 1, wherein the coating has corrosion-inhibiting activity.

5. A method according to claim 1, wherein the coating improves the wear resistance and scratch resistance of the surface.

6. A method according to claims 1-5, wherein the amount of water is 0.1% by volume or more, preferably 0.5% by volume or more, based on the volume of the atmosphere.

7. A method according to claims 1-6, wherein the amount of water is not more than 5% by volume.

8. A method according to claims 1-7, wherein as substrate a polyester or a polyolefin material is used.

9. A method according to claim 8, wherein as substrate a polyalkylene terephthalate or a polypropylene material is used.

10. A method according to claims 1-9, wherein the chemically reactive compound is a reactive silicon compound, preferably a silane or a siloxane.

11. A method according to claim 10, wherein the compound is tetraethoxysilane.

12. A method according to claims 1-11, wherein the corona discharge occurs by applying a voltage of at least 5 kV.

13. A substrate coated with a coating formed from a reactive chemical compound, obtainable by the use of the method according to claims 1-12.

AMENDED CLAIMS

[received by the International Bureau on 3 February 2000 (03.02.00);
original claims 1-13 replaced by new claims 1-13 (2 pages)]

1. A method for applying a coating to at least one surface of a substrate, wherein said substrate is introduced into an atmosphere which contains at least one chemically reactive compound and water, and subsequently, using a corona discharge, on the surface of the substrate a coating is formed from said reactive compound and wherein said coating has an inhibiting effect on the permeability to vapor and/or gas.

2. A method according to claim 1 , wherein said coating has an inhibiting effect on the permeability to water vapor, CO_2 and/or oxygen.

3. A method according to claim 1 or 2, wherein the coating has corrosion-inhibiting activity.

4. A method according to claim 1, wherein the coating improves the wear resistance and scratch resistance of the surface.

5. A method according to claims 1-4, wherein the amount of water is 0.1% by volume or more, preferably 0.5% by volume or more, based on the volume of the atmosphere.

6. A method according to claims 1-5, wherein the amount of water is not more than 5% by volume.

7. A method according to claims 1-6, wherein as substrate a polyester or a polyolefin material is used.

8. A method according to claim 7, wherein as substrate a polyalkylene terephthalate or a polypropylene material is used.

9. A method according to claims 1-8, wherein the chemically reactive compound is a reactive silicon compound, preferably a silane or a siloxane.

10. A method according to claim 9, wherein the compound is tetraethoxysilane.

11. A method according to claims 1-10, wherein the corona discharge occurs by applying a voltage of at least 5 kV.

12. A substrate coated with a coating formed from a reactive chemical compound, obtainable by the use of the method according to claims 1-11.

13. Use of water in an atmosphere which contains at least one chemically reactive compound, in a method for forming a coating from said reactive compound on a substrate using a corona discharge, for inhibiting the permeability of the coated surface to vapor and/or gas.

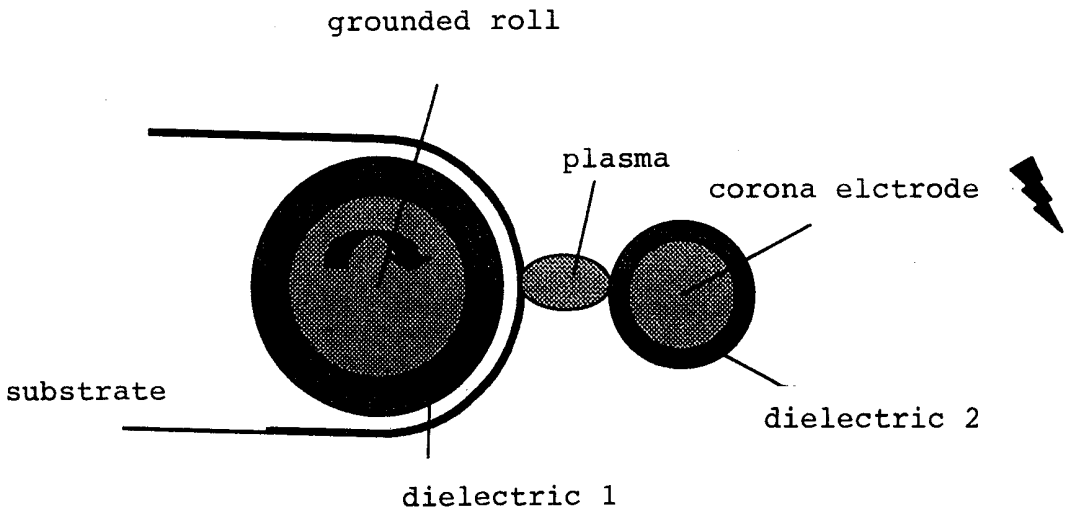

grounded roll
plasma
corona elctrode
substrate
dielectric 2
dielectric 1

Fig. 1

INTERNATIONAL SEARCH REPORT

Int. tional Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C16/40 C23C16/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X Y	US 5 527 629 A (GASTIGER MICHEL-JACQUES ET AL) 18 June 1996 (1996-06-18) column 2, line 1 - line 27; example 1	13 5,8,9, 11,12
X Y	EP 0 577 447 A (AIR LIQUIDE) 5 January 1994 (1994-01-05) column 1, line 1 - line 10 column 2, line 16 - line 26; example 1	13 4,11,12

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
24 November 1999	03/12/1999

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INTERNATIONAL SEARCH REPORT

Int. tional Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	THYEN R ET AL: "Plasma-enhanced chemical-vapour-deposition of thin films by corona discharge at atmospheric pressure" FIFTH INTERNATIONAL CONFERENCE ON PLASMA SURFACE ENGINEERING, GARMISCH-PARTENKIRCHEN, GERMANY, 9-13 SEPT. 1996, vol. 97, no. 1-3, pages 426-434, XP002101532 ISSN 0257-8972, Surface and Coatings Technology, Dec. 1997, Elsevier, Switzerland	13
A	paragraph '0002!	1-12

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ational Application No
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