PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D06M 10/02, 14/18, D21H 19/16, 23/44, B29C 59/14

A1

(11) International Publication Number: **WO 98/58117**

(43) International Publication Date: 23 December 1998 (23.12.98)

(21) International Application Number: PCT/GB98/01702

(22) International Filing Date: 11 June 1998 (11.06.98)

(30) Priority Data:

9712338.4	14 June 1997 (14.06.97)	GB
9720078.6	23 September 1997 (23.09.97)	GB

(71) Applicant *(for all designated States except US)*: THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation & Research Agency, Ively Road, Farnborough, Hampshire GU14 0LX (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: BADYAL, Jas, Pal, Singh [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB). COULSON, Stephen, Richard [GB/GB]; University of Durham, Science Laboratories, South Road, Durham DH1 3LE (GB). WILLIS, Colin, Robert [GB/GB]; CBDE, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). BREWER, Stuart, Anson [GB/GB]; CBDE, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB).

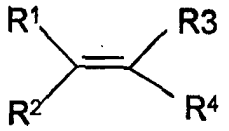
(74) Agent: SKELTON, S., R.; D/IPR, Formalities Section (Procurement Executive), Poplar 2, MOD Abbey Wood # 19, Bristol BS34 8JH (GB).

(81) Designated States: AU, CA, CN, GB, JP, NZ, SG, SI, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
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.

(54) Title: SURFACE COATINGS

(57) Abstract



(I)

A method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising a monomeric unsaturated organic compound which comprises a chain of carbon atoms, which are optionally substituted by halogen; provided that where the compound is a perhalogenated alkene, it has a chain of at least 5 carbon atoms; so as to form an oil or water repellent coating on said substrate. Suitable compounds for use in the methods are compounds of formula (I) where R^1, R^2 and R^3 are independently selected from hydrogen, alkyl, haloalkyl or aryl optionally substituted by halo; provided that at least one of R^1, R^2 or R^3 is hydrogen, and R^4 is a group $X–R^5$ where R^5 is an alkyl or haloalkyl group and X is a bond; a group of formula $–C(O)O(CH_2)_nY–$ where n is an integer of from 1 to 10 and Y is a bond or a sulphonamide group; or a group $–(O)_pR^6(O)_q(CH_2)_t–$ where R^6 is aryl optionally substituted by halo, p is 0 or 1, q is 0 or 1 and t is 0 or an integer of from 1 to 10, provided that where q is 1, t is other than 0. The method is particularly useful in the production of oil– and/or water repellent fabrics.

Jiangsu Favored Ex. 1022

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		

Surface Coatings

The present invention relates to the coating of surfaces, in particular to the production of oil- and water- repellent surfaces, as well as to coated articles obtained thereby.

Oil- and water- repellent treatments for a wide variety of surfaces are in widespread use. For example, it may be desirable to impart such properties to solid surfaces, such as metal, glass, ceramics, paper, polymers etc. in order to improve preservation properties, or to prevent or inhibit soiling.

A particular substrate which requires such coatings are fabrics, in particular for outdoor clothing applications, sportswear, leisurewear and in military applications. Their treatments generally require the incorporation of a fluoropolymer into or more particularly, fixed onto the surface of the clothing fabric. The degree of oil and water repellency is a function of the number and length of fluorocarbon groups or moieties that can be fitted into the available space. The greater the concentration of such moieties, the greater the repellency of the finish.

In addition however, the polymeric compounds must be able to form durable bonds with the substrate. Oil- and water-repellent textile treatments are generally based on fluoropolymers that are applied to fabric in the form of an aqueous emulsion. The fabric remains breathable and permeable to air since the treatment simply coats the fibres with a very thin, liquid-repellent film. In order to make these finishes durable, they are sometimes co-applied with cross-linking resins that bind the fluoropolymer treatment to fibres. Whilst good levels of durability towards

laundering and dry-cleaning can be achieved in this way, the cross-linking resins can seriously damage cellulosic fibres and reduce the mechanical strength of the material. Chemical methods for producing oil- and water-repellent textiles are disclosed for example in WO 97/13024 and British patent No 1,102,903 or M. Lewin et al., 'Handbood of Fibre Science and Technology' Marcel and Dekker Inc., New York, (1984) Vol 2, Part B Chapter 2.

Plasma deposition techniques have been quite widely used for the deposition of polymeric coatings onto a range of surfaces. This technique is recognised as being a clean, dry technique that generates little waste compared to conventional wet chemical methods. Using this method, plasmas are generated from small organic molecules, which are subjected to an ionising electrical field under low pressure conditions. When this is done in the presence of a substrate, the ions, radicals and excited molecules of the compound in the plasma polymerise in the gas phase and react with a growing polymer film on the substrate. Conventional polymer synthesis tends to produce structures containing repeat units which bear a strong resemblance to the monomer species, whereas a polymer network generated using a plasma can be extremely complex.

The success or otherwise of plasma polymerisation depends upon a number of factors, including the nature of the organic compound. Reactive oxygen containing compounds such as maleic anhydride, has previously been subjected to plasma polymerisation (Chem. Mater. Vol. 8, 1, 1996).

US Patent No 5,328,576 describes the treatment of fabric or paper surfaces to impart liquid repellent properties by

subjecting the surfaces to a pre-treatment with an oxygen plasma, followed by plasma polymerisation of methane.

However, plasma polymerisation of the desirable oil and water repellent fluorocarbons have proved more difficult to achieve. It has been reported that cyclic fluorocarbons undergo plasma polymerisation more readily than their acyclic counterparts (H. Yasuda et al., J. Polym. Sci., Polym. Chem. Ed. 1977, 15, 2411). The plasma polymerization of trifluoromethyl-substituted perfluorocyclohexane monomers has been reported (A. M. Hynes et al., Macromolecules, 1996, 29, 18-21).

A process in which textiles are subjected to plasma discharge in the presence of an inert gas and subsequently exposed to an F-containing acrylic monomer is described in SU-1158-634. A similar process for the deposition of a fluroalkyl acrylate resists on a solid substrate is described in European Patent Application No. 0049884.

Japanese application no. 816773 describes the plasma polymerisation of compounds including fluorosubstituted acrylates. In that process, a mixture of the fluorosubstituted acrylate compounds and an inert gas are subjected to a glow discharge.

The applicants have found an improved method of producing polymer and particular halopolymer coatings which are water and/or oil repellent on surfaces.

According to the present invention there is provided a method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising a monomeric unsaturated organic compound which

comprises an optionally substituted hydrocarbon group, wherein the optional substituents are halogen; provided that where the compound is a straight chain perhalogenated alkene, it includes at least 5 carbon atoms; so as to form an oil or water repellent coating on said substrate.

Unsaturated organic compounds are those which contain at least one double bond which is capable of reacting to form a polymeric compound. The compounds used in the method of the invention suitably include at least one optionally substituted hydrocarbon chain. Suitable chains, which may be straight or branched, have from 3 to 20 carbon atoms, more suitably from 6 to 12 carbon atoms

Monomeric compounds used in the method may include the double bond within a chain and so comprise alkenyl compounds. Alternatively, the compounds may comprise an alkyl chain, optionally substituted by halogen, as a substitutent which is attached to an unsaturated moiety either directly or by way of an functional group, such as a ester or sulphonamide group.

As used therein the term "halo" or "halogen" refers to fluorine, chlorine, bromine and iodine. Particularly preferred halo groups are fluoro. The term hydrocarbon includes to alkyl, alkenyl or aryl groups. The term "aryl" refers to aromatic cyclic groups such as phenyl or napthyl, in particular phenyl. The term "alkyl" refers to straight or branched chains of carbon atoms, suitably of up to 20 carbon atoms in length. The term "alkenyl" refers to straight or branched unsaturated chains suitably having from 2 to 20 carbon atoms.

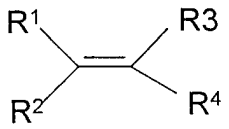
Monomeric compounds where the chains comprise unsubstituted alkyl or alkenyl groups are suitable for producing coatings which are water repellent. By substituting at least some of the hydrogen atoms in these chains with at least some halogen atoms, oil repellency may also be conferred by the coating.

Thus in a preferred aspect, the monomeric compounds include haloalkyl moieties or comprise haloalkenyls. Therefore, preferably the plasma used in the method of the invention will comprise a monomeric unsaturated haloalkyl containing organic compound.

Suitable plasmas for use in the method of the invention include non-equilibrium plasmas such as those generated by radiofrequencies (Rf), microwaves or direct current (DC). They may operate at atmospheric or sub-atmospheric pressures as are known in the art.

The plasma may comprise the monomeric compound alone, in the absence of other gases or in mixture with for example an inert gas. Plasmas consisting of monomeric compound alone may be achieved as illustrated hereinafter, by first evacuating the reactor vessel as far as possible, and then purging the reactor vessel with the organic compound for a period sufficient to ensure that the vessel is substantially free of other gases.

Particularly suitable monomeric organic compounds are those of formula (I)



(I)

where R^1, R^2 and R^3 are independently selected from hydrogen, alkyl, haloalkyl or aryl optionally substituted by halo; and R^4 is a group X-R^5 where R^5 is an alkyl or haloalkyl group and X is a bond; a group of formula $-C(O)O(CH_2)_nY-$ where n is an integer of from 1 to 10 and Y is a bond or a sulphonamide group; or a group $-(O)_pR^6(O)_q(CH_2)_t-$ where R^6 is aryl optionally substituted by halo, p is 0 or 1, q is 0 or 1 and t is 0 or an integer of from 1 to 10, provided that where q is 1, t is other than 0.

Suitable haloalkyl groups for R^1, R^2, R^3 and R^5 are fluoroalkyl groups. The alkyl chains may be straight or branched and may include cyclic moieties.

For R^5, the alkyl chains suitably comprise 2 or more carbon atoms, suitably from 2-20 carbon atoms and preferably from 6 to 12 carbon atoms.

For R^1, R^2 and R^3, alkyl chains are generally preferred to have from 1 to 6 carbon atoms.

Preferably R^5 is a haloalkyl, and more preferably a perhaloalkyl group, particularly a perfluoroalkyl group of formula C_mF_{2m+1} where m is an integer of 1 or more, suitably from 1-20, and preferably from 6-12 such as 8 or 10.

Suitable alkyl groups for R^1, R^2 and R^3 have from 1 to 6 carbon atoms.

Preferably however, at least one of R^1, R^2 and R^3 is hydrogen and preferably R^1, R^2, R^3 are all hydrogen.

Where X is a group $-C(O)O(CH_2)_nY-$, n is an integer which provides a suitable spacer group. In particular, n is from 1 to 5, preferably about 2.

Suitable sulphonamide groups for Y include those of formula $-N(R^7)SO_2^-$ where R^7 is hydrogen or alkyl such as C_{1-4}alkyl, in particular methyl or ethyl.

In a preferred embodiment, the compound of formula (I) is a compound of formula (II)

$$CH_2=CH-R^5 \qquad (II)$$

where R^5 is as defined above in relation to formula (I).

In compounds of formula (II), X in formula (I) is a bond.

In an alternative preferred embodiment, the compound of formula (I) is an acrylate of formula (III)

$$CH_2=CR^7C(O)O(CH_2)_nR^5 \qquad (III)$$

where n and R^5 as defined above in relation to formula (I) and R^7 is hydrogen or C_{1-6} alkyl, such as methyl.

Using these compounds, coatings with water hydrophobicity values of up to 10 and oleophobicity values of up to 8 have been achieved as illustrated hereinafter.

Other compounds of formula (I) are styrene derivatives as are well known in the polymer art.

All compounds of formula (I) are either known compounds or they can be prepared from known compounds using conventional methods.

The surface coated in accordance with the invention may be of any solid substrate, such as fabric, metal, glass, ceramics, paper or polymers. In particular, the surface comprises a fabric substrate such as a cellulosic fabric, to which oil- and/or water-repellency is to be applied. Alternatatively, the fabric may be a synthetic fabric such as an acrylic/nylon fabric.

The fabric may be untreated or it may have been subjected to earlier treatments. For example, it has been found that treatment in accordance with the invention can enhance the water repellency and confer a good oil-repellent finish onto fabric which already has a silicone finish which is water repellent only.

Precise conditions under which the plasma polymerization takes place in an effective manner will vary depending upon factors such as the nature of the polymer, the substrate etc. and will be determined using routine methods and/or the techniques illustrated hereinafter. In general however, polymerisation is suitably effected using vapours of compounds of formula (I) at pressures of from 0.01 to 10 mbar, suitably at about 0.2mbar.

A glow discharge is then ignited by applying a high frequency voltage, for example at 13.56MHz.

The applied fields are suitably of average power of up to 50W. Suitable conditions include pulsed or continuous

fields, but are preferably pulsed fields. The pulses are applied in a sequence which yields very low average powers, for example of less than 10W and preferably of less than 1W. Examples of such sequences are those in which the power is on for 20μs and off for from 10000μs to 20000μs.

The fields are suitably applied for a period sufficient to give the desired coating. In general, this will be from 30 seconds to 20 minutes, preferably from 2 to 15 minutes, depending upon the nature of the compound of formula (I) and the substrate etc.

Plasma polymerisation of compounds of formula (I), particularly at low average powers has been found to result in the deposition of highly fluorinated coatings which exhibit super-hydrophobicity. In addition, a high level of structural retention of the compound of formula (I) occurs in the coating layer, which may be attributed to the direct polymerisation of the alkene monomer for instance a fluoroalkene monomer via its highly susceptible double bond.

It has been noted, particularly in the case of the polymerisation of compounds of formula (III) above, that low power pulsed plasma polymerisation produces well-adhered coatings which exhibit excellent water and oil repellency. The greater level of structural retention in the case of pulsed plasma polymerisation can be attributed to free radical polymerisation occurring during the duty cycle off-time and less fragmentation during the on-time.

In a particularly preferred embodiment of the invention, a surface is exposing a surface to a plasma comprising a compound of formula (III) as defined above, wherein the

plasma being created by a pulsed voltage also as described above.

Suitably the compound of formula (I) includes a perfluoroalkylated tail or moiety, the process of the invention may have oleophobic as well as hydrophobic surface properties.

Thus the invention further provides a hydrophobic or oleophobic substrate which comprises a substrate comprising a coating of a alkyl polymer and particularly a haloalkyl polymer which has been applied by the method described above. In particular, the substrates are fabrics but they may be solid materials such as biomedical devices.

The invention will now be particularly described by way of example with reference to the accompanying diagrammatic drawings in which:

Figure 1 shows a diagram of the apparatus used to effect plasma deposition;

Figure 2 is a graph showing the characteristics of continuous wave plasma polymerisation of 1H, 1H, 2H-pefluoro-1-dodecene;

Figure 3 is a graph showing the characteristics of pulsed plasma polymerisation of 1H, 1H, 2H-pefluoro-1-dodecene at 50W P_P, T_{on}=20μs and T_{off}= 10000μs for 5 minutes; and

Figure 4 is a graph showing the characteristics of (a) continuous and (b) pulsed plasma polymerisation of 1H, 1H, 2H, 2H-heptadecafluorodecyl acrylate.

Example 1

Plasma Polymerisation of Alkene

1H, 1H, 2H-perfluoro-1-dodecene ($C_{10}F_{21}CH=CH_2$) (Fluorochem F06003, 97% purity) was placed into a monomer tube (I) (Fig. 1) and further purified using freeze-thaw cycles. A series of plasma polymerisation experiments were carried out in an inductively coupled cylindrical plasma reactor vessel (2) of 5cm diameter, 470cm^3 volume, base pressure of 7x10^{-3}mbar, and with a leak rate of better than 2x10^{-3} cm^{3}min^{-1}. The reactor vessel (2) was connected by way of a "viton" O-ring (3), a gas inlet (4) and a needle valve (5) to the monomer tube (1).

A thermocouple pressure gauge (6) was connected by way of a Young's tap (7) to the reactor vessel (2). A further Young's tap (8) connected with an air supply and a third (9) lead to an E2M2 two stage Edwards rotary pump (not shown) by way of a liquid nitrogen cold trap (10). All connections were grease free.

An L-C matching unit (11) and a power meter (12) was used to couple the output of a 13.56 Mhz R.F. generator (13), which was connected to a power supply (14), to copper coils (15) surrounding the reactor vessel (2). This arrangement ensured that the standing wave ratio (SWR) of the transmitted power to partially ionised gas in the reactor vessel (2) could be minimised. For pulsed plasma deposition, a pulsed signal generator (16) was used to trigger the R.F power supply, and a cathode ray oscilloscope (17) was used to monitor the pulse width and amplitude. The average power <P> delivered to the system during pulsing is given by the following formula:

$$\langle P \rangle = P_{cw}\{T_{on}/(T_{on} + T_{off})\}$$

where $T_{on}/(T_{on} + T_{off})$ is defined as the duty cycle and P_{cw} is the average continuous wave power.

In order to carry out polymerization/deposition reactions the reactor vessel (2) was cleaned by soaking overnight in a chloros bleach bath, then scrubbing with detergent and finally rinsing with isopropyl alcohol followed by oven drying. The reactor vessel (2) was then incorporated into the assembly as shown in Figure 1 and further cleaned with a 50W air plasma for 30 minutes. Next the reactor (2) vessel was vented to air and the substrate to be coated (19), in this case a glass slide, was placed in the centre of the chamber defined by the reactor vessel (2) on a glass plate (18). The chamber was then evacuated back down to base pressure (7.2×10^{-3}mbar).

Perfluoroalkene vapour was then introduced into the reaction chamber at a constant pressure of ~0.2mbar and allowed to purge the plasma reactor, followed by ignition of the glow discharge. Typically 2-15 minutes deposition time was found to be sufficient to give complete coverage of the substrate. After this, the R.F generator was switched off and the perfluoroalkene vapour allowed to continue to pass over the substrate for a further 5 minutes before evacuating the reactor back down to base pressure, and finally venting up to atmospheric pressure.

The deposited plasma polymer coatings were characterised immediately after deposition by X-ray photoelectron spectroscopy (XPS). Complete plasma polymer coverage was confirmed by the absence of any Si (2p) XPS signals showing through from the underlying glass substrate.

A control experiment, where the fluoroalkene vapour was allowed to pass over the substrate for 15 minutes and then pumped down to base pressure was found to show the presence of a large Si (2p) XPS signal from the substrate. Hence the coatings obtained during plasma polymerisation are not just due to absorption of the fluoroalkene monomer onto the substrate.

The experiments were carried out with average powers in the range of from 0.3 to 50W. The results of the XPS spectrum of a 0.3W continuous wave plasma polymer deposition onto a glass slide for 13 minutes is shown in Figure 2.

It can be seen that in this instance, $\underline{C}F_2$ and $\underline{C}F_3$ groups are the prominent environments in the C(1s) XPS envelope:-

$\underline{C}F_2$ (291.2eV) 61%

$\underline{C}F_3$ (293.3eV) 12%

The remaining carbon environments comprised partially fluorinated carbon centres and a small amount of hydrocarbon ($\underline{C}_xH_y$). The experimental and theoretically expected (taken from the monomer) values are given in Table 1

Table 1

	Experimental	Theoretical
F:C ratio	1.70 ± 0.3	1.75
%$\underline{C}F_2$ group	61% ± 2%	75%
%$\underline{C}F_3$ group	12% ± 2%	8%

The difference between theoretical and experimental $\underline{C}F_2$ group and $\underline{C}F_3$ group percentages can be attributed to a small amount of fragmentation of the perfluoroalkene monomer.

Figure 3 shows the C (1s) XPS spectrum for a 5 minute pulsed plasma polymerisation experiment where:- P_{cw} = 50W

T_{on} = 20μs

T_{off} = 10000μs <P> = 0.1W

The chemical composition of the deposited coating for pulsed plasma deposition is given in Table 2 below.

Table 2

	Experimental	Theoretical
F:C ratio	1.75 ± 0.7	1.75
%$\underline{C}F_2$ group	63% ± 2%	75%
%$\underline{C}F_3$ group	10% ± 2%	8%

It can be seen that the $\underline{C}F_2$ region is better resolved and has greater intensity which means less fragmentation of the perfluoroalkyl tail compared to continuous wave plasma polymerisation.

Surface energy measurements were carried out on slides produced in this way using dynamic contact angle analysis. The results showed that the surface energy was in the range of 5-6mJm^{-1}.

Example 2

Oil and Water Repellency Test

The pulsed plasma deposition conditions described in Example 1 above were used to coat a piece of cotton (3x8cm) which was then tested for wettability using "3M Test Methods" (3M oil repellency Test 1, 3M Test Methods Oct.1, 1988). As a Water repellency test, the 3M water repellency Test II, water/alcohol drop test, 3M Test 1, 3M Test Methods, October 1, 1988 was used. These tests are designed to detect a fluorochemical finish on all types of fabrics by measuring:

(a) aqueous stain resistance using mixtures of water and isopropyl alcohol.

(b) the fabric's resistance to wetting by a selected series of hydrocarbon liquids of different surface tensions.

These tests are not intended to give an absolute measure of the fabric's resistance to staining by watery or oily materials, since other factors such as fabric construction, fibre type, dyes, other finishing agents, etc., also influence stain resistance. These tests can, however, be used to compare various finishes. The water repellency tests comprises placing 3 drops of a standard test liquid consisting of specified proportions of water and isopropyl alcohol by volume onto the plasma polymerised surface. The surface is considered to repel this liquid if after 10 seconds, 2 of the 3 drops do not wet the fabric. From this, the water repellency rating is taken as being the test liquid with the greater proportion of isopropyl alcohol which passes the test. In the case of the oil repellency test, 3 drops of hydrocarbon liquid are placed on the coated

surface. If after 30 seconds no penetration or wetting of the fabric at the liquid-fabric interface occurs around 2 of the 3 drops is evident, then the test is passed.

The oil repellency rating is taken to be the highest-numbered test liquid which does not wet the fabric surface (where the increasing number corresponds to decreasing hydrocarbon chain and surface tension).

The ratings obtained for the pulsed plasma deposition of 1H, 1H, 2H perfluoro-1-dodecene onto cellulose were:-

Water	9	(10% water, 90% isopropyl alcohol)
Oil	5	(dodecane)

These values compare well with commercial treatments.

Example 3

Plasma Polymerisation of Acrylates

The method of Example 1 described above was repeated using 1H, 1H, 2H, 2H-heptadecafluorodecyl acrylate (Fluorochem F04389E, 98% purity) in place of the perfluoroalkene. As in Example 1, low average powers were used for continuous wave and pulsed plasma polymerisation experiments. For example, the XPS spectrum of a 1W continuous wave plasma polymer deposited onto a glass slide for 10 minutes is shown in Figure 4(a). Figure 4(b) shows the C(1s) XPS spectrum for a 10 minutes pulsed plasma polymerisation experiment where

P_{cw} = 40W (average continuous wave power)

T_{on} = 20μs (pulsed time on)

T_{off} = 20000μs (pulsed time off)

$\langle P \rangle$ = 0.04W (average pulsed power)

Table 3 compares the theoretical (taken from the monomer, $CH_2=CHCO_2CH_2CH_2C_8F_{17}$) environments with what is actually found for polymer coatings.

Table 3

Environment	eV	Theoretical percentages	Experimental percentages
$\underline{C}F_3$	293.2	7.7	7.8
$\underline{C}F_3$	291.2	53.8	47.0
O-$\underline{C}$=O	289.0	7.7	13.0
$\underline{C}F$	287.8	--	0.7
$\underline{C}$-CF_n/C-O	286.6	15.4	13.4
$\underline{C}$-C(O)=O	285.7	7.7	3.9
$\underline{C}_xC_y$	285.0	7.7	7.2

It can be seen that the $\underline{C}F_2$ group is the prominent environment in the C(1s) XPS envelope at 291.2eV. The remaining carbon environments being $\underline{C}F_3$, partially fluorinated and oxygenated carbon centres and a small amount of hydrocarbon ($\underline{C}_xH_y$). The chemical composition of the coatings deposited for continuous wave and pulsed plasma conditions are given below in Table 4 (excluding satellite percentages) along with the theoretically expected compositions).

Table 4

	Theoretical	CW Plasma	Pulsed Plasma
F:C ratio	1.31	0.94	1.49
%$\underline{C}F_2$ group	53.8%	27.2%	47.0%
%$\underline{C}F_3$ group	7.7%	3.8%	7.8%

It can be seen from Figure 4(b) that the $\underline{C}F_2$ region is better resolved and has greater intensity, which means less fragmentation of the perfluoroalkyl tail occurs during pulsed plasma conditions compared to continuous wave plasma polymerisation. In the case of the continuous wave plasma experiments, the low percentages of $\underline{C}F_2$ and $\underline{C}F_3$ groups occur.

Surface energy measurements as described in Example 1 shows a surface energy of $6mJm^{-1}$.

Example 4

Oil and Water Repellency Test

Using the pulsed plasma deposition conditions of Example 3 except that these were applied for 15 minutes, pieces of cotton (3x 8cm) were coated with 1H, 1H, 2H, 2H-heptadecafluorodecyl acrylate. Similar pieces of cotton were coated with the same compound using a continuous wave at 1W fo 15 minutes. These were then subjected to oil and water repellency tests as described in Example 2 above.

Samples were then subjected to a benzotrifluoride Soxhlet extraction for either 1 or 7 hours and the oil and water repellency tests repeated. The results, expressed as described in Example 2,

Time (hours)	Continuous wave		Pulsed wave	
	Oil-repellency	Water repellency	Oil repellency	Water repellency
0	7	4	8	10
1	-	2	6	7
7	-	2	5	7

Hence these coatings are highly hydrophobic and oleophobic and the coatings have good durability.

Example 5

Treatment of silicone coated synthetic fabric

A sample of a modifed acrylic/nylon fabric which already contained a silicone coating to impart water repellency, was subjected to the a pulsed acrylate plasma consisting of the compound $CH_2=CHCOO(CH_2)_2C_8F_{17}$ and using the conditions described in Example 3.

A sample of the same material was subjected to a two stage deposition process in which the fabric was first exposed to a continuous wave 30W air plasma for 5 seconds followed by exposure to the same acrylate vapour only.
The products were then tested for oil and water repellency as described in Example 2.

In addition, the durability of the coating was tested by then subjecting the products to a 1 hour Soxhlet extraction with trichloroethylene.

The results are as shown in Table 5

Table 5

Treatment	Repellency Ratings		
	Before Plasma	After Plasma	After extraction with solvent
Pulsed phase acrylate plasma	W2	O7, W10	O6, W8
Air plasma followed by exposure to acylate monomer	W2	O1, W3	O1(borderline) W2

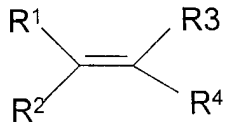
It appears therefore that the process of the invention can not only enhance the water repellency of such as fabric, and also confer oil repellency, the durability of the coating is higher than that obtained using the known two step grafting polymerisation process.

Claims

1. A method of coating a surface with a polymer layer, which method comprises exposing said surface to a plasma comprising a monomeric unsaturated organic compound which comprises an optionally substituted hydrocarbon group wherein any optional substituents are halogen; provided that where the compound is a straight chain perhalogenated alkene, it comprises at least 5 carbon atoms; so as to form an oil or water repellent coating on said substrate.

2. A method according to claim 1 wherein the organic compound is substituted by halogen.

3. A method according to claim 1 wherein the said organic compound is a compound of formula (I)



(I)

where R^1, R^2 and R^3 are independently selected from hydrogen, alkyl, haloalkyl or aryl optionally substituted by halo; and R^4 is a group $X-R^5$ where R^5 is an alkyl or haloalkyl group and X is a bond; a group of formula $-C(O)O(CH_2)_nY-$ where n is an integer of from 1 to 10 and Y is a bond or a sulphonamide group; or a group $-(O)_pR^6(O)_q(CH_2)_t-$ where R^6 is aryl optionally substituted by halo, p is 0 or 1, q is 0 or 1 and t is 0 or an integer of from 1 to 10, provided that where q is 1, t is other than 0.

4. A method according to claim 3 wherein R^5 is a haloalkyl group.

5. A method according to claim 4 wherein R^5 is a perhaloalkyl group.

6. A method according to claim 5 wherein R^5 is a perfluoroalkyl group of formula C_mF_{2m+1} where m is an integer of 1 or more.

7. A method according to claim 6 wherein m is from 1-20.

8. A method according to claim 7 wherein m is from 6-12.

9. A method according to any one of the preceding claims wherein R^1, R^2 and R^3 are independently selected from hydrogen or a C_{1-6}alkyl or haloC_{1-6}alkyl group.

10. A method according to claim 9 wherein at least one of R^1, R^2 and R^3 is hydrogen.

11. A method according to claim 10 wherein R^1, R^2, R^3 are all hydrogen.

12. A method according to claim 3 wherein X is a group of formula $-C(O)O(CH_2)_nY-$ and Y is a sulphonamide group of formula $-N(R^6)SO_2-$ where R^6 is hydrogen or alkyl.

13. A method according to claim 3 wherein the compound of formula (I) comprises a compound of formula (II)

$$CH_2=CH-R^5 \qquad (II)$$

where R^5 is as defined in claim 3.

14. A method according to claim 3 wherein the compound of formula (I) is an acrylate of formula (III)

$$CH_2=CR^7C(O)O(CH_2)_nR^5 \qquad (III)$$

where n and R^5 as defined in claim 2 and R^7 is hydrogen or C_{1-6} alkyl.

15. A method according to any one of the preceding claims wherein the surface is a surface of a fabric, metal, glass, ceramics, paper or polymer substrate.

16. A method according to claim 15 wherein the substrate is a fabric.

17. A method according to any one of the preceding claims wherein the gas pressure of the organic compound is from 0.01 to 10 mbar.

18. A method according to any one of the preceding claims wherein a glow discharge is ignited by applying a high frequency voltage.

19. A method according to claim 18 wherein the voltage is applied as a continuous field.

20. A method according to claim 18 wherein the voltage is applied as a pulsed field.

21. A method according to claim 20 wherein pulses are applied in a sequence which yields low average power.

22. A method according to claim 21 wherein the sequence is such that the power is on for 20μs and off for from 10000μs to 20000μs.

23. A method according to any one of the preceding claims wherein the plasma polymerisation takes place for from 2 to 15 minutes.

24. A method according to claim 1, which method comprises exposing a surface to a plasma comprising a compound of formula (III) as defined in claim 14, said plasma being created by a pulsed voltage.

25. A hydrophobic or oleophobic substrate which comprises a substrate comprising a coating of a polymer which has been applied by the method according to any one of claims 1 to 24.

26. A hydrophobic or oleophobic substrate according to claim 25 wherein the polymer is a haloalkyl polymer.

27. A substrate according to claim 25 or claim 26 which is a fabric.

28. An item of clothing which comprises a fabric according to claim 27.

Fig.1.

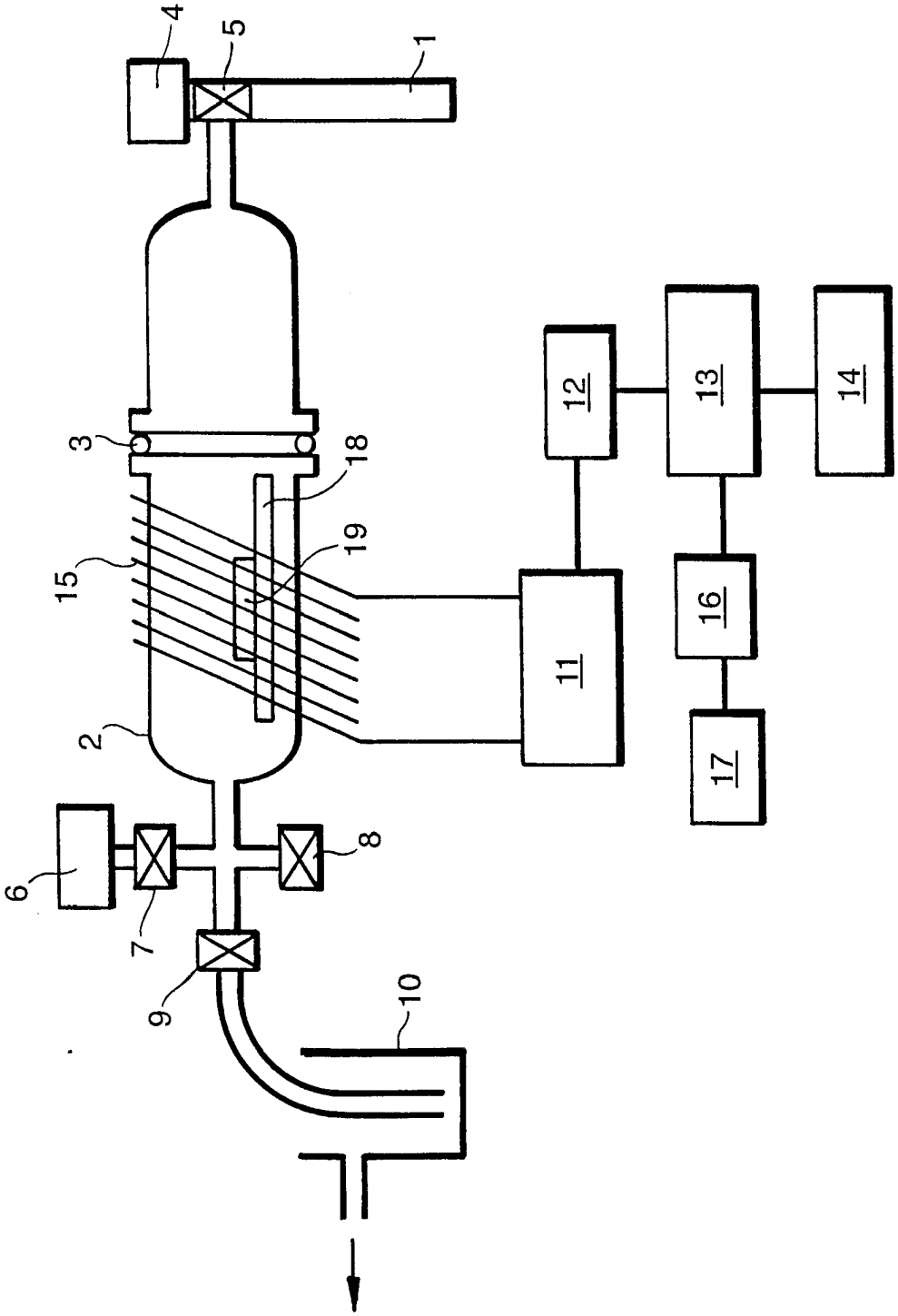


Fig.2.

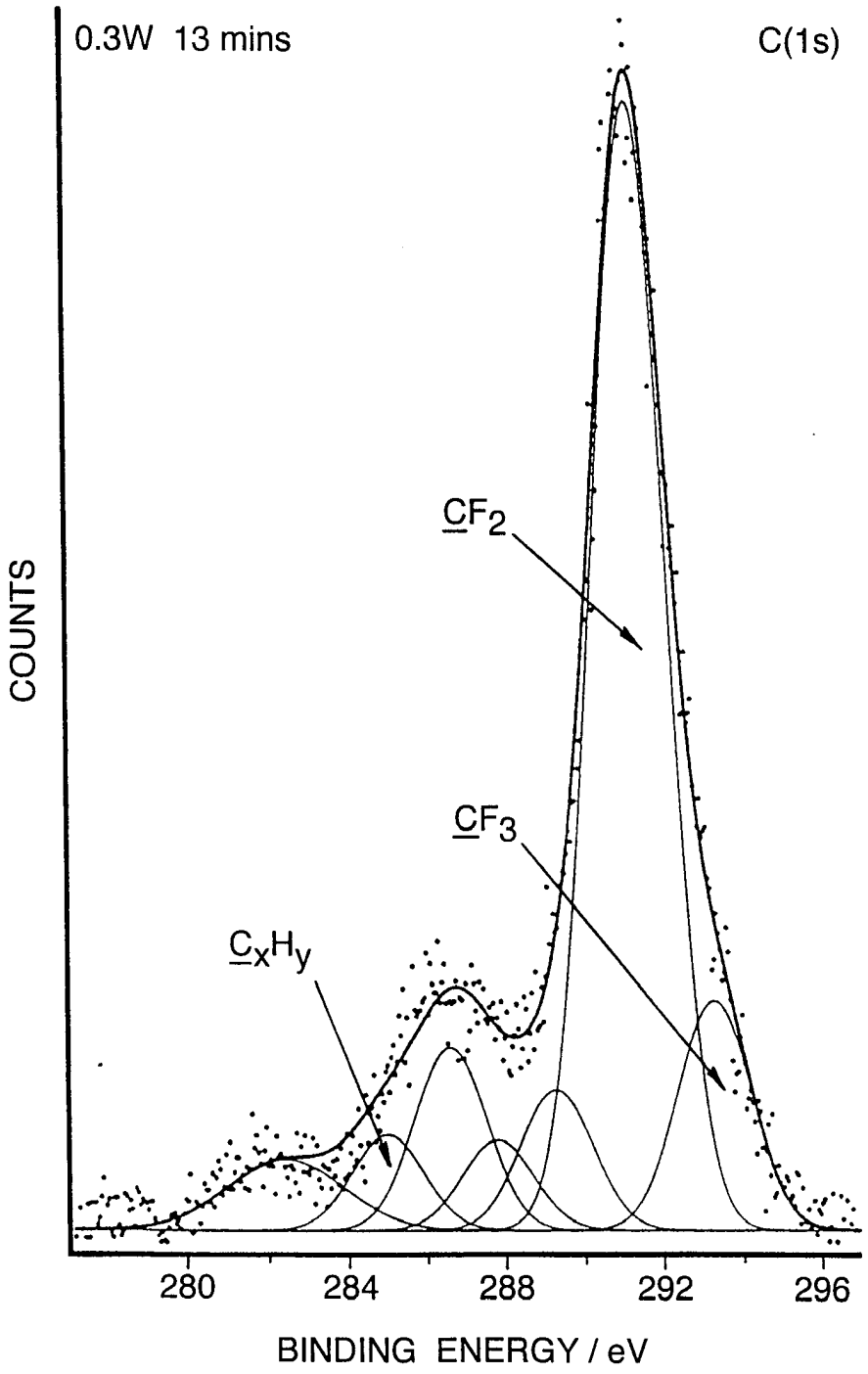

0.3W 13 mins
C(1s)
COUNTS
CF2
CF3
CxHy
280
284
288
292
296
BINDING ENERGY / eV

Fig.3.

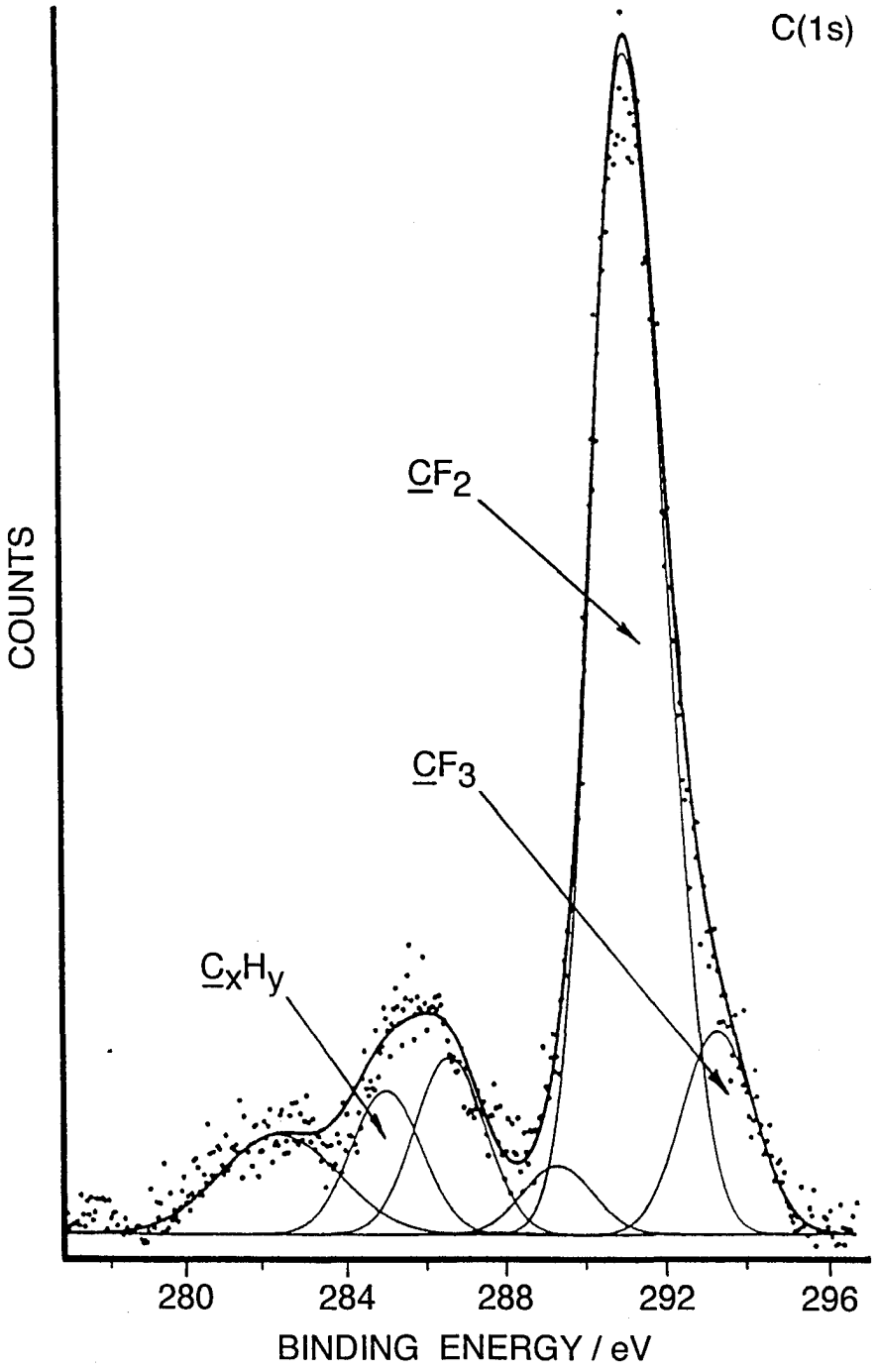
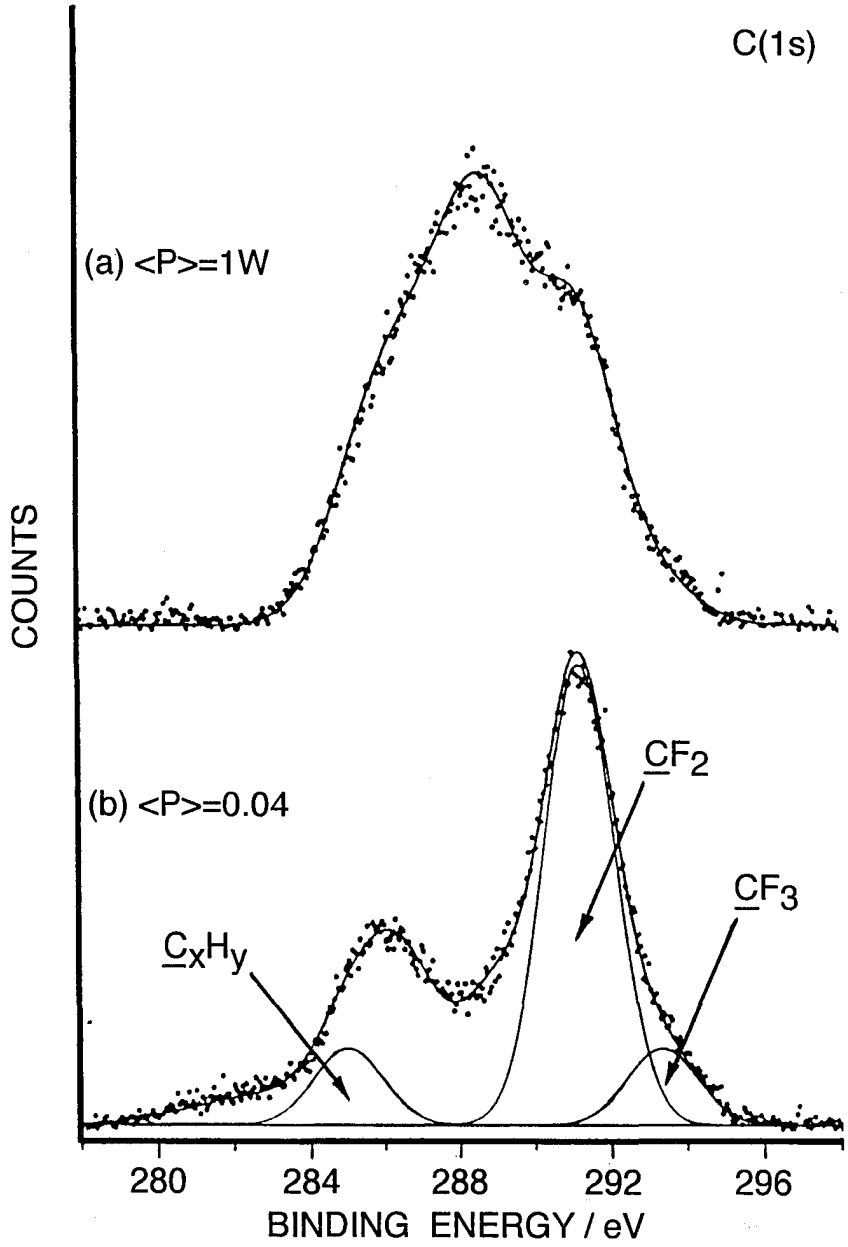


Fig.4.


C(1s)
(a) <P>=1W
COUNTS
(b) <P>=0.04
CF2
CF3
CxHy
280
284
288
292
296
BINDING ENERGY / eV

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/GB 98/01702

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D06M10/02 D06M14/18 D21H19/16 D21H23/44 B29C59/14

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 6 D06M D21H B29C B05D

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 [1]	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 8235 Derwent Publications Ltd., London, GB; AN 82-73505E XP002079483 & JP 57 119906 A (DAIKIN KOGYO KK) , 26 July 1982 see abstract ---	1-11,14, 15,17, 18,25,26
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 242 (C-0721), 23 May 1990 & JP 02 061176 A (WAKAYAMA PREEF GOV), 1 March 1990 see abstract ---	1,15,16, 25,27,28

-/--

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

[X] Patent family members are listed in annex.

[1] 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	Date of mailing of the international search report
5 October 1998	14/10/1998

Name and mailing address of the ISA	Authorized officer
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	Koegler-Hoffmann, S

3

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/01702

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 0 049 884 A (DAIKIN IND LTD) 21 April 1982 cited in the application see page 1, line 22 - page 4, line 11 see page 5, line 16 - page 6, line 32 ---	1-11,14, 15,17-26
X	US 5 041 304 A (KUSANO YUKIHIRO ET AL) 20 August 1991 see column 2, line 22 - column 5, line 29; claims ---	1,2,15, 16,25-28
X	DATABASE WPI Week 8505 Derwent Publications Ltd., London, GB; AN 85-027803 XP002079484 & JP 59 222340 A ((NIPQ) DAINIPPON PRINTING CO LTD), 14 December 1984 see abstract ---	1,2,15, 25,26
X	US 5 290 378 A (KUSANO YUKIHIRO ET AL) 1 March 1994 see column 2, line 47 - column 5, line 10; claims -----	1,15

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ional Application No
PCT/GB 98/01702

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0049884 A	21-04-1982	JP 1596594 C	27-12-1990
		JP 2022370 B	18-05-1990
		JP 58005734 A	13-01-1983
		JP 1596595 C	27-12-1990
		JP 2022371 B	18-05-1990
		JP 58005735 A	13-01-1983
		JP 57089753 A	04-06-1982
		US 4382985 A	10-05-1983
		US 4421842 A	20-12-1983
		US 4421843 A	20-12-1983
US 5041304 A	20-08-1991	JP 3202145 A	03-09-1991
US 5290378 A	01-03-1994	JP 3263444 A	22-11-1991