

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 June 2008 (26.06.2008)

PCT

(10) International Publication Number
WO 2008/074823 A1

(51) International Patent Classification:
C08J 5/18 (2006.01) *C09D 183/04* (2006.01)

(74) Agent: **WEBER, Wolfgang**; Evonik Degussa GmbH,
Postcode 84/339, Rodenbacher Chaussee 4, 63457 Hanau
(DE).

(21) International Application Number:
PCT/EP2007/064191

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(22) International Filing Date:
19 December 2007 (19.12.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
06126485.9 19 December 2006 (19.12.2006) EP

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): **DE-GUSSA NOVARA TECHNOLOGY S.P.A.** [IT/IT]; Via Pisacane 7/B, I-20016 Pero (MI) (IT).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **FREGONESE, Daniele** [IT/IT]; Via Monte Grappa, 9 Tembelle di Vigonove, I-30030 Vigonovo (VE) (IT).

Published:
— *with international search report*

(54) Title: SOL GEL PROCESS FOR PRODUCING PROTECTIVE FILMS FOR POLYMERIC SUBSTRATES

(57) Abstract: Sol gel process for producing protective films for polymeric substrates Sol gel process for producing protective films for polymeric substrates, the process relates to the sol gel reaction of a metal or semi-metal alkoxide carried out in certain conditions. The sols obtained were, without limiting, spin- or dip-coated onto polymeric substrates then thermally cured into transparent-abrasion resistant coating. Such coating transmit visible light, but absorb wavelengths of ultraviolet light which cause degradation of the substrate surface and resultant adhesion-loss of the protective coating upon weathering.



WO 2008/074823 A1

Sol gel process for producing protective films for polymeric substrates

The subject of the invention is a process for the preparation of transparent films on substrates.

- 5 Plastic materials, such as polycarbonate (PC) and polymethylmethacrylate (PMMA), are nowadays used in many application areas such as automotive, constructions, electronics, headlamps, and sunroofs among the others.
- 10 Further development of their possibilities to enter new markets is hindered by the lack of surface hardness and abrasion resistance.

Other uses of the polymeric materials, such as glazing, decorative architectural panels and mirrors,
15 are also limited because of this lack of abrasion resistance. In this sense a lot of work has been devoted to the development of coating to solve this issue, for instance it has been proposed to use scratch resistant coatings, such as silica-containing
20 solutions and polysilicic acid fluorinated copolymer compositions. But these materials have found only limited commercial use because they are difficult to apply, poor in humidity resistance or expensive (U.S. Pat. No. 3,986,997).

- 25 Moreover those studies concerned film transparent in the UV region, more in particular at wavelength higher close to 287 nm which causes a breakdown in carbonate linkages accompanied by liberation of carbon monoxide and carbon dioxide and depolymerization of the
30 substrate. Ultraviolet radiation from the sun can reach the surface of a substrate coated with an ultraviolet radiation-transparent coating and cause it to degrade. As a result, the protective coating loses

adhesion and begins to flake off as the article weathers.

Another approach is that proposed by Ward Brown from Rohm and Haas Corp. US patent 2003/0134949 which
5 describes the use of autoxidable alkoxysilane. Those alkoxysilane boost the resistance to weathering of plastic object and yet they do not provide enough radiation stability.

A transparent and abrasion resistant coating
10 compositions is described in the US patent 4,500,669 with is made of a colloidal dispersion of metals, alloy, salts and oxides, but does not provide solution to damage caused by UV radiation.

Very few authors have tried to combine Sol-gel
15 techniques and UV stability in order to obtain coating systems that are at the same time abrasion resistant and UV stable.

Moreover, it is clear that it would be a perfect match to have a glassy coating which combines the
20 outstanding properties of glass such as electrical conductivity and thermal stability (e.g., polycarbonate $T_g = 145^\circ \text{C.}$) with some UV protection.

The subject of the invention is a process for making a vitreous coating on plastic substrates such as
25 polycarbonate, polymethylmetacrylates and polyolefins among the others.

The technology used is the sol-gel techniques already described in our previous patent WO 2004/007384.

The sol-gel techniques for making coatings consists in
30 making a suspension in alcoholic medium by mixing the component at room temperature, let the suspension gelling under controlled conditions and finally there

is the drying step which could be considered like a curing step.

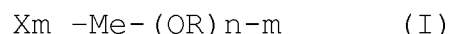
In reality this is a very general procedure because every type of coating requires a specific preparation
5 process i.e. suspension composition, application of the suspension on the substrate (dip or spray or spin coating techniques) gelling conditions (T) and the drying procedure, solvent evaporation, T of curing, rate of drying.

10 The literature describes the use sol -gel techniques-based coating for several supports but the industrialisation of such methods have been always seen as problematic because of the high temperature required for curing, see for instance the patents
15 6,017,389, 6,130,152 and the Italian patent NO98 A00004.

The subject of the invention is a method to manufacture sol-gel based coating with abrasion resistance and UV stability properties which requires
20 mild conditions for the manufacturing and the application on the substrate.

The subject of the invention is a process for the preparation of transparent films on substrates comprising the following steps:

25 - preparation of a solution in a solvent of one or more alcoxides corresponding to the formula:



where Me is a metal belonging to 3., 4. or 5. groups of the periodic system; n is the valence of Me;
30 X is R1 or OR1, with R1 equal or different from R, m is either zero or an integer number equal to or lower than 3;

R and R1 are hydrocarbon radicals with a number of carbon atoms equal to or lower than 12;

- hydrolysis of the obtained solution in the presence of a catalyst;
- 5 - eventual addition of a compound with ultraviolet radiation absorbing properties
- eventual addition of a hydrophobic agent
- eventual addition of an antistatic and reducing reflectance agent
- 10 - eventual addition of a compound with photocatalytic properties
- eventual addition of a polymer as thickening agent
- eventual addition of a compound with antibacterial properties
- 15 - deposition of the sol on the substrate of interest;
- final drying and curing of the coating;

The solution obtained by hydrolysis of a solution in an inorganic solvent of one or more alkoxides responding to the formula (I) can be a stable
20 colloidal solution.

The alkoxide preferably can be selected among tetramethylorthosilane, tetraethylorthosilane, tetraethoxyorthosilicate, tetrapropylorthosilicates, tetrabutylorthosilicate, ethyltriethoxysilane,
25 methyltrimethoxysilane, methyltriethoxysilane or a mixture of the same.

The alkoxide solution where the organic solvent preferably can be chosen among acetone, tetrahydrofuran, dioxane and more preferably ethanol.

The concentration of the solution can be in a percentage 10 and 55 by weight.

The compound with ultraviolet radiation absorbing property can be selected from the group of

- 5 benzotriazoles, the s-triazines, the oxanilides, the salicylates, the hydroxybenzophenones, the benzoates and the α -cyanoacrylates and inorganic molecules from the group TiO_2 and ZnO . It can be in a percentage 0.7 and 8 by weight.

- 10 The compound with hydrophobic agent can be a tetrafluorooctyltriethoxysilane. It can be in a percentage 0.1 and 6 by weight.

The compound with antistatic and reducing reflectance properties can be selected from the group of tin

- 15 oxide, indium oxide, antimony tin oxide and titanium oxide. It can be in a percentage between 0.1 and 5 by weight.

The polymer with thickening properties can be selected from the group polystyrene, polyvinylalcohol,

- 20 polyvinylacetate, polyethyleneglycole with molecular weight between 300 and 12000. The percentage can be between 0.5% to 10%, more preferably between 2 and 5% by weight.

The compound with photocatalytic properties can be

- 25 selected from the group titanium dioxide, zinc oxide. It can be in a percentage between 0.5% and 7% by weight.

The compound with antibacterial properties can be AgO . It can be in percentage between 0.05 and 5 by weight.

- 30 The alkoxide solution or mixture in the solvent can be between 20% and 60% by weight.

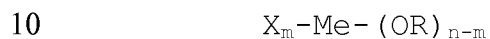
The hydrolysis of the alkoxide can be performed by addition of a controlled quantity of water.

The molar ratio H_2O/Me can be between 0.3 and 6, preferably between 1.5 and 3.

- 5 The catalyst can be an acid selected among the mineral acid and organic acids with K_a between 0.1 and 3.

The drying temperature can be between 60 and 200°C.

The process concerns the preparation of a sol in solution of one or more alkoxides having the formula:



where M is a metal belonging to 3. 4. or 5. groups, n is the metal's valence

- X is R_1 or OR_1 , where R_1 is equal or different from R, and m is an integer number of either zero or an
15 integer number equal or inferior to 3,
R and R_1 are hydrocarbon moieties with atom carbon chain length up to 12.

- According to the invention it has been found that the alkoxide is miscible in solvent such as
20 tetrahydrofuran, acetone and ethanol.

- In accordance with the invention, a hydrophobic agent and functional additive are employed to chemically modify the surfaces. Hydrophobic agents conventionally used in the art may be silicon-based agents including
25 siloxane, silane or silicon; F-based hydrophobic agents such as fluorosilanes, fluoroalkylsilanes (FAS), polytetrafluoroethylene, polytrifluoroethylene, polyvinylfluoride, or functional fluoroalkyl compounds, preferred hydrophobic agent is Dynasil
30 F8261 supplied by Degussa AG Germany.

Afterwards the hydrolysis is initiated by adding water solution of an acid. The hydrolysis reaction is exothermic and for this reason the temperature raises some degrees, the increase is very much dependent on
5 batch size and hydrolysis conditions. As the maximal temperature is reached the organic UV-filter is added to the batch under stirring.

As soon as the solution has been prepared it is applied to a substrate by, for instance, dip coating
10 or spin coating method.

Unlike the process described in the already cited patent 6,017,389 the obtained solution is not refluxed for 1.5 hours but just stirred for few minutes, furthermore the molar ratio TEOS :Ethanol is always
15 bigger than 1.2 whereas in the cited patent is lower. In the same patent it is claimed that the porous layer of silica is obtained in two steps process which concern two different solvents The process that the authors are here reporting is also different from what
20 has been reported in the US patent 3986997 (example 6) in which is reported a multi-steps process to manufacture the sol using a bigger than 1 molar ratio TEOS / Ethanol, whereas the authors suggest to use more ethanol than TEOS.

25 The mentioned UV-filter could be any of hydrobenzophenone, hydroxybenzotriazol or hydroxyl-phenyl-triazine derivatives EP 0 818 450.

Afterwards there is the gellation step which is catalysed by organic or inorganic acid.

30 Deposition of the sol on the substrate which can be done either just after hydrolysis or while later just before the gelation takes place.

The substrate can be any known polymer.

In a preferred form of the invention the substrate can be elected from the group of polycarbonate, polymethylmetacrylate, polystyrene, polyethylene, polypropylene, polyvinylchloride,
5 polyethylenephthalate, ABS, CR39 or nylon.

Preferred the substrate can be polycarbonate (PC), polystyrene or polymethylmetacrylate (PMMA).

The final step is the curing or drying of the sol already on the substrate surface. It is important that
10 the temperature of curing is higher than 70 °C, preferably 35 to 120 °C. The curing can be done either in an oven where air is blown at high efficiency or under IR lamps or in any industrial method used to cure polymeric coatings, whereby the temperature is to
15 be adapted to the substrate. I.e. for PMMA is better to have 80 °C while for PC is better to have 110 °C.

The formulation is in general terms fixed by the height of the layer to be obtained. For the PC the thickness is 800 nanometer while for PMMA is 500
20 nanometer.

Examples

Example 1

A 1 l round flask containing a magnetic stir bar is
25 loaded with 261.8 g of ethanol and 197.28 g of tetraethoxysilane supplied by Degussa AG under the trade name Dynasil (TEOS).

At room temperature and under constant and strong stirring are then added very slowly 39.72g of HCl 1M.
30 The temperature increase due to the hydrolysis reaction is of 20 °C.

The solution so obtained is then applied by dip coating (dipping speed 0.39cm/s) on rectangular polycarbonate plate (10cm length, 15 cm with, 0.3 cm thickness). The plate is then dried for 12 hours at 120 °C in an oven. The plate so obtained has undergone characterisation tests:

	Hardness according to ASTM method	Transmittance at 300 nm (%)	Grid adhesion test	Surface roughness RA (nm)
Polycarbonate untreated	F	71	NA	25.7
Polycarbonate with coating	F	72	Fail	23.0

Chemical stability towards butylacetate, acetone and tetrahydrofuran of the coated polycarbonate plate is unchanged when compared to the uncoated polycarbonate.

The hardness is measured according to method ASTM D336 by using a series of pencils with different hardness from 8B (the most soft) to 8H (the hardest).

The coating adhesion was evaluated by grid adhesion test based on JIS K5400. A one-hundred-section grid was cut on the coated surface. Adhesive tape was applied to the grid, and then sharply removed (vertical to the surface). "Pass" means that no damages have been observed, conversely, "Fail" means at least one section damaged.

Surface roughness is determined by profilometer Taylor Mod. 222.

Chemical stability of coated material of the coated polycarbonate is checked by dipping the plate into pure solvent and checking visually if the solvent has

changed the aesthetic of surface. Solvents tested: acetone, butylacetate and tetrahydrofuran.

The uncoated polycarbonate is not stable in those solvents.

5 Example 2

A 1 l round flask containing a magnetic stir bar is loaded with 254.17g of ethanol and 191.53 g of tetraethoxysilane supplied by Degussa AG under the trade name Dynasil (TEOS).

- 10 At room temperature and under constant stirring are then added very slowly 39.72 g of HCl 1M. The temperature increase due to the hydrolysis reaction is of 20°C. When the temperature reached the maximum 14.56 g of Tinuvin 1130 Bis(-β-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-terbutylphenil]-propionic acid-
15 polyethylenglycol)300-ester supplied by Ciba have been added to the solution.

- The mixture so obtained is then applied by dip coating (dipping speed 0.39cm/s) on rectangular polycarbonate
20 plate (10cm length, 15 cm with, 0.3 cm thickness). The plate is then dried for 12 hours at 120 °C in an oven. The plate so obtained has undergone characterisation tests:

	Hardness according to ASTM method	Transmittance at 300 nm (%)	Grid adhesion test	Surface roughness RA (nm)
Polycarbonate untreated	F	71	NA	25.7
Polycarbonate with coating	3H	9	Pass	12.6

Chemical stability towards butylacetate, acetone and tetrahydrofuran of the coated polycarbonate plate is improved when compared to the uncoated polycarbonate plate. The coated polycarbonate under visual
5 inspection did not change the surface appearance.

Example 3

A 1 l round flask containing a magnetic stir bar is loaded with 261.09g of ethanol, 176.79 g of tetraethoxysilane supplied by Degussa AG under the
10 trade name Dynasil A (TEOS) and 11.34 triethoxyphenylsilane supplied by Degussa AG Germany under the trade name Dynasil 9265.

At room temperature and under constant stirring are then added very slowly 40.78 g of HCl 1M. The
15 temperature increase due to the hydrolysis reaction is of 20 °C.

The mixture so obtained is then applied by dip coating (dipping speed 0.39cm/s) on rectangular polycarbonate plate (10cm length, 15 cm with, 0.3 cm thickness). The
20 plate is then dried for 12 hours at 120 °C in an oven. The plate so obtained has undergone characterisation tests:

	Hardness according to ASTM method	Transmittance at 300 nm (%)	Grid adhesion test	Surface roughness RA (nm)
Polycarbonate untreated	F	71	NA	25.7
Polycarbonate with coating	H	70	Pass	18.0

Chemical stability towards butylacetate, acetone and
25 tetrahydrofuran of the coated polycarbonate plate is

unchanged when compared to the uncoated polycarbonate plate.

Example 4

- A 1 l round flask containing a magnetic stir bar is loaded with 253.48 g of ethanol, 181.34 g of tetraethoxysilane supplied by Degussa AG under the trade name Dynasil A (TEOS) and 11.01 g of triethoxyphenylsilane supplied by Degussa AG Germany under the trade name Dynasil 9265.
- At room temperature and under constant stirring are then added very slowly 39.59 g of HCl 1M. The temperature increase due to the hydrolysis reaction is of 20°C. When the temperature reached the maximum 14.56 g of Tinuvin 1130 Bis(-β-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-terbutylphenyl]-propionic acid-polyethylenglycol)300-ester supplied by Ciba have been added to the solution.

The mixture so obtained is then applied by dip coating (dipping speed 0.39cm/s) on rectangular polycarbonate plate (10cm length, 15 cm with, 0.3 cm thickness). The plate is then dried for 12 hours at 120 °C in an oven. The plate so obtained has undergone characterisation tests:

	Hardness according to ASTM method	Transmittance at 300 nm (%)	Grid adhesion test	Surface roughness RA (nm)
Polycarbonate untreated	F	71	NA	25.7
Polycarbonate with coating	4H	8	Pass	9.6

Chemical stability towards butylacetate, acetone and tetrahydrofuran of the coated polycarbonate plate is improved when compared to the uncoated polycarbonate plate. The coated polycarbonate under visual
5 inspection did not change the surface appearance.

Example 5

A 1 l round flask containing a magnetic stir bar is loaded with 253.48g of ethanol, 181.34 g of tetraethoxysilane supplied by Degussa AG under the
10 trade name Dynasil A (TEOS) and 11.01 g of triethoxyphenylsilane supplied by Degussa AG Germany under the trade name Dynasil 9265.

At room temperature and under constant stirring are then added very slowly 39.59g of HCl 1M. The
15 temperature increase due to the hydrolysis reaction is of 20°C. When the temperature reached the maximum 14.56 g of Tinuvin 1130 Bis(-β-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-terbutylphenil]-propionic acid-polyethylenglycol)300-ester supplied by Ciba have been
20 added to the solution.

The mixture so obtained is then applied by dip coating (dipping speed 0.39cm/s) on rectangular polymethylmetacrylate plate (PMMA) (10cm length, 15 cm with, 0.3 cm thickness). The plate is then dried for
25 12 hours at 120 °C in an oven. The plate so obtained has undergone characterisation tests:

	Hardness according to ASTM method	Transmittance at 300 nm (%)	Grid adhesion test	Surface roughness RA (nm)
Polycarbonate untreated	F	21	NA	17.5
Polycarbonate with coating	4H	3	Pass	12

Chemical stability towards dichloromethane of the coated PMMA plate is improved when compared to the uncoated PMMA plate. The coated polymethylmetacrylate plate under visual inspection did not change the surface appearance.

Example 6

A 1 l round flask containing a magnetic stir bar is loaded with 250.98 g of ethanol, 181.34 g of tetraethoxysilane supplied by Degussa AG under the trade name Dynasil A (TEOS), 11.01 g of triethoxyphenylsilane supplied by Degussa AG Germany under the trade name Dynasil 9265 and 2.5 g Dynasil F8261 (tetrafluorooctyltriethoxysilane) supplied by Degussa AG.

At room temperature and under constant stirring are then added very slowly 39.59g of HCl 1M. The temperature increase due to the hydrolysis reaction is of 20°C. When the temperature reached the maximum 14.56 g of Tinuvin 1130 Bis(-β-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-terbutylphenil]-propionic acid-polyethylenglycol)300-ester supplied by Ciba have been added to the solution.

The mixture so obtained is then applied by dip coating (dipping speed 0.39cm/s) on rectangular polycarbonate plate (PC) (10cm length, 15 cm with, 0.3 cm thickness). The plate is then dried for 12 hours at 120 °C in an oven. The plate so obtained has undergone characterisation tests:

	Hardness according to ASTM method	Transmittance at 300 nm (%)	Grid adhesion test	Surface roughness RA (nm)
Polycarbonate untreated	F	71	NA	25.7
Polycarbonate with coating	2H	11	Pass	6.1

Chemical stability towards butylacetate, acetone and tetrahydrofuran of the coated polycarbonate plate is improved when compared to the uncoated polycarbonate plate. The coated polycarbonate under visual inspection did not change the surface appearance.

Example 7

A 1 l round flask containing a magnetic stir bar is loaded with 250.98 g of ethanol, 181.34 g of tetraethoxysilane supplied by Degussa AG under the trade name Dynasil A (TEOS), 11.01 g of triethoxyphenylsilane supplied by Degussa AG Germany under the trade name Dynasil 9265 and 2.5g tin oxide (ITO).

At room temperature and under constant stirring are then added very slowly 39.59g of HCl 1M. The temperature increase due to the hydrolysis reaction is of 20°C. When the temperature reached the maximum 14.56 g of Tinuvin 1130 Bis(-β-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-terbutylphenyl]-propionic acid-polyethylenglycol)300-ester supplied by Ciba have been added to the solution.

The mixture so obtained is then applied by dip coating (dipping speed 0.39cm/s) on rectangular polycarbonate

plate (PC) (10cm length, 15 cm with, 0.3 cm thickness). The plate is then dried for 12 hours at 120 °C in an oven. The plate so obtained has undergone characterisation tests:

	Hardness according to ASTM method	Transmittance at 300 nm (%)	Grid adhesion test	Surface roughness RA (nm)
Polycarbonate untreated	F	71	NA	25.7
Polycarbonate with coating	H	11	Pass	21

5

The obtained coating has a porous aspect and is characterized by antireflecting properties such as minimum reflectance measured in the range 450 - 750 nm.

10 Example 8

A 1 l round flask containing a magnetic stir bar is loaded with 254.17g of ethanol and 191.53 g of tetraethoxysilane supplied by Degussa AG under the trade name Dynasil (TEOS).

- 15 At room temperature and under constant stirring are then added very slowly 39.72g of HCl 1M. The temperature increase due to the hydrolysis reaction is of 20°C. When the temperature reached the maximum 14.56 g of Tinuvin 1130 Bis(-β-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-terbutylphenil]-propionic acid-
- 20 polyethylenglycol)300-ester supplied by Ciba have been added to the solution with a solution made of 14 g THF plus 14 g of polystyrene.

The mixture so obtained is then applied by dip coating

25 (dipping speed 0.39cm/s) on rectangular polycarbonate

plate (10 cm length, 15 cm with, 0.3 cm thickness). The plate is then dried for 12 hours at 120 °C in an oven. The plate so obtained has undergone characterisation tests:

5

	Hardness according to ASTM method	Transmittance at 300 nm (%)	Grid adhesion test	Surface roughness RA (nm)
Polycarbonate untreated	F	71	NA	25.7
Polycarbonate with coating	H	9	Pass	11

The thickness of the coating is 3 micron whereas the same formulation without polymer has a thickness of 0.8 micron (see example 3).

- 10 Based on the obtained results one can infer that the basic coating formulation solvent, TEOS and acid can be strongly improved, performance-wise, by adding either the UV filter or the modified the ethoxysilane.

- Without wishing to be bound to any theory it is
15 believed that both component work as plasticisers making the glassy coating less fragile.

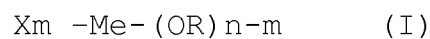
In the example 6 it has been listed also the Dynasil F8261 as agent for better hydrophobic effect.

- These coatings are useful in a variety of substrate,
20 here have been listed only PC and PMMA but in reality the process is suitable also, without limiting the scope of this invention, for polyethylene, polypropylene, polyvinylchloride, polyethylene-tereftalate, acrylnitrilebutadienstyrene (ABS),
25 allyldiglycolcarbonate (CR39) and nylon.

Claims:

1. A process for the preparation of transparent films on substrates comprising the following steps:

- 5 - preparation of a solution in a solvent of one or more alcoxides corresponding to the formula:



10 where Me is a metal belonging to 3., 4. or 5. groups of the periodic system; n is the valence of Me;

X is R1 or OR1, with R1 equal or different from R, m is either zero or an integer number equal to or lower than 3;

15 R and R1 are hydrocarbon radicals with a number of carbon atoms equal to or lower than 12;

- hydrolysis of the obtained solution in the presence of a catalyst;

20 - eventual addition of a compound with ultraviolet radiation absorbing properties;

- eventual addition of a hydrophobic agent;

- eventual addition of an antistatic and reducing reflectance agent;

25 - eventual addition of a compound with photocatalytic properties;

- eventual addition of a polymer as thickening agent;

- eventual addition of a compound with antibacterial properties;

- deposition of the sol on the substrate of interest;
 - final drying and curing of the coating.
2. Process for the preparation of transparent films
5 substrates according to claim 1 in which the alkoxide is selected among tetramethyl-orthosilane, tetraethylorthosilane, tetraethoxyorthosilicate, tetrapropylorthosilicates, tetrabutylorthosilicate, ethyltriethoxysilane, methyltrimethoxysilane,
10 methyltriethoxysilane, or a mixture of the same.
 3. Process for the preparation of transparent films according to claim 1 where the organic solvent solution of the alkoxide is preferably chosen among
15 acetone, tetrahydrofuran, dioxane and more ethanol.
 4. Process for the preparation of transparent films according to claim 1 where the compound with ultraviolet radiation absorbing property is
20 selected from the group of benzotriazoles, the s-triazines, the oxanilides, the salicylates, the hydroxybenzophenones, the benzoates and the α -cyanoacrylates and inorganic molecules from the group TiO_2 and ZnO .
 5. Process for the preparation of transparent films
25 according to claim 1 where the compound with hydrophobic agent is a tetrafluorooctyltriethoxysilane.
 6. Process for the preparation of transparent films according to claim 1 where the compound with
30 antistatic and reducing reflectance properties is selected from the group tin oxide, indium oxide, antimony tin oxide and titanium oxide.

7. Process for the preparation of transparent films according to claim 1 where the polymer with thickening properties is selected from the group polystyrene, polyvinylalcohol, polyvinylacetate,
5 polyethyleneglycole with molecular weight between 300 and 12000.
8. Process for the preparation of transparent films according to claim 1 where the compound with photocatalytic properties is selected from the
10 group titanium dioxide, zinc oxide.
9. Process for the preparation of transparent films according to claim 1 where the compound with antibacterial properties is AgO.
10. Process for the preparation of films according to
15 claim 1 where the alkoxide solution or mixture in the solvent is between 20% and 60% by weight.
11. Process for the preparation of films according to claim 1 where the hydrolysis of the alkoxide is performed by addition of a controlled quantity of
20 water.
12. Process for the preparation of films according to claim 12 where the molar ratio H_2O/Me is between 0.3 and 6.
13. Process for the preparation of films according to
25 claim 1 where the catalyst is an acid selected among the mineral acid and organic acids with K_a between 0.1 and 3.
14. Process for the preparation of films according to
30 claim 1 where the drying temperature is between 60 and 200°C.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/064191

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J5/18 C09D183/04

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)

C08J C09D C03C G09F B32B C01G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 986 997 A (CLARK HAROLD A) 19 October 1976 (1976-10-19) column 1, line 48 - column 5, line 21; claims 1-14; examples 1-10	1-4, 6-8; 10-14
A		5, 9
X	US 6 017 389 A (SCHMIDT HELMUT [DE] ET AL.) 25 January 2000 (2000-01-25) column 1, line 4 - column 4, line 41; claims 1-17; examples 1-3	1-4, 6-8, 10-14
A		5, 9
X	WO 2004/007384 A (NOVARA TECHNOLOGY S R L [IT]; COSTA FULVIO [IT]; COSTA LORENZO [IT]) 22 January 2004 (2004-01-22) page 1, line 5 - page 9, line 31; claims 1-20; examples 1-3	1-4, 6-8, 10-14
A		5, 9
	-/--	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

11 March 2008

Date of mailing of the international search report

19/03/2008

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

olde Scheper, Bernd

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/064191

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 029 827 A1 (NIPPON SHEET GLASS CO LTD [JP]) 23 August 2000 (2000-08-23) claims 1-34	1,4,6,8
X	WO 2004/107297 A (KONICA MINOLTA HOLDINGS INC [JP]; OKUBO YASUSHI [JP]; KIYOHARA KAZUTO) 9 December 2004 (2004-12-09) page 18, line 22 - page 19, line 12	1,4
P,X	& US 2007/009674 A1 (OKUBO YASUSHI [JP] ET AL) 11 January 2007 (2007-01-11) paragraph [0115]	1,4
X	US 6 139 613 A (HENDRICKSON WILLIAM A [US] ET AL) 31 October 2000 (2000-10-31) column 11, lines 21-59	1,7
A	EP 1 449 811 A (CATALYSTS & CHEM IND CO [JP]) 25 August 2004 (2004-08-25) paragraph [0187]	9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/064191

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3986997	A	19-10-1976	AT 340017 B	25-11-1977
			AT 17875 A	15-03-1977
			AU 7323074 A	18-03-1976
			BE 821403 A1	23-04-1975
			CA 1026504 A1	21-02-1978
			CH 621818 A5	27-02-1981
			DE 2446279 A1	08-01-1976
			FR 2276360 A1	23-01-1976
			GB 1454960 A	10-11-1976
			HK 33479 A	25-05-1979
			JP 910684 C	14-06-1978
			JP 51002736 A	10-01-1976
			JP 52039691 B	06-10-1977
			NL 7412522 A	30-12-1975
			SE 410865 B	12-11-1979
			SE 7411424 A	29-12-1975
			SU 621319 A3	25-08-1978
US 6017389	A	25-01-2000	AT 201665 T	15-06-2001
			DE 59607013 D1	05-07-2001
			WO 9711035 A1	27-03-1997
			EP 0851845 A1	08-07-1998
			ES 2157008 T3	01-08-2001
			JP 11514960 T	21-12-1999
WO 2004007384	A	22-01-2004	AU 2003266231 A1	02-02-2004
			CA 2492256 A1	22-01-2004
			CN 1668542 A	14-09-2005
			EP 1521724 A1	13-04-2005
			HK 1082494 A1	01-06-2007
			HR 20050030 A2	28-02-2005
			IT N020020009 A1	12-01-2004
			JP 2005532974 T	04-11-2005
			TW 233938 B	11-06-2005
			US 2005215076 A1	29-09-2005
EP 1029827	A1	23-08-2000	WO 9925660 A1	27-05-1999
			US 6340646 B1	22-01-2002
WO 2004107297	A	09-12-2004	US 2007009674 A1	11-01-2007
US 2007009674	A1	11-01-2007	WO 2004107297 A1	09-12-2004
US 6139613	A	31-10-2000	NONE	
EP 1449811	A	25-08-2004	CN 1599697 A	23-03-2005
			WO 03037798 A1	08-05-2003
			US 2004265587 A1	30-12-2004