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Description

[0001] 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.

[0002] 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.

[0003] 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.

[0004] 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., 'Handbook of Fibre Science and Technology' Marcel and Dekker Inc., New York, (1984) Vol 2, Part B Chapter 2.

[0005] 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.

[0006] 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).

[0007] 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.

[0008] 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).

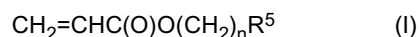
[0009] A process in which textiles are subjected to plasma discharge in the presence of an inert gas and subsequently exposed to an F-containing acyclic monomer is described in SU-1158-634. A similar process for the deposition of a fluoroalkyl acrylate resists on a solid substrate is described in European Patent Application No. 0049884.

[0010] 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.

[0011] US 5 041 304 discloses plasma polymerisation of partially fluorinated alkenes and perfluorinated alkenes and cycloalkanes at atmospheric pressure by glow discharge of a gas mixture containing an inert gas. The compounds mentioned include, for example, fluoropropylene, difluoropropylene etc, difluorobutene, trifluorobutene etc, but perfluorinated compounds such as hexafluoropropylene and octafluorocyclobutane are preferred.

[0012] The applicants have found an improved method of producing halopolymer coatings which are water and/or oil repellent on surfaces.

[0013] According to the present invention there is provided a method of coating a surface with an oil and water repellent polymer layer, which method comprises exposing said surface to a continuous wave plasma field comprising the compound of formula (I)



[0014] Wherein the average power of the field is less than 1W, n is an integer of from 1 to 10 and R⁵ is a C6-20

perhaloalkyl group.

[0015] As used therein the term "halo" or "halogen" refers to fluorine, chlorine, bromine and iodine. Particularly preferred halo groups are fluoro. Preferably, R^5 is a perfluoroalkyl group of formula C_mF_{2m+1} where m is an integer from 6 to 12, such as 8 or 10.

[0016] The term hydrocarbon includes to alkyl, alkenyl or aryl groups. The term "aryl" refers to aromatic cyclic groups such as phenyl or naphthyl, 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.

[0017] 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.

[0018] 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.

[0019] 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.

[0020] All compounds of formula (I) are either known compounds or they can be prepared from known compounds using conventional methods.

[0021] 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. Alternatively, the fabric may be a synthetic fabric such as an acrylic/nylon fabric.

[0022] 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.

[0023] 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 hereafter. 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.

[0024] A glow discharge is then ignited by applying a high frequency voltage, for example at 13.56MHz.

[0025] Suitable conditions include continuous 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 20 μ s and off for from 10000 μ s to 20000 μ s.

[0026] 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.

[0027] 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 via its highly susceptible double bond.

[0028] Because the compound of formula (I) includes a perfluorinalkylated tail or moiety, the process of the invention may have oleophobic as well as hydrophobic surface properties.

[0029] Thus the invention further provides a hydrophobic or oleophobic substrate which comprises a substrate comprising a coating of 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.

[0030] 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-perfluoro-1-decene;

Figure 3 is a graph showing the characteristics of pulsed plasma polymerisation of 1H, 1H, 2H-perfluoro-1-dodecene at 50W P_p , $T_{on} = 20 \mu s$ and $T_{off} = 10000 \mu s$ 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.

Comparative Example 1

Plasma Polymerisation of Alkene

[0031] 1H, 1H, 2H-perfluoro-1-dodecene ($C_{10}F_{21}CH=CH_2$) (Fluorochem F06003, 97% purity) was placed into a monomer tube (1) (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 5 cm diameter, 470 cm³ volume, base pressure 7×10^{-3} mbar, and with a leak rate better than 2×10^{-3} cm³min⁻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).

[0032] 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.

[0033] 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 $\langle P \rangle$ 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.

[0034] In order to carry out polymerization/deposition reactions the reactor vessel (2) was cleaned by soaking overnight in a chlorox 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 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).

[0035] Perfluoroalkene vapour was then introduced into the reaction chamber at a constant pressure of ~ 0.2 mbar 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.

[0036] 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.

[0037] 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.

[0038] The experiments were carried out with average powers in the range from 0.3 to 50W. The results of the XPS spectrum of a 0.3 W continuous wave plasma polymer deposition onto a glass slide for 13 minutes is shown in Figure 2.

[0039] It can be seen that in this instance, \underline{CF}_2 and \underline{CF}_3 groups are the prominent environments in the C(1s) XPS envelope:-

\underline{CF}_2	(291.2 eV)	61%
\underline{CF}_3	(293.3 eV)	12%

[0040] 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 I

Table 1

	Experimental	Theoretical
F:C ratio	1.70 ± 0.3	1.75
% CF_2 group	$61\% \pm 2\%$	75%
% CF_3 group	$12\% \pm 2\%$	8%

[0041] The difference between theoretical and experimental CF_2 group and CF_3 group percentages can be attributed to a small amount of fragmentation of the perfluoroalkene monomer.

[0042] Figure 3 shows the C (1s) XPS spectrum for a 5 minute pulsed plasma polymerisation experiment where: $P_{\text{CW}} = 50 \text{ W}$

$$T_{\text{on}} = 20 \mu\text{s}$$

$$T_{\text{off}} = 10000 \mu\text{s} \quad \langle P \rangle = 0.1 \text{ W}$$

[0043] The chemical composition of the deposited coating for pulsed plasma deposition is given in Table 2 below.

Table 2

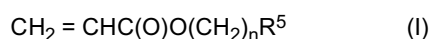
	Experimental	Theoretical
F:C ratio	1.75 ± 0.7	1.75
% CF_2 group	$63\% \pm 2\%$	75%
% CF_3 group	$10\% \pm 2\%$	8%

[0044] It can be seen that the CF_2 region is better resolved and has greater intensity which means less fragmentation of the perfluoroalkyl tail compared to continuous wave plasma polymerisation.

[0045] 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 $5\text{-}6 \text{ mJm}^{-1}$.

Claims

1. A method of coating a surface with an oil and water repellent polymer layer, which method comprises exposing said surface to a continuous wave plasma field comprising the compound of formula (I)

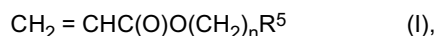


wherein the average power of the field is less than 1 W , n is an integer of from 1 to 10, and R^5 is a C_{6-20} perhaloalkyl group.

2. A method according to Claim 1, wherein R^5 is a perfluoroalkyl group of formula $\text{C}_m\text{F}_{2m+1}$ where m is an integer of from 6 to 12.
3. A method according to Claim 1 or Claim 2, in which the surface is a surface of a fabric, metal, glass, ceramic, paper or polymer substrate.
4. A method according to Claim 3, in which the substrate is a fabric.
5. A method according to any preceding Claim, in which the plasma treatment is provided by a glow discharge ignited in an atmosphere containing the compound at a gas pressure from 0.01 to 10 mbar by a high frequency voltage.
6. A method according to any preceding Claim, wherein the plasma polymerisation takes place for from 2 to 15 minutes.

Patentansprüche

1. Verfahren zur Beschichtung einer Oberfläche mit einer öl- und wasserabweisenden Polymerschicht, wobei das Verfahren umfasst, die Oberfläche einem CW(continuous wave)-Plasmafeld auszusetzen, welches eine Verbindung der Formel (I) umfasst:

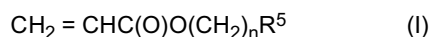


wobei die mittlere Leistung des Feldes weniger als 1W beträgt, n eine ganze Zahl von 1 bis 10 und R⁵ eine C₆₋₂₀-Perhalogenalkylgruppe ist.

2. Verfahren nach Anspruch 1, wobei R⁵ eine Perfluoralkylgruppe der Formel C_mF_{2m+1} ist, worin m eine ganze Zahl von 6 bis 12 ist.
3. Verfahren nach Anspruch 1 oder 2, wobei es sich bei der Oberfläche um eine Oberfläche eines Textilsubstrats, Metallsubstrats, Glassubstrats, Keramiksubstrats, Papiersubstrats oder Polymersubstrats handelt.
4. Verfahren nach Anspruch 3, wobei das Substrat eine Textilie ist.
5. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Plasmabehandlung durch eine Glimmentladung realisiert wird, die in einer Atmosphäre, welche die Verbindung bei einem Gasdruck von 0,01 bis 10 mbar enthält, mit Hilfe einer Hochfrequenzspannung gezündet wird.
6. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Plasmapolymerisation 2 bis 15 Minuten lang stattfindet.

Revendications

1. Méthode de revêtement d'une surface avec une couche de polymère repoussant l'huile et l'eau, laquelle méthode comprend l'exposition de ladite surface à un champ de plasma à ondes continues comprenant le composé de formule (I)



dans laquelle la puissance moyenne du champ est inférieure à 1 W, n est un nombre entier de 1 à 10 et R⁵ est un groupe perhalogénoalkyle en C₆-C₂₀.

2. Méthode selon la revendication 1, dans laquelle R⁵ est un groupe perfluoroalkyle de formule C_mF_{2m+1}, où m est un nombre entier de 6 à 12.
3. Méthode selon la revendication 1 ou la revendication 2, dans laquelle la surface est une surface d'un substrat en tissu, en métal, en verre, en céramique, en papier ou en polymère.
4. Méthode selon la revendication 3, dans laquelle le substrat est un tissu.
5. Méthode selon une quelconque revendication précédente, dans laquelle le traitement au plasma est fourni par une décharge lumineuse allumée dans une atmosphère contenant le composé à une pression gazeuse de 0,01 à 10 mbar par une tension à haute fréquence.
6. Méthode selon une quelconque revendication précédente, dans laquelle la polymérisation au plasma a lieu pendant 2 à 15 minutes.

Fig.1.

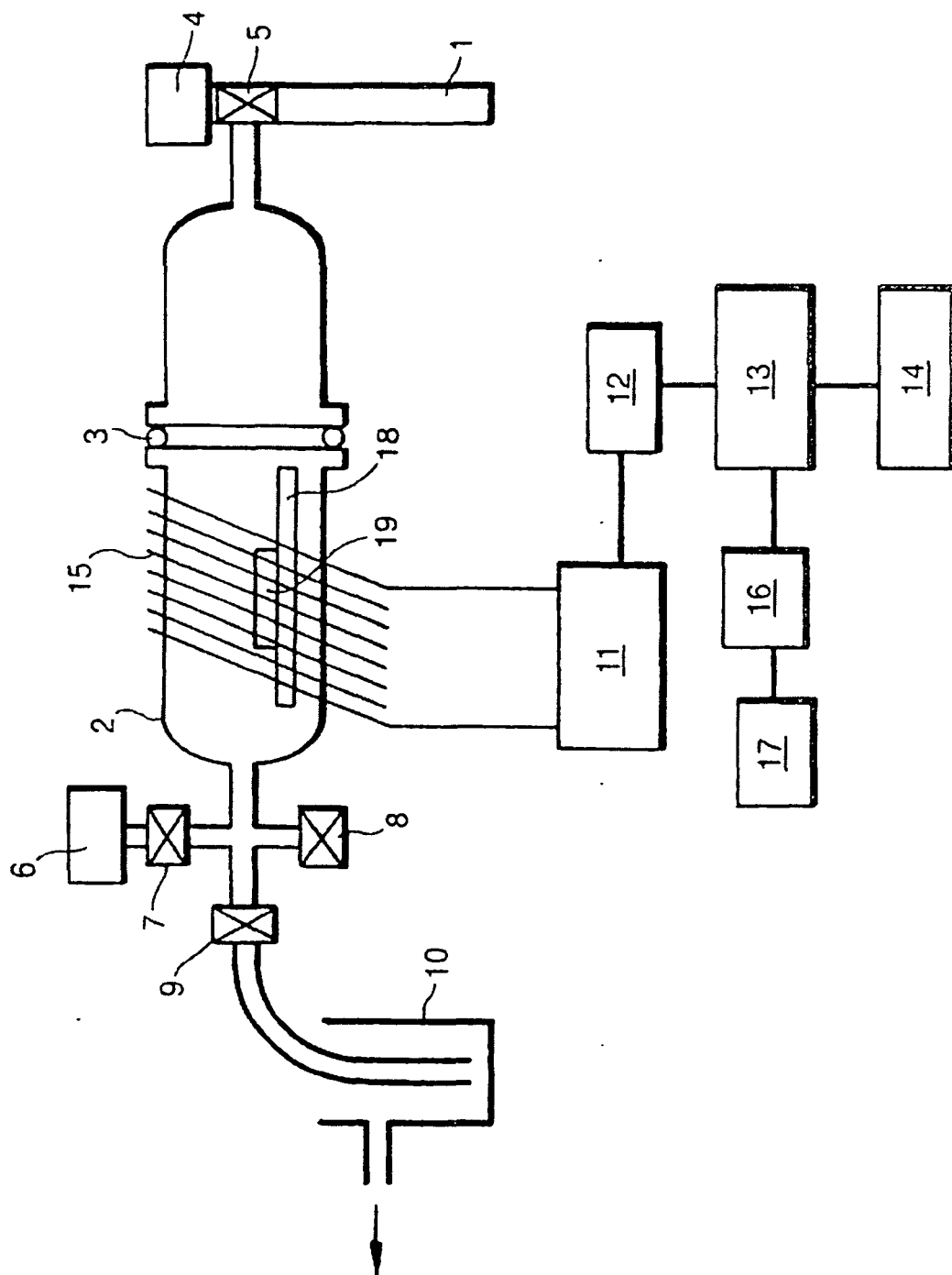


Fig.2.

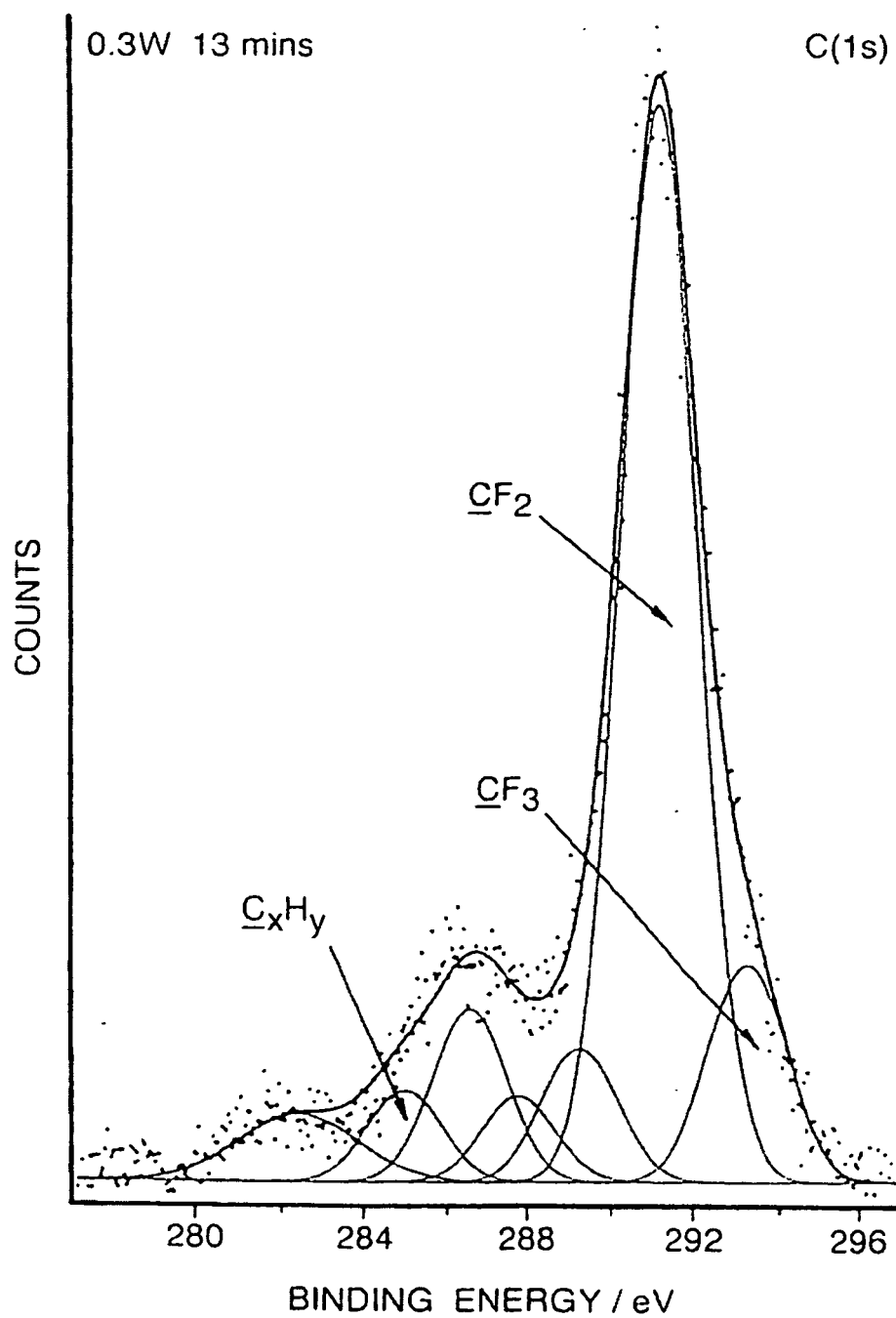


Fig.3.

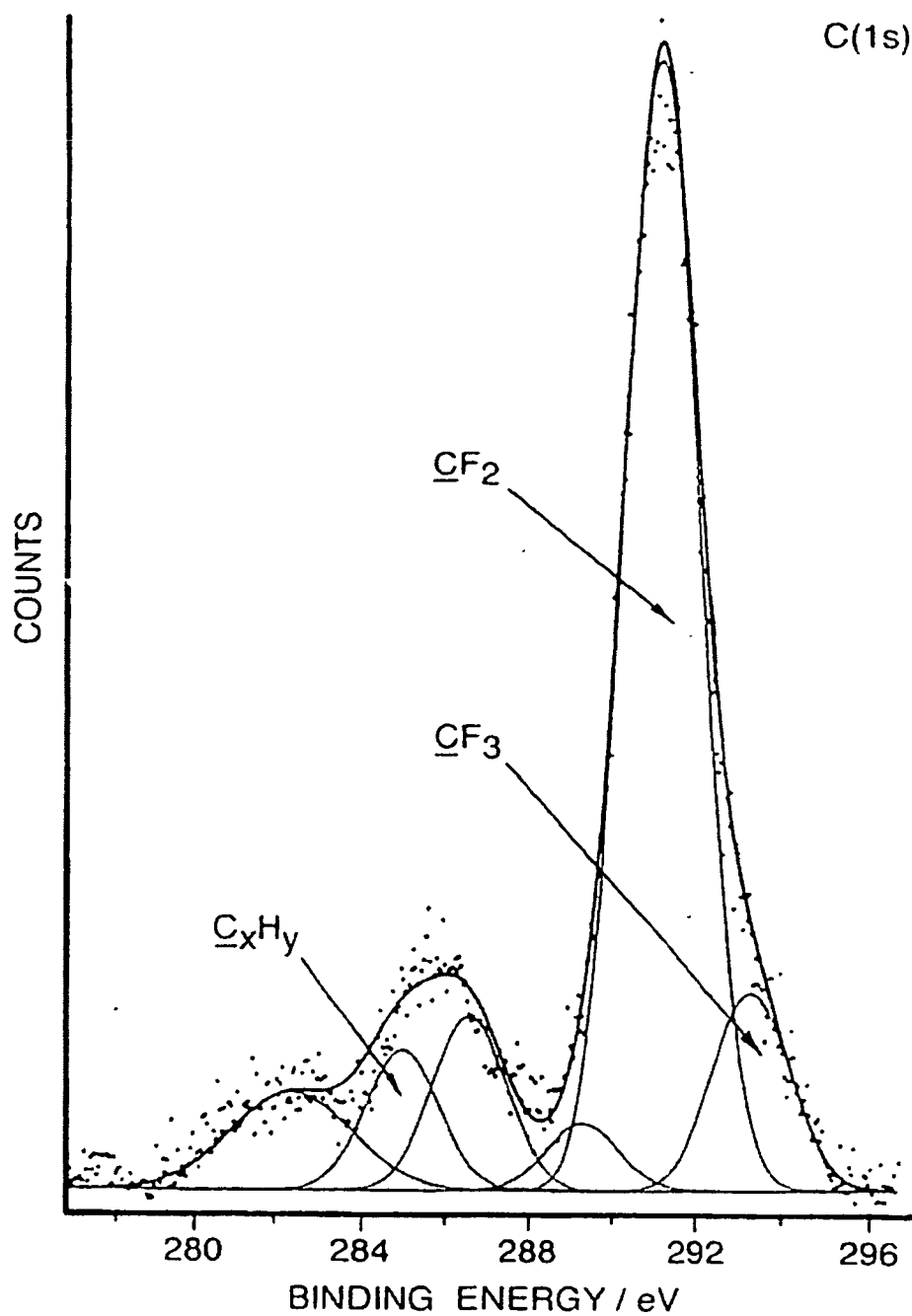
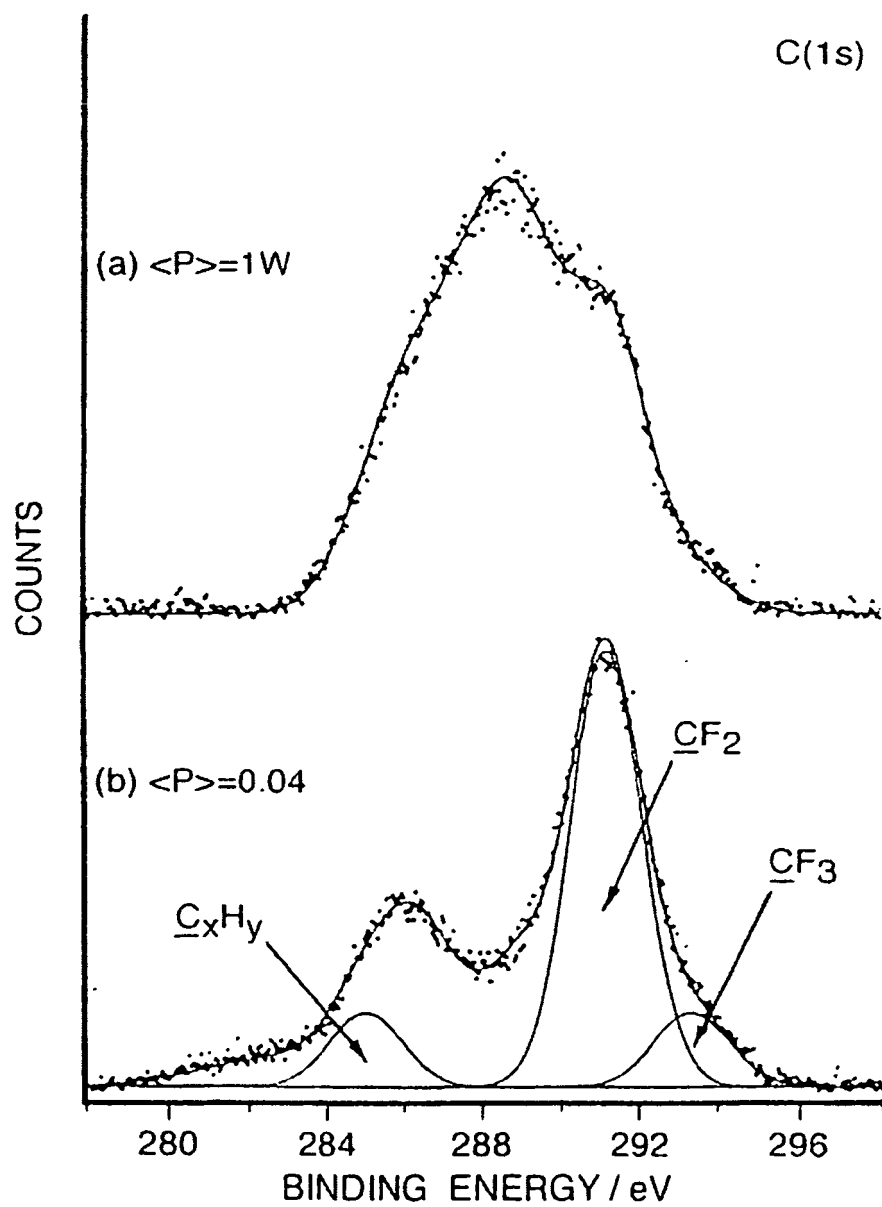


Fig.4.



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