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(54) Title: CLEANING WIPES HAVING A COVALENTLY BOUND OLEOPHILIC COATING THEIR USE AND PROCESSES
FOR THEIR MANUFACTURE

(57) Abstract: Wipes for cleaning oily surfaces comprise an oleophilic material covalently bonded to the surface of the wipe sub-
strate. The wipes retain absorbency, clean oily soil with reduced residues or streaks and retain their properties after washing. A
process for coating the wipes employs atmospheric discharge.



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CLEANSING WIPES HAVING A COVALENTLY BOUND OLEOPHILIC COATING, THEIR USE AND PROCESSES FOR THEIR MANUFACTURE

The present invention is concerned with improvements to
5 cleansing wipes. In particular it relates to wipes which
have an oleophilic coating and to a method of forming an
oleophilic coating onto wipes. It is also concerned with the
use of such wipes for the cleaning of oily surfaces.

- 10 Wipes used for cleaning tasks include wipes made from a base
or substrate material including cloth, woven and non-woven
textiles, sponge and paper. Throughout this specification,
the term "wipe substrate" is used to refer to the base
material from which the body of the wipe is formed.
15 Cleansing wipes are used in the cleansing of hard surfaces
such as floors, work surfaces, furniture, kitchen and
bathroom surfaces.

- By household use is meant household hard surface cleaners
20 (including but not limited to glass, ceramic, wood and
plastics cleaners), household surface cleaners with
antimicrobial and or disinfecting and or antiseptic
activity, insecticides or insect repellents for household
use, air care products including malodour neutralisers,
25 anti-allergenic agents and fragrancing delivered into
household and automotive air spaces, polishes (including but
not limited to those for polishing the floor furniture, shoe
and metal), automatic dishwashing products including "in
machine" wash and pre/post-treatment products and fabric
30 care products for water softening in washing machines,
carpet cleaners and stain removal pre-wash treatments

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Polymeric coatings are widely used to coat cleansing wipes because they are easily applied to give conformal, filmic coatings on a wide range of substrates. The functionality of the polymer is often provided to the substrate coated. An extensive range of methods is used for the delivery and/or curing of films of polymeric coatings. As an example a polymer melt or solution is typically applied by mechanical coating or immersion of a substrate with the resulting polymeric coating being converted to a film by a suitable curing technique such as for example by the application of heat, radiation and/or pressure.

However, the application of a polymer film to a cleansing wipe, although it may make the surface oleophilic, generally leads to a decrease in the absorbency of the wipe for taking up water. Moreover the polymer film is generally unable to absorb oily soil. Although the film comprises molecules covalently bonded to each other, the molecules of the polymer file are not generally covalently bound to the wipe substrate.

Where cleansing wipes have the intended purpose of the removal of oily soil, they may be used in combination with an aqueous cleansing composition, or with an oleophilic solvent intended to disperse or dissolve the oily soil. For this reason it is preferred if such wipes are absorbent, particularly water-absorbent.

To achieve cleansing, it is necessary not only to mobilise the oily soil, but also to remove it from the surface to be cleansed. Hence it is also desirable if the oily soil can be

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bound to the wipe surface during the cleansing process. However, the requirements of water-absorbency and oleophilicity have, until now, seemed mutually incompatible.

5 It has now been found that by covalently bonding an oleophilic coating to the surface of a cleansing wipe substrate, a cleansing wipe can be obtained which is particularly effective at oily soil removal while reducing the risk of streaks or residues on the cleansed surface.

10

Another advantage of the cleansing wipes of the invention is that after their use for cleansing soiled surfaces, the wipes may be cleaned and regenerated by washing in conventional detergent solutions without significant loss in
15 performance.

20

In a first aspect, the invention provides cleansing wipe having an oleophilic coating comprising an oleophilic material which has been covalently bound to the surface of the wipe substrate.

25

According to a second aspect of the present invention, there is provided a process for bonding an oleophilic material to the surface of a cleansing wipe substrate comprising the steps of:

30

- i) introducing an oleophilic material in the form of a gas, vapour, droplets or particles, the oleophilic material being capable of forming a free radical within a plasma environment, into an atmospheric or low pressure plasma discharge and/or an excited gas stream resulting therefrom,

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whereby a highly reactive oleophilic material is formed, and

- 5 ii) exposing the cleansing wipe substrate to the resulting highly reactive oleophilic material whereby the material is deposited onto the surface of the cleansing wipe substrate to form a covalently bonded oleophilic coating.

10

Surprisingly, it has been found that a cleansing wipe which has an oleophilic coating covalently bonded to the substrate of the wipe has many of the advantages of enhanced oily soil removal of a wipe impregnated with an oleophilic solvent.

15 Moreover, the wipe retains the ability to absorb moisture and the oleophilic coating remains bonded to the wipe even after repeated washing with aqueous detergents, retaining its properties. A further advantage over conventional, impregnated wipes is that the oleophilic coating material is
20 not left behind to form oily smears on surfaces which have been treated with the wipe.

In other words, the oleophilic coating acts as a stable layer which can improve the take up of oily soil onto the
25 wipe without itself depositing onto the surface to be cleaned.

Without wishing to be bound by theory, it is thought that polymer coatings of the prior art consist essentially of
30 molecules covalently bound to each other whereas in the oleophilic coatings according to the invention, the

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molecules are covalently bound to the wipe substrate rather than to other coating molecules.

The present invention will now be further described.

5

A preferred method for forming the covalently bound oleophilic coating is plasma deposition.

Conformal polymer films can also be applied to a substrate via the process of plasma polymerisation or plasma enhanced chemical vapour deposition (PE-CVD). Conventional chemical Vapour Deposition is the deposition of a solid on a heated substrate from a chemical reaction in the vapour phase near or on the heated substrate. The chemical reactions which take place may include thermal decomposition, oxidation, carburisation and nitridation. Typically the sequence of events for a CVD reaction comprises the following sequentially:-

- 20 (i) Introduction of reactant gases into a reactor by appropriate introduction means e.g. forced flow,
 (ii) diffusion of the gases through the reactor towards a substrate surface,
 (iii) contact of gases with substrate surface,
25 (iv) chemical reaction takes place between gases and/or one or more gases and the substrate surface leading to covalent bonding of the material to the surface,
 (v) desorption and diffusion away from substrate surface of reaction by-products.
- 30

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In the case of plasma enhanced CVD the gases are directed so as to diffuse through a plasma. Any appropriate plasma may be utilised. Non-thermal equilibrium plasma such as for example glow discharge plasma may be utilised. The glow
5 discharge may be generated at low pressure, i.e. vacuum glow discharge or in the vicinity of atmospheric pressure - atmospheric pressure glow discharge. In respect of the present invention the latter is preferred. Glow discharge plasma is generated in a gas, such as helium by a high
10 frequency electric field.

Typically the plasma is generated in a gap between two electrodes, at least one of which is encased or coated or the like in a dielectric material. PE-CVD may be utilised
15 at any suitable temperature e.g. a plasma at a temperature of from room temperature to 500°C. The ability to achieve chemical bonding to a substrate at room temperature makes this process particularly advantageous when the substrate is sensitive to degradation on heating, such as is the case
20 with many cleansing wipes.

Yasuda, H. Plasma Polymerization; Academic Press: Orlando, 1985 describes how vacuum glow discharge has been used to polymerise gas phase polymer precursors into continuous
25 films. As an example, the plasma enhanced surface treatment and deposition of fluorocarbons has been investigated for the preparation of oleophobic surfaces since the 1970's. Initially, simple fluorocarbon gas precursors such a carbon tetrafluoride were used; this improved hydrophobicity but
30 did not significantly improve oleophobicity. Subsequently, as described in EP 0049884 higher molecular weight

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fluorinated precursors such as the perfluoroalkyl substituted acrylates were used.

- These early processes typically resulted in fragmentation of the precursor and insertion of fluorine into the surface rather than formation of a polymerized fluorocarbon coating. The development of pulsed plasma polymerization (or modulated discharge) as described in Ryan, M., Hynes, A., Badyal, J., Chem. Mater. 1996, 8(1), 37-42 and Chen, X., Rakeshwar, K., Timmons, R., Chen, J., Chiyan, O., Chem. Mater. 1996, 8(5), 1067-77 produced polymerised coatings in which the properties and/or functionalities of the monomer are substantially retained resulting in the production of a polymeric coating, retaining many properties of the bulk polymer. Coulson S.R., Woodward I.S., Badtal J.P.S., Brewer S.A., Willis C., Langmuir, 16, 6287-6293, (2000) describe the production of highly oleophobic surfaces using long chain perfluoroacrylate or perfluoroalkene precursors.
- Vacuum glow discharge processes have been investigated as routes to encapsulation and controlled release for example Colter, K.D.; Shen, M.; Bell, A.T. Biomaterials, Medical Devices, and Artificial Organs (1977), 5(1), 13-24 describes a method where fluoropolymer coatings are applied to reduce the diffusion of a steroid active through a poly(dimethylsiloxane) elastomer. Kitade, Tatsuta; Kitamura, Kieseke; Hozumi, Kei. Chemical & Pharmaceutical Bulletin (1987), 35(11), 4410-17 describes the application of vacuum glow discharge plasma to coat a powdered active with a PTFE based coating for controlled dissolution.

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WO 9910560 describes a further vacuum plasma method where precursor vapour is introduced to the plasma to produce coatings for the purpose of encapsulation.

- 5 A drawback for vacuum plasma methods is that the necessity for a vacuum requires the coating process to be operated in a batch wise manner.

- Both Atmospheric Pressure Glow Discharge (APGD) and
10 Dielectric Barrier Discharge (DBD) offer an alternative homogeneous plasma source, which have many of the benefits of vacuum plasma methods, while operating at atmospheric pressure. The use of APGD was significantly developed
1980's, e.g. as described in Kanazawa S., Kogoma M.,
15 Moriwaki T., Okasaki S., J. Phys. D: Appl. Phys., 21, 838-840 (1988) and Roth J.R., Industrial Plasma Engineering Volume 2 Applications to Nonthermal Plasma Processing, Institute of Physics Publishing, 2001, pages 37-73.
WO 01 59809 and WO 02 35576 describe a series of wide area
20 APGD systems, which provides a uniform, homogeneous plasma at ambient pressure by application of a low frequency RF voltage across opposing parallel plate electrodes separated by ~10 mm. The ambient pressure and temperature ensures compatibility with open perimeter, continuous, on-line
25 processing.

- Considerable work has been done on the stabilisation of atmospheric pressure glow discharges, described in
"Appearance of stable glow discharge in air, argon, oxygen
30 and nitrogen at atmospheric pressure using a 50 Hz source"
by Satiko Okazaki, Masuhiro Kogoma, Makoto Uehara and Yoshihisa Kimura, J. Phys. D: Appl. Phys. 26 (1993) 889-892.

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Further, there is described in US 5414324 (Roth et al) the generation of a steady-state glow discharge plasma at atmospheric pressure between a pair of insulated metal plate electrodes spaced up to 5 cm apart and radio frequency
5 (R.F.). energised with a room mean square (rms) potential of 1 to 5 kV at 1 to 100 kHz. This patent specification describes the use of electrically insulated metallic plate electrodes. This patent specification also describes a number of problems relating to the use of plate electrodes
10 and the need to discourage electrical breakdown at the tips of electrodes.

These ambient temperature, atmospheric plasma systems have also been used to demonstrate the deposition of plasma
15 coatings from vapour phase monomers - in effect atmospheric PE-CVD. For example EP 0431951 describes surface treatment with silane and disilane vapour and US 6146724 describes the deposition of a barrier coating from siloxane vapour precursors.

20 WO 02/28548 describes a process for enabling the introduction of a solid or liquid precursor into an atmospheric pressure plasma discharge and/or an ionised gas stream resulting therefrom in order to form a coating on a
25 substrate. The substrates mentioned include metal, ceramic, plastic, woven or non-woven fibres, natural fibres, synthetic fibres, cellulosic material and powders.

Any suitable means for generating the plasma environment may
30 be used. Any conventional means for generating an atmospheric pressure plasma glow discharge may be used, for example, atmospheric pressure plasma jet, atmospheric

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pressure microwave glow discharge and atmospheric pressure glow discharge.

Preferably, the present invention uses equipment similar to that described in WO 02/28548, wherein liquid coating-forming materials are introduced as an aerosol into an atmospheric plasma discharge or the excited species resulting from such a discharge.

10 For typical plasma generating apparatus, the plasma is generated between a pair of electrodes within a gap of from 3 to 50mm, for example 5 to 25mm. The generation of steady-state glow discharge plasma at atmospheric pressure is preferably obtained between adjacent electrodes which may be
15 spaced up to 5 cm apart, dependent on the process gas used. The electrodes being radio frequency energised with a root mean square (rms) potential of 1 to 100 kV, preferably between 1 and 30 kV at 1 to 100 kHz, preferably at 15 to 50 kHz. The voltage used to form the plasma will typically be
20 between 1 and 30 kVolts, most preferably between 2.5 and 10 kV however the actual value will depend on the chemistry/gas choice and plasma region size between the electrodes.

Any suitable electrode systems may be utilised. Each
25 electrode may comprise, for example, a metal plate or metal gauze which is in contact with a dielectric material. Suitable electrode are described in WO 02/35576. Thus, there may be provided electrode units containing an electrode and an adjacent a dielectric plate and a cooling
30 liquid distribution system for directing a cooling conductive liquid onto the exterior of the electrode to cover a planar face of the electrode. Each electrode unit

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may comprise a watertight box having one side in the form of a dielectric plate to which a metal plate or gauze electrode is attached on the inside of the box. There may also be a liquid inlet and a liquid outlet fitted to a liquid

5 distribution system comprising a cooler and a recirculation pump and/or a sparge pipe incorporating spray nozzles. The cooling liquid preferably covers the face of the electrode remote from the dielectric plate. The cooling conductive liquid is preferably water and may contain conductivity
10 controlling compounds such as metal salts or soluble organic additives. Ideally, the electrode is a metal plate or mesh electrode in contact with the dielectric plate. The dielectric plate extends beyond the perimeter of the electrode and the cooling liquid is also directed across the
15 dielectric plate to cover at least that portion of dielectric bordering the periphery of the electrode. Preferably, all the dielectric plate is covered with cooling liquid. The water acts to electrically passivate any boundaries, singularities or non-uniformity in the metal
20 electrodes such as edges, corners or mesh ends where the wire mesh electrodes are used.

In an alternative system, each electrode may be of the type described in PCT/EP2004/001756. Thus, each electrode may
25 comprise housing having an inner and outer wall, wherein at least the inner wall is formed from a dielectric material, and which housing contains an at least substantially non-metallic electrically conductive material in direct contact with the inner wall instead of the "traditional" metal plate
30 or mesh. Electrodes of this type are preferred because the inventors have identified that by using electrodes in accordance with the present invention to generate a Glow

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Discharge, the resulting homogeneous glow discharge can be generated with reduced inhomogeneities when compared to systems utilizing metal plate electrodes. A metal plate is never fixed directly to the inner wall of an electrode in the present invention and preferably, the non-metallic electrically conductive material is in direct contact with the inner wall of the electrode.

Suitable dielectric materials include polycarbonate, polyethylene, glass, glass laminates, epoxy filled glass laminates and the like. Preferably, the dielectric has sufficient strength in order to prevent any bowing or disfigurement of the dielectric by the conductive material in the electrode. Preferably, the dielectric used is machinable and is provided at a thickness of up to 50mm in thickness, more preferably up to 40mm thickness and most preferably 15 to 30mm thickness. In instances where the selected dielectric is not sufficiently transparent, a glass or the like window may be utilized to enable diagnostic viewing of the generated plasma.

The electrodes may be spaced apart by means of a spacer or the like, which is preferably also made from a dielectric material which thereby effects an increase in the overall dielectric strength of the system by eliminating any potential for discharge between the edges of the conductive liquid.

In one embodiment, the electrode comprises a housing having an inner and outer wall, wherein the inner wall is formed from a dielectric material. The housing contains at least one substantially non-metallic electrically conductive

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material in direct contact with the inner wall instead of the "traditional" metal plate or mesh.

The substantially non-metallic electrically conductive material may be a liquid such as a polar solvent for example water, alcohol and/or glycols or aqueous salt solutions and mixtures thereof, but is preferably an aqueous salt solution. When water is used alone, it preferably comprises tap water or mineral water. Preferably, the water contains up to a maximum of about 15% by weight of a water soluble salt such as an alkali metal salt, for example sodium or potassium chloride or alkaline earth metal salts. This is because the conductive material present in such an electrode has substantially perfect conformity and thereby a homogeneous surface potential at the dielectric surface.

Alternatively, the substantially non-metallic electrically conductive material may be in the form of one or more conductive polymer compositions, which may typically be supplied in the form of pastes. Such pastes are currently used in the electronics industry for the adhesion and thermal management of electronic components, such as microprocessor chip sets. These pastes typically have sufficient mobility to flow and conform to surface irregularities.

Suitable polymers for the conductive polymer compositions in accordance with the present invention may include silicones, polyoxypolyolefin elastomers, a hot melt based on a wax such as a, silicone wax, resin/polymer blends, silicone polyamide copolymers or other silicon-organic copolymers or the like or epoxy, polyimide, acrylate, urethane or

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isocyanate based polymer. The polymers will typically contain conductive particles, typically of silver but alternative conductive particles might be used including gold, nickel, copper, assorted metal oxides and/or carbon including carbon nanotubes; or metallised glass or ceramic beads. Specific examples polymers which might be used include the conductive polymer described in EP 240648 or silver filled organopolysiloxane based compositions such as Dow Corning® DA 6523, Dow Corning® 6524, Dow Corning® DA 6526 BD, and Dow Corning® 6533 sold by Dow Corning Corporation or silver filled epoxy based polymers such as Ablebond® 8175 from (Ablestik Electronic Materials & Adhesives) Epo-Tek® H20E-PFC or Epo-Tek® E30 (Epoxy Technology Inc).

One example of the type of assembly which might be used on an industrial scale is described in WO 03/086031.

In a preferred embodiment, the electrodes are vertically arrayed.

Whilst the atmospheric pressure glow discharge assembly may operate at any suitable temperature, it preferably operates at a temperature between room temperature (20°C) and 70°C and is typically utilized at a temperature in the region of 30 to 50°C.

The coating-forming material may be atomised (meaning formed into finely divided particles or droplets) using any conventional means, for example an ultrasonic nozzle. The material to be atomised is preferably in the form of a liquid, a solid or a liquid/solid slurry. The atomiser

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preferably produces a coating-forming material drop size of from 10 to 100 micrometres, more preferably from 10 to 50 micrometres. Suitable atomisers for use in the present invention are ultrasonic nozzles from Sono-Tek Corporation,
5 Milton, New York, USA or Lechler GbH of Metzingen Germany.

The process gas used to generate a plasma suitable for use in the present invention may be any suitable gas but is preferably an inert gas or inert gas based mixture such as,
10 for example helium, a mixture of helium and argon and an argon based mixture additionally containing ketones and/or related compounds. These process gases may be utilized alone or in combination with potentially reactive gases such as, for example, nitrogen, ammonia, O₂, H₂O, NO₂, air or
15 hydrogen. Most preferably, the process gas will be Helium alone or in combination with an oxidizing or reducing gas. The selection of gas depends upon the plasma processes to be undertaken. When an oxidizing or reducing process gas is required, it will preferably be utilized in a mixture
20 comprising 90-99% noble gas and 1 to 10% oxidizing or reducing gas.

Under oxidising conditions the present method may be used to form an oxygen containing coating on the substrate.
25

In a nitrogen containing atmosphere nitrogen can bind to the substrate surface, and in an atmosphere containing both nitrogen and oxygen, nitrates can bind to and/or form on the substrate surface. Such gases may also be used to pre-treat
30 the substrate surface prior to exposure to a coating forming substance. For example, oxygen containing plasma treatment of the substrate may provide improved adhesion with the

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applied coating. The oxygen containing plasma being generated by introducing oxygen-containing materials to the plasma such as oxygen gas or water.

5

Any suitable non-thermal equilibrium plasma equipment may be used to undertake the method of the present invention. However atmospheric pressure glow discharge, dielectric barrier discharge (DBD), low pressure glow discharge, which
10 may be operated in either continuous mode or pulse mode are preferred.

The plasma equipment may also be in the form of a plasma jet as described in WO 03/085693. Where the substrate is placed
15 downstream and remote from the plasma source.

Any conventional means for generating an atmospheric pressure glow discharge may be used in the method of the present invention, for example atmospheric pressure plasma
20 jet, atmospheric pressure microwave glow discharge and atmospheric pressure glow discharge. Typically, such means will employ helium as the process gas and a high frequency (e.g. >1kHz) power supply to generate a homogeneous glow discharge at atmospheric pressure via a Penning ionisation
25 mechanism, (see for example, Kanazawa et al, J. Phys. D: Appl. Phys. 1988, 21, 838, Okazaki et al, Proc. Jpn. Symp. Plasma Chem. 1989, 2, 95, Kanazawa et al, Nuclear Instruments and Methods in Physical Research 1989, B37/38, 842, and Yokoyama et al., J. Phys. D: Appl. Phys. 1990, 23,
30 374).

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In the case of low pressure discharge plasma, liquid precursor and the active material is preferably either retained in a container or is introduced into the reactor in the form of an atomised liquid spray as described above.

5 The low pressure plasma may be performed with coating-forming material heating and/or pulsing of the plasma discharge, but is preferably carried out without the need for additional heating. If heating is required, the method in accordance with the present invention using low pressure
10 plasma techniques may be cyclic, i.e. the coating-forming material plasma treated with no heating followed by heating with no plasma treatment, etc., or may be simultaneous, i.e. coating-forming material heating and plasma treatment occurring together. The plasma may be generated by way of
15 the electromagnetic radiations from any suitable source, such as radio frequency, microwave or direct current (DC). A radio frequency (RF) range between 8 and 16 MHz is suitable with an RF of 13.56 MHz preferred. In the case of low pressure glow discharge any suitable reaction chamber
20 may be utilized. The power of the electrode system may be between 1 and 100 W, but preferably is in the region of from 5 to 50 W for continuous low pressure plasma techniques. The chamber pressure may be reduced to any suitable pressure for example from 0.1 to 0.001 mbar but preferably is between
25 0.05 and 0.01 mbar.

A particularly preferred pulsed plasma treatment process involved pulsing the plasma discharge at room temperature. The plasma discharge is pulsed to have a particular "on"
30 time and "off" time, such that a very low average power is applied, for example a power of less than 10W and preferably less than 1W. The on-time is typically from 10 to 10000 μ s,

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preferably 10 to 1000 μ s, and the off-time typically from 1000 to 10000 μ s, preferably from 1000 to 5000 μ s. The oleophilic coating material may be introduced into the vacuum with no additional gases, i.e. by direct injection, however additional process gases such as helium or argon may also be utilized as carriers where deemed necessary.

In the case of the low pressure plasma options the process gas for forming the plasma may be as described for the atmospheric pressure system but may alternatively not comprise noble gases such as helium and/or argon and may therefore purely be oxygen, air or an alternative oxidising gas.

The oleophilic material is an organic material comprising an oleophilic group. Suitably, the oleophilic group comprises at least 8 carbon atoms, preferably, at least 10 carbon atoms, more preferably at least 12 carbon atoms.

Without wishing to be bound by any theory, it is believed that the oleophilic coating-forming material becomes chemically grafted onto the substrate by covalent bond formation under plasma conditions, forming an oleophilic coating on the surface of the wipe substrate. A portion of oleophilic coating-forming material may be bonded to the substrate whilst the remainder (e.g. the oleophilic group) of the material may dangle freely from the substrate surface. Suitably, some of the oleophilic coating-forming material is deposited in an unpolymerised state. Preferably 50% or more by weight of the oleophilic coating-forming material is in an unpolymerised state, preferably 60% or more, more preferably 70% or more.

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The oleophilic coating-forming material may be an unsaturated hydrocarbon. Preferably the unsaturated hydrocarbon is an alkene. The alkene may have at least 8 carbon atoms, preferably, at least 10 carbon atoms, more preferably, at least 12 carbon atoms, for example, 12 to 30 carbon atoms, preferably 14 to 24 carbon atoms. In a preferred embodiment, dodecene and/or hexadecene is employed. Alpha-olefins are particularly preferred alkenes.

- 10 The hydrocarbon may be straight-chain, branched or cyclic. Preferably straight chain hydrocarbons are employed.

The oleophilic coating-forming material may be suitably be a hydrocarbon chain with a terminal group such as an alcohol, aldehyde, halide or fatty acid. Alternatively, esters of short-chain alcohols and fatty acids are suitable and preferred. Examples of suitable short chain alcohols include methanol, ethanol, ethylene glycol, propylene glycol and glycerol. Suitable fatty acids have typically from 12 to 30 carbon atoms, preferably 14 to 24. Where the alcohol is a polyhydric alcohol, the ester may be a mono-ester or a polyester. Particularly suitable as a coating-forming material are triglycerides. Examples of suitable triglycerides are oils and fats, preferably vegetable oils such as corn oil, sunflower oil, rapeseed oil, olive oil, castor oil, soybean oil. Sunflower oil has been found to be particularly suitable.

The wipe substrate may be a woven or knitted cloth, a non-woven textile or paper or a natural or synthetic sponge. The wipe may be for hard surface cleaning, such as furniture, floor or multisurface cleaning or

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The wipe or cloth substrate may be woven or non-woven, and may comprise synthetic or natural fibres or a mixture thereof, or be made of a sponge material. Typical materials for the fibres are cotton, cellulose, wool, polyethylene, polypropylene, acetate, polyamide, rayon, viscose and/or polyacrtoylonitrile. Reinforcing threads may be present, if desired. Typically the wipe has a weight of from 40 to 80g per m³, preferably 50 to 70g per m³, and a size of from 15 to 40 cm by 15 to 40 cm.

The wipe substrate is preferably water-absorbent, by which it is meant that the substrate is capable of taking up and retaining within its structure a certain amount of water. This may suitably be measured by weighing a sheet of dry wipe substrate, immersing the wipe substrate in demineralised water at 20°C for 2 minutes, then placing the wet wipe substrate, without squeezing, onto a horizontal wire grid made up of 1 cm squares of rigid, interlocked 0.5mm piano wire and allowing it to drain for 2 minutes. The absorbency is equal to the weight of the water in the drained, saturated substrate divided by the weight of the dry substrate, expressed as a percentage.

Suitably the wipe substrate has a water-absorbency of 100% or more, preferably, 300% or more, more preferably 600% or more.

Suitably, the cleansing wipe of the invention, including the oleophilic coating has a water-absorbency, measured by the same method, of 80% or more, preferably 240% or more, more preferably 480% or more.

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The wipe according to the invention may be supplied in a packaged form pre-impregnated by a component such as water or a cleaning composition as disclosed in, for example, GB-A-2,368,590.

5

In another aspect, the invention provides a method of cleaning an oily surface by wiping the surface with a cleansing wipe having an oleophilic coating which is covalently bound to the surface of the wipe substrate.

10 A further aspect of the invention is concerned with the use of a cleansing wipe having an oleophilic coating which is covalently bound to the surface of the wipe substrate for the cleaning of oily surfaces.

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CLAIMS

1. A cleansing wipe having an oleophilic coating
comprising an oleophilic material which has been covalently
5 bound to the surface of the wipe substrate.

2. A cleansing wipe according to claim 1, wherein the
oleophilic material comprises an oleophilic group comprising
at least 10 carbon atoms.

10

3. A cleansing wipe according to claim 1 or 2 wherein the
oleophilic material is an alpha-olefin.

4. A cleansing wipe according to claim 1 or 2 wherein the
15 oleophilic material is a triglyceride.

5. A process for bonding an oleophilic material to the
surface of a cleansing wipe substrate comprising the steps
of:

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ii) introducing an oleophilic material in the form of
a gas, vapour, droplets or particles, the
oleophilic material being capable of forming a
free radical within a plasma environment, into an
25 atmospheric or low pressure plasma discharge
and/or an excited gas stream resulting therefrom,
whereby a highly reactive oleophilic material is
formed, and

25

30 ii) exposing the cleansing wipe substrate to the
resulting highly reactive oleophilic material
whereby the material is deposited onto the surface

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of the cleansing wipe substrate to form a covalently bonded oleophilic coating.

5 6. A method according to claim 5, wherein the oleophilic coating-forming material is introduced into the plasma discharge as liquid droplets by means of one or more atomisers.

10 7. A method as claimed in any one of the claims 5 or 6, wherein the cleansing wipe is passed through the plasma and/or excited gas stream resulting therefrom.

8. A method according to any one of claims 5 to 7, wherein
15 the oleophilic material comprises an oleophilic group comprising at least 10 carbon atoms.

9. A method according to claim 8 wherein the oleophilic material is an alpha-olefin.

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10. A method according to claim 8 wherein the oleophilic material is a triglyceride.

11. A cleansing wipe having a oleophilic coating covalently
25 bonded to the surface of the wipe, the wipe being obtainable by a method as claimed in any one of the preceding claims.

12. A method of removing a soil from a surface, the method comprising wiping the soil with a cleansing wipe according
30 to any one of claims 1 to 4 or claim 11.

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13. The use of a cleansing wipe according to any one of claims 1 to 4 or claim 11 for the cleaning of an oily surface.

INTERNATIONAL SEARCH REPORT

PCT/GB2005/001853

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D17/04 D06M10/02 D06M14/18 D06M13/03 D06M13/224

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 C11D D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98/58117 A (THE SECRETARY OF STATE FOR DEFENCE) 23 December 1998 (1998-12-23) page 4, lines 7-13; claims; examples page 5, line 29 - page 7, line 31 page 8, line 6 - line 12	1,5
X	EP 0 695 622 A (FRAUNHOFER-GESELLSCHAFT ZUR FOERDERUNG DER ANGEWANDTEN FORSCHUNG E.V.) 7 February 1996 (1996-02-07) column 1, lines 3-11; claims column 3, line 31 - line 45 ----- -/--	1,5,11

☒ 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.

Z document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

PCT/GB2005/001853

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	THOMAS H ET AL: "TEXTILVEREDLUNG MIT NIEDERTEMPERATURPLASMEN" MELLIAND TEXTILBERICHTE, INTERNATIONAL TEXTILE REPORTS, MELLIAND TEXTILBERICHTE, FRANKFURT AM MAIN, DE, vol. 79, no. 5, May 1998 (1998-05), pages 350-352, XP000765141 ISSN: 0341-0781 paragraphs '0003!, '0004! -----	1,5,11
X	VOHRER U ET AL: "HYDROPHOBIERUNG POLYMERER MATERIALIEN MITTELS PLASMA" TEXTILVEREDLUNG, SVF SVCC, BASEL, CH, vol. 37, no. 9/10, September 2002 (2002-09), pages 5-6,8,10, XP001225408 ISSN: 0040-5310 the whole document -----	1,5,11

INTERNATIONAL SEARCH REPORT

PCT/GB2005/001853

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9858117	A	23-12-1998	AU 738802 B2	27-09-2001
			AU 8028498 A	04-01-1999
			CA 2294644 A1	23-12-1998
			CN 1265714 A ,C	06-09-2000
			EP 0988412 A1	29-03-2000
			WO 9858117 A1	23-12-1998
			GB 2341864 A ,B	29-03-2000
			JP 2002510363 T	02-04-2002
			NZ 501791 A	28-09-2001
			US 6551950 B1	22-04-2003
EP 0695622	A	07-02-1996	DE 4432919 A1	25-01-1996
			AT 208700 T	15-11-2001
			DE 59509823 D1	20-12-2001
			EP 0695622 A2	07-02-1996