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Industry Canada

CA 2673329 A1 2008/06/26

(21) **2 673 329**

**(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION**

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2007/12/19
(87) Date publication PCT/PCT Publication Date: 2008/06/26
(85) Entrée phase nationale/National Entry: 2009/06/18
(86) N° demande PCT/PCT Application No.: EP 2007/064191
(87) N° publication PCT/PCT Publication No.: 2008/074823
(30) Priorité/Priority: 2006/12/19 (EP06126485.9)

(51) Cl.Int./Int.Cl. *C08J 5/18* (2006.01),
C09D 183/04 (2006.01)

(71) **Demandeur/Applicant:**
DEGUSSA NOVARA TECHNOLOGY S.P.A., IT

(72) **Inventeurs/Inventors:**
FREGONESE, DANIELE, IT;
COSTA, FULVIO, IT

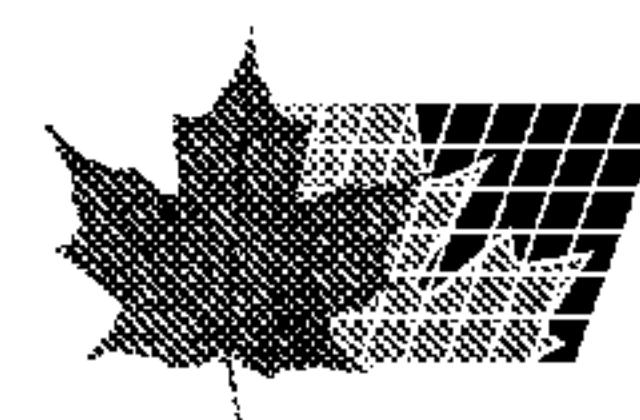
(74) **Agent:** MARKS & CLERK

(54) Titre : PROCEDE SOL-GEL POUR FABRIQUER DES FILMS PROTECTEURS POUR DES SUBSTRATS
POLYMERES

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

(57) Abrégé/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.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(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)(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).

(25) Filing Language: English

(26) Publication Language: English

Published:

— with international search report

(30) Priority Data:
06126485.9 19 December 2006 (19.12.2006) EP(71) Applicant (for all designated States except US): **DEGUSSA 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 Viganove, I-30030 Viganovo (VE) (IT).

WO 2008/074823 A1

(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.

**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.

15 Other uses of the polymeric materials, such as glazing, decorative architectural panels and mirrors, 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 alkoxy silane. Those alkoxy silane 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.

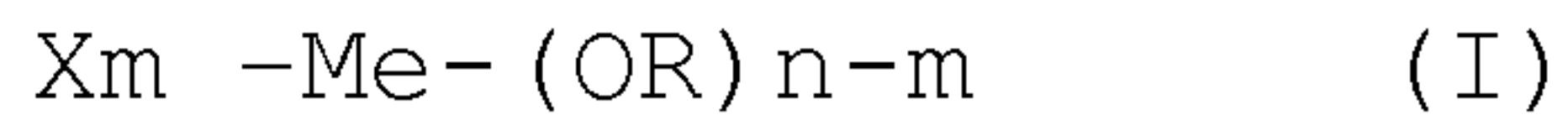
10 The literature describes the use sol -gel techniques-based coating for several supports but the industrialisation of such methods have been always seen as problematic because of the high temperature required for curing, see for instance the patents
15 6,017,389, 6,130,152 and the Italian patent N098 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 a 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 tetrafluoroctyltriethoxysilane. 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 H₂O/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 Ka 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:

10 X_m-Me- (OR)_{n-m}

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

X is R₁ or OR₁, where R₁ 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 R₁ 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 siloxane, silane or silicon; F-based hydrophobic

25 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 gelation 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 5 120 °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

10 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).

15 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 20 at least one section damaged.

Surface roughness is determined by profilometer Taylor Mod. 222.

25 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-tertbutylphenyl]-propionic acid-polyethyleneglycol)300-ester supplied by Ciba have been added to the solution.

15

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

20 plate (10cm length, 15 cm width, 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 width, 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

5 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.

10 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-15 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

20 plate (10cm length, 15 cm width, 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 Tinuvil 1130 Bis(-β-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-terbutylphenyl]-propionic acid-polyethyleneglycol)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 polymethylmethacrylate plate (PMMA) (10cm length, 15 cm width, 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 polymethylmethacrylate plate under visual inspection did not change the 5 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 10 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 (tetrafluoroctyltriethoxysilane) supplied by Degussa AG.

15 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- 20 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 25 plate (PC) (10cm length, 15 cm width, 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 percarbonate plate is 5 improved when compared to the uncoated percarbonate 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 10 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 15 (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 20 14.56 g of Tinuvin 1130 Bis(-β-[3-(2-H-Benzotriazole-2-yl)-4-hydroxy-5-terbutylphenyl]-propionic acid-polyethyleneglycol)300-ester supplied by Ciba have been added to the solution.

The mixture so obtained is then applied by dip coating 25 (dipping speed 0.39cm/s) on rectangular polycarbonate

plate (PC) (10cm length, 15 cm width, 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-terbutylphenyl]-propionic acid-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.

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

plate (10 cm length, 15 cm width, 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.

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

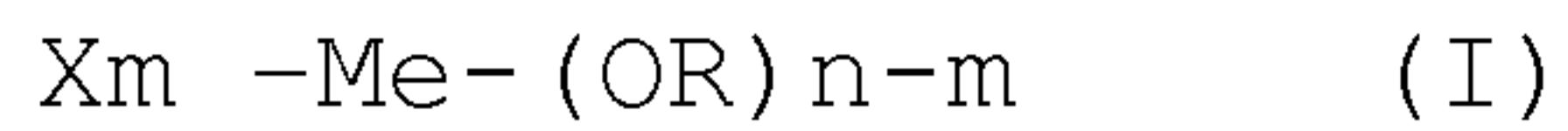
In the example 6 it has been listed also the Dynasil F8261 as agent for better hydrophobic effect.

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), allyldiglycolcarbonate (CR39) and nylon.

Claims:

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

- preparation of a solution in a solvent of one or
- 5 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;

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 a antistatic and reducing reflectance agent;

25 - eventual addition of a compound with photocatalitic 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 or the preparation of transparent films

5 substrates according to claim 1 in which the alkoxide is selected among tetramethyl-orthosilane, tretraethylorthosilane, tetraethoxyorthosilicate, tetrapropylorthosilicates, tetrabutylorthosilicate, ethyltryethoxysilane, 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 acetone, tetrahydrofuran, dioxane and more 15 ethanol.

4. Process for the preparation of transparent films according to claim 1 where the compound with ultraviolet radiation absorbing property is selected from the group of benzotriazoles, the s- 20 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 tetrafluoroctyltriethoxy- silane.

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 20 claim 1 where the hydrolysis of the alkoxide is performed by addition of a controlled quantity of water.
12. Process for the preparation of films according to claim 12 where the molar ratio H₂O/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 Ka between 0.1 and 3.
14. Process for the preparation of films according to claim 1 where the drying temperature is between 60 30 and 200°C.