



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁷ : C23C 16/50, 16/30, B05D 7/24, C03C 17/28, C04B 41/48</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/14298</p> <p>(43) International Publication Date: 16 March 2000 (16.03.00)</p>
<p>(21) International Application Number: PCT/US99/20923</p> <p>(22) International Filing Date: 7 September 1999 (07.09.99)</p> <p>(30) Priority Data: 98116895.8 7 September 1998 (07.09.98) EP</p> <p>(71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): CORZANI, Italo [IT/IT]; Via Fontevecchia, 40, I-66100 Chieti (IT). DATTA, Saswati [US/US]; 11636 Plumhill Lane, Cincinnati, OH 45249 (US). FRANCE, Paul, Amaat, Raymond, Gerard [BE/US]; 8375 Todd Creek Circle, West Chester, OH 45069 (US). MARCHESINI, Maurizio [IT/IT]; Via Danubio, 9, I-65010 Spoltore (IT). PALUMBO, Gianfranco [DE/DE]; Georgenfeld 7, D-61348 Bad Homburg (DE). D'AGOSTINO, Riccardo [IT/IT]; Via Orabona, 4, I-70126 Bari (IT). FAVIA, Pietro [IT/IT]; Via Orabona, 4, I-70126 Bari (IT). LAMENDOLA, Ritalba [IT/IT]; Via Orabona, 4, I-70126 Bari (IT). RADOMYSELSKIY, Arseniy Valerevich [UA/US]; 1031 Delta Avenue 31, Cincinnati, OH 45208 (US). SCHONE,</p>	<p>Rainer, Walter, Max [DE/DE]; Romberweg 15, D-61462 Königstein (DE).</p> <p>(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).</p> <p>(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: ARTICLES WITH HARD SURFACES HAVING SUPER HYDROPHOBIC COATING</p>		
<p>(57) Abstract</p> <p>The present invention relates to articles with hard surfaces as for example ceramics such as tiles, dishes, soup bowls, sanitary equipment like toilets, urinals, washing basins, shower cabins; glass/finished surfaces such as windows, hard contact lenses, drinking glasses, building surfaces, marble, painted surfaces e.g. on buildings, cars, airplanes; plastic/metal surfaces; appliances such as dishwashers, dryers, laundry machines, mixers, telephones, computer keyboards; inside and/or outside of containers for aqueous or hydrophilic materials such as liquid detergent bottles, shampoo bottles, beverage containers, liquid tanks, flowable particle tanks (e.g. flour tanks). Such articles with hard surfaces are treated to have at least part of their surface provided with super hydrophobicity.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

Articles with hard surfaces
having super hydrophobic coating

5

10

15

Field of the invention

The present invention relates to articles with hard surfaces as for example ceramics such as tiles, dishes, soup bowls, sanitary equipment like toilets, urinals, washing basins, shower cabins; glass/finished surfaces such as windows, optical
20 lenses, hard contact lenses, drinking glasses, building surfaces, marble, painted surfaces e.g. on buildings, cars, airplanes; plastic/metal surfaces; appliances such as dishwashers, dryers, laundry machines, mixers, telephones, computer keyboards; inside and/or outside of containers for aqueous or hydrophilic materials such as liquid detergent bottles, shampoo bottles, beverage containers,
25 liquid tanks, flowable particle tanks (e.g. flour tanks). Such articles with hard surfaces are treated to have at least part of their surface provided with super hydrophobicity.

Background of the invention

30

For instance, U.S. Pat. No. 3,498,527 teaches that paper board containers for liquids can be waterproofed by application of a waterproofing coating such as wax or polyethylene, and a similar method is shown in U.S. Pat. No. 2,708,645 for waterproofing paper drinking cups and in U.S. Pat. No. 3,212,697 for paper
35 grocery sacks. In U.S. Pat. No. 3,597,313, temporary wet strength is imparted to paper by coating it with a polymeric alcohol-polymeric aldehyde reaction product.

Coating processes, by themselves, have been used to produce disposable articles of sanitary clothing. In U.S. Pat. No. 3,078,849, a disposable sanitary napkin is disclosed which consists of an adsorbent layer having a liquid-repellent backing of polyvinyl alcohol or similar material capable of initially repelling water but eventually solubilizing. The degree of water-repellency, therefore the lifetime of the napkin, is controlled by varying the thickness of the backing. Because the necessary life of the napkin cannot be predicted by manufacturer or user, the backing must be sufficiently thick to take account of all normal contingencies. U.S. Pat. No. 3,542,028 is directed to a flushable sanitary napkin consisting of a cellulosic sheet treated with a fluoropolymer coating. U.S. Pat. No. 3,559,650 teaches the preparation of a sanitary napkin having two flush-disposable sides separated by a waterproof film too thin to support itself once both faces of the napkin have disintegrated upon disposal.

15 Analogous to the process of coating a surface with a waterproofing substance is the concept of reacting a surface with another material so as to form a reaction product on the surface which has water-repellent properties. For example, U.S. Pat. Nos. 2,130,212 and 3,137,540 teach that materials such as polymeric alcohols may be reacted with other materials to increase their water-repellent properties. The latter patent teaches treating polyvinyl alcohol articles with an aqueous emulsion of an aldehyde to impart water-repellency thereto. U.S. Pat. No. 3,626,943 teaches that disposable diapers can be made from polyvinyl alcohol and waterproofed on one side by reaction with formaldehyde. These reaction-type coating processes suffer from drawbacks. They are carried out in the aqueous phase which is complicated and requires relatively large quantities of reagents. Most of the processes which employ some form of in situ chemical reaction to produce a water-repellent surface are carried out in the liquid phase, some vapor phase treatments are taught by U.S. Pat. Nos. 2,306,222; 2,961,388; and 3,017,290.

A known method of water and oil repellent finishing of textiles, described in USSR Patent 1,158,634, includes plasma treatment in a glow discharge in an atmosphere of inorganic gases, followed by treatment with a fluorine containing acrylic monomer in gas phase. Another prior method of achieving film plasma polymerization, described in U.S. Pat. No. 4,188,426, includes treatment in a glow discharge of per-fluoro-cyclo-butane or hexafluoroethane to reduce the friction coefficient and to improve the surface hydrophobia of organic and inorganic substrates (e.g. polyethylene films, metals). However these disclosures do not achieve a level of water repellency as the present invention.

Plasma-deposited fluorocarbon coatings are often cited in the literature as "teflon-like coatings" because their CF_x ($0 < x \leq 2$) composition and surface energy can be made very close to that of polytetrafluoroethylene (PTFE, $-(CF_2-CF_2-)_n$), known on the market as Teflon®.

Plasma coating processes of metals, polymers, and other substrates, with fluorocarbon films are known in the art. As an example, it is known from USP 4 869 922 and from other sources, that deposition from continuous (i.e. non modulated) radiofrequency (RF) glow discharges fed with fluorocarbons provides films, layers, tapes, plates, and differently shaped articles made of plastics, metals or other materials, with a thin fluorocarbon coating, with no other material interposed between the coating itself and the substrate. Such coatings are claimed to have very good adherence to the items processed, to be void-free, to be uniform or not porous, and to show controlled wettability characteristics, which depend on their surface chemical composition. The non modulated, continuous plasma process of the above mentioned patent leads to coatings characterized by static water contact angle (WCA) values lower than 120° .

Glow discharges treatments are also considered in US-A-5 462 781 for improving the bondability of an implantable polymer medical device or for changing the wettability of a polymer fabric. Several of the references discussed in this patent

confirm non modulated, continuous plasma treatments as a means for varying the inherent WCA of a surface.

5 US-A-5 034 265 discloses a non modulated, continuous plasma treatment for improving the biocompatibility of vascular grafts with a CF_x fluorocarbon coating deposited at the inside wall of the grafts in a proper plasma reactor fed with tetrafluoroethylene (C_2F_4 , TFE) at 0.2 Torr. In the preferred embodiment of the invention no other materials are interposed between the substrate and the coating.

10 U.S. Pat No 5,328,576 discloses a method for imparting water and oil repellent surface properties to fabrics or paper that includes pretreatment in a low pressure oxygen plasma in the presence of water vapor followed by plasma polymerization of methane in a high frequency glow discharge carried out in the same treatment chamber. This method doesn't deliver durable, permanent coatings with a WCA
15 higher than about 120° .

U.S. Pat. No. 5,262,208 discloses an gas plasma treatment for archival preservation of paper manuscripts by a thin film protective polymer film. The treatment time is ranging from 30-3600 seconds. Other methods have been used
20 to obtain thin coatings on the web materials with short treatment periods. Providing surface treatment is disclosed in US Patent No. 4,842,893 and 4,954,371 which describe a process for high speed coating of substrates with a complete and uniformly adhering layer and using electron beam radiation curing of the vapor deposited monomers for multilayer capacitors. U.S. Pat. No.
25 4,842,893 discloses high speed coating process including flash vaporization system and electron beam curing. Both of these electron beam disclosures are incorporated herein by reference. Other uses of electron beam coatings in the electronic industry field have been reported by Westinghouse science & technology center USA (Adv. Mat. Newsletter Volume 13, No 9, 1991 page 4).

30 It has now been found that providing at least part of the hard surface of articles with hard surfaces with a hydrophobicity at heretoforth unachievable levels can provide a tremendous benefit to the use of such articles.

Summary of the invention

5 The present invention relates to articles with hard surfaces as for example ceramics such as tiles, dishes, soup bowls, sanitary equipment like toilets, urinals, washing basins, shower cabins; glass/finished surfaces such as windows, optical lenses, hard contact lenses, drinking glasses, building surfaces, marble, painted surfaces e.g. on buildings, cars, airplanes; plastic/metal surfaces; appliances such as dishwashers, dryers, laundry machines, mixers, telephones, computer
10 keyboards; inside and/or outside of containers for aqueous or hydrophilic materials such as liquid detergent bottles, shampoo bottles, beverage containers, liquid tanks, flowable particle tanks (e.g. flour tanks). Such articles with hard surfaces are treated to have at least part of their surface provided with super hydrophobicity. In particular the present invention relates to articles with hard
15 surfaces which are coated by means of modulated plasma deposition of fluorocarbons.

Specifically, the present invention, having the features mentioned in the annexed claims, relates to articles with hard surfaces having at least part of their surface
20 coated with a thin, well adherent, nonporous, fluorocarbon coating with super hydrophobic properties, i.e. characterized by static water contact angle (WCA) values, measured on a smooth and plane surface, higher than about 120° , preferably higher than 130° , more preferably higher than 150° . For example, hard surfaces being treated with this method have their hydrophobicity markedly
25 improved. They can for example provide improvements in water repellency, soil/dirt sticking prevention, reduced build-up on surface, complete emptying of containers, no build-up in appliances e.g. detergent dispensers, reduced cleaning needed for surfaces, easy cleaning or ageing/rust reduction.

30 The present invention deals with articles with hard surfaces having part of their surface treated i.e. characterized by static water contact angle (WCA) values higher than about 120° , preferably higher than 130° , more preferably higher than 150° . The hard surfaces are preferably subjected to a modulated glow discharge plasma treatment performed with a fluorocarbon gas or vapor compound fed in a
35 properly configured reactor vessel where the hard surfaces are positioned. The plasma process deposits a continuous, fluorocarbon thin film with super hydrophobic surface characteristics, tightly bound to the hard surface of the article.

Alternatively a more conventional thin film coating process followed by high energy surface curing can be used. This is the method of using a high speed vacuum coating process for producing durable and thin water-repellent coatings on a hard surface. It uses e.g. a movable support such as rotating drum in a vacuum chamber. The surface of the support is maintained at a temperature sufficient to permit condensation of a vaporized material deposited in the chamber. The material is a curable monomer with a relatively low molecular weight. The monomer vapor is created using a flash vaporizer. The desired amount of curable monomer is metered to a heated flash vaporizer system where the material is vaporized. It is then transported e.g. by its inherent pressure, to the article with hard surface resting on the rotating drum and condensed on the hard surface. According to the method the article with hard surface is then transported to a curing means such as an energy source which emits an electron beam, UV-light radiation or exposure to an electro magnetic field. Alternative the curable monomer can also be transferred into radicals by passing through a plasma zone (zone of high voltage discharge). The curing of the monomer by the curing means then provides a coating on the hard surface which has a static water contact angle of more than 120°.

20

The method for delivering the curable monomer to the hard surface for minimizing the amount of monomers can use an ultrasonic atomizer producing micro droplets of curable monomer. They are released into a vaporization tube heated by band heaters. The atomized droplets impinge on the inner wall of the vaporization tube and are instantaneously vaporized, i.e., flash vaporized. This reduces the opportunity for polymerization prior to being deposited on the article with hard surface.

"Plasma," as used herein, is used in the sense of "low-temperature plasma" or "cold plasma" produced by igniting a glow discharge in a low pressure gas through a power supply. Glow discharges contain a variety of species chemically active and energetic enough to cause chemical reactions with surfaces exposed, i.e. covalent bonding to a suitable substrate material. Cold plasmas, or glow discharges, are generally produced with high frequency (from KHz to MHz and

30

GHz) power supply (HF plasmas). Electrons, positive and negative ions, atoms, excited molecules, free radicals, and photons of various energies are formed in a cold plasma.

5 "Modulated plasma" means a non continuous plasma, HF plasma, i.e. a glow discharge whose driving power is pulsed between a maximum value and zero (ON/OFF pulse) or a fraction of it, at a certain frequency, with a proper pulse generator connected to the main power supply. In the case of ON/OFF pulsed systems, the time ON and time OFF values are among the experimental
10 parameters of the process. Superimposing a triggering ON/OFF pulse to the main high frequency field which generally drives a glow discharge, alternates short continuous discharges with plasma OFF time intervals where active species still exists in the gas phase, but the effects of ions and electrons are strongly reduced. This alternating exposure to two different processes leads to unique surface
15 modifications of the articles, which can be very different from those of continuous plasma process, as it will be shown.

"Plasma deposition" or "plasma polymerization" is the plasma process that leads to the formation of thin (0.01 - 2 μm), partly crosslinked, void-free, continuous
20 coatings well adherent to surfaces. The molecules of the gas phase are fragmented by energetic electrons, which are able to break chemical bonds; this process leads to radicals and other chemical species which are able to deposit at surfaces inside the vacuum chamber and form a thin, uniform film. The action of the plasma may also affect the surface of a polymer article in the early deposition
25 time; energetic species may break bonds in the surface with possible evolution of gas products, such as hydrogen, and formation of free radical sites which contribute to form covalent bonds between the growing film and the surface.

It has been found that it is possible to deposit thin fluorocarbon films with super
30 hydrophobic characteristics, i.e. showing a surprisingly high static water contact angle (WCA) value, even up to about 165°. The present invention thus refers to articles with hard surfaces coated with fluorocarbon films characterized by a WCA value higher than 120°, preferably higher than 130°, more preferably higher than 150°.

35

In particular fluorocarbon coatings with F/C ratio from about 1.50 to about 2.00 deposited on different surfaces and characterized by WCA values higher than about 120°, such as between about 155° and about 165°, find useful application in

articles with hard surfaces, especially if the coatings have been deposited at the surface of different polymer substrates such as polyethylene (PE), polypropylene (PP) polyethyleneterephthalate (PET). It should be noted that the F/C ratio could be theoretically up to 3, if the coating would be formed only by a mono-molecular layer of CF_3 groups. But the formation of intermolecular cross-links and the formation of claims (containing CF_2 fragments) which are grafted onto the surface lowers the above theoretical value so that the obtained coatings, notwithstanding the fact that they contain many CF_3 groups, have a general F/C ratio in the range of about 1.50 to about 2.00.

The thickness of the coatings depends on the duration of the plasma process at different conditions, and can be kept between 0.01 and 2 μm . It has been found that the nature of the substrate materials does not influence the chemical composition or the thickness of the coatings. Coatings with WCA values up to about 165° (e.g. $165^\circ \pm 5^\circ$) were obtained.

Hard surfaces to be treated are subjected to modulated plasma gas discharge in the presence of at least one fluorocarbon gas or vapor. Specifically, fluorocarbon gases or vapors such as tetrafluoroethylene (TFE, C_2F_4), hexafluoropropene (HFP, C_3F_6), perfluoro-(2-trifluoromethyl-)pentene, perfluoro-(2-methylpent-2-ene) or its trimer may be used, TFE being the presently preferred choice. The plasma deposition process is preferably performed by positioning the hard surface in a properly arranged plasma reactor, connecting the reactor to a source of a fluorocarbon gas or vapor, regulating flow and pressure of the gas inside the reactor, and sustaining a glow discharge in the reactor with a high frequency electric field in a pulsed (modulated) mode by means of a suitable pulsed power supply. The parameters which define the glow discharge treatment includes the feed gas or vapor, its flow rate, its pressure, the position of the articles with hard surfaces inside the reactor, the design of the reactor, the exciting frequency of the power supply, the input power, the time ON and the time OFF of the pulsing system. Articles with hard surfaces may be positioned in the "glow" region of the discharge, i.e. directly exposed to the plasma, or in the "afterglow" region, i.e. downstream in respect to the visible glow. The two positions generally result in coatings with different composition and properties; treating the hard surface with modulated glow discharge results also in different coatings respect to continuous treatments.

Brief description of the drawings

The invention will now be described, purely by way of example, with reference to the enclosed figures of drawing, wherein:

- Figure 1 compares a conventional "continuous" RF glow discharge with an ON/OFF "modulated" RF glow discharge;

- Figure 2 portrays a typical scheme of a plasma reactor adapted for use within the context of the invention;

- Figure 3 shows a C1s ESCA signal of an uncoated polyethylene surface wherein the signal is due only to C-H, C-C bonds of the substrate;

- Figure 4 shows a C1s ESCA signal of a PE surface coated with a fluorocarbon coating deposited as described in example 1 (glow position, continuous mode), with WCA of $100 \pm 5^\circ$; the signal is composed by components due to CF₃, CF₂, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination;

- Figure 5 shows a C1s ESCA signal of a PE surface coated with a fluorocarbon coating deposited as described in example 1 (afterglow position, continuous mode), with WCA of $120 \pm 5^\circ$; the signal is composed by components due to CF₃, CF₂, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination; and

- Figure 6 shows a C1s ESCA signal of a PE surface coated with a fluorocarbon coating deposited as described in example 1 (glow position, modulated mode), with WCA of $165 \pm 5^\circ$; the signal is composed by components due to CF₃, CF₂, CF and CCF bonds of the fluorocarbon coating, and to C-H, C-C bonds due to surface contamination.

Detailed description of the invention

Figure 1 compares a conventional "continuous" plasma (figure 1a) with the modulated process of the invention, (figure 1b) showing pulsed alternating plasma ON with plasma OFF (i.e. no plasma) times. The two processes are schematized by referring to their driving signals.

The reactor 1 schematically shown in figure 2 was utilized not exclusively for developing the deposition method object of the present invention. The reactor vacuum chamber 1 is made of Pyrex glass, is provided with an external RF powered electrode 2 and an internal grounded electrode 3. The external electrode is connected to a power supply 4 (typically a radiofrequency generator operating at e.g. 13.56 MHz) through a matching network and an ON/OFF pulse generator

5. The articles can be treated in the "glow" region of the reactor, onto the grounded electrode 3, as well as in its "afterglow" position i.e. at an afterglow articles holder 6. The gas/vapor is fed through a proper mass flowmeter through a gas/vapor feeding manifold 7, and its pressure, measured at the pump out exit 8 of the reactor, kept at a certain constant value with a manual valve on the vacuum connection between the reactor and its pumping unit. Even though the arrangement shown in the drawing represents a presently preferred choice, those skilled in the art will immediately recognize that pulsed energization of the plasma reactor can be achieved by different means such as direct energization by means of pulsed RF generators commonly used in radar and telecommunication techniques.

Preferably, the deposition process is performed with an RF (13.56 MHz) generator. The RF power delivered to the external electrode of the reactor is kept in the 1-500 Watts range for a power density of 0.02-10 Watt/cm². The reactor is fed with a fluorocarbon compound at a 1-100 sccm flow rate and is kept at a constant pressure of 50-1000 mTorr during the process. Preferably, the glow discharges are modulated through the pulse generator, preferably at 1-500 ms time ON and 1-1000 ms time OFF values, with respective values of about 10 ms and about 190 ms being the most preferred choice at present. The deposition process may range from a few seconds to many hours; during this time a uniform fluorocarbon coating is deposited on the hard surfaces of the articles positioned in the glow as well as on those in the afterglow region. The deposition rate, a typical one being in the 20 - 400 Å/min range, was measured by weighing (weight/time) the articles before and after the discharge, or by measuring the thickness of the coatings (thickness/time) with an Alpha Step profilometer. The deposition rate and the chemical composition of the coating depend on the experimental conditions (pressure, power, article position, time ON, time OFF, gas feed and flow rate) of the discharge.

The coatings obtained are uniform over the entire surface of the article; when deposited on flat (i.e. plane), smooth surfaces, their hydrophobic character has been estimated through their static WCA value, as measured with a WCA goniometer. The measurement is done on a flat, i.e. plane, and smooth surface of a substrate after coating. The term smooth as used herein for water contact angle measurements refers to a roughness of no more than 5 microns in accordance with standard roughness measurements on continuous surfaces. WCA values in

the range about 120° to about 165°, corresponding to a critical surface tension lower than that of PTFE (18 dynes/cm) have been measured for fluorocarbon CF_x coatings, when x ranges between about 1.50 and about 2.00. The chemical composition of coatings is preferably determined by Electron Spectroscopy for
5 Chemical Analysis (ESCA) within the sampling depth of the technique (about 100 Å). The adherence of the coating to the surface is very good.

The following examples are given for the purpose of still better illustrating the inventive concept of the present invention, and for highlighting the advantages of
10 using modulated over continuous treatments.

EXAMPLE 1

15 Three sets of materials having a "hard surface" and being provided by silicon, PE and PP, were positioned onto the grounded electrode 3 of the reactor schematized in Figure 2. The areas per material were in the range of 2 - 10 cm². A similar set of articles was positioned in the afterglow position at 6. C₂F₄ was set to feed continuously the reactor at 6 sccm, and the pressure set at 300 mTorr.
20 The RF generator was connected to the reactor and allowed to sustain the discharge with 50 Watt of input power for 90 min, then switched off.

Another glow discharge was subsequently run with a similar set of articles positioned in the glow position and no articles in the afterglow position, under the
25 same conditions described above except for the fact that modulation was effected at 10 ms time ON and 190 ms time OFF through the pulse generator.

At the end of the two discharges the articles were extracted from the reactor and the WCA of their surface measured. The WCA values shown in Table 1 were
30 found, which are compared to the WCA values of the unprocessed articles. A deposition rate of 30 ± 5 Å/min was measured for the coatings deposited in the modulated mode.

Other articles, treated in the two modes, were analysed with the ESCA technique.
35 Their surface composition resulted to be entirely composed by carbon and fluoride (fluorine as element), according to the results shown in Tables 2a-c. No other elements were detected (e.g. Si for silicon), which means that the coatings are

continuous. The C1s spectrum of the uncoated PE substrate is shown in Figure 3, while the C1s spectra of PE samples coated as described above are shown in Figures 4, 5 and 6, respectively.

5 Table 1

SUBSTRATE	Si	PE	PP
WCA unprocessed	$15^{\circ} \pm 3^{\circ}$	$95^{\circ} \pm 3^{\circ}$	$85^{\circ} \pm 3^{\circ}$
WCA continuous discharge (glow position)	$100^{\circ} \pm 5^{\circ}$	$100^{\circ} \pm 5^{\circ}$	$100^{\circ} \pm 5^{\circ}$
WCA continuous discharge (afterglow position)	$120^{\circ} \pm 5^{\circ}$	$120^{\circ} \pm 5^{\circ}$	$120^{\circ} \pm 5^{\circ}$
WCA modulated discharge (glow position)	$165^{\circ} \pm 5^{\circ}$	$165^{\circ} \pm 5^{\circ}$	$165^{\circ} \pm 5^{\circ}$

Table 2a

ESCA results for the continuous discharge (glow position) of Example 1

10

COATED SUBSTRATE	Si	PE	PP
carbon atomic %	43.3	42.4	42.9
fluorine atomic %	56.7	57.6	57.1
F/C ratio	1.31	1.36	1.33

Table 2b

ESCA results for the continuous discharge (afterglow position) of Example 1

COATED SUBSTRATE	Si	PE	PP
carbon atomic %	34.4	33.8	34.1
fluorine atomic %	65.6	66.2	65.9
F/C ratio	1.91	1.96	1.93

15

Table 2c

ESCA results for the modulated discharge (glow position) of Example 1

COATED SUBSTRATE	Si	PE	PP
carbon atomic %	36.4	36.2	36.7
fluorine atomic %	63.6	63.8	63.3

F/C ratio	1.75	1.76	1.72
-----------	------	------	------

EXAMPLE 2

5 Three sets of surfaces of glass, silicon and PE, of areas in the range of 2-10 cm² per article, were positioned onto the grounded electrode 3 of the reactor schematized in Figure 2. A similar set of articles was positioned in the afterglow position. C₃F₆ was set to feed continuously the reactor at 5 sccm, and the pressure set at 300 mTorr. The RF generator was connected to the reactor and
10 allowed to sustain the discharge with 50 Watt of input power for 60 min, then switched off.

Another glow discharge was subsequently run with a similar set of articles positioned in the glow position and no articles in the afterglow, under the same
15 conditions described above except for the fact that modulation was effected at 10 ms time ON and 90 ms time OFF through the pulse generator.

At the end of the two discharges the articles were extracted from the reactor and their WCA measured. The WCA values shown in Table 3 were found, which are
20 compared to the WCA values of the unprocessed articles. A deposition rate of 70 ± 5 Å/min was measured for the coatings deposited in the modulated mode.

Other articles, treated in the two modes, were analysed with the ESCA technique; their surface composition resulted to be entirely composed by carbon and fluoride
25 (fluorine as element), according to the results shown in Tables 4a-c. Also for this case, since no other elements were detected (e.g. Si for silicon and glass substrates), the coatings were assumed to be continuous.

30 Table 3

SUBSTRATE	glass	Si	PE
WCA unprocessed	35° ± 3°	15° ± 3°	95° ± 3°
WCA continuous discharge (glow position)	105° ± 5°	105° ± 5°	105° ± 5°
WCA continuous discharge (afterglow position)	120° ± 5°	120° ± 5°	120° ± 5°

WCA modulated discharge (glow position)	120° ± 5°	120° ± 5°	120° ± 5°
--	-----------	-----------	-----------

Table 4 a

5 ESCA results for the continuous discharge (glow position) of Example 2

COATED SUBSTRATE	glass	Si	PE
carbon atomic %	42.7	42.1	41.5
fluorine atomic %	57.3	57.9	58.5
F/C ratio	1.34	1.37	1.41

Table 4 b

10 ESCA results for the continuous discharge (afterglow position) of Example 2

COATED SUBSTRATE	glass	Si	PE
carbon atomic %	37.1	38.3	38.1
fluorine atomic %	62.9	61.7	61.9
F/C ratio	1.69	1.61	1.62

Table 4 c

15 ESCA results for the modulated discharge (glow position) of Example 2

COATED SUBSTRATE	glass	Si	PE
carbon atomic %	38.1	39.9	39.2
fluorine atomic %	61.9	60.1	60.8
F/C ratio	1.62	1.51	1.55

As an alternative to provide the article with hard surface of the present invention the method of thin film coating with a monomer followed by surface curing can be used.

20 The coating formed by the method of the present invention has a thickness of less than 5 microns, and preferably less than 2 microns and most preferably in the range of 0.001 to 1 microns. The coatings are formed by depositing a vapor of curable monomer, under vacuum, on a movable article with hard surface which is

mounted in thermal contact with a support, for continuous processing preferably a rotating drum, which is maintained at a temperature below the boiling point of the vaporized monomer under the environmental conditions in vacuum chamber. As a result of this temperature differential, the monomer vapor condenses on the hard surface. The monomer materials utilized in the present invention are relatively low in molecular weight, between 150 and 1000 Atomic Mass Units (AMU), and preferably in the range 200 to 300 AMU. Polyfunctional fluoro-carbons and especially fluoroacrylates or mixtures of monofunctional fluoroacrylates and polyfunctional fluoroacrylates are preferred. The monomers or monomer mixtures employed have an average of about two or more double bonds (i.e., a plurality of olefinic groups) and have a vapor pressure such that they condense on the article with hard surface. Such vapor pressures are for example pressure between about $1.33 \cdot 10^{-6}$ mbar and $1.33 \cdot 10^{-1}$ mbar, most preferably a vapor pressure of approximately $1.33 \cdot 10^{-2}$ mbar at standard temperature and pressure, (i.e., relatively low boiling materials) are selected.

These high-vapor-pressure monomers can be flash vaporized already at low temperatures and thus are not degraded (cracked) by the heating process. The absence or low amount of unreactive degradation products results in coatings with a reduced level of volatile components in which substantially all of the deposited monomer is reactive and will cure to form an integral film when exposed to a source of radiation. These properties make it possible to provide a substantially continuous coating despite the fact that the deposited film is very thin. The cured films exhibit excellent adhesion and are resistant to chemical attack by organic solvents and inorganic salts.

The high speed vacuum coating process for producing water vapour permeable substrates with exceptional water repellent properties require a curable monomer component. Desirably, the curable monomer for obtaining water-repellent coatings comprises fluoro-containing group.

In one embodiment, any suitable fluoromonomer may be used, including, but not limited to, fluoroacrylate monomers, fluoro olefin monomers, fluorostyrene monomers, fluoroalkylene oxide monomers (e.g., perfluoropropylene oxide, perfluorocyclohexene oxide), fluorinated vinyl alkyl ether monomers, and the
5 copolymers thereof with suitable comonomers, wherein the comonomers are fluorinated or unfluorinated. Fluoromonomers which are polymerized by a free radical polymerization process are preferred.

In one embodiment, fluorostyrenes and fluorinated vinyl alkyl ether monomers
10 which may be used in the method of the present invention include, but are not limited to, α -fluorostyrene; β -fluorostyrene; α , β -difluorostyrene; β , β -difluorostyrene; α , β , β -trifluorostyrene; α -trifluoromethylstyrene; 2,4,6-Tris (trifluoromethyl)styrene; 2,3,4,5,6-pentafluorostyrene; 2,3,4,5,6-pentafluoro- α -methylstyrene; and 2,3,4,5,6-pentafluoro- β -methylstyrene.

15

In yet another embodiment, tetrafluoroethylene can also be used in the method of the present invention and include, but are not limited to, tetrafluoroethylene-hexafluoropropylene copolymers, tetrafluoroethylene-perfluorovinyl ether
20 copolymers (e.g., copolymers of tetrafluoroethylene with perfluoropropyl vinyl ether), tetrafluoroethylene-ethylene copolymers, and perfluorinated ionomers (e.g., perfluorosulfonate ionomers; perfluorocarboxylate ionomers).

In still another embodiment, fluorocarbon elastomers (see, e.g., 7 Encyclopedia of Polymer Science & Engineering 257) are a group of fluoro olefin polymers which
25 can also be used in the process of the present invention and include, but are not limited to, poly(vinylidene fluoride-co-hexafluoropropylene); poly(vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene); poly[vinylidene fluoride-co-tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly[tetrafluoroethylene-co-perfluoro(methyl vinyl ether)]; poly(tetrafluoroethylene-co-propylene); and
30 poly(vinylidene fluoride-co-chlorotrifluoroethylene).

In the preferred embodiment, because of their reactivity, physical properties, and the properties of cured films formed from such components, fluoroacrylates are particularly useful monomeric materials. The term "fluoroacrylate monomer," as used herein, refers to esters of acrylic acid ($H_2C = CHCOOH$) or methacrylic acid ($H_2C = CCH_3 - COOH$), where the esterifying group is a fluorinated group such as perfluoroalkyl. A specific group of fluoroacrylate monomers useful in the method of the invention are compounds represented by formula (I): $H_2C = CR_1 - COO (CH_2)_n R_2$ (I) wherein: n is 1 or 2;

10 R_1 is hydrogen or methyl; and R_2 is a perfluorinated aliphatic or perfluorinated aromatic group, such as a perfluorinated linear or branched, saturated or unsaturated C_1 to C_{10} alkyl, phenyl, or naphthyl.

In a particular embodiment of the invention, R_2 is a C_1 to C_8 perfluoroalkyl or $-CH_2 - NR_3 - SO_2 - R_4$, wherein R_3 is C_1 - C_2 alkyl and R_4 is C_1 to C_8 perfluoroalkyl. The term "perfluorinated," as used herein, means that all or essentially all hydrogen atoms on an organic group are replaced with fluorine. Monomers illustrative of Formula (I) above, and their abbreviations, include the following:

2-(N-ethylperfluorooctanesulfonamido) ethyl acrylate ("EtFOSEA");

20 2-(N-ethylperfluorooctanesulfonamido) ethyl methacrylate ("EtFOSEMA");

2-(N-methylperfluorooctanesulfonamido) ethyl acrylate ("MeFOSEA");

2-(N-methylperfluorooctanesulfonamido) ethyl methacrylate ("MeFOSEMA");

1,1-Dihydroperfluorooctyl acrylate ("FOA"); and

1,1-Dihydroperfluorooctyl methacrylate ("FOMA").

25

Alternatively, the curable monomer component can also include polyfunctional acrylates, which are set forth in U.S. Patent 4,842,893.

30

Benefits of the invention

Without wishing to be bound by theory it is believed that the benefits of the present invention are obtainable by the mechanism indicated below. In the following the particular benefits of the present invention, i.e. the benefits of articles with hard surfaces which hard surfaces have superhydrophobic coatings, will be discussed.

Ceramics such as tiles, dishes, soup bowls, sanitary equipment like toilets, urinals, washing basins, shower cabins are often exposed to aqueous liquid which is contaminated or loaded with various components which are known to build up over time or immediately and thus leave after a short period or even after a single use of this article an unclean or stained surface. Such surfaces therefore require frequently cleaning. The frequency of this cleaning and therefore the quantity of soiling residue and build up on the surface of such articles can drastically be reduced when reducing the time available for residue build up by rendering the surface so hydrophobic that aqueous liquids will not stay on such surfaces. For example the build up of soap and dirt residues in washing basins can be drastically reduced when rendering such basins superhydrophobic such that liquid carrying these soilings has an increased flow off speed.

Similarly glass and finished surfaces such as windows, optical lenses, hard contact lenses, drinking glasses, building surfaces, marble, painted surfaces for example on buildings, cars or air planes, plastic or metal surfaces, appliances share similar problems and therefore benefit in a similar way from the present invention. Such surfaces are all more or less frequently exposed to water and soilings or contaminates. For example glass windows or building surfaces are exposed to the airborne dirt and particular contamination's, e.g. along high traffic roads, which cause the need for frequent repainting or cleaning of these surfaces.

This situation is further aggravated by rain falling onto this surfaces and causing the dirt to stick even firmer to the surface. With the introduction of the superhydrophobic coating however such build up does not adhere as strongly to the surface. In addition the increased speed in rainwater flow off from such surfaces can carry dirt away easier. This combined action of reduced adherence and increased transport speed with rainwater flow off does provide a substantial reduction in the frequency of cleaning of such surfaces. Obviously the same is true for appliances (which are usually not exposed to rain water) but for which a wipe cleaning becomes more effective and therefore easier and less time consuming for the person cleaning such an appliance.

The same considerations as above apply to containers on their outside. However an additional benefit has been identified when coating containers on their inside. Since the superhydrophobicity actively drives aqueous liquids away from the superhydrophobic surface it becomes possible to completely empty such
5 containers without the previously necessary effort. Especially for liquid consumer goods like shampoos, liquid detergents but also beverages and industrial size beverage tanks it becomes very efficient to use super hydrophobic coatings on the inside of the container such that it can be emptied without much effort by simple
10 gravitational flow. In a similar way containers holding a material having liquid flow characteristics (such as flour) can benefit from such superhydrophobic inside coating of a container (for example the tanks in which flour is transported).

When considering the above the benefit of the present invention for articles with
15 hard surfaces treated to be superhydrophobic is based on the combined action of reduced ability of undesired material to stick to the article (this is at least partially attributed to the reduced friction coefficient), i.e. creating less build up on such a treated surface, and the increased speed in run off of aqueous liquids from such surfaces. It should also be mentioned that due to the thickness of the coating no
20 change in optical performance (transparency, color, surface texture) is caused.

Claims

1. An article with a hard surface which article is characterized in that at least
5 part of said hard surface is treated with a coating and said treated hard surface
has a static water contact angle (WCA) higher than about 120°, preferably higher
than about 130°, most preferably between about 150° and about 165°.
2. An article according to claim 1 characterized in that said coating is a
10 fluorocarbon coating.
3. An article according to claim 2 characterized in that said coating exhibits a
fluorine/carbon ratio (F/C) of between about 1.50 and about 2.00, preferably
between about 1.60 and about 1.95.
15
4. An article according to any of the claims 1-3 wherein said article is a
ceramic article.
5. An article according to any of the claims 1-3 wherein said article is a
20 glass article.
6. An article according to any of the claims 1-3 wherein said article is an
article with a finished hard surface.
- 25 7. An article according to any of the claims 1-3 wherein said article is a
container for liquids.
8. An article according to claim 7 wherein the inside of said article is treated
with said coating.
30
9. An article according to any of the claims 1-3 wherein said article is an
appliance.
35

1/6

CONTINUOUS RF GLOW DISCHARGE

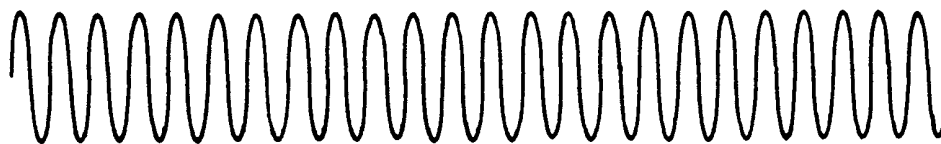


FIG. 1a

MODULATED RF GLOW DISCHARGE

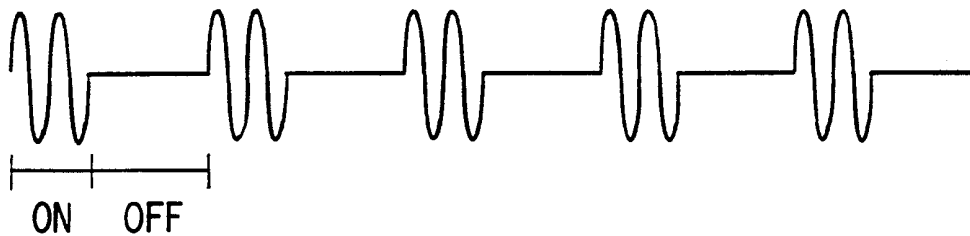


FIG. 1b

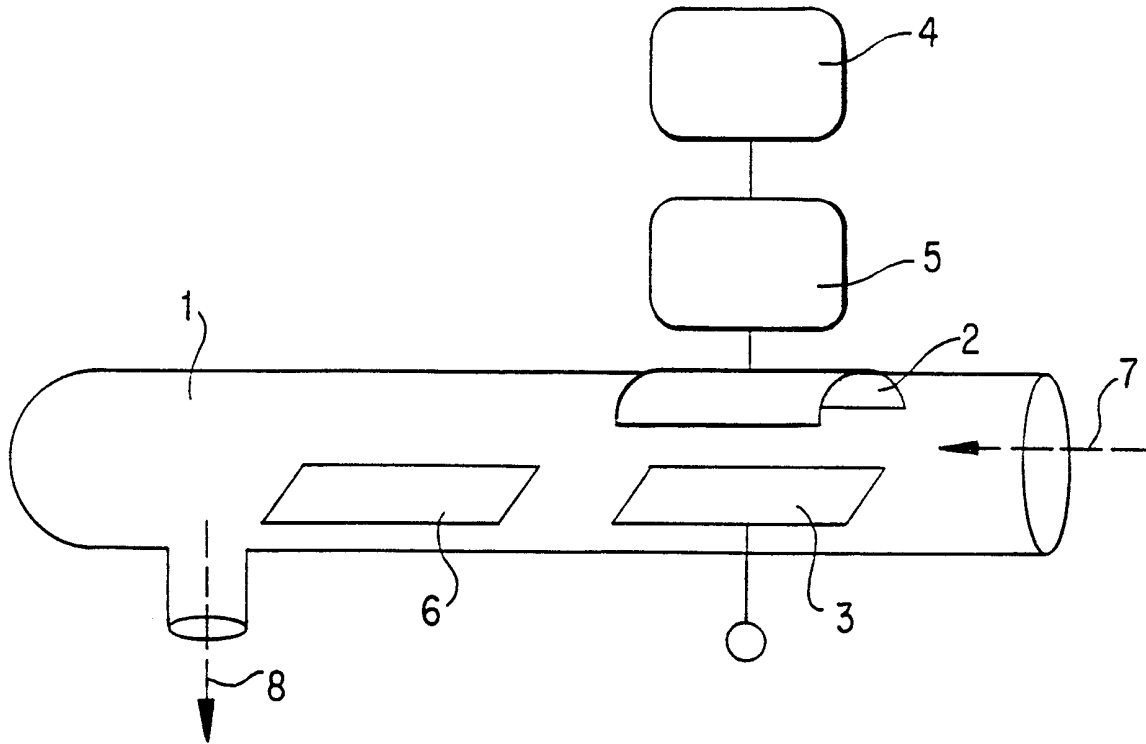


FIG. 2

3/6

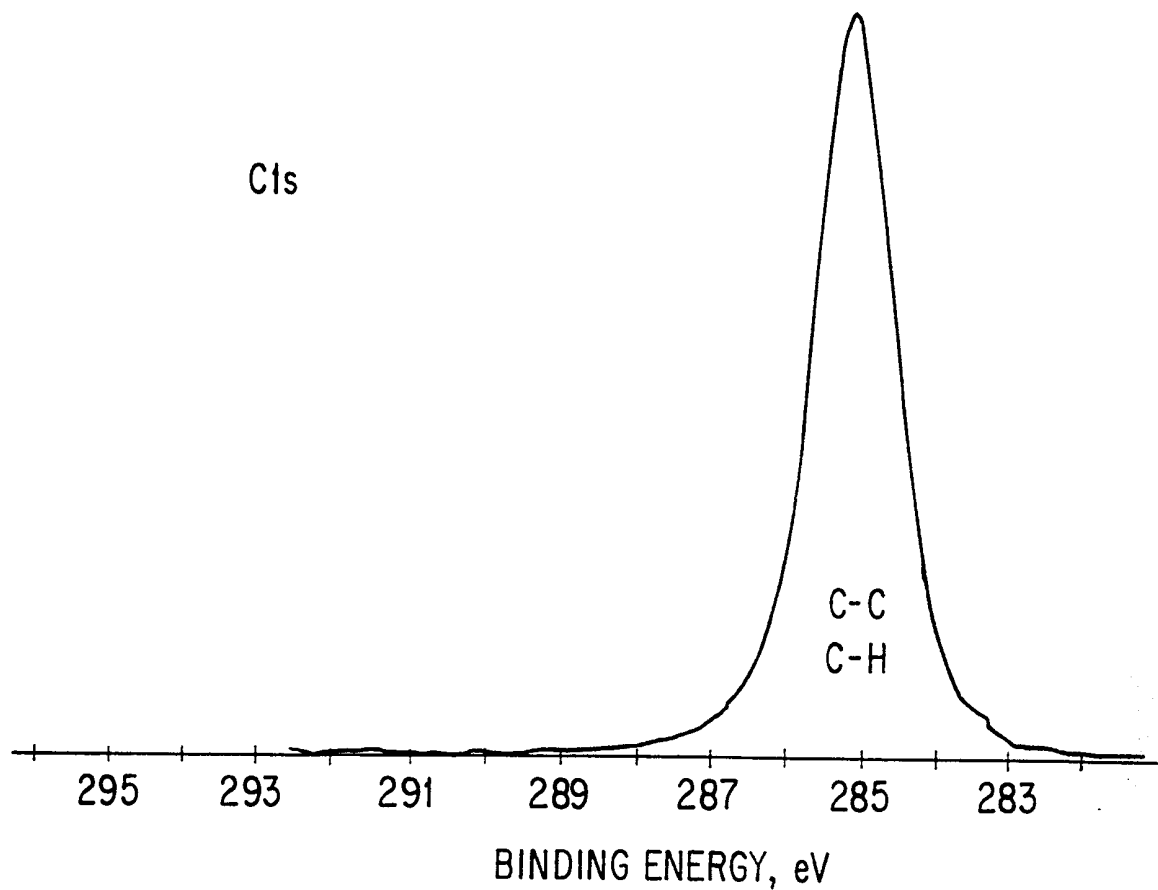


FIG. 3

4/6

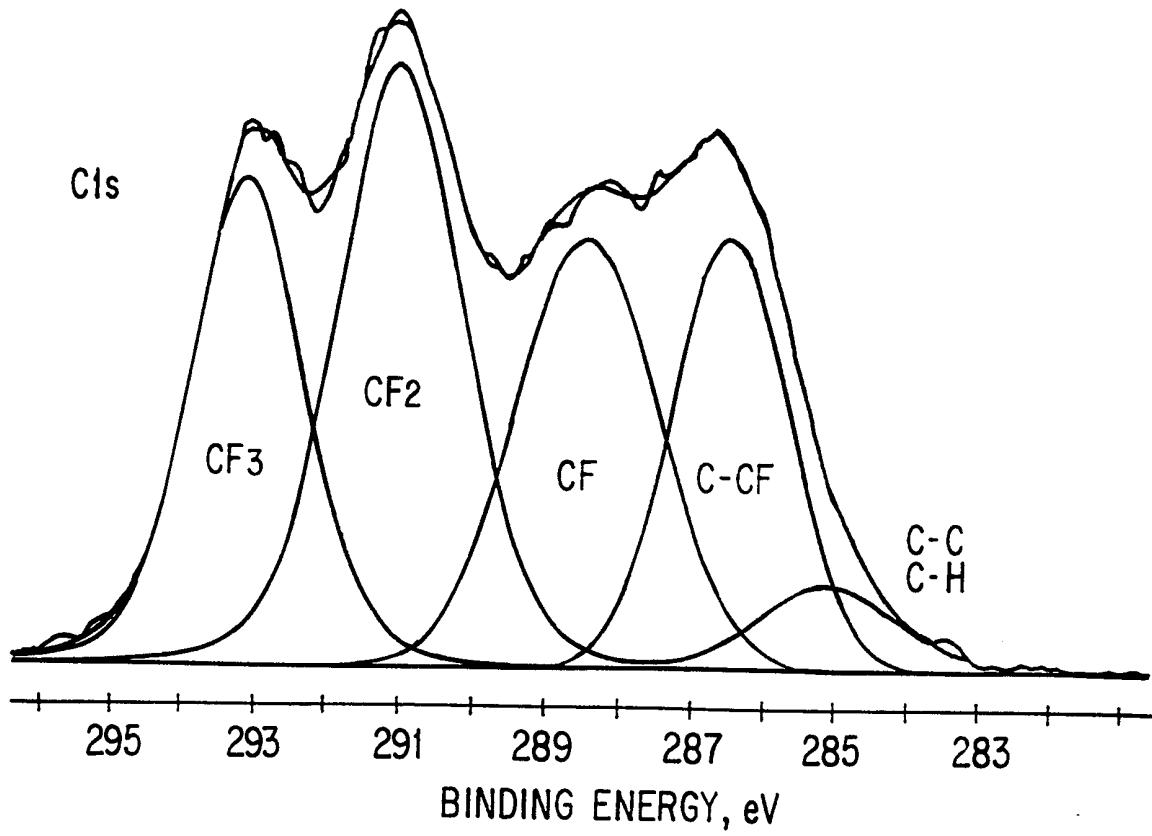


FIG. 4

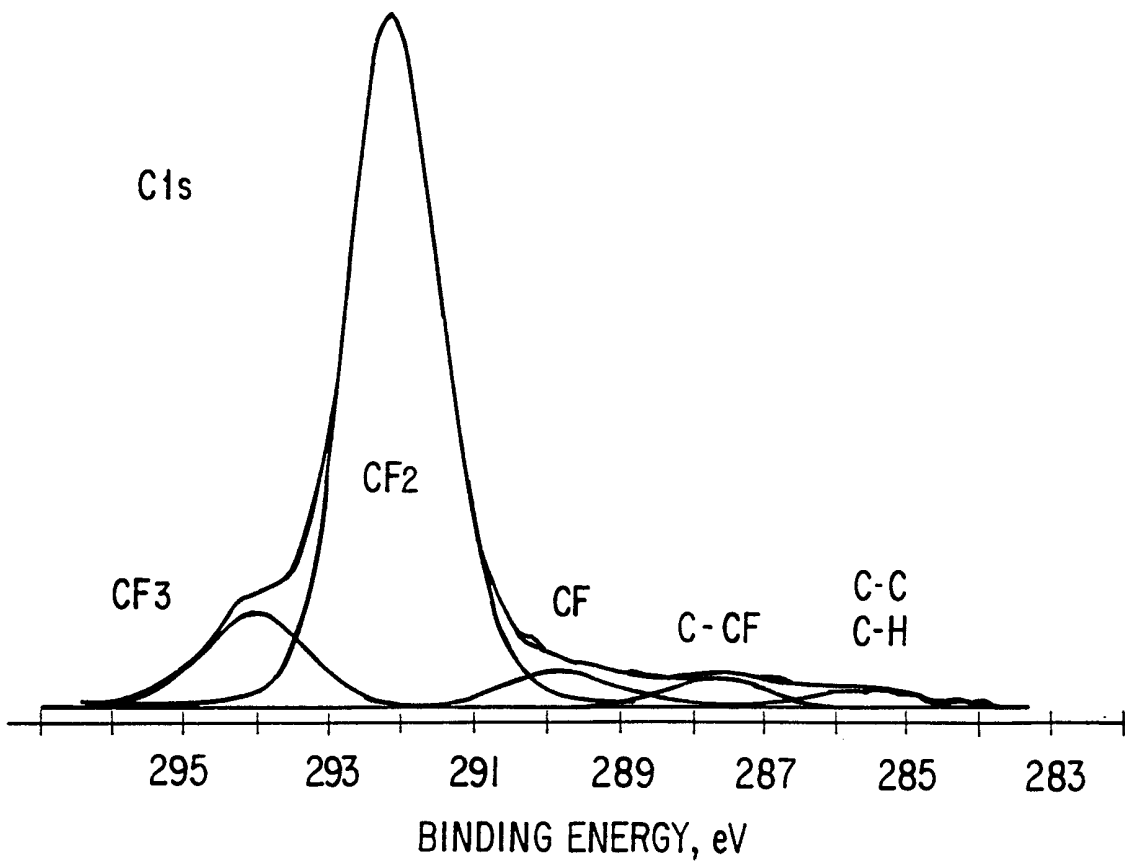


FIG. 5

6/6

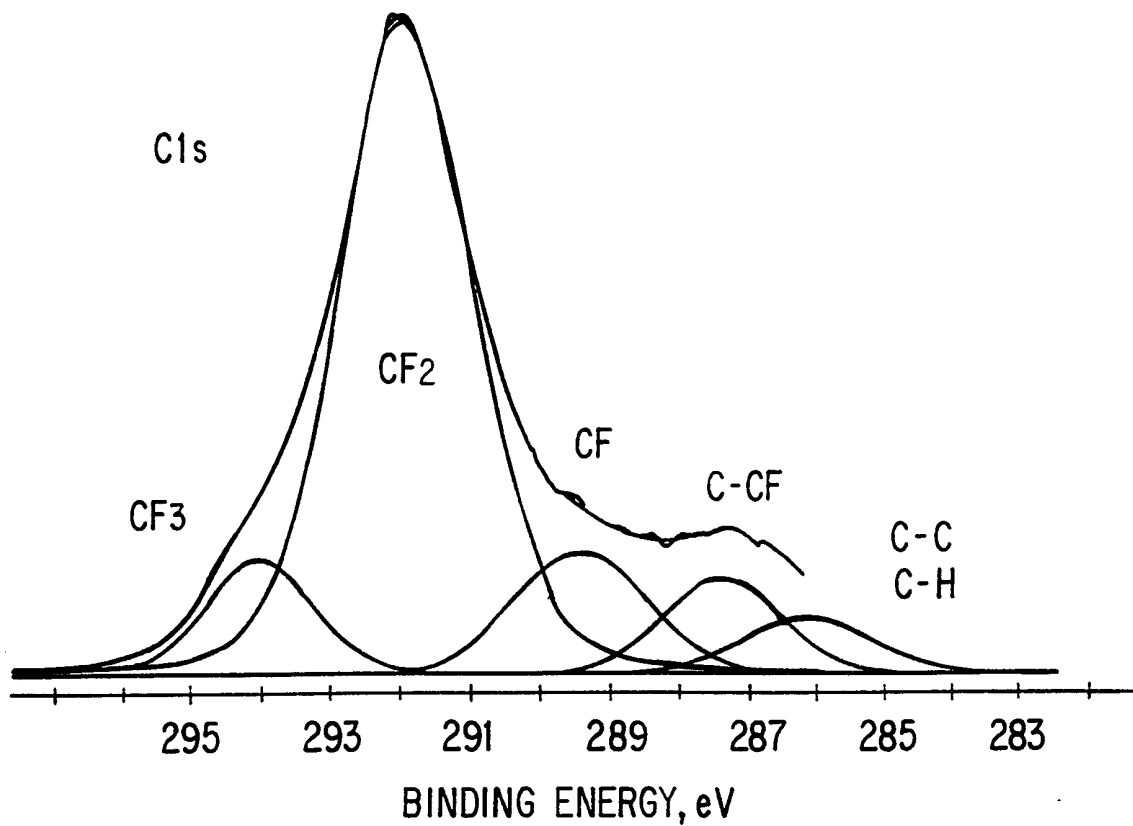


FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/20923

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C16/50 C23C16/30 B05D7/24 C03C17/28 C04B41/48

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.
X	EP 0 531 029 A (GEN ELECTRIC) 10 March 1993 (1993-03-10) column 4, line 6 - line 38; claims 9-13; example	1, 2, 4-6, 9
X	EP 0 492 545 A (MATSUSHITA ELECTRIC IND CO LTD) 1 July 1992 (1992-07-01) example 1	1, 5, 6
A	US 4 632 842 A (KARWOSKI THEODORE ET AL) 30 December 1986 (1986-12-30) column 9, line 3 - column 12, line 19	1-3
A	GB 760 573 A (TH. GOLDSCHMIDT AG) 7 November 1956 (1956-11-07) the whole document	5-8

Further documents are listed in the continuation of box C.

Patent family members are listed in 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 January 2000

Date of mailing of the international search report

20/01/2000

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

Patterson, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/20923

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0531029 A	10-03-1993	AU 2128992 A	04-03-1993
		CA 2072384 A	01-03-1993
		CN 1069778 A	10-03-1993
		JP 5230659 A	07-09-1993
		US 5380557 A	10-01-1995
		ZA 9206153 A	29-05-1993

EP 0492545 A	01-07-1992	JP 2500152 B	29-05-1996
		JP 4255345 A	10-09-1992
		JP 2506234 B	12-06-1996
		JP 4221630 A	12-08-1992
		JP 2690876 B	17-12-1997
		JP 8092402 A	09-04-1996
		US 5580605 A	03-12-1996
		CA 2058341 A	26-06-1992
		DE 69129145 D	30-04-1998
		DE 69129145 T	16-07-1996
		KR 9702941 B	13-03-1996

US 4632842 A	30-12-1986	NONE	

GB 760573 A		CH 320698 A	
		NL 85087 C	
