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GB 2451176 A
EP 1557489 A1
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WO 2004/065684 A1

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(54) Title of the Invention: **Novel product and method**
Abstract Title: **Plasma polymerization for coating wool**

(57) A method of treating wool in the form of a fibre, yarn, sliver, fabric or garment. A polymer coating is applied by plasma polymerization to prevent shrinkage due to felting due to laundering. The method may include a pre-treatment step, for example application of a continuous plasma of inert gas, application of nano particles to the fibre surface or coating the fibre surface with a polymer. The polymer may be a fluoropolymer such as that formed from 1H, 1H, 2H, 2H-heptadecafluorodecylacrylate.

Application No. GB0920620.2 **RTM** Date :25 March 2010

The following terms are registered trademarks and should be read as such wherever they occur in this document:

Hercosett

Novel Product and Method

The present invention relates to the treatment of wool and wool blend fabrics to improve laundering performance, in particular to reduce shrinkage due to felting during laundering.

The term 'wool' includes not only the fibres derived from the Caprinae family, such as sheep, but also the hair of certain other species of mammals, such as goats, llamas, alpacas and rabbits (e.g. cashmere, mohair or angora).

Wool fibre is a popular material for making garments, due to its appearance and handling qualities, as well as its thermal insulating properties. However, the disadvantage of wool and wool blends is that it can shrink during laundering.

The problem of shrinkage is due to felting caused by wool fibre's complex structure, consisting on an inner cortex and outer surface cuticle. It is this outer surface cuticle which is primarily responsible for felting shrinkage.

The cuticle comprises an epicuticle which includes fatty lipids covalently bound to a protein surface, which provide some natural water repellency. The cuticle also comprises an exocuticle which has a rigid surface structure comprising of overlapping scales which protect the wool fibre from mechanical damage. This rigid surface structure of the exocuticle is responsible for a 'directional frictional effect' (DFE) which leads to wool felting during laundering.

When the fibres are being laundered, they are subject to water, heat and mechanical agitation, causing the fibres to interlock. Due to the nature of the exocuticle, fibres can slide more easily in one direction than the other leading to preferential unidirectional movement which causes felting.

The coefficient of friction in the 'with' scale direction is less than in the 'against' scale direction due to the hardness of the scale edge and its lack of deformability when it comes into contact with other fibres. The result of the DFE is that the fibres progressively lock together, the yarns closes up and the fabric shrinks irreversibly.

The major method of treating wool to make it machine washable is the chlorine Hercosett process, which aims to "mask and smooth" the surface scales hence eliminating the DFE. The process involves a series of aqueous baths; starting with acid chlorination to modify the epicuticle and thereby impart wettability, create reactive functionality for the reactive polymer bonding and raise surface energy to allow the polymer coating to spread. A subsequent step is antichlorination / neutralisation which creates further reactive functionality for the reactive polymer bonding and removes residual chlorine from the fibre. This step is followed by application of the polymer, softening and drying.

The Hercosett polymer is a soft, cationic reactive epichlorohydrin polyamide which exhausts onto the negatively charged wool fibre and covalently bonds to the fibre surface. It masks the scale edges so eliminating the DFE.

The Chlorine Hercosett process is described in more detail in T. Shaw & M. A. White, Chapter 5, P.346 (1984), Handbook of Fiber Science & Fiber Technology, Vol. II, Chemical Processing of Fibers & Fabrics, Functional Finishes, Part B, Edited by M. Lewin & S. B. Sello. Marcel Dekker Inc., New York. ISBN 0-8247-7118. The Chlorine Hercosett process is also described in both J. Lewis, Wool Science Review, 54, 2 (1977) and also H. J. Katz, G. F. Wood & M.T. Goldsmith, Textile Manufacturer, 95, 84 (1969).

The Chlorine Hercosett process has the disadvantage that adsorbable organohalogens (AOX) are produced in the chlorination stage, causing other solutions to be sought.

Durable water repellent coatings (DWR) are often added to fabrics to make them water resistant, for example Fluoropel and Olephobol are two typical fluoropolymers coatings applied by wet chemistry techniques to give water repellency. Durable water repellent coatings are discussed in E. Kissa, Chapter 2, P.143 (1984), Handbook of Fiber Science & Fiber Technology, Vol. II, Chemical Processing of Fibers & Fabrics, Functional Finishes, Part B, Edited by M. Lewin & S. B. Sello. Marcel Dekker Inc., New York. ISBN 0-8247-7118 and also F. Audenaert, H. Lens, D. Rolly and P. Van der Elst, Fluorochemical Textile Repellents – Synthesis, and Applications: A 3M Perspective, J. Text. Inst., 90, 3, 76 (1999).
The water repellency of these fluoropolymers coatings tends to be reduced after laundering, due to reorientation of the fluorocarbon polymer chain. This is caused by movement of the polymer to enable the hydrophobic fluorine functional groups to "re-position" into the coating sub-surface, away from the water used in cleaning. Hot pressing (e.g. ironing) or hot drying of the fabric is required to restore water repellency.

Plasma deposition techniques have been used for the deposition of polymeric coatings onto a range of surfaces, and in particular onto fabric 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 organic molecules, which are subjected to an electrical field. When this is done in the presence of a substrate, the radicals of the compound in the plasma polymerise on the substrate. Conventional polymer synthesis tends to produce structures containing repeat units that bear a strong resemblance to the monomer species, whereas a polymer network generated using a plasma can be extremely complex. The properties of the resultant coating can depend upon the nature of the substrate as well as the nature of the monomer used and conditions under which it is deposited.

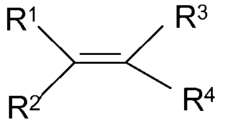
A first aspect of the present invention provides a method of treating wool in the form of fibre, sliver, yarn, fabric or garment comprising said fibre or yarn, to prevent shrinkage due to felting during laundering, the method comprising applying a polymer coating by plasma polymerisation.

A sliver is carded and combed wool formed into a tube of fibres. The Textile Institute define a sliver as an assemblage of fibres in continuous form without twist.

The fibre, yarn, sliver, fabric or garment may comprise pure wool or a wool / polymer blend.

Any monomer that undergoes plasma polymerisation or modification of the surface to form a suitable polymeric coating layer may suitably be used. Examples of such monomers include those known in the art to be capable of producing hydrophobic polymeric coatings on substrates by plasma polymerisation including, for example, carbonaceous compounds having reactive functional groups, particularly substantially $-CF_3$ dominated perfluoro compounds (see WO 97/38801), perfluorinated alkenes (Wang et al., Chem Mater 1996, 2212-2214), hydrogen containing unsaturated compounds optionally containing halogen atoms or perhalogenated organic compounds of at least 10 carbon atoms (see WO 98/58117), organic compounds comprising two double bonds (WO 99/64662), saturated organic compounds having an optionally substituted alky chain of at least 5 carbon atoms optionally interposed with a heteroatom (WO 00/05000), optionally substituted alkynes (WO 00/20130), polyether substituted alkenes (US 6,482,531B) and macrocycles containing at least one heteroatom (US 6,329,024B), the contents of all of which are herein incorporated by reference.

A particular group of monomers which may be used to produce the coating of the present invention include compounds of formula (I)



(I)

where R^1, R^2 and R^3 are independently selected from hydrogen, halo, 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 $-C(O)O-$, a group of formula $-C(O)O(CH_2)_nY-$ where n is an integer of from 1 to 10 and Y is 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.

As used therein the term "halo" or "halogen" refers to fluorine, chlorine, bromine and iodine. Particularly preferred halo groups are fluoro. 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. "Haloalkyl" refers to alkyl chains as defined above which include at least one halo substituent.

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 4 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 4-12 such as 4, 6 or 8.

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

In one embodiment, at least one of R^1, R^2 and R^3 is hydrogen. In a particular embodiment R^1, R^2, R^3 are all hydrogen. In yet a further embodiment however R^3 is an alkyl group such as methyl or propyl.

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

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

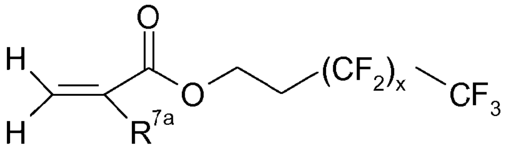
where R^5 is as defined above in relation to formula (I).

In compounds of formula (II), 'X' within the X-R^5 group in formula (I) is a bond.

However in a preferred embodiment, the compound of formula (I) is an acrylate of formula (III)

$$CH_2=CR^{7a}C(O)O(CH_2)_nR^5 \quad (III)$$

where n and R^5 as defined above in relation to formula (I) and R^{7a} is hydrogen, C_{1-10} alkyl, or C_{1-10}haloalkyl. In particular R^{7a} is hydrogen or C_{1-6}alkyl such as methyl. A particular example of a compound of formula (III) is a compound of formula (IV)

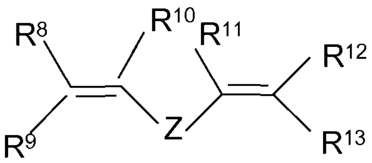


(IV)

where R^{7a} is as defined above, and in particular is hydrogen and x is an integer of from 1 to 9, for instance from 4 to 9, and preferably 7. In that case, the compound of formula (IV) is 1H,1H,2H,2H-heptadecafluorodecylacrylate.

According to a particular embodiment, the polymeric coating is formed by exposing the fibre, yarn, sliver, fabric or garment to plasma comprising one or more organic monomeric compounds, at least one of which comprises two carbon-carbon double bonds for a sufficient period of time to allow a polymeric layer to form on the surface.

Suitably the compound with more than one double bond comprises a compound of formula (V)

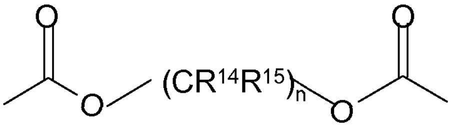


(V)

where R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} are all independently selected from hydrogen, halo, alkyl, haloalkyl or aryl optionally substituted by halo; and Z is a bridging group.

Examples of suitable bridging groups Z for use in the compound of formula (V) are those known in the polymer art. In particular they include optionally substituted alkyl groups which may be interposed with oxygen atoms. Suitable optional substituents for bridging groups Z include perhaloalkyl groups, in particular perfluoroalkyl groups.

In a particularly preferred embodiment, the bridging group Z includes one or more acyloxy or ester groups. In particular, the bridging group of formula Z is a group of sub-formula (VI)



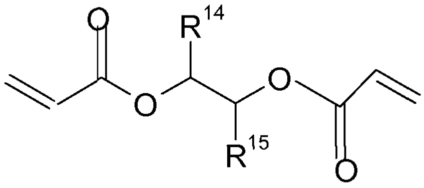
(VI)

where n is an integer of from 1 to 10, suitably from 1 to 3, each R^{14} and R^{15} is independently selected from hydrogen, halo, alkyl or haloalkyl.

Suitably R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} are haloalkyl such as fluoroalkyl, or hydrogen. In particular they are all hydrogen.

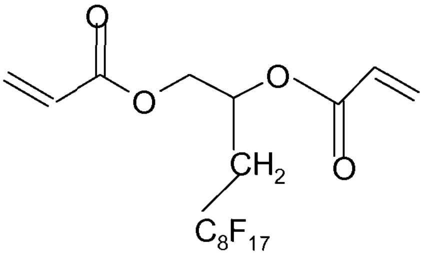
Suitably the compound of formula (V) contains at least one haloalkyl group, preferably a perhaloalkyl group.

Particular examples of compounds of formula (V) include the following:



A

wherein R^{14} and R^{15} are as defined above and at least one of R^{14} or R^{15} is other than hydrogen. A particular example of such a compound is the compound of formula B.

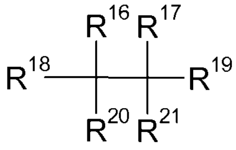


B

In a further embodiment, the polymeric coating is formed by exposing the fibre, yarn, sliver, fabric or garment to plasma comprising a monomeric saturated organic compound, said compound comprising an optionally substituted alkyl chain of at least 5 carbon atoms optionally interposed with a heteroatom for a sufficient period of time to allow a polymeric layer to form on the surface.

The term "saturated" as used herein means that the monomer does not contain multiple bonds (i.e. double or triple bonds) between two carbon atoms which are not part of an aromatic ring. The term "heteroatom" includes oxygen, sulphur, silicon or nitrogen atoms. Where the alkyl chain is interposed by a nitrogen atom, it will be substituted so as to form a secondary or tertiary amine. Similarly, silicons will be substituted appropriately, for example with two alkoxy groups.

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



$$R^{18}-C(R^{16})(R^{20})-C(R^{17})(R^{21})-R^{19}$$

(VII)

where R^{16}, R^{17}, $R^{18,}$ R^{19} and R^{20} are independently selected from hydrogen, halogen, alkyl, haloalkyl or aryl optionally substituted by halo; and R^{21} is a group $X-R^{22}$ where R^{22} is an alkyl or haloalkyl group and X is a bond or a group of formula $-C(O)O(CH_2)_xY-$ where x is an integer of from 1 to 10 and Y is a bond or a sulphonamide group; or a group $-(O)_pR^{23}(O)_s(CH_2)_t-$ where R^{23} is aryl optionally substituted by halo, p is 0 or 1, s is 0 or 1 and t is 0 or an integer of from 1 to 10, provided that where s is 1, t is other than 0.

Suitable haloalkyl groups for R^{16}, R^{17}, R^{18}, R^{19}, and R^{20} are fluoroalkyl groups. The alkyl chains may be straight or branched and may include cyclic moieties and have, for example from 1 to 6 carbon atoms.

For R^{22}, the alkyl chains suitably comprise 1 or more carbon atoms, suitably from 1-20 carbon atoms and preferably from 6 to 12 carbon atoms.

Preferably R^{22} is a haloalkyl, and more preferably a perhaloalkyl group, particularly a perfluoroalkyl group of formula C_zF_{2z+1} where z is an integer of 1 or more, suitably from 1-20, and preferably from 6-12 such as 8 or 10.

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

Suitable sulphonamide groups for Y include those of formula $-N(R^{23})SO_2^-$ where R^{23} is hydrogen, alkyl or haloalkyl such as C_{1-4}alkyl, in particular methyl or ethyl.

The monomeric compounds used preferably comprises a C_{6-25} alkane optionally substituted by halogen, in particular a perhaloalkane, and especially a perfluoroalkane.

According to another aspect, the polymeric coating is formed by exposing the fibres, yarn, sliver, fabric or garment to plasma comprising an optionally substituted alkyne for a sufficient period to allow a polymeric layer to form on the surface.

Suitably the alkyne compounds used comprise chains of carbon atoms, including one or more carbon-carbon triple bonds. The chains may be optionally interposed with a heteroatom and may carry substituents including rings and other functional groups. Suitable chains, which may be straight or branched, have from 2 to 50 carbon atoms, more suitably from 6 to 18 carbon atoms. They may be present either in the monomer used as a starting material, or may be created in the monomer on application of the plasma, for example by the ring opening

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

$$R^{24}\text{-}C{\equiv}C\text{-}X^{1}\text{-}R^{25} \qquad \text{(VIII)}$$

where R^{24} is hydrogen, alkyl, cycloalkyl, haloalkyl or aryl optionally substituted by halo; X^1 is a bond or a bridging group; and R^{25} is an alkyl, cycloalkyl or aryl group optionally substituted by halogen.

Suitable bridging groups X^1 include groups of formulae $-(CH_2)_s-$, $-CO_2(CH_2)_p-$, $-(CH_2)_pO(CH_2)_q-$, $-(CH_2)_pN(R^{26})CH_2)_q-$, $-(CH_2)_pN(R^{26})SO_2-$, where s is 0 or an integer of from 1 to 20, p and q are independently selected from integers of from 1 to 20; and R^{26} is hydrogen, alkyl, cycloalkyl or aryl. Particular alkyl groups for R^{26} include C_{1-6} alkyl, in particular, methyl or ethyl.

Where R^{24} is alkyl or haloalkyl, it is generally preferred to have from 1 to 6 carbon atoms.

Suitable haloalkyl groups for R^{24} include fluoroalkyl groups. The alkyl chains may be straight or branched and may include cyclic moieties. Preferably however R^{24} is hydrogen.

Preferably R^{25} is a haloalkyl, and more preferably a perhaloalkyl group, particularly a perfluoroalkyl group of formula C_rF_{2r+1} where r is an integer of 1 or more, suitably from 1-20, and preferably from 6-12 such as 8 or 10.

In a particular embodiment, the compound of formula (VIII) is a compound of formula (IX)

$$CH{\equiv}C(CH_2)_s\text{-}R^{27} \qquad (IX)$$

where s is as defined above and R^{27} is haloalkyl, in particular a perhaloalkyl such as a C_{6-12} perfluoro group like C_6F_{13}.

In another embodiment, the compound of formula (VIII) is a compound of formula (X)

$$CH{\equiv}C(O)O(CH_2)_pR^{27} \quad (X)$$

where p is an integer of from 1 to 20, and R^{27} is as defined above in relation to formula (IX) above, in particular, a group C_8F_{17}. Preferably in this case, p is an integer of from 1 to 6, most preferably about 2.

Other examples of compounds of formula (I) are compounds of formula (XI)

$$CH{\equiv}C(CH_2)_pO(CH_2)_qR^{27}, \qquad (XI)$$

where p is as defined above, but in particular is 1, q is as defined above but in particular is 1, and R^{27} is as defined in relation to formula (IX), in particular a group C_6F_{13};

or compounds of formula (XII)

$$CH\equiv C(CH_2)_pN(R^{26})(CH_2)_q\ R^{27} \qquad (XII)$$

where p is as defined above, but in particular is 1, q is as defined above but in particular is 1, R^{26} is as defined above an in particular is hydrogen, and R^{27} is as defined in relation to formula (IX), in particular a group C_7F_{15};

or compounds of formula (XIII)

$$CH\equiv C(CH_2)_pN(R^{26})SO_2R^{27} \qquad (XIII)$$

where p is as defined above, but in particular is 1,R^{26} is as defined above an in particular is ethyl, and R^{27} is as defined in relation to formula (IX), in particular a group C_8F_{17}.

In an alternative embodiment, the alkyne monomer used in the process is a compound of formula (XIV)

$$R^{28}C\equiv C(CH_2)_n\ SiR^{29}R^{30}R^{31} \qquad (XIV)$$

where R^{28} is hydrogen, alkyl, cycloalkyl, haloalkyl or aryl optionally substituted by halo, R^{29}, R^{30} and R^{31} are independently selected from alkyl or alkoxy, in particular C_{1-6} alkyl or alkoxy.

Preferred groups R^{28} are hydrogen or alkyl, in particular C_{1-6} alkyl.

Preferred groups R^{29}, R^{30} and R^{31} are C_{1-6} alkoxy in particular ethoxy.

In general, the fibres, yarn, sliver, fabric or garment to be treated is placed within a plasma chamber together with the material to be deposited in a gaseous state, a glow discharge is ignited within the chamber and a suitable voltage is applied, which may be pulsed.

The polymeric coating may be produced under both pulsed and continuous-wave plasma deposition conditions but pulsed plasma may be preferred as this allows closer control of the coating, and so the formation of a more uniform polymeric structure.

As used herein, the expression "in a gaseous state" refers to gases or vapours, either alone or in mixture, as well as aerosols.

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 fibres, yarn, sliver, fabric or garment treated and will be determined using routine methods and/or the techniques.

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. In particular however, they are generated by radiofrequencies (RF).

Various forms of equipment may be used to generate gaseous plasmas. Generally these comprise containers or plasma chambers in which plasmas may be generated. Particular examples of such equipment are described for instance in WO2005/089961 and WO02/28548, but many other conventional plasma generating apparatus are available.

The gas present within the plasma chamber may comprise a vapour of the monomer alone, but it may be combined with a carrier gas, in particular, an inert gas such as helium or argon, if required. In particular helium is a preferred carrier gas as this can minimise fragmentation of the monomer.

When used as a mixture, the relative amounts of the monomer vapour to carrier gas are suitably determined in accordance with procedures which are conventional in the art. The amount of monomer added will depend to some extent on the nature of the particular monomer being used, the nature of the substrate being treated, the size of the plasma chamber etc. Generally, in the case of conventional chambers, monomer is delivered in an amount of from 50-250mg/minute, for example at a rate of from 100-150mg/minute. It will be appreciated however, that the rate will vary depending on the reactor size chosen and the number of substrates required to be processed at once; this in turn depends on considerations such as the annual through-put required and the capital outlay.

Carrier gas such as helium is suitably administered at a constant rate for example at a rate of from 5-90 standard cubic centimetres per minute (sccm), for example from 15-30sccm. In some instances, the ratio of monomer to carrier gas will be in the range of from 100:0 to 1:100, for instance in the range of from 10:0 to 1:100, and in particular about 1:0 to 1:10. The precise ratio selected will be so as to ensure that the flow rate required by the process is achieved.

In some cases, a preliminary continuous power plasma may be struck for example for from 15 seconds to 10 minutes, for example from 2-10 minutes within the chamber. This may act as a surface pre-treatment step, ensuring that the monomer attaches itself readily to the surface, so that as polymerisation occurs, the coating "grows" on the surface. The pre-treatment step may be conducted before monomer is introduced into the chamber, in the presence of only an inert gas. In one embodiment, the inert gas comprises argon.

The plasma is then suitably switched to a pulsed plasma to allow polymerisation to proceed, at least when the monomer is present.

In all cases, a glow discharge is suitably ignited by applying a high frequency voltage, for example at 13.56MHz. This is applied using electrodes, which may be internal or external to the chamber, but in the case of larger chambers are generally internal.

Suitably the gas, vapour or gas mixture is supplied at a rate of at least 1 standard cubic centimetre per minute (sccm) and preferably in the range of from 1 to 100sccm.

In the case of the monomer vapour, this is suitably supplied at a rate of from 80-300mg/minute, for example at about 120mg/minute depending upon the nature of the monomer, the size of the chamber and the surface area of the product during a particular run whilst the pulsed voltage is applied. It may however, be more appropriate for industrial scale use to have a fixed total monomer delivery that will vary with respect to the defined process time and will also depend on the nature of the monomer and the technical effect required.

Gases or vapours may be delivered into the plasma chamber using any conventional method. For example, they may be drawn, injected or pumped into the plasma region. In particular, where a plasma chamber is used, gases or vapours may be drawn into the chamber as a result of a reduction in the pressure within the chamber, caused by use of an evacuating pump, or they may be pumped, sprayed, dripped, electrostatically ionised or injected into the chamber as is common in liquid handling.

Polymerisation is suitably effected using vapours of compounds for example of formula (I), which are maintained at pressures of from 0.1 to 400mtorr, suitably at about 10-100mtorr.

The applied fields are suitably of power of from 5 to 500W for example from 20 to 500W, suitably at about 100W peak power, applied as a continuous or pulsed field. Where used, pulses are suitably applied in a sequence which yields very low average powers, for example in a sequence in which the ratio of the time on : time off is in the range of from 1:100 to 1:1500, for example at about 1:650. Particular examples of such sequence are sequences where power is on for 20-50μs, for example about 30μs, and off for from 1000μs to 30000μs, in particular about 20000μs. Typical average powers obtained in this way are 0.1 - 0.2 W.

The fields are suitably applied from 30 seconds to 90 minutes, preferably from 5 to 60 minutes, depending upon the nature of the compound of formula (I) and the fibres, yarn, sliver, fabric or garment being treated.

Suitably a plasma chamber used is of sufficient volume to accommodate multiple fibres, yarn, slivers, fabrics or garments.

A particularly suitable apparatus and method for producing coated fibre, yarn, sliver, fabric or garments in accordance with the invention is described in WO2005/089961, the content of which is hereby incorporated by reference.

In particular, when using high volume chambers of this type, the plasma is created with a voltage as a pulsed field, at an average power of from 0.001 to 500W/m^3, for example at from 0.001 to 100W/m^3 and suitably at from 0.005 to 0.5W/m^3.

These conditions are particularly suitable for depositing good quality uniform coatings, in large chambers, for example in chambers where the plasma zone has a volume of greater than 500cm^3, for instance 0.1m^3 or more, such as from 0.5m^3-10m^3 and suitably at about 1m^3. The layers formed in this way have good mechanical strength.

The dimensions of the chamber will be selected so as to accommodate the particular fibres, yarn, sliver, fabric or garment being treated. For instance, generally cuboid chambers may be suitable for a wide range of applications, but if necessary, elongate or rectangular chambers may be constructed or indeed cylindrical, or of any other suitable shape.

The chamber may be a sealable container, to allow for batch processes, or it may comprise inlets and outlets for the fibre, yarn, sliver, fabric or garment, to allow it to be utilised in a continuous process as an in-line system. In particular in the latter case, the pressure conditions necessary for creating a plasma discharge within the chamber are maintained using high volume pumps, as is conventional for example in a device with a "whistling leak". However it will also be possible to process fibres, yarn, slivers, fabrics or garments at atmospheric pressure, or close to, negating the need for "whistling leaks".

A second aspect of the present invention provides use of a polymer coating obtained by plasma polymerisation on a wool containing fibre, yarn, sliver, fabric or garment made from said fibre or yarn to reduce shrinkage due to felting during laundering.

A third aspect of the present invention provides a wool containing fibre, yarn, sliver, fabric or garment made from said fibre or yarn, wherein the fibre, yarn, sliver, fabric or garment has been treated according to the method as described above to prevent shrinkage due to felting during laundering.

A fifth aspect of the present invention provides use of a polymer coating obtained by plasma polymerisation on a wool containing fibre, yarn, sliver, fabric or garment made from said fibre or yarn as a water and/or oil repellent coating which does not require post laundering refreshing.

Preferred features of the second, third, fourth and fifth aspects of the invention may be as described above in connection with the first aspect.

Throughout the description and claims of this specification, the words “comprise” and “contain” and variations of the words, for example “comprising” and “comprises”, mean “including but not limited to”, and do not exclude other moieties, additives, components, integers or steps.

Throughout the description and claims of this specification, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the specification is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Other features of the present invention will become apparent from the following example. Generally speaking the invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims and drawings). Thus features, integers, characteristics, compounds, chemical moieties or groups described in conjunction with a particular aspect, embodiment or example of the invention are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith.

Moreover unless stated otherwise, any feature disclosed herein may be replaced by an alternative feature serving the same or a similar purpose.

The invention will now be particularly described by way of examples.

In order to analyse the effect of different fluoropolymers coatings on wool and wool blend fabrics, three different wool-containing fabrics samples underwent different surface treatments. The resulting coated fabrics were then tested for water and oil repellency, fluorine content and mechanical properties.

The fabrics samples tested were untreated wool, Chlorine-Hercosett treated wool and polyester/wool blend fabrics, containing hollow and solid polyester filaments. These samples were treated with "traditional" fluorocarbon technology and with a plasma polymerisation system. The resulting coated samples were then evaluated for liquid repellency after washing, dry cleaning and flat abrasion and the results of the different fluorocarbon coating compared.

The three different wool containing fabrics were: 100% wool botany serge (190g/m^2, supplied by Whaleys, Bradford), plain weave chlorine-Hercosett treated wool (100% wool, 210 g/m^2) supplied by Bulmer & Lumb, Bradford and undyed wool/polyester (60/4) blend fabrics (yarn count 60/2, 160 g/m^2) also supplied by Bulmer & Lumb, Bradford.

The "traditional" fluorochemicals used were Oleophobol SL-A 01, generously donated by Ciba, and Fluorepel OWS from Devan-PPT Limited. (These are standard commercial fluorocarbon polymer finishes.)

The SDC ECE phosphate-based reference detergent, without optical brightening agents, was used during the wash fastness tests. It was used as the washing powder addition because it is the standard detergent in the ISO C06 wash fastness tests to simulate domestic laundering.

Prior to finishing, the wool fabrics were washed with an aqueous non-ionic detergent solution to remove any possible impurities which could potentially interfere with the subsequent surface treatment; and then air dried.

The "traditional" fluorocarbons were applied to the samples by the following method. Fabric samples were treated using a pad-dry-cure method with either 50g/l Oleophobol SL-A or 50g/l Fluorepel OWS. The pad bath was set at pH 6-7 and the wet pick-up was 70%. The padded fabrics were dried at 100°C for 2 minutes (100% wool fabrics) or 1 minute (blend fabrics), and then cured for 5 minutes at 150°C or 1 minute at 170°C for the wool and blend fabrics, respectively.

The plasma polymerisation coating was applied by the following method. The plasma polymerization experiments were performed in an inductively coupled glow discharge reactor with a base pressure of 6.13×10^{-3} mbar, a leak rate of better than 6×10^{-9} mol s^{-1} and a monomer flow rate 4mg/min or 3.2 mol s^{-1}. This was connected to a two stage Edwards rotary pump via a liquid nitrogen cold trap, a thermocouple pressure gauge, and a monomer tube containing the 1H, 1H, 2H, 2H-heptadecafluorodecyl acrylate monomer. All connections were grease free. An L-C matching unit was used to minimize the standing wave ratio (SWR) of the transmitted power between a 13.56 MHz radio frequency (RF) generator and the electrical discharge. For pulsed plasma deposition experiments, the RF source was triggered by a signal generator, and an oscilloscope was used to monitor the pulse width and amplitude.

The substrate to be coated was placed into the centre of the reactor, followed by evacuation back down to the base pressure. The fluoro-monomer vapour was then introduced at a constant pressure of ~0.2 mbar and allowed to purge through the system for 5 minute, followed by ignition of the glow discharge. The pressure on the reactor outlet was found to be steady, which is consistent with sufficient monomer flow rate. Deposition was terminated after enough time to form a film, based on the previous trials, on the substrates surface. The monomer vapour was allowed to continue to pass over the substrate for a further 5 minute and subsequently the plasma chamber was evacuated back down to the base pressure and then vented to the atmosphere. The optimum pulsing conditions were determined using factorial experimental design, followed by simplex optimization. Accordingly, the peak power (Pp = 40 W), pulse on-period (t_{on} = 30 µs), and pulse off-period (t_{off} = 20000 µs) for plasma polymer deposition had been optimized to yield a critical surface energy on a flat glass substrate of γc = 4.3 mN/ m.

In addition some samples were pre-treated with an argon plasma prior to the fluoro-monomer plasma polymerisation in order to potentially improve the repellency performance. The reactor was purged with argon (BOC 99.5% purity) for 4 minute at pressure around 80 mtorr and then by using a continuous wave at 300 W the samples were treated for, 60, 120, 240, and 480 seconds, respectively.

Both the water and oil repellency of different Chlorine Hercosett treated fabric samples were evaluated and the results are shown in tables 1 and 2 respectively.

The abrasion resistance of finished fabrics was measured according to BS 12947-2: 1999, on a Martindale Wear & Abrasion Tester and the repellency properties evaluated after 3,000 rubs.

In order to evaluate the re-orientation of the fluorocarbon polymer chains after laundering, dry-cleaning and flat abrasion the fabrics were hot-pressed using an Elnapress/SDL with the standard wool temperature setting. A hot press treatment is identified as HP in the results tables.

The water repellency of the fabrics samples was determined using the 3M water repellency test using a series of water/isopropyl alcohol solutions.

Table 1 below shows the results for the 3M water repellency analysis of fluorocarbon treated Chlorine/Hercosett Wool Fabrics.

After-Treatments	**Scoured Fabric**	**Oleophobol Treated Fabric**	**Fluorepel Treated Fabric**	**Argon Pre-treatment Time (Minutes) Followed By Plasma Polymerization**		
				0	**1**	**2**
Original	1	10	10	9-10	10	10
3 Wash Cycles	W	3	2	2	8	8
3 Washes & HP*	W	10	10	9	9	9
5 Wash Cycles	W	2	2	2	6	6
5 Washes & HP	W	10	10	9	9	10
1 Dry Clean Cycle	W	9	9	8	10	10
1 Dry Clean & HP	W	10	10	10	10	10
3 Dry Clean Cycle	0	8	7	7	10	10
3 Dry Cleans & HP	0	10	10	9	10	10
Flat Abrasion	1	6	6	3	6	7
Flat Abrasion & HP	2	10	10	7	7	8

Table 1 3M Water Repellency Analysis of Fluorocarbon Treated Chlorine/Hercosett Wool Fabrics.

Examination of Table 1 indicates the effectiveness of the plasma polymerisation of the fluoro-monomer on the Chlorine Hercosett treated wool fabric in imparting water repellency relative to the traditional wet chemical fluorocarbon applications.
The table shows the different results when an argon plasma pre-treatment is applied for 1, 2 or 3 minutes respectively. It is apparent that the argon plasma pre-treatment prior to plasma polymerisation system has introduced much better polymer re-orientation behaviour at room temperature, hence not requiring a hot press for restoring the water repellency performance after laundering.

Similarly after dry cleaning the argon plasma pre-treatment prior to plasma polymerisation system again has introduced much better polymer re-orientation behaviour at room temperature and again appears to negate the requirement for a heat treatment to restore effective water repellency performance.

The effect of flat abrasion on the treated fabrics was to reduce the water repellency however again the heat post-treatment restores the repellency.

Pre-treating the wool with an argon plasma has a beneficial effect in eliminating/reducing the need for a post-heat treatment but the abraded plasma treated wool fabrics appear to have lost some repellency performance probably due to the thinner PP coating layer relative to the traditional fluorocarbon finishes.

The oil repellency of the fabric was determined using the AATCC 118-2007 oil repellency test using a series of eight standard hydrocarbon solutions. The oil repellency grade is the highest numbered test liquid which does not wet the fabric surface. Table 2 below shows the results of the 3M Oil Repellency Analysis of Fluorocarbon Treated Chlorine/Hercosett Wool Fabrics.

After-Treatments	**Scoured Fabric**	**Oleophobol Treated Fabric**	**Fluorepel Treated Fabric**	**Argon Pre-treatment Time (Minutes) Followed By Plasma Polymerization**		
				0	**1**	**2**
Original	0	7	7	7	7	7
3 Wash Cycles	0	1	0	0	5	5
3 Washes & HP*	0	7	7	7	7	7
5 Wash Cycles	0	0	0	0	3	4
5 Washes & HP	0	7	7	7	7	7
1 Dry Clean Cycle	0	7	7	5	7	7
1 Dry Clean & HP	0	7	7	7	7	7
3 Dry Clean Cycle	0	6	6	3	7	7
3 Dry Clean & HP	0	7	7	7	7	7
Flat Abrasion	0	4	4	1	7	7
Flat Abrasion & HP	0	7	7	5	7	7

Table 2 3M Oil Repellency Analysis of Fluorocarbon Treated Treated Chlorine/Hercosett Wool Fabrics.

Examination of Table 2 indicates the effectiveness of the plasma polymerisation of the fluoro-monomer on the Chlorine Hercosett treated wool fabric in imparting oil repellency relative to the traditional wet chemical fluorocarbon applications.

It is also apparent that the argon plasma pre-treatment prior to plasma polymerisation system has introduced much better polymer re-orientation behaviour at room temperature, hence not requiring a hot press for restoring the oil repellency performance after laundering. In contrast the traditional fluorocarbon finishes require a hot press to restore oil repellency after a washing cycle.

In terms of dry cleaning the performance of both systems is comparable but the argon plasma pre-treatment does again improve performance and removes the necessity for a heat treatment to restore effective oil repellency performance

The effect of flat abrasion is to reduce the oil repellency of the traditional wet chemical fluorocarbons however again the heat treatment restores the repellency. Pre-treating the wool with an argon plasma has a beneficial effect in eliminating the need for a heat treatment. (Flat abrasion resulted in no less oil repellence in samples which underwent plasma treatment).

The various tests were repeated on wool blend fabric samples and the results are given in tables 7 to 10 below.

After-Treatments	**Scoured Fabric**	**Oleophobol Treated Fabric**	**Fluorepel Treated Fabric**	**FPP**	**Ar & FPP**
Original	1	10	10	10	10

3 Wash Cycles	1	5	5	6	8
3 Washes & HP*	1	10	9	10	10
5 Wash Cycles	1	5	5	5	6
5 Washes & HP	1	9	9	10	10
3 Dry Clean Cycle	1	4	3	10	10
3 Dry Clean & HP	1	8	6	10	10

Table 7 3M Water Repellency Analysis of Wool/Polyester Blend Fabric (40/60, Solid Polyester Filaments)

After-Treatments	**Scoured Fabric**	**Oleophobol Treated Fabric**	**Fluorepel Treated Fabric**	**FPP**	**Ar & FPP**
Original	1	10	10	10	10
3 Wash Cycles	1	5	5	4	6
3 Washes & HP*	1	10	9	10	10
5 Wash Cycles	1	5	5	2	6
5 Washes & HP	1	9	9	9	10
3 Dry Clean Cycle	1	3	2	9	10
3 Dry Clean & HP	1	5	5	9	9

Table 8. 3M Water Repellency Analysis of Wool/Polyester Blend Fabric (40/60, Hollow Polyester Filaments)

After-Treatments	**Scoured Fabric**	**Oleophobol Treated Fabric**	**Fluorepel Treated Fabric**	**FPP**	**Ar & FPP**
Original	0	8	8	8	8
3 Wash Cycles	0	0	0	5	5
3 Washes & HP*	0	8	7	7	7
5 Wash Cycles	0	0	0	2	3
5 Washes & HP	0	7	7	7	7
3 Dry Clean Cycle	0	2	1	7	7
3 Dry Clean & HP	0	7	4	7	8

Table 9 3M Oil Repellency Analysis of Wool/Polyester Blend Fabric (40/60, Solid Polyester Filaments)

After-Treatments	**Scoured Fabric**	**Oleophobol Treated Fabric**	**Fluorepel Treated Fabric**	**FPP**	**Ar & FPP**
Original	0	8	8	8	8
3 Wash Cycles	0	0	0	5	5
3 Washes & HP*	0	8	8	7	7
5 Wash Cycles	0	0	0	2	3
5 Washes & HP	0	7	7	7	7

3 Dry Clean Cycle	0	0	0	7	7
3 Dry Clean & HP	0	4	5	8	8

Table 10 3M Oil Repellency Analysis of Wool/Polyester Blend Fabric (40/60, Hollow Polyester Filaments)

Similar trends were observed with the wool/polyester blend fabrics as with the pure wool although the decrease in water repellency is less after aqueous washing and may be related to the natural water repellency of the polyester blend component. In contrast the water and oil repellence performance after repeated dry cleaning for the plasma treated blend fabric is significantly better than the traditional fluorocarbon finished fabrics.

Samples of Chlorine Hercosett treated fabrics with different fluorocarbon treatments underwent surface analysis using both X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS).

ToF-SIMS analyses were carried out using a PHI 7000 instrument operating at a base pressure of less than 4.0×10^{-8} Torr. The instrument was equipped with a reflectron analyser, a Cs^+ ion source (8 keV; pulsed length 1.25 ns) and a pulsed electron flood source (50-70 eV) for charge compensation. Both positive and negative secondary ion mass spectra were acquired from areas measuring 250 µm × 250 µm over the mass range 0-2000. For each sample analysis, the total primary ion dose was less than 1×10^{12} ions/cm^2, which lies below the threshold value for static SIMS of 1×10^{13} ions/cm^2.

Studies of the Chlorine-Hercosett treated wool fabric indicates the loss of the 18-methyleicosanoic acid signal at $m/z = 341^-$ in the negative ion spectrum suggesting a combination of chemical scission of the 18-MEA and the presence of a polymer coating overlayer. (The acid chlorination stage of the Chlorine Hercosett process removes the covalently bound hydrophilic 18-methyleicosanoic acid (18-MEA) from the epicuticle). However the amide signal at $m/z = 42^-$ is still apparent but will be derived from the polymer and possibly any uncoated exposed wool protein. In contrast the reduction in the sulphur signal at $m/z = 32^-$ due to the protein has reduced in intensity suggesting the polymer coating has masked the underlying protein. Other species evident in the ToF-SIMS negative ion spectrum are at $m/z = 265^-$, 293^-, 311^-, 325^-, and 339^-.and are attributed to alkyl sulphates and linear alkylbenzene sulphonates surfactants. In addition in the positive ion spectrum there are softener signals detected at $m/z = 494^+$ $[N^+(CH_3)_2\ (C_{16}H_{33})_2]$, 522^+ $[N^+(CH_3)_2\ (C_{16}H_{33})\ (C_{18}H_{37})]$, and 550^+ $[N^+(CH_3)_2\ (C_{18}H_{37})_2]$.

Examination of the plasma polymerised treated wool indicates a strong signal at $m/z = 19^-$ due to F^- in the negative ion spectrum and in the positive ion spectrum a complex polymer fragmentation pattern is observed and reflects the heterogeneity of the polymer polymerisation process for heptadecafluorodecyl acrylate. During the plasma process the monomer may undergo fragmentation and re-formation processes giving rise to a complex polymer structure. Nevertheless a series of characteristic positive ions are evident: $C_3F_5^+$, $C_3F_5H_2^+$, $C_4F_5^+$, $C_5F_7^+$, $C_5F_9^+$, $C_7F_{13}^+$, $C_8F_{17}^+$, $C_8F_{17}CH_2CH_2^+$, $C_{10}F_{15}H_2^+$ etc.

XP spectra were obtained using a Kratos Axis Ultra XPS instrument with an Al Kα-alpha x-ray source. The samples (300×800 µm) were attached to sample bar with double sided adhesive. Wide scan spectra were recorded at a 80 eV pass energy. High resolution spectra in the S(2p), C(1s), N(1s), O(1s), and F(1s) regions were obtained at a 20 eV pass energy. To overcome the insulation problems of textile fibres during the analyses, the charge neutraliser flood gun provided a constant stream of electrons in order to neutralize the charge build up. Binding energy values were calculated relative to the C(1s) photoelectron peak at 285.0 eV. The samples surface elemental composition and atomic ratios were obtained by Casa XPS software and Wagner's sensitivity factors.

The results of the XPS analysis are shown in table 3.

Treatment	**Atomic Composition (%) Fluorine**
Untreated	0.5
Oleophobol Treated*	36.9
Oleophobol 3 x Wash Cycles	25.5
Oleophobol 3 x Wash Cycles & Hot Pressed	38.7
Oleophobol Flat Abraded*	13.6
Fluoro-Plasma Polymerised (FPP)	43.8
FPP 3 Wash Cycles	19.7
FPP 3 Wash Cycles & Hot Pressed	38.9
FPP 5 Wash Cycles	10.8
FPP 5 Wash Cycles & Hot Pressed	34.2
FPP Flat Abraded*	6.9
FPP Flat Abraded* & Hot Pressed	8.1
Argon Plasma (AR) Pre-treated & FPP	46.8
AR & FPP 3 Wash Cycles	30.6

AR & FPP 3 Wash Cycles & Hot Pressed	51.0
AR & FPP 5 Wash Cycles	18.1
AR & FPP 5 Wash Cycles & Hot Pressed	40.0
AR & FPP Flat Abraded*	15.4
AR & FPP Flat Abraded* & Hot Pressed	16.7

*: Treated sample after flat abrasion for 3000 rubs.

Table 3 XPS Surface Elemental Composition of Fluorocarbon Treated Chlorine-Hercosett Wool Fabrics

The XPS (X-ray photoelectron spectroscopy) data of the plasma treated sample indicates obvious incorporation of fluorocarbon into the surface of the fibre with the fluorine content increasing up to 47%, when an argon pretreatment is used.

It is evident that following washing, dry cleaning and flat abrasion the surface fluorine decreases but subsequent heat treatments bring about the fluoropolymer re-orientation.

The argon plasma treated samples also exhibited this behaviour even though the water and oil repellency performance of the laundered, and not heated, samples showed only a relatively small reduction in repellency performance.
Interestingly the XPS spectra of the fluoropolymer PP fabrics shows an absence of surface nitrogen suggesting a surface fluorocarbon overlayer masking the nitrogen containing Hercosett polymer.

The tensile properties of the fabrics were determined according to the BS 13934-1:1999 test method on an Instron model 5564, with gauge length of 100 mm, crosshead speed of 50mm/min, and each value presented is the average of 10 measurements.

The influence of the treatments on the fabric's mechanical (handle) properties both before and after treatment was objectively assessed using the Kawabata Evaluation System (KES). The 20x20cm samples were conditioned at 20°C and 65% R.H. (Relative Humidity) prior to testing the tensile, shear, and bending properties.

Table 4 shows the tensile strength of wool fabrics treated with plasma and fluorocarbons, whilst table 5 shows the results for KES-F analysis of the selected mechanical properties of the Chlorine Hercosett treated wool fabrics.

Treatment	**Ar Plasma Time (Minutes)**	**Tensile Strength (kN/m)**
Scoured	-	6.8 ± 0.11
Oleophobol SL-A	-	6.8±0.22
Fluorepel OWS	-	6.7±0.20
Argon Plasma Pre-treatment	1	6.7 ± 0.19
	2	7.0 ± 0.14
	4	7.3 ± 0.16
	8	7.3 ± 0.16
Argon Plasma Pre-treatment + FPP	0	6.8 ± 0.10
	1	6.5 ± 0.14
	2	6.7 ± 0.19
	4	7.1 ± 0.29
	8	7.0 ± 0.10

Table 4 Tensile Strength of Wool Fabrics Treated with Plasma and Fluorocarbons

	Scoured	**Oleophobol**	**Fluorapel**	**AR Pre-Treat**		**AR & FPP**		
				1min.	**2min.**	**0min.**	**1min.**	**2min.**

EMT	7.51	7.71	7.07	8.30	8.06	7.86	7.59	8.22
LT	0.491	0.550	0.573	0.471	0.473	0.484	0.479	0.460
WT	8.92	10.23	9.77	9.50	9.38	9.28	8.94	9.22
RT	64.64	65.29	63.04	69.04	72.11	69.46	71.31	70.14
B	0.0777	0.078	0.084	0.099	0.095	0.091	0.090	0.092
2HB	0.0268	0.042	0.037	0.040	0.037	0.0395	0.0371	0.0442
G	0.33	0.36	0.41	0.45	0.40	0.42	0.36	0.38
2HG5	0.95	0.92	1.00	1.38	1.03	1.14	0.94	0.94

*EMT - Extensibility; LT - Tensile Linearity; WT - Tensile Work; RT - Tensile Resilience; B - Bending Rigidity; 2HB - Bending Hysteresis;
G - Shear Stiffness; 2HG5 - Shear Hysteresis at 5°

Table 5 KES-F Analysis of the Selected Mechanical Properties of the Chlorine Hercosett Treated Wool Fabrics

The effect of the fluorocarbon treatments on the fabric tensile strength is marginal, although interestingly there is a small improvement in strength for some of the argon plasma treated samples which may be related to increased surface friction.

On plasma polymerising the fluoropolymer onto the fibre surface the lubricating effect of the fluorocarbon surface coating reduces the tensile strength. This lubricating effect is also observed in the KES-F data where the shear hysteresis at 5°, 2HG5, decreases from 1.38 to 0.94, similar to the untreated sample (see table 5). 2HG5 is a measure of interyarn friction and any damage to the wool surface increases the value, whilst conversely any lubrication reduces the value. Overall the fluorocarbon treatments produce a marginal stiffening of the fabric handle.

The felting shrinkage of the wool fabrics was determined using a Wascator FOM 71P, with a standard 5A wash programme. Fabric shrinkage was determined after each wash cycle by measuring the new fabric area and comparing it with the initial area value. The fabric samples were dry cleaned in accordance with the BS EN ISO 3175:1998 test method, by PPT Company, Ambergate, and their repellency properties were determined after 1 and 3 cycles. The results are shown in table 6.

Fabric Treatment	**% Area Shrinkage**				
	1 X 5A	**2 X 5A**	**3 X 5A**	**4 X 5A**	**5 X 5A**
Scoured & Undyed	24.8	40.3	53.6	59.6	63.4
Oleophobol SL-A	12.0	34.7	50.6	60.5	63.7
Fluorepel OWS	7.3	29.2	47.8	51.9	59.0
FPP	-2.5	0.0	4.4	12.3	14.6
Scoured & Dyed	3.3	4.6	6.3	11.6	12.3
Oleophobol SL-A	3.8	3.8	7.9	11.4	12.4
Fluorepel OWS	1.3	2.5	8.7	12.5	14.1
FPP	0.1	0.5	5.1	4.2	3.3

Table 6 Felting Shrinkage of Fluorocarbon Treated Scoured Wool Fabrics

While the Chlorine/Hercosett treated wool fabric is machine washable and will not shrink, untreated wool will shrink extensively depending on fabric structure and processing. Examination of Table 6 indicates the untreated wool fabric shrinks progressively up to 63.4% area shrinkage after 5x5A wash cycles. The traditional fluorocarbon coatings have no beneficial effect in reducing felting but in contrast the fluoro-monomer plasma polymerised wool sample has much lower felting shrinkage. The reduction in felting is very encouraging and potentially creates an opportunity to achieve a dual effect of combined liquid repellency and machine washability.

Treatment of wool fabrics with traditional fluorocarbon coatings and with plasma polymerised (PP) fluoropolymers results in imparting water repellency and oil repellency to the fabrics with the initial performance of both finishing treatments being comparable. Subsequent repeated launderings or dry clean cycles results in a decrease in repellency but this can be re-established after a heat treatment which produces molecular re-orientation of the fluoropolymer at the surface interface.

While the PP samples offer better ambient drying re-orientation than the traditional fluorocarbon coatings, an argon plasma pre-treatment prior to PP further enhances this repellency recovery performance. This effect is related to the creation of optimum surface interface chemistry with the plasma coating and minimising the energy required for fluoropolymers re-orientation. The outer 1-10nms of the treated fabrics has been characterised by surface sensitive analytical techniques such as XPS and ToF-SIMS and an increase in the surface fluorine content clearly demonstrated. Polymer re-orientation after hot pressing is demonstrated using XPS by the increase in the surface fluorine concentration. Analysis of the surface of the plasma polymerised fabric surface indicated the loss of 19-MEA and a decrease in sulphur and nitrogen content suggesting a fluoropolymer overlayer is masking the underlying protein or Hercosett polymer. The ToF-SIMS spectra of the PP fabrics also indicate the presence of characteristic perfluoro ions.

The Chlorine Hercosett treated wool is machine washable and the PP treatment does not affect this vital performance criteria. Interestingly the untreated wool fabric shrinks by 63% in area with repeated launderings and the Oleophobol and Fluorepel coatings do not affect this level of felting shrinkage. In contrast the fluoropolymer PP treatment significantly reduces the felting shrinkage. The effect of the fluorocarbon treatments on the tensile strength of the fabrics is marginal, while the KES-F analysis of the fabrics indicated the Oleophobol and Fluorepel finishes impart some fabric stiffening, in contrast the PP treatment appears to have a beneficial effect on fabric handle on the blend fabrics.

The effect of silica nanoparticles on the wool was also determined, as described in more detail below. Silica nanoparticles were applied to a wool sample before a fluoropolymers coating was added. The shrinkage, water and oil repellency, colour of the wool samples and KES-F analysis were then tested.

The wool sample was 100% wool botany serge (190g/m2) was supplied by Whaleys, Bradford. The 'traditional' fluorochemical used was Oleophobol SL-A 0, Ciba and the shrink proofing polymer Synthapret BAP was supplied by Bayer. The SDC ECE non-phosphate reference determgent, without O.B.A, was used during was fastness tests.

1H,1H,2H,2H-heptadecaluorodecyl acrylate (H2C=CHCO2CH2CH2(DF2)7CF3) (Fluorochem, 98% purity, further purified using multiple freeze-thaw cycles) was used as the feed monomer in the plasma reactor.

The fabric samples were padded with a bath containing 0.3% on weight of fabric, o.w.f., nanoparticles and 5ml/l iso-propanol, at 70% wet pick up. The different sized nanoparticles are shown in table 11. The padded fabrics were dried at 100°C for 2 minutes and then cured for 4 minutes at 140°C.

Fabric samples were treated with the 'traditional' fluorochemicals using a pad-dry-cure method with 18g/l Synthapret BAP, 24g/l Oleophobol SL-A, 0.3% on weight of fabric, o.w.f., nanoparticles and 5ml/l iso-propanol.

The pad bath was set at pH6-7, using acetic acid, and the wet pick-up was 70%. The padded fabrics were dried at 100°C for 2 minutes and then cured for 4 minutes at 140°C.

Fabric samples were also treated by plasma polymerisation as described above.

Nano-particle Tradename (Nissan)	**Particle Size (nm)**
Snowtex OS (OS)	4-6
Snowtex O (O)	10-20
Snowtex OL (OL)	40-50
MP-1040	100
MP-4540	430

Table 11 Nano-particle Size Range and Commercial Tradenames

The felting shrinkage of the wool fabrics was determined using a Wascoator FOM 71P, with a standard 5A wash programme as described above. Table 12 shows the fabric shrinkage for the wool coated with silica nanoparticles with different fluoropolymers coatings. The tests have been repeated for both dyed and undyed samples.

As can be seen in the results in table 6, the fluoropolymers plasma polymerisation has the beneficial effect in reduction of felting shrinkage.

Table 12 shows the effect of silica nanoparticles on felting shrinkage in combination with different treatments.

Fabric Treatment	**% Area Shrinkage 5 X 5A**	**Fabric Treatment & Plasma Polymerisation**	**% Area Shrinkage 5 X 5A**
Untreated	60.4	Untreated	29.2
Synthapret BAP (BAP)	41.9	Synthapret BAP	N/D
Oleophobol SL-A (SL)	51.1	Oleophobol SL-A	15.3
Snowtex OS (4-6nm)	57.2	Snowtex OS (4-6nm)	20.6
Snowtex O (10-20nm)	56.2	Snowtex O (10-20nm)	23.1
Snowtex OL (40-50nm)	55.0	Snowtex OL (40-50nm)	13.9
MP-1040 (100nm)	60.0	MP-1040 (100nm)	12.0
MP-4540 (430nm)	58.1	MP-4540 (430nm)	16.6
Snowtex OS + BAP	42.9	Snowtex OS + BAP	12.7
Snowtex O + BAP	38.4	Snowtex O + BAP	15.2
Snowtex OL + BAP	34.9	Snowtex OL + BAP	27.1
MP-1040 + BAP	35.4	MP-1040 + BAP	26.5
MP-4540 + BAP	35.5	MP-4540 + BAP	8.0
Snowtex OS + SL	53.2	Snowtex OS + SL	14.9
Snowtex O + SL	55.5	Snowtex O + SL	22.5

Snowtex OL + SL	51.4	Snowtex OL + SL	17.4
MP-1040 + SL	52.4	MP-1040 + SL	20.0
MP-4540 + SL	54.7	MP-4540 + SL	17.8
Snowtex OS + BAP + SL	33.1	Snowtex OS + BAP + SL	19.5
Snowtex O + BAP + SL	32.5	Snowtex O + BAP + SL	12.0
Snowtex OL + BAP + SL	31.5	Snowtex OL + BAP + SL	11.1
MP-1040 + BAP + SL	29.1	MP-1040 + BAP + SL	15.9
MP-4540 + BAP + SL	33.9	MP-4540 + BAP + SL	6.5

Table 12. Felting Shrinkage of Fluorocarbon and Nano-particle Treated Scoured Wool Fabrics

Examination of table 12 indicates that incorporation of the nanoparticles into the Synthapret BAP/Oleophobol SL-A formulation does further reduce the felting shrinkage but this effect is only fully developed after a subsequent fluoropolymer plasma polymerisation.

This effect may be due to the fluoropolymer plasma coating lubricating the surface protrusions. Similarly on plasma polymerising the fluorocarbon over the nanoparticles there is a significant reduction in felting shrinkage. Surprisingly in general it appears the larger nanoparticles have the better effect and it may be related to the particles providing a stand off protective mechanism.

The fabric samples underwent the 3M water repellency analysis and AATCC Oil Repellency Analysis. The results for 'traditional' fluorocarbon treated samples are illustrated in tables 13 and 14 and for plasma treated sample in tables 15 and 16.

	Original	**5 Wash Cycles**	**5 Washes & HP**	**3 Dry Clean Cycle**	**3 Dry Clean & HP**
Untreated	2	0	2	2	2
BAP	ND	ND	ND	ND	ND
Oleophobol	10	2	7	2	6
Snowtex OS	W	2	2	2	2
Snowtex O	W	2	2	1	2
Snowtex OL	W	2	2	2	2
MP-1040	W	2	2	2	2
MP-4540	1	2	2	2	2
OS + BAP	1	2	2	2	2
O + BAP	1	2	2	2	2
OL + BAP	1	2	2	2	2
MP-1040 + BAP	2	2	2	2	2
MP-4540 + BAP	2	2	2	2	2
OS + SL	6	2	4	2	2
O + SL	9	2	6	2	2
OL + SL	10	2	9	2	2
MP-1040 + SL	10	2	6	2	2
MP-4540 + SL	10	2	7	2	4
OS + BAP +	7	2	4	2	3

SL					
O + BAP + SL	10	2	6	2	5
OL + BAP+ SL	10	2	7	2	7
MP-1040 + BAP + SL	9	2	7	2	7
MP-4540 + BAP + SL	10	2	8	3	7

Table 13. 3M Water Repellency Analysis of Fluorocarbon Treated Untreated Wool Fabrics.

	Original	**5 Wash Cycles**	**5 Washes & HP**	**3 Dry Clean Cycle**	**3 Dry Clean & HP**
Untreated	0	0	0	0	0
BAP	ND	ND	ND	ND	ND
Oleophobol	8	0	5	0	7
Snowtex OS	0	0	0	0	0
Snowtex O	0	0	0	0	0
Snowtex OL	0	0	0	0	0
MP-1040	0	0	0	0	0
MP-4540	0	0	0	0	0
OS + BAP	0	0	0	0	0
O + BAP	0	0	0	0	0
OL + BAP	0	0	0	0	0
MP-1040 + BAP	0	0	0	0	0
MP-4540 + BAP	0	0	0	0	0

OS + SL	5	0	0	0	0
O + SL	7	0	6	0	0
OL + SL	8	0	8	0	0
MP-1040 + SL	7	0	5	0	0
MP-4540 + SL	8	0	5	0	1
OS + BAP + SL	6	0	0	0	1
O + BAP + SL	8	0	4	0	5
OL + BAP+ SL	7	0	5	0	6
MP-1040 + BAP + SL	7	0	5	0	6
MP-4540 + BAP + SL	7	0	5	0	7

Table 14. AATCC Oil Repellency Analysis of Fluorocarbon Treated Untreated Wool Fabrics.

	Original	**5 Wash Cycles**	**5 Washes & HP**	**3 Dry Clean Cycle**	**3 Dry Clean & HP**
Untreated	10	**2**	**9**	10	10
BAP	ND	ND	ND	ND	ND
Oleophobol	10	3	10	4	9
Snowtex OS	10	2	5	7	8
Snowtex O	10	2	6	7	7
Snowtex OL	10	2	9	9	10

MP-1040	9	**3**	9	8	7
MP-4540	10	**4**	**10**	8	10
OS + BAP	10	2	9	9	10
O + BAP	10	3	9	9	10
OL + BAP	10	3	9	9	10
MP-1040 + BAP	10	3	10	9	10
MP-4540 + BAP	10	3	9	9	10
OS + SL	10	2	10	9	10
O + SL	10	3	10	9	10
OL + SL	10	2	10	8	10
MP-1040 + SL	10	2	9	7	9
MP-4540 + SL	10	3	9	7	9
OS + BAP + SL	10	2	10	9	10
O + BAP + SL	10	2	10	8	10
OL + BAP+ SL	10	2	9	9	10
MP-1040 + BAP + SL	10	3	10	8	9
MP-4540 + BAP + SL	10	3	9	8	9

Table 15. 3M Water Repellency Analysis of Nanoparticle & Fluoropolymer Plasma Polymerised Wool Fabrics.

	Original	**5 Wash**	**5 Washes**	**3 Dry**	**3 Dry**

		Cycles	& HP	Clean Cycle	Clean & HP
Untreated	7	**0**	7	7	7
BAP	ND	ND	ND	ND	ND
Oleophobol	7	1	7	1	7
Snowtex OS	7	0	3	7	7
Snowtex O	7	0	5	7	7
Snowtex OL	7	**2**	7	7	7
MP-1040	7	**2**	7	7	5
MP-4540	8	**2**	7	7	7
OS + BAP	7	0	7	7	7
O + BAP	7	1	7	7	7
OL + BAP	7	1	7	7	7
MP-1040 + BAP	7	1	7	7	7
MP-4540 + BAP	7	0	7	7	7
OS + SL	7	0	7	7	7
O + SL	7	1	7	7	7
OL + SL	7	0	7	7	7
MP-1040 + SL	7	0	7	5	7
MP-4540 + SL	7	0	7	5	7
OS + BAP + SL	7	0	7	7	7
O + BAP + SL	7	0	7	7	7
OL + BAP+ SL	7	0	7	7	7
MP-1040 +	8	1	7	7	7

BAP + SL					
MP-4540 + BAP + SL	8	1	7	7	7

Table 16. AATCC Oil Repellency Analysis of Nanoparticle & Fluoropolymer Plasma Polymerised Wool Fabrics.

Examination of the water and oil repellency performance of the fabrics with the nanoparticles incorporated into the traditional fluorocarbon finish, Oleophobol SL, indicated that the nanoparticles have relatively little effect in improving the repellency performance. Similarly the effect of incorporating the nanoparticles into the fluoropolymers plasma polymerisation system is marginal except for the samples where the plasma polymerisation is directly onto nanoparticle along pre-treated fabric (highlighted in tables).

The fabric colour was measured using a Datacolor Reflectance Spectrophotometer. The samples were triple folded and an average of four valued used to provide the mean. The results are illustrated in tables 17 and 18.

Fabric Treatment	**Whiteness Index (WID)**	**ΔWID**	**Yellowness Index (YID)**	**ΔYID**
Untreated	-10.7	0	26.9	0
Synthapret BAP	ND		ND	
Oleophobol SL-A	-10.5	0.2	26.2	-0.7
Snowtex OS (4-6nm)	-10.9	-0.1	26.6	-0.3
Snowtex O (10-20nm)	-10.9	-0.2	26.6	-0.3
Snowtex OL (40-50nm)	-6,4	4.3	24.1	-2.8

MP-1040 (100nm)	-4.7	6.0	23.3	-3.5
MP-4540 (430nm)	-1.7	9.1	21.9	-5.0
Snowtex OS + BAP	-10.5	0.2	26.4	-0.5
Snowtex O + BAP	-11.4	-0.7	26.8	-0.1
Snowtex OL + BAP	-10,7	0.0	26.6	-0.3
MP-1040 + BAP	-11.1	-0.4	26.7	-0.2
MP-4540 + BAP	-8.8	1.9	25.5	-1.4
Snowtex OS + SL	-13.7	-3.0	28.4	1.5
Snowtex O + SL	-13.9	-3.2	28.4	1.5
Snowtex OL + SL	-12.1	-1.4	27.5	0.6
MP-1040 + SL	-12.8	-2.1	27.9	1.0
MP-4540 + SL	-11.0	-0.2	26.9	0.0
Snowtex OS + BAP + SL	-13.1	-2.3	28.0	1.1
Snowtex O + BAP + SL	-12.5	-1.8	27.5	0.7
Snowtex OL + BAP+ SL	-13.2	-2.5	28.0	1.1
MP-1040 + BAP + SL	-11.3	-0.5	27.0	-0.1
MP-4540 + BAP + SL	-11.4	-0.7	27.1	0.2

Table 17. Whiteness & Yellowness Indices of Nanoparticle & Fluorocarbon Treated Wool Fabrics.

Fabric Treatment & Plasma Polymerisation	**Whiteness Index (WID)**	**ΔWID**	**Yellowness Index (YID)**	**ΔYID**

Untreated	-10.4	0	26.5	0
Synthapret BAP	ND		ND	
Oleophobol SL-A	-15.8	-5.4	29.5	3.0
Snowtex OS (4-6nm)	-11.9	-1.5	27.2	0.7
Snowtex O (10-20nm)	-10.6	-0.2	26.6	0.1
Snowtex OL (40-50nm)	-9,8	0.6	26.2	-0.3
MP-1040 (100nm)	-5.1	5.3	23.6	-2.9
MP-4540 (430nm)	1.3	11.7	20.6	-5.9
Snowtex OS + BAP	-10.7	-0.3	26.4	-0.1
Snowtex O + BAP	-11.7	-1.3	27.0	0.5
Snowtex OL + BAP	-11,8	1.4	27.0	0.5
MP-1040 + BAP	-10.8	-0.4	26.6	0.1
MP-4540 + BAP	-10.0	0.4	26.1	-0.4
Snowtex OS + SL	-11.7	-1.3	27.2	0.7
Snowtex O + SL	-13.9	-3.5	28.4	1.9
Snowtex OL + SL	-13.8	-3.4	28.3	1.8
MP-1040 + SL	-14.5	-4.1	28.9	2.4
MP-4540 + SL	-12.2	-1.8	27.5	1.0
Snowtex OS + BAP + SL	-13.4	-3.0	28.2	1.7
Snowtex O + BAP + SL	-13.5	-3.1	28.1	1.6
Snowtex OL + BAP+ SL	-14.5	-4.1	28.8	2.3
MP-1040 + BAP + SL	-12.0	-1.6	27.2	0.7
MP-4540 + BAP + SL	-11.8	-1.4	27.1	0.6

Table 18. Whiteness & Yellowness Indices of Nanoparticle & Fluoropolymer Plasma Polymerised Wool Fabrics.

The effect on fabric whiteness/yellowness of incorporating the nanoparticles into the fabric structure is dependent on the particle size. With the larger particle size there is an obvious whitening effect and clearly this will impact on any coloured products. In contrast with the smaller particle nanoparticles the lightening effect is relatively small.

Finally the mechanical properties were also tested and the results shown in table 19.

Fabric Treatment	**Bending Rigidity B**	**Shear Stiffness G**	**Shear Hysteresis at 5°, 2HG5**
Untreated	0.1022	0.34	0.57
Synthapret BAP	ND	ND	ND
Oleophobol SL-A	0.1046	0.35	0.67
Snowtex OL (40-50nm)	0.1084	0.36	1.10
MP-1040 (100nm)	0.1008	0.34	0.96
MP-4540 (430nm)	0.0987	0.35	0.78
Snowtex OL + BAP+ SL	0.1027	0.34	0.59
MP-1040 + BAP + SL	0.1020	0.35	0.52
MP-4540 + BAP + SL	0.1058	0.34	0.53
Fabric Treatment & Plasma Polymerisation			
Untreated	0.1063	0.34	0.86
Synthapret BAP	ND	ND	ND
Oleophobol SL-A	0.1018	0.35	0.79

Snowtex OL (40-50nm)	0.1073	0.37	1.52
MP-1040 (100nm)	0.1022	0.39	1.54
MP-4540 (430nm)	0.1029	0.37	1.17
Snowtex OL + BAP+ SL	0.1028	0.34	0.70
MP-1040 + BAP + SL	0.1141	0.36	0.86
MP-4540 + BAP + SL	0.1130	0.35	0.79

Table 19. KES-F Analysis of the Selected Mechanical Properties of Nanoparticle & Fluoropolymer Plasma Polymerised Wool Fabrics.

The effect of the nanoparticles on the mechanical properties of the treated fabric is variable. If applied alone or alone followed by a plasma polymerisation process the 2HG5 value (the indicator of interyarn friction and softness) increases; probably due to the protruding particles causing increased frictional interaction. In contrast, if the nanoparticles are incorporated with the shrinkproofing or water/oil repellent finish, the mechanical properties are similar to the control fabric.

The application of incorporation of nanoparticles into fluorocarbon systems applied to wool fabric offers only marginal benefits in terms of water and oil repellency but this performance is improved with argon plasma pre-treatment. The felting shrinkage of the wool fabric, particularly after plasma polymerisation, is reduced by incorporating nanoparticles into the coating and is probably related to a stand-off mechanism where the fibre scales cannot engage. The effect of the nanoparticles on fabric handle is variable depending on the application condition. However, where the nanoparticles are relatively “exposed” it appears the surface protrusions increase interyarn friction and harshen fabric handle. SEM analysis indicated the distribution of the nanoparticles is uneven, either located at the scale edges or within the fluoropolymers film. Argon plasma pre-treatment improves the distribution of the nanoparticles on the wool fabric.

Claims

1. A method of treating wool in the form of fibre, sliver, yarn, fabric or garment comprising said fibre or yarn, to prevent shrinkage due to felting during laundering, the method comprising applying a polymer coating by plasma polymerisation.

2. A method according to claim 1 wherein the polymer is a fluoropolymer.

3. A method according to any of claims 1 or 2 wherein in a preliminary step before the plasma polymerisation, a continuous power plasma is applied in the presence of an inert gas.

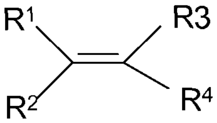
4. A method according to claim 3, wherein the inert gas comprises argon.

5. A method according to any one of the preceding claims wherein the fibre, yarn, sliver, fabric or garment undergoes a pre-treatment to coat the fibre surface with a polymer.

6. A method according to claim 5 wherein the pre-treatment comprises the Chlorine / Hercosett process.

7. A method according to any one claims 1 to 4, wherein the method further comprises the application of silicon nanoparticles to the fibre, yarn, sliver, fabric or garment.

8. A method according to any one of the preceding claims wherein the plasma comprises a monomeric compound which undergoes plasma polymerisation to form a polymer, wherein the monomeric 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 $-C(O)O-$, a group of formula $-C(O)O(CH_2)_nY-$ where n is an integer of from 1 to 10 and Y is 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.

9. A method according to claim 8 wherein the compound of formula (I) is a compound of formula (II)

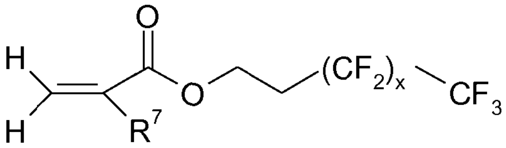
$CH_2=CH-R^5$ (II)

where R^5 is as defined above in relation to formula (I), or the compound of formula (I) is an acrylate of formula (III)

$CH_2=CR^{7a}C(O)O(CH_2)_nR^5$ (III)

where n and R^5 as defined above in relation to formula (I) and R^{7a} is hydrogen, C_{1-10} alkyl, or C_{1-10}haloalkyl. In particular R^{7a} is hydrogen or C_{1-6}alkyl such as methyl.

10. A method according to claim 9 wherein the compound of formula (III) is a compound of formula (IV)

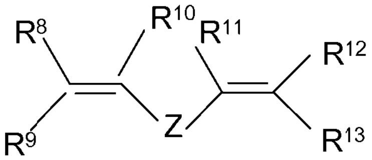


(IV)

where R^7 is where R^7 is hydrogen or alkyl, and x is an integer of from 1 to 9.

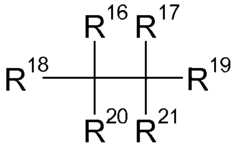
11. A method according to claim 10 wherein the compound of formula (IV) is 1H,1H,2H,2H-heptadecafluorodecylacrylate.

12. A method according to any one of claims 1-7 wherein the plasma comprises a monomeric compound which undergoes plasma polymerisation to form a polymer, wherein the monomeric compound is a compound of formula (V)



(V)

where R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} are all independently selected from hydrogen, halo, alkyl, haloalkyl or aryl optionally substituted by halo; and Z is a bridging group, or a a compound of formula (VII)



(VII)

where R^{16}, R^{17}, $R^{18,}$ R^{19} and R^{20} are independently selected from hydrogen, halogen, alkyl, haloalkyl or aryl optionally substituted by halo; and R^{21} is a group X-R^{22} where R^{22} is an alkyl or haloalkyl group and X is a bond; a group of formula -C(O)O$(CH_2)_x$Y- where x is an integer of from 1 to 10 and Y is a bond or a sulphonamide group; or a group $-(O)_pR^{23}(O)_s(CH_2)_t-$ where R^{23} is aryl optionally substituted by halo, p is 0 or 1, s is 0 or 1 and t is 0 or an integer of from 1 to 10, provided that where s is 1, t is other than 0, or a compound of formula (VIII)

$R^{24}-C\equiv C-X^1-R^{25}$ (VIII)

where R^{24} is hydrogen, alkyl, cycloalkyl, haloalkyl or aryl optionally substituted by halo;
X^1 is a bond or a bridging group; and
R^{25} is an alkyl, cycloalkyl or aryl group optionally substituted by halogen.

13. A method according to any one of the preceding claims which is carried out in a plasma deposition chamber, a glow discharge is ignited within said chamber, and a voltage applied as a pulsed field.

14. A method according to claim 13 wherein applied voltage is at a power of from 5 to 500W.

15. A method according to claim 13 or claim 14 wherein the voltage is pulsed in a sequence in which the ratio of the time on : time off is in the range of from 1:500 to 1:1500.

16. A method according to claim 15 wherein the voltage is pulsed in a sequence where power is on for 20-50µs, and off for from 1000µs to 30000µs.

17. A method according to any one of claims 13 to 16 wherein the voltage is applied as a pulsed field at for a period of from 30 seconds to 90 minutes.

18. A method according to any one of the preceding claims wherein the fibre, yarn, sliver, fabric or garment comprises 100% wool.

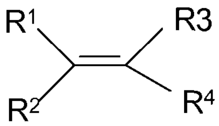
19. A method according to any one of the preceding claims wherein the fibre, yarn, sliver, fabric or garment comprises a wool / polymer blend.

20. Use of a polymer coating obtained by plasma polymerisation on a wool containing fibre, yarn, sliver, fabric or garment made

from said fibre or yarn to reduce shrinkage due to felting during laundering.

21. Use according to claim 19 wherein the polymer is a fluoro polymer.

22. Use according to any one of claims 20 or 21 wherein the polymer coating is formed by exposing the fabric or a yarn from which it is constructed to comprising 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 _$-C(O)O-$, $-C(O)O(CH_2)_nY-$ 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, for a sufficient period of time to allow a protective polymeric layer to form on the surface of the fabric or yarn.

23. Use of a polymer coating obtained by plasma polymerisation on a wool containing fibre, yarn, sliver, fabric or garment made from said fibre or yarn as a water and/or oil repellent coating which does not require post laundering refreshing.

24. A wool containing fibre, yarn, sliver, fabric or garment made from said fibre or yarn, wherein the fibre, yarn, sliver, fabric or garment has been treated according to the method of any of claims 1 to 19 to prevent shrinkage due to felting during laundering.

Application No:	GB0920620.2	**Examiner:**	Dr J.P. Bellia
Claims searched:	1-24	**Date of search:**	24 March 2010

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-4, 8-24	WO2007/083124 A1 (P2I) See paragraphs 19-20 and 37-42
X	1-4, 8-24	WO2004/065684 A1 (PROCTER & GAMBLE) See page 8 line 7-21 and page 15 line 5-page 16 line 10.
X	1-4, 8-24	GB2451176 A (P2I) See page 4 line 1-page 14 line 5
X	1, 5, 8	EP1557489 A1 (SECRETARY OF STATE FOR DEFENCE) See paragraphs 35, 36 and Example 5

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

D06M

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI

International Classification:

Subclass	Subgroup	Valid From
D06M	0014/24	01/01/2006