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COATING, COATING COMPOSITION AND METHOD OF FORMING COATING

The present invention relates to providing a surface, such as a surface of the nozzle plate of an ink jet print head, with a layer having a predetermined surface property, especially a non-wetting property.

In the manufacture of ink jet print heads, it is desirable for at least a part of the surface of the nozzle plate, and in particular a zone surrounding a nozzle orifice, to be resistant to wetting by the ink; otherwise the ink tends to form a pool round the orifice and this pool can interfere with the proper operation of the printer. The nozzle plate may be an integral part of the print head or a separate entity which is attached to the print head.

For a surface to be resistant to wetting by a liquid, its critical wetting tension or "surface energy" should be significantly less than that of the liquid. Many inks favoured for ink jet printing are based on solvents having relatively low surface energies, eg. 20 or 25 to 35mN.m⁻¹, whereas the materials from which the print heads are formed, eg. polyesters, polyimides, glass, ceramics and metal, tend to have a higher surface energy, e.g. greater than 40mN.m⁻¹. It is therefore necessary to provide those portions of the surface which are desired to be resistant to wetting by the ink with a suitable coating. For purposes of simplicity such coatings are referred to hereinafter as non-wetting coatings.

One class of coating material that is particularly favoured for its non-wetting properties comprises fluorinated organic compounds; however these are notoriously difficult to bond to many of the materials from which ink jet print heads are formed and there have been



many proposals for solving the problem. One solution is provided by EP-A-0367438 which describes selecting a fluorinated organosilane as the non-wetting material and bonding it to the substrate surface by means of an interlayer comprising cured siloxane. While very good adhesion is achieved with the process, still further improvement is desired and it would also be desirable to simplify the coating procedure.

We have now discovered a method of providing a strongly bonded non-wetting coating based on organosilane which can be applied to a substrate in a single step. The invention also provides a coating composition and a method of forming the coating from the coating composition.

In its broadest aspect, the invention provides a method of providing a substrate with a desired surface property, e.g. a non-wetting property, which comprises forming on said surface a crosslinked copolysiloxane coating containing X- and X'- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'-.

As indicated above, the invention is particularly concerned with coating the nozzle plates of ink jet print heads, and especially providing a non-wetting coating.

In accordance with this aspect of the invention, there is provided a non-wetting crosslinked copolysiloxane coating on a substrate, said copolysiloxane containing $\text{CF}_3\text{Z-}$



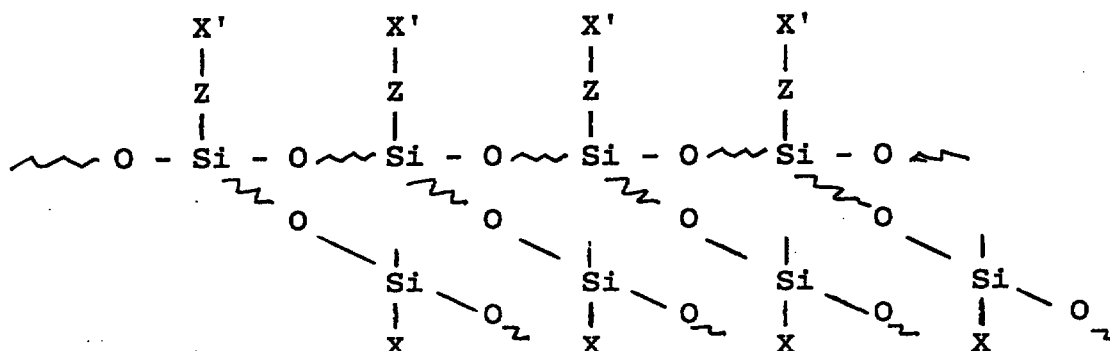
and X- groups attached to different Si atoms wherein each Z is a divalent organic group and each X is a monovalent organic group reactive with a group on the coated substrate surface.

Thus, the copolysiloxane contains at least two different kinds of repeat units. The first comprises the monovalent organic group X', e.g. $\text{CF}_3\text{Z}-$, attached to a silicon atom which in turn is attached to at least one oxygen atom attached to another silicon atom in the copolysiloxane and the second comprises the monovalent organic group X attached to a silicon atom which in turn is attached to at least one oxygen atom attached to another silicon atom in the copolysiloxane.

The crosslinked copolysiloxane coating may be formed by applying to a substrate a crosslinkable composition of silicon compounds including a silicon compound containing the group X' and a silicon compound containing the group X and causing or allowing the said silicon compounds to crosslink. The coating so formed exhibits excellent adhesion to the substrate and a surface which has the desired surface property provided by the group X'. Thus, where X' is $\text{CF}_3\text{Z}-$, a surface is provided which has excellent non-wetting properties even towards non-aqueous inks. While not wishing to be bound by this theory, it is believed that during the formation of the crosslinked polysiloxane from the crosslinkable composition of the silicon compounds, effective partition of the X' and X groups occurs whereby the silicon-containing molecules tend to orient themselves with X' groups tending to concentrate at the coating/atmosphere interface while the X groups tend to concentrate at the coating/substrate interface, e.g. as shown very diagrammatically below.



ATMOSPHERE



SUBSTRATE

In the above diagram, it is to be understood that each  can represent a direct or indirect link.

In any event, where $X' = \text{CF}_3\text{Z}-$, coatings have been obtained according to the invention wherein the surface energy is close to that which has been measured for a monolayer of close-packed CF_3- groups.

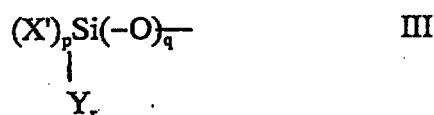
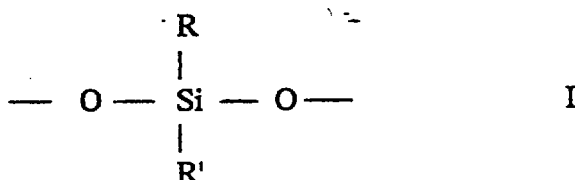
Preferably, the crosslinked polysiloxane will also include other siloxane units in addition to those containing the groups $X'-$ and $X-$, to enhance other desirable properties in the coating such as tensile strength, abrasion resistance, hardness and fracture toughness.

Suitable units will be known to those skilled in the art but for cost and availability of the compounds from which they are derived, they will generally comprise silicon atoms to which groups selected from monovalent hydrocarbon and monovalent hydrocarbyloxy groups are attached. It is preferred that these silicon atoms form a major part of the



crosslinked polysiloxane because of the relatively greater cost of silicon compounds containing the groups X'- and X-, especially where X'- is CF₃Z-. Suitably these silicon atoms form a major proportion of the total number of silicon atoms of the crosslinked polysiloxane and provide the backbone of the copolysiloxane to which the silicon atoms containing the X'- groups and the silicon atoms containing the X- groups are attached.

Thus in accordance with one preferred embodiment, the crosslinked copolysiloxane includes the following repeating units



wherein each R and each R' is selected from monovalent hydrocarbyl groups, monovalent hydrocarbyloxy groups and -O-, X and X' are as defined above, each Y is an inert monovalent atom or group, l is 1 or 2, m is 1, 2 or 3, n is 0, 1 or 2, the total of l, m and n being 4; and p is 1 or 2, q is 1, 2 or 3 and r is 0, 1 or 2, the total of p, q and r being 4.

In unit I preferred hydrocarbyl and hydrocarbyloxy groups for R and/or R' are alkyl and alkoxy groups, and more preferably the lower alkyl and alkoxy groups e.g. those having 1



to 4 carbon atoms, especially methyl and ethoxy.

So that the product is crosslinked, it will be understood that in at least some of the units, the Si atom must be attached to at least three -O- groups; that is to say in at least some of the units I, at least one of R and R' must be -O- and/or in at least some of the units II, m must be 3 and/or in at least some of the units III, q must be 3. Preferably, the crosslinking is provided mainly by providing units of the kind I wherein at least one of R and R' is -O-.

It will be understood that other units may also be included in the copolysiloxane, if desired, provided that they do not interfere unacceptably with the film-forming properties of the copolysiloxane, the bonding of the copolysiloxane to the substrate and the desired surface property of the coating.

The units of the structure II, and more particularly the groups X- thereof, provide the means whereby the copolysiloxane is bonded to the substrate. While in these units it is sufficient for m to be 1, so that the units are chemically bound to the body of the copolysiloxane, it is preferred that m is greater than 1, e.g. 2 or 3, to reduce the possibility of such units becoming detached from the body of the copolysiloxane by bond scission, thereby reducing the strength of the bond of the copolysiloxane to the substrate. For similar reasons, it is preferred that units of the structure II provide at least 0.1% of the total number silicon atoms in the copolysiloxane, and preferably from 0.1 to 10%, more preferably 0.4 to 3%. Above 10%, no further improvement in bond strength is obtained and other desirable properties of the coating may be adversely affected.



The units of the Structure III provide the desired surface properties and for the same reason as are given above for the units of structure II, while q may be 1, it is much preferred that it is 2 or 3, more preferably, 3. The number of silicon atoms in the copolysiloxane provided by units having the structure III will depend upon the nature of the group X' but in general will be at least that number that is just enough experimentally to provide a monolayer of the terminal groups of the X' group on the surface of the coating. In the particular case where X' is $\text{CF}_3\text{Z}-$ so as to provide a non-wetting coating, units of the structure III will preferably provide from 0.01% to 15%, more preferably from 0.1 to 5%, of the silicon atoms in the copolysiloxane. Above 15%, little improvement is likely and other properties of the coating may be adversely affected.

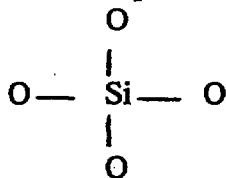
The units of structure I are preferably chosen to provide the important physical properties of the coating and it is also preferred that the desired level of crosslinking is achieved largely by means of these units. Preferably, therefore, they provide a major part (i.e. over 50%), and more preferably at least 75%, of the silicon atoms of the copolysiloxane. The maximum proportion of these units in the copolysiloxane is generally controlled by the number of units II, units III and any optional units that are also present but in general units of structure I will not provide more than about 99.8%, and more preferably not more than about 99%, of the total number of silicon atoms.

The thickness of the coating can also be controlled by the number of units of the structure I present, the larger numbers producing the thicker coatings by increasing the number of intermediate siloxane layers in the copolysiloxane linking the upper layer containing units of structure III to the lower layer (that is, the layer adjacent the substrate)



containing units of structure II. It will be understood that within the ranges of concentration given above for units of structure II and III, the actual concentration desired will depend upon the thickness of the coating. With increase in thickness, the number of units of structure I relative to the number of units of structures II and III will increase, and vice versa.

In the units of the structure I, it will be understood that those wherein at least one of R and R' is -O- will contribute to the crosslinking. Thus, physical properties of the coating may be varied by varying the ratio of units wherein neither R and R' is -O-, to the number of units where at least one of R and R' is -O-. Decreasing the ratio will increase the crosslink density and thus the rigidity and hardness of the coating while increasing the ratio will reduce crosslink density and introduce elastomeric properties. However, it is generally preferred that unit I contributes, and more preferably contributes mainly or entirely, to the crosslinking, in which case it is essential that in at least some of the units I, that is to say in at least about 50 % and preferably at least 75 % of the units at least one of R and R' is -O-. Of these units, it will generally be preferred that in most, if not all, only one of R and R' is -O-, because of the difficulty of forming coating compositions containing compounds that will provide units having the structure.



when employing the preferred method of depositing the coating from solution.

In the units of the structure II, X contains a group which is reactive with a group on the substrate surface eg. to form π - π bonds, hydrogen bonds or ionic or covalent bonds and the nature of X will therefore be chosen according to the nature of the surface to be coated. For example, where the surface is oxidised metal or glass, X may contain an -OH group or a -COOH group; where the surface is polyester or polyimide, X may contain an active hydrogen atom. In another alternative, X may contain a polymerisable ethylenically unsaturated group, for example a vinyl group, e.g. to enable bonding of the coating to the substrate by grafting. However, in the preferred case where the surface is polyimide, polycarbonate or linear polyester, the strongest bonds have been obtained when X contains at least one Zerewitinoff hydrogen atom attached to a nitrogen atom e.g. as in primary and secondary amino groups, imino groups, amide groups and monosubstituted amide groups. In general, it will be preferred that l is 1 because where more than one X- group is present, steric hindrance which interferes with the ability of X to bond with the substrate may occur. The units may also include one, or even two, Y groups where Y is a monovalent inert atom or group by which we mean an atom or group that is inert to X and does not interfere with the formation of the copolysiloxane. Examples are hydrogen, hydrocarbyl such as alkyl, e.g. methyl, or phenyl and hydrocarbyloxy, e.g. alkoxy. However, as indicated above m is preferably 2 or 3 and for best results, it is preferred that l is 1 and m is 3, in which case it will be understood that the units II will contribute to the crosslinking.

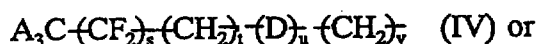
Examples of X groups having a Zerewitinoff hydrogen atom attached to a nitrogen atom



are aminoalkyl, N-alkylaminoalkyl, alkylene amide alkylene N-alkylamide and N-alkylene substituted polyalkylene imine; e.g. aminopropyl, N-methyl aminopropyl, 3-amidopropyl, 3-(N-methylamido)propyl and propyl substituted polyethyleneimine.

In the units of the structure III, X' is a monovalent organic group chosen to provide a desired surface property. In the preferred case where non-wetting characteristics are required, X' is preferably $\text{CQ}_3\text{Z}-$ where each Q is H or F and Z is a divalent organic group. Thus CQ_3- may be CF_3- , $\text{CF}_2\text{H}-$, CFH_2 or CH_3- . Where a particularly low surface energy surface is required, e.g. to exhibit good non-wetting properties even towards non-aqueous inks such as those where the diluent is selected from hydrocarbons and esters, it is preferred that essentially all the CQ_3- groups are CF_3- groups. However, it has unexpectedly been found that good non-wetting coatings for such inks are still obtainable where at least some of the CF_3- groups are replaced by groups where one or more of the fluorine atoms have been replaced by hydrogen atoms. In particular, at least some of the CF_3- groups may be replaced by CH_3- groups. For aqueous inks, adequate non-wetting may be obtainable where the CQ_3- groups are CH_3- groups.

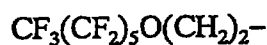
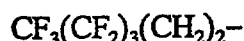
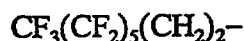
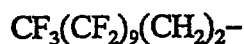
Divalent group Z preferably has a chain of carbon, or carbon and oxygen, atoms between the free valencies. More preferably, the group $\text{CQ}_3\text{Z}-$ has the structure



where each A is F or CF_3- , D is a divalent atom or group, eg. $-\text{O}-$, and each of s, t and v



is zero or a positive integer with the total of s plus t plus v being at least one and u is 0 or 1. For optimum non-wetting properties, in structure IV each A is preferably F, t and u are each 0, v is 2 and s is 1 to 9. In structure V, u is preferably 0 and t plus v is a whole number from 1 to 9. Specific examples of $\text{CQ}_3\text{Z}-$ are



Preferably, p is 1 because steric hindrance may interfere with the desired surface properties of the coating if p is greater than 1. The units may also include one or even two Y groups where Y is an inert atom or group by which we mean here an atom or group that is inert to X' and does not interfere with the formation of the copolysiloxane. Examples are hydrogen, hydroxy, hydrocarbyl, e.g. methyl or phenyl, and hydrocarbyloxy, e.g. alkoxy. As indicated above, however, q is preferably 2 and more preferably 3.

The coatings of the invention are formed from film-forming compositions comprising at least one hydrolysable silicon compound containing at least one X'- group and at least one hydrolysable silicon compound containing at least one X- group. In general, the composition will also include a hydrolysable silicon compound known to form polysiloxane films.

The silicon compounds are preferably provided in the composition as a solution in a



suitable solvent which is preferably readily removable from the coating, eg. by evaporation, and is of low surface tension. Suitable solvents are alcohols eg. ethyl alcohol, and alkanes, eg. hexane. Preferably, the solution also includes a higher boiling component to promote self-levelling of the coating. Examples include n-hexanol and 2-butoxyethanol.

To enable the silicon components to hydrolyse, the coating composition will also contain water. Sufficient water should be included to permit complete hydrolysis of the hydrolysable silicon compounds but if too much water is present the resultant solution, after hydrolysis of the silicon compounds, may not adequately wet the substrate to be coated, especially where this is formed of certain synthetic polymers. For example, where the surface is polyimide, it has been found that the water content of the composition prior to hydrolysis of the silicon compounds should preferably be not more than 350% of that required for the total hydrolysis.

In a preferred embodiment, the coating composition comprises

- (i) at least one film-forming silicon compound A selected from those having the structure $\text{Si}(\text{R}'')_4$, $\text{RSi}(\text{R}'')_3$ and $\text{RR}'\text{Si}(\text{R}'')_2$ where each of R and R' is selected from monovalent hydrocarbyl and hydrocarbyloxy groups and R'' is a hydrolysable group.
- (ii) at least one silicon compound B having the structure $\text{X}_l\text{SiY}_n\text{R}''_m$ where X, Y, l, n and m are each as defined above and each R'' is a hydrolysable group; and
- (iii) at least one silicon compound C having the structure $\text{X}'_p\text{SiY}_r\text{R}''_q$ where X',



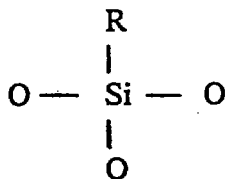
Y, p, q and r are each as defined above and each R" is a hydrolysable group;

and wherein at least some of the molecules contain at least three hydrolysable groups whereby to achieve crosslinking.

Preferred hydrolysable groups are alkoxy and chloride groups.

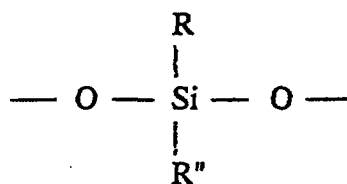
It will be understood that compounds A having the structure $RR'Si(R'')_2$ will provide units of structure III in the crosslinked copolysiloxane. In the preferred case where crosslinking is provided mainly by units of the structure I, it will be understood that at least some of the molecules of compound A will be of the structure $Si(R'')_4$ or, more preferably, $RSi(R'')_3$.

It is possible that not all of the hydrolysable groups of the compounds in the coating composition will be hydrolysed. Thus, for example, a compound A having the structure $RSi(R'')_3$ may give rise to units in the crosslinked copolysiloxane having not only the structure

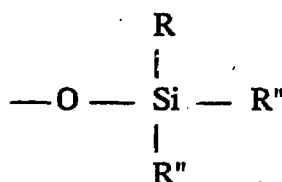


but also the units having the structure





and even



Compound A is preferably a compound which on hydrolysis and cross-linking will provide a strong hard film able to withstand temperatures of at least 100°C without deteriorating. Particular examples of A are methyltriethoxysilane and tetraethoxysilane. Partially polymerised materials such as polydialkyl- and polydialkoxysilanes may also be used as, or as part of, component A provided that they can be provided as emulsions or, more preferably, solutions in a solvent for the other components of the composition.

While compound B in principle requires only one hydrolysable group R'', it is preferred that it contains at least two and preferably three such groups and only one group X.

Where it contains two hydrolysable groups, it may contain two X groups or one X group and one Y group. Particular examples are 3-aminopropyl triethoxysilane, trimethoxysilylpropyl substituted polyethyleneimine, dimethoxy methyl silyl propyl substituted polyethylene imine and carboxyamide silanes such as those sold as Prosil 9214 and Prosil 9215 by Fluorochem Ltd of Old Glossop, Derbyshire, England.



Compound C preferably contains at least 2, and preferably 3, hydrolysable groups R".

Specific examples where X' is $\text{CO}_3\text{Z}-$ are octyl triethoxy silane, decyl triethoxy silane, fluorinated derivatives such as 1H,1H,2H,2H-perfluorooctyl triethoxysilane and 1H,1H,2H,2H perfluorodecyl triethoxysilane and the corresponding compounds wherein one or more of the ethoxy groups are replaced by chlorine, e.g. 1H,1H,2H,2H perfluorooctyl dimethyl chlorosilane. Mixtures of 1H,1H,2H,2H perfluoroalkyl triethoxysilanes having 8, 10 and 12 carbon atoms in the perfluoroalkyl chain may also be used.

Hydrolysis of the silicon compounds of the coating composition and subsequent cross-linking may be promoted by acid or basic conditions. It is therefore preferred that the coating composition also include an additive which shifts the pH of the composition above or below 7. Where the group X of component B is basic, it is preferred that the additive is an acid which will promote protonation of X since this is believed to promote the partition of X and the X' group of component C, at least where X' is $\text{CO}_3\text{Z}-$. Examples of suitable acids are mineral acids such as hydrochloric and organic acids such as acetic. The amount of acid employed is not believed to be critical provided that it is sufficient to neutralise all of any base present and ensure acidic conditions. Mixtures of acids may be used.

The composition should be formed under clearly acid or basic conditions and therefore it is preferred to add the hydrolysable silicon compounds to an acidic (or basic) solution.



Prior to application to the substrate to form the coating, the coating composition should be aged to ensure at least partial hydrolysis of the hydrolysable groups. It is particularly important that compound A be at least partially hydrolysed and it is desirable that compounds B and C are also at least partially hydrolysed so as to reduce the possibility of evaporation during the curing required to effect the formation of the crosslinked film. This ageing also improves the mechanical properties of the resulting coating. The ageing may suitably be achieved by allowing the composition to stand at room temperature for several hours. The ageing process might also be accelerated by heat but care must be taken not to induce premature crosslinking leading to the formation of insolubles. The presence of such insolubles will be seen as the formation of cloudiness in the composition. In general, ageing for 1-2 days at room temperature has been found satisfactory. If the ageing step is omitted, the coating may suffer from pinholes or other defects and this is believed to be due to the presence of excess water in the composition which has not been consumed in the hydrolysis.

The at least partially hydrolysed composition may then be applied to the substrate and cured to effect or complete crosslinking. While the substrate may consist of any suitable material whose surface is required to be made non-wetting, the invention is particularly applicable to the treatment of nozzle plates of ink jet print heads. Thus, materials to which the coating may be applied include, in particular, metals (including metals whose surface has been oxidised by atmospheric oxygen), glass, ceramics and synthetic plastics. The invention is particularly applicable to glass, metals and laser-ablatable plastics such as polyimides, polycarbonates, saturated polyesters eg. polyethylene terephthalate and polybutylene naphthenate, and polyether ether ketones.



Prior to coating, it is preferred that the surface be pre-treated to clean it and, preferably, also increase its surface energy since this has been found to improve adhesion, especially of polyimide surfaces. One preferred pre-treatment for polyimides is to soak the surface in an aqueous alkaline solution, eg. for about an hour, rinse with water and then dry. The coating may then be applied in any suitable manner eg. roller coating, doctor knife coating or spraying. One preferred method is by meter bar whereby the composition is spread over the surface by means of a wire-wound bar. Preferably, the coating is applied as soon as possible after completion of the pre-treatment. The preferred wet coating thickness is 2 to 10 microns. At thicknesses below 2 microns, the coating may be incomplete and no apparent additional benefit is obtained from coatings more than 10 microns thick. Excessive thickness is preferably avoided if the coating is subsequently to be treated, e.g. by laser ablation, to remove some of it. A preferred dry thickness is 0.3 to 1 microns.

The coating is then caused or allowed to cure. Suitably, the cure is accelerated by application of heat and heating may conventionally be effected in an oven at a temperature which will depend upon the choice of the components for the composition but will generally be in the range 60°C to 100°C, preferably about 70 to 95°C. To ensure completion of the formation of the cross-linked film, cure times of several hours, eg. 3 to 24 hours are recommended. Cure may be enhanced if it is effected in an atmosphere of high humidity.

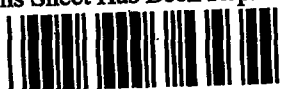
Preferably, the coating is aged prior to the heating step, e.g. by allowing it to stand at room temperature for a few minutes e.g. 5 to 30 minutes, since this has been found to



improve the properties of the resultant film, and in particular its surface properties and the strength of bond to the substrate. It is believed that this is because the ageing permits partition or "self assembly" of the molecules whereby those carrying the group X- concentrate at the coating/substrate interface where those carrying the group X'- concentrate at the interface of the coating with the atmosphere.

By means of the invention, coatings are obtainable which are strongly bonded to the substrate and provide the desired surface properties. In particular, non-wetting coatings may be obtained which exhibit excellent non-wetting characteristics to a range of ink jet ink compositions including those based on low surface energy solvents such as alkylene glycols, polyalkylene glycols and ethers thereof and hydrocarbons. The required surface energy (mN.m^{-1}) of the coating to provide the desired non-wettability will depend upon the nature of the ink but in general will be less than 20 and preferably less than 10 for non-aqueous inks, and less than 45 and preferably less than 35 for aqueous inks. The coatings moreover are thermally stable up to temperatures as high as 200°C and resistant to abrasion. They also remain undamaged by exposure to pre- and post-ablation treatments such as cleansing with solvents such as acetone and propan-2-ol. A particularly important feature of the coatings where X- is $\text{CO}_3\text{Z-}$ is their inertness to inks and their substantial freedom from defects.

In a modification of the invention, at least some of the Si atoms in the copolysiloxane may be replaced by tetravalent metal atoms, e.g. Zr and Ti. It is also envisaged that a minor proportion of the Si atoms may be replaced by di- or trivalent metal or metalloid atoms, e.g. B and Al.



The invention is now illustrated but in no way limited by the following Example in which all parts are expressed by volume except where indicated otherwise.

EXAMPLE

A coating composition was prepared from the following components by first mixing the solvents and acids and then adding the silicon compounds

ethanol	30 parts
glacial acetic acid	0.9 part
hexanol	2.0 parts
hydrochloric acid (0.01 mol/dm ³)	5 parts
methyl triethoxysilane	5 parts
3-aminopropyl triethoxysilane	0.5 part
1H,1H,2H,2H perfluorooctyl triethoxysilane	0.5 part.

The solution so formed was then allowed to stand for 2 days to allow hydrolysis of the silicon compounds.

A sheet of polyimide is washed with about 1 mol/dm³ NaOH, rinsed well with water and dried by wiping with a clean room wipe and then the aged solution is applied to the surface of the sheet using a meter bar to form a wet coating approximately 4 microns thick. The coated sheet is allowed to stand for 5 minutes and then placed in a humid atmosphere in an oven at 95°C for 3 hours. The resulting coating thickness was of the order of 0.6 microns.



An ink jet print head nozzle plate was then formed from the coated sheet by laser ablation.

The resistance of the nozzle plate to wiping was evaluated by measuring its receding meniscus velocity (RMV) in the following manner. An ink-soaked polyurethane foam pad is drawn across the non-wetting coating surface at a measured velocity. The velocity at which the ink just fails to follow the foam pad and begins to leave a trail of ink upon the non-wetting coating is taken to be the RMV. The minimum RMV for adequate wiping performance is 1.0mm sec^{-1} . The measured RMV was 2.7mm sec^{-1} . The RMV was still greater than 1.0mm sec^{-1} after six weeks' immersion in the ink, indicating a very low level of interaction between the ink and the coating. By way of comparison, prior coatings tended to turn grey after a similar immersion treatment due to adhesion of components of the ink to the coating. The ink employed in the above-mentioned tests was an ink jet printer ink comprising a colloidal dispersion of carbon black in tripropylene glycol monomethyl ether containing a polymeric dispersant.

In a further test, the coated nozzle plate was wiped 50 times with a cotton bud soaked in acetone. No visible damage was perceived.

In another test, the abrasion resistance of the coated nozzle plate was evaluated by rubbing it with a foam pad soaked in ink. The coating survived 1,100 wipes before any loss of non-wetting properties was observed. Examination showed that the loss of performance was due to scratching and not as a result of attack by or absorbance of the ink. The same coating survived over 150,000 rubs with a silicone wiper blade.



The coating remained non-wetting after heating to 200°C and was still effective after the equivalent of more than 3 months continuous use of a printer fitted with the coated nozzle plate.

Coatings strongly bonded to the substrate were also obtained when the procedure described above was repeated but replacing the perfluorooctyl triethoxysilane with n-octyl triethoxysilane and with a mixture of perfluorooctyl triethoxysilane and n-octyl triethoxysilane.





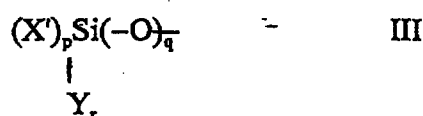
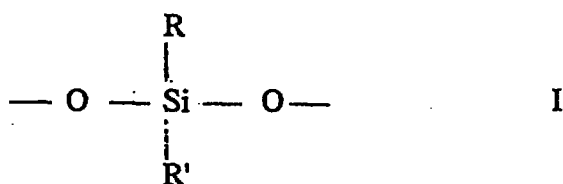
CLAIMS

1. A coating on a substrate to endow said substrate with a desired surface property, said coating comprising a crosslinked copolysiloxane containing X'- and X- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'-.
2. A non-wetting crosslinked copolysiloxane coating wherein said polysiloxane contains X'- and X- groups attached to different Si atoms wherein each X' has the formula CQ_3Z- where each Z is a divalent organic group and each X is a monovalent organic group reactive with a group on the substrate surface and has a higher surface tension than the group CF_3Z- .
3. A modification of the coating as claimed in claim 2 wherein in at least some of the CF_3Z- groups one or more of the fluorine atoms are replaced by hydrogen atoms.
4. A coating as claimed in claim 2 or claim 3 wherein the X'- groups are selected from the CH_3- groups, CF_3- groups and a mixture of such groups.
5. A coating as claimed in any one of claims 1 to 4 in which the Si atoms carrying the X'- groups and the Si atoms carrying the X- groups are separated by one or more siloxane layers.





6. A coating as claimed in claim any one of claims 1 to 5 wherein said copolysiloxane comprises the following repeating units



wherein each of R and R' is selected from monovalent hydrocarbyl groups, monovalent hydrocarbyloxy groups and ---O--- , each Y is an inert monovalent atom or group, l is 1 or 2, m is 1, 2 or 3, n is 0, 1 or 2, the total of l, m and n being 4; and p is 1 or 2, q is 1, 2 or 3 and r is 0, 1 or 2, the total of p, q and r being 4, provided that in at least some of the said repeating units a silicon atom is attached to at least three ---O--- groups.

7. A coating as claimed in claim 6 containing units of the structure I wherein at least one of R and R' is ---O--- .
8. A coating as claimed in claim 7 wherein in most or all of the units of structure I in which at least one of R and R' is ---O--- , only one of R and R' is ---O--- .
9. A coating as claimed in claim 6, claim 7 or claim 8 further including repeating



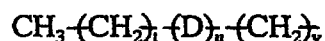
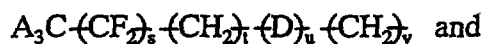


units containing a polymerisable ethylenically unsaturated group attached to an Si atom.

10. A coating as claimed in any one of claims 6 to 9 wherein
- each R is a lower alkyl or alkoxy group;
 - each X is selected from groups containing at least one Zerewitinoff hydrogen atom attached to a nitrogen atom;
 - each Y is hydrogen, a hydrocarbyl group or a hydrocarbyloxy group;
 - and each group X' is a group having the structure $\text{CF}_3\text{Z}-$ where Z is a divalent organic group.

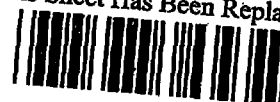
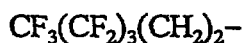
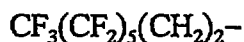
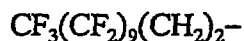
11. A modification of the coating as claimed in claim 10 wherein in at least some of the CF_3- groups, at least one of the fluorine atoms is replaced by a hydrogen atom.

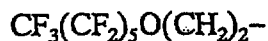
12. A coating as claimed in claim 10 or claim 11 wherein each X' is selected from groups having the structure



where each A is F or CF_3 , di s a divalent atom or group, each of s, t and v is zero or a positive integer with the total of $s + t + v$ being at least one, and u is zero or one.

13. A coating as claimed in claim 12 wherein X' is selected from





14. A coating as claimed in any one of claims 6 to 13 wherein X contains an amine group.
15. A coating as claimed in claim 14 wherein X is aminoalkyl.
16. A coating as claimed in any one of claim 6 to 15 wherein l and p are each 1 and m and q are each 3.
17. A coating as claimed in any one of claims 6 to 16 wherein the silicon atoms of units I, II and III form from 75 to 99.1%, from 0.1 to 10% and from 0.01 to 15%, respectively, of the total number of silicon atoms in the copolysiloxane.
18. A coating as claimed in any one of claims 1 to 17 on an ink jet printer nozzle plate.
19. A coating as claimed in claim 18 which is a non-wetting coating and is on a zone of the nozzle plate surrounding a nozzle.
20. A crosslinkable film-forming coating composition for forming a coating as claimed in any one of claims 1 to 19, said composition comprising at least one hydrolysable silicon compound containing the group X' and at least one hydrolysable silicon compound



containing the group X.

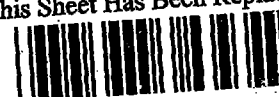


21. A composition as claimed in claim 20 further including (i) a solvent for the silicon compounds present in the composition and (ii) water.
22. A composition as claimed in claim 21 containing water in an amount of from 100 to 350 mole % of that required to effect complete hydrolysis of the hydrolysable groups.
23. A composition as claimed in claim 20, claim 21 or claim 22 comprising
- (i) at least one film-forming silicon compound A selected from those having the structure $\text{Si}(\text{R}'')_4$, $\text{RSi}(\text{R}'')_3$ and $\text{RR}'\text{Si}(\text{R}'')_2$ where each R'' is a hydrolysable group,
 - (ii) at least one silicon compound B having the structure $\text{X}_l\text{SiY}_n\text{R}''_m$ where each R'' is a hydrolysable group, l is 1 or 2, m is 1, 2 or 3 and n is 1 or 2, and
 - (iii) at least one silicon compound C having the structure $(\text{X}')_p\text{SiY}_r\text{R}''_q$ where each R'' is a hydrolysable group, p is 1 or 2, q is 1, 2 or 3 and r is 1 or 2, provided that at least some of the molecules contain at least three hydrolysable groups.
24. A composition as claimed in claim 23 which includes compounds having the structure $\text{RSi}(\text{R}'')_3$.
25. A composition as claimed in claim 23 or claim 24 wherein X is a basic group, said composition further including an acid.





26. A composition as claimed in any one of claims 23 to 25 in which at least component A is in at least partially hydrolysed form.
27. A method of providing a substrate with a desired surface property which comprises forming on said surface a crosslinked copolysiloxane coating containing X- and X'- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'-.
28. A method as claimed in claim 26 which comprises applying to a substrate a crosslinkable composition of silicon compounds including a silicon compound containing the group X' and a silicon compound containing the group X and causing or allowing the said silicon compounds to crosslink.
29. A method as claimed in claim 27 or claim 28 for forming a coating on a substrate comprising applying a composition as claimed in claim 26 to a substrate and causing or allowing the components to form a crosslinked film.
30. A method as claimed in claim 28 comprising the steps of
- (i) forming a solution of the composition of claim 23 or claim 24 in a solvent therefor containing water to hydrolyse the hydrolysable groups,
 - (ii) causing or permitting at least partial hydrolysis of at least component A,
 - (iii) applying the solution obtained from step (ii) to a substrate, and





(iv) causing and permitting the components to form a crosslinked film.

31. A method as claimed in claim 30 in which the coating obtained in step (iii) is allowed to stand before initiating step (iv).

32. A method as claimed in any one of claims 27 to 31 wherein the substrate is selected from glass, metal, ceramics and ablatable synthetic polymers.

33. A method as claimed in claim 32 wherein the substrate is selected from polyimide, polyethylene terephthalate and polybutylene naphthalate.

34. A method as claimed in any one of claims 27 to 33 wherein the substrate is an ink jet printer nozzle plate.

35. A method as claimed in claim 34 wherein the coating is applied to a zone of the nozzle plate surrounding a nozzle.



COATING, COATING COMPOSITION AND
METHOD OF FORMING COATING

ABSTRACT

A coating on a substrate which endows the substrate with a desired surface property, the coating comprising a cross-linked polysiloxane containing X'- and X- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'-, said coating being bonded to said substrate by reaction of X- groups with substrate surface groups reactive therewith. In one embodiment a non-wetting coating is provided wherein the X'-group has the formula CF_3Z where Z is a divalent organic group or the formula $\text{CH}_3(\text{CH}_2)_t$ where t is at least 3.



REPLACED SHEETS	SG
☐ Description : paged to paged	
☒ Claim(s) : paged <u>22</u> to paged <u>28</u>	
☐ Drawing(s) : paged to paged	
☐ Abstract : paged to paged	
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REPLACEMENT SHEETS	SG
☒ Description : paged <u>1</u> to paged <u>21</u>	
☒ Claim(s) : paged <u>22</u> to paged <u>28</u>	
☐ Drawing(s) : paged to paged	
☒ Abstract : paged <u>29</u> to paged <u>30</u>	
DATE OF RECEIPT <u>17/9/96</u>	

COATING, COATING COMPOSITION AND METHOD OF FORMING COATING

The present invention relates to providing a surface, such as a surface of the nozzle plate of an ink jet print head, with a layer having a predetermined surface property, especially a non-wetting property.

In the manufacture of ink jet print heads, it is desirable for at least a part of the surface of the nozzle plate, and in particular a zone surrounding a nozzle orifice, to be resistant to wetting by the ink; otherwise the ink tends to form a pool round the orifice and this pool can interfere with the proper operation of the printer. The nozzle plate may be an integral part of the print head or a separate entity which is attached to the print head.

For a surface to be resistant to wetting by a liquid, its critical wetting tension or "surface energy" should be significantly less than that of the liquid. Many inks favoured for ink jet printing are based on solvents having relatively low surface energies, eg. 20 or 25 to 35mN.m⁻¹, whereas the materials from which the print heads are formed, eg. polyesters, polyimides, glass, ceramics and metal, tend to have a higher surface energy, e.g. greater than 40mN.m⁻¹. It is therefore necessary to provide those portions of the surface which are desired to be resistant to wetting by the ink with a suitable coating. For purposes of simplicity such coatings are referred to hereinafter as non-wetting coatings.

One class of coating material that is particularly favoured for its non-wetting properties comprises fluorinated organic compounds; however these are notoriously difficult to bond to many of the materials from which ink jet print heads are formed and there have been

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many proposals for solving the problem. One solution is provided by EP-A-0367438 which describes selecting a fluorinated organosilane as the non-wetting material and bonding it to the substrate surface by means of an interlayer comprising cured siloxane. While very good adhesion is achieved with the process, still further improvement is desired and it would also be desirable to simplify the coating procedure.

We have now discovered a method of providing a strongly bonded non-wetting coating based on organosilane which can be applied to a substrate in a single step. The invention also provides a coating composition and a method of forming the coating from the coating composition.

In its broadest aspect, the invention provides a method of providing a substrate with a desired surface property, e.g. a non-wetting property, which comprises forming on said surface a crosslinked copolysiloxane coating containing X- and X'- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'-.

As indicated above, the invention is particularly concerned with coating the nozzle plates of ink jet print heads, and especially providing a non-wetting coating.

In accordance with this aspect of the invention, there is provided a non-wetting crosslinked copolysiloxane coating on a substrate, said copolysiloxane containing $\text{CF}_3\text{Z-}$

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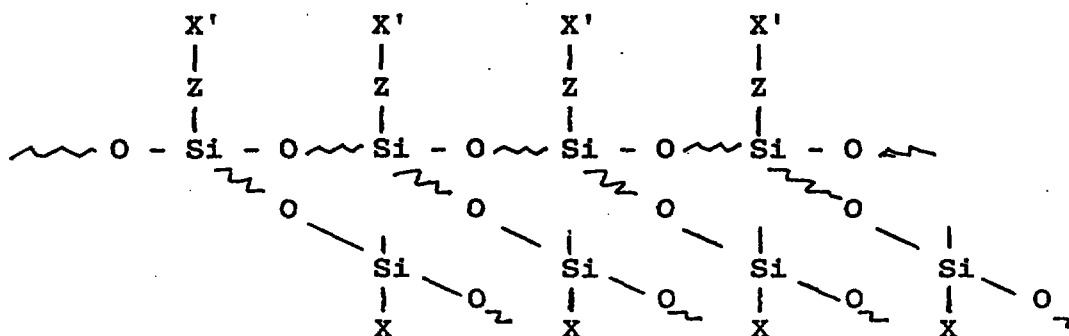
and X- groups attached to different Si atoms wherein each Z is a divalent organic group and each X is a monovalent organic group reactive with a group on the coated substrate surface.

Thus, the copolysiloxane contains at least two different kinds of repeat units. The first comprises the monovalent organic group X', e.g. $\text{CF}_3\text{Z}-$, attached to a silicon atom which in turn is attached to at least one oxygen atom attached to another silicon atom in the copolysiloxane and the second comprises the monovalent organic group X attached to a silicon atom which in turn is attached to at least one oxygen atom attached to another silicon atom in the copolysiloxane.

The crosslinked copolysiloxane coating may be formed by applying to a substrate a crosslinkable composition of silicon compounds including a silicon compound containing the group X' and a silicon compound containing the group X and causing or allowing the said silicon compounds to crosslink. The coating so formed exhibits excellent adhesion to the substrate and a surface which has the desired surface property provided by the group X'. Thus, where X' is $\text{CF}_3\text{Z}-$, a surface is provided which has excellent non-wetting properties even towards non-aqueous inks. While not wishing to be bound by this theory, it is believed that during the formation of the crosslinked polysiloxane from the crosslinkable composition of the silicon compounds, effective partition of the X' and X groups occurs whereby the silicon-containing molecules tend to orient themselves with X' groups tending to concentrate at the coating/atmosphere interface while the X groups tend to concentrate at the coating/substrate interface, e.g. as shown very diagrammatically below.

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ATMOSPHERESUBSTRATE

In the above diagram, it is to be understood that each  can represent a direct or indirect link.

In any event, where $X' = \text{CF}_3\text{Z}-$, coatings have been obtained according to the invention wherein the surface energy is close to that which has been measured for a monolayer of close-packed CF_3- groups.

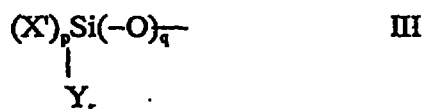
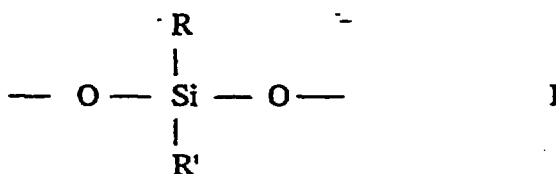
Preferably, the crosslinked polysiloxane will also include other siloxane units in addition to those containing the groups $X'-$ and $X-$, to enhance other desirable properties in the coating such as tensile strength, abrasion resistance, hardness and fracture toughness. Suitable units will be known to those skilled in the art but for cost and availability of the compounds from which they are derived, they will generally comprise silicon atoms to which groups selected from monovalent hydrocarbon and monovalent hydrocarbyloxy groups are attached. It is preferred that these silicon atoms form a major part of the

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crosslinked polysiloxane because of the relatively greater cost of silicon compounds containing the groups X' - and X -, especially where X' - is CF_3Z -. Suitably these silicon atoms form a major proportion of the total number of silicon atoms of the crosslinked polysiloxane and provide the backbone of the copolysiloxane to which the silicon atoms containing the X' - groups and the silicon atoms containing the X - groups are attached.

Thus in accordance with one preferred embodiment, the crosslinked copolysiloxane includes the following repeating units



wherein each R and each R' is selected from monovalent hydrocarbyl groups, monovalent hydrocarbyloxy groups and $-\text{O}-$, X and X' are as defined above, each Y is an inert monovalent atom or group, l is 1 or 2, m is 1, 2 or 3, n is 0, 1 or 2, the total of l, m and n being 4; and p is 1 or 2, q is 1, 2 or 3 and r is 0, 1 or 2, the total of p, q and r being 4.

In unit I preferred hydrocarbyl and hydrocarbyloxy groups for R and/or R' are alkyl and alkoxy groups, and more preferably the lower alkyl and alkoxy groups e.g. those having 1

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to 4 carbon atoms, especially methyl and ethoxy.

So that the product is crosslinked, it will be understood that in at least some of the units, the Si atom must be attached to at least three $-O-$ groups; that is to say in at least some of the units I, at least one of R and R' must be $-O-$ and/or in at least some of the units II, m must be 3 and/or in at least some of the units III, q must be 3. Preferably, the crosslinking is provided mainly by providing units of the kind I wherein at least one of R and R' is $-O-$.

It will be understood that other units may also be included in the copolysiloxane, if desired, provided that they do not interfere unacceptably with the film-forming properties of the copolysiloxane, the bonding of the copolysiloxane to the substrate and the desired surface property of the coating.

The units of the structure II, and more particularly the groups X- thereof, provide the means whereby the copolysiloxane is bonded to the substrate. While in these units it is sufficient for m to be 1, so that the units are chemically bound to the body of the copolysiloxane, it is preferred that m is greater than 1, e.g. 2 or 3, to reduce the possibility of such units becoming detached from the body of the copolysiloxane by bond scission, thereby reducing the strength of the bond of the copolysiloxane to the substrate. For similar reasons, it is preferred that units of the structure II provide at least 0.1% of the total number silicon atoms in the copolysiloxane, and preferably from 0.1 to 10%, more preferably 0.4 to 3%. Above 10%, no further improvement in bond strength is obtained and other desirable properties of the coating may be adversely affected.

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The units of the Structure III provide the desired surface properties and for the same reason as are given above for the units of structure II, while q may be 1, it is much preferred that it is 2 or 3, more preferably, 3. The number of silicon atoms in the copolysiloxane provided by units having the structure III will depend upon the nature of the group X' but in general will be at least that number that is just enough experimentally to provide a monolayer of the terminal groups of the X' group on the surface of the coating. In the particular case where X' is CF_3Z- so as to provide a non-wetting coating, units of the structure III will preferably provide from 0.01% to 15%, more preferably from 0.1 to 5%, of the silicon atoms in the copolysiloxane. Above 15%, little improvement is likely and other properties of the coating may be adversely affected.

The units of structure I are preferably chosen to provide the important physical properties of the coating and it is also preferred that the desired level of crosslinking is achieved largely by means of these units. Preferably, therefore, they provide a major part (i.e. over 50%), and more preferably at least 75%, of the silicon atoms of the copolysiloxane. The maximum proportion of these units in the copolysiloxane is generally controlled by the number of units II, units III and any optional units that are also present but in general units of structure I will not provide more than about 99.8%, and more preferably not more than about 99%, of the total number of silicon atoms.

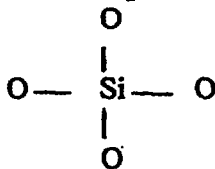
The thickness of the coating can also be controlled by the number of units of the structure I present, the larger numbers producing the thicker coatings by increasing the number of intermediate siloxane layers in the copolysiloxane linking the upper layer containing units of structure III to the lower layer (that is, the layer adjacent the substrate)

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containing units of structure II. It will be understood that within the ranges of concentration given above for units of structure II and III, the actual concentration desired will depend upon the thickness of the coating. With increase in thickness, the number of units of structure I relative to the number of units of structures II and III will increase, and vice versa.

In the units of the structure I, it will be understood that those wherein at least one of R and R' is -O- will contribute to the crosslinking. Thus, physical properties of the coating may be varied by varying the ratio of units wherein neither R and R' is -O-, to the number of units where at least one of R and R' is -O-. Decreasing the ratio will increase the crosslink density and thus the rigidity and hardness of the coating while increasing the ratio will reduce crosslink density and introduce elastomeric properties. However, it is generally preferred that unit I contributes, and more preferably contributes mainly or entirely, to the crosslinking, in which case it is essential that in at least some of the units I, that is to say in at least about 50 % and preferably at least 75 % of the units at least one of R and R' is -O-. Of these units, it will generally be preferred that in most, if not all, only one of R and R' is -O-, because of the difficulty of forming coating compositions containing compounds that will provide units having the structure.



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when employing the preferred method of depositing the coating from solution.

In the units of the structure II, X contains a group which is reactive with a group on the substrate surface eg. to form π - π bonds, hydrogen bonds or ionic or covalent bonds and the nature of X will therefore be chosen according to the nature of the surface to be coated. For example, where the surface is oxidised metal or glass, X may contain an -OH group or a -COOH group; where the surface is polyester or polyimide, X may contain an active hydrogen atom. In another alternative, X may contain a polymerisable ethylenically unsaturated group, for example a vinyl group, e.g. to enable bonding of the coating to the substrate by grafting. However, in the preferred case where the surface is polyimide, polycarbonate or linear polyester, the strongest bonds have been obtained when X contains at least one Zerewitinoff hydrogen atom attached to a nitrogen atom e.g. as in primary and secondary amino groups, imino groups, amide groups and monosubstituted amide groups. In general, it will be preferred that l is 1 because where more than one X- group is present, steric hindrance which interferes with the ability of X to bond with the substrate may occur. The units may also include one, or even two, Y groups where Y is a monovalent inert atom or group by which we mean an atom or group that is inert to X and does not interfere with the formation of the copolysiloxane. Examples are hydrogen, hydrocarbyl such as alkyl, e.g. methyl, or phenyl and hydrocarbyloxy, e.g. alkoxy. However, as indicated above m is preferably 2 or 3 and for best results, it is preferred that l is 1 and m is 3, in which case it will be understood that the units II will contribute to the crosslinking.

Examples of X groups having a Zerewitinoff hydrogen atom attached to a nitrogen atom

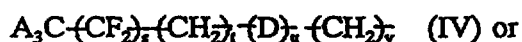
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are aminoalkyl, N-alkylaminoalkyl, alkylene amide alkylene N-alkylamide and N-alkylene substituted polyalkylene imine; e.g. aminopropyl, N-methyl aminopropyl, 3-amidopropyl, 3-(N-methylamido)propyl and propyl substituted polyethyleneimine.

In the units of the structure III, X' is a monovalent organic group chosen to provide a desired surface property. In the preferred case where non-wetting characteristics are required, X' is preferably $\text{CQ}_3\text{Z}-$ where each Q is H or F and Z is a divalent organic group. Thus CQ_3- may be CF_3- , $\text{CF}_2\text{H}-$, CFH_2 or CH_3- . Where a particularly low surface energy surface is required, e.g. to exhibit good non-wetting properties even towards non-aqueous inks such as those where the diluent is selected from hydrocarbons and esters, it is preferred that essentially all the CQ_3- groups are CF_3- groups. However, it has unexpectedly been found that good non-wetting coatings for such inks are still obtainable where at least some of the CF_3- groups are replaced by groups where one or more of the fluorine atoms have been replaced by hydrogen atoms. In particular, at least some of the CF_3- groups may be replaced by CH_3- groups. For aqueous inks, adequate non-wetting may be obtainable where the CQ_3- groups are CH_3- groups.

Divalent group Z preferably has a chain of carbon, or carbon and oxygen, atoms between the free valencies. More preferably, the group $\text{CQ}_3\text{Z}-$ has the structure

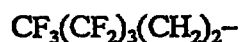
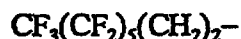
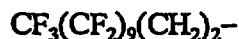


where each A is F or CF_3- , D is a divalent atom or group, eg. $-\text{O}-$, and each of s, t and v

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is zero or a positive integer with the total of s plus t plus v being at least one and u is 0 or 1. For optimum non-wetting properties, in structure IV each A is preferably F, t and u are each 0, v is 2 and s is 1 to 9. In structure V, u is preferably 0 and t plus v is a whole number from 1 to 9. Specific examples of $\text{CQ}_3\text{Z}-$ are



Preferably, p is 1 because steric hindrance may interfere with the desired surface properties of the coating if p is greater than 1. The units may also include one or even two Y groups where Y is an inert atom or group by which we mean here an atom or group that is inert to X' and does not interfere with the formation of the copolysiloxane. Examples are hydrogen, hydroxy, hydrocarbyl, e.g. methyl or phenyl, and hydrocarbyloxy, e.g. alkoxy. As indicated above, however, q is preferably 2 and more preferably 3.

The coatings of the invention are formed from film-forming compositions comprising at least one hydrolysable silicon compound containing at least one $\text{X}'-$ group and at least one hydrolysable silicon compound containing at least one $\text{X}-$ group. In general, the composition will also include a hydrolysable silicon compound known to form polysiloxane films.

The silicon compounds are preferably provided in the composition as a solution in a

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suitable solvent which is preferably readily removable from the coating, eg. by evaporation, and is of low surface tension. Suitable solvents are alcohols eg. ethyl alcohol, and alkanes, eg. hexane. Preferably, the solution also includes a higher boiling component to promote self-levelling of the coating. Examples include n-hexanol and 2-butoxyethanol.

To enable the silicon components to hydrolyse, the coating composition will also contain water. Sufficient water should be included to permit complete hydrolysis of the hydrolysable silicon compounds but if too much water is present the resultant solution, after hydrolysis of the silicon compounds, may not adequately wet the substrate to be coated, especially where this is formed of certain synthetic polymers. For example, where the surface is polyimide, it has been found that the water content of the composition prior to hydrolysis of the silicon compounds should preferably be not more than 350% of that required for the total hydrolysis.

In a preferred embodiment, the coating composition comprises

- (i) at least one film-forming silicon compound A selected from those having the structure $\text{Si}(\text{R}'')_4$, $\text{RSi}(\text{R}'')_3$ and $\text{RR}'\text{Si}(\text{R}'')_2$ where each of R and R' is selected from monovalent hydrocarbyl and hydrocarbyloxy groups and R'' is a hydrolysable group.
- (ii) at least one silicon compound B having the structure $\text{X}_l\text{SiY}_n\text{R}''_m$ where X, Y, l, n and m are each as defined above and each R'' is a hydrolysable group; and
- (iii) at least one silicon compound C having the structure $\text{X}'_p\text{SiY}_q\text{R}''_r$ where X',

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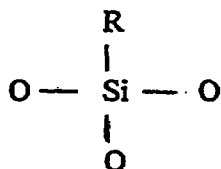
Y, p, q and r are each as defined above and each R" is a hydrolysable group;

and wherein at least some of the molecules contain at least three hydrolysable groups whereby to achieve crosslinking.

Preferred hydrolysable groups are alkoxy and chloride groups.

It will be understood that compounds A having the structure $RR'Si(R'')_2$ will provide units of structure III in the crosslinked copolysiloxane. In the preferred case where crosslinking is provided mainly by units of the structure I, it will be understood that at least some of the molecules of compound A will be of the structure $Si(R'')_4$ or, more preferably, $RSi(R'')_3$.

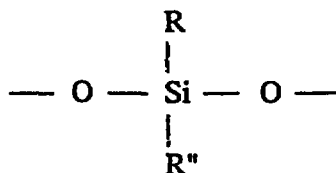
It is possible that not all of the hydrolysable groups of the compounds in the coating composition will be hydrolysed. Thus, for example, a compound A having the structure $RSi(R'')_3$ may give rise to units in the crosslinked copolysiloxane having not only the structure



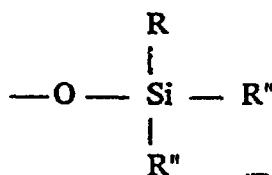
but also the units having the structure

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and even



Compound A is preferably a compound which on hydrolysis and cross-linking will provide a strong hard film able to withstand temperatures of at least 100°C without deteriorating. Particular examples of A are methyltriethoxysilane and tetraethoxysilane. Partially polymerised materials such as polydialkyl- and polydialkoxy-silanes may also be used as, or as part of, component A provided that they can be provided as emulsions or, more preferably, solutions in a solvent for the other components of the composition.

While compound B in principle requires only one hydrolysable group R'', it is preferred that it contains at least two and preferably three such groups and only one group X. Where it contains two hydrolysable groups, it may contain two X groups or one X group and one Y group. Particular examples are 3-aminopropyl triethoxysilane, trimethoxysilylpropyl substituted polyethyleneimine, dimethoxy methyl silyl propyl substituted polyethylene imine and carboxyamide silanes such as those sold as Prosil 9214 and Prosil 9215 by Fluorochem Ltd of Old Glossop, Derbyshire, England.

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Compound C preferably contains at least 2, and preferably 3, hydrolysable groups R".

Specific examples where X' is $\text{CQ}_3\text{Z}-$ are octyl triethoxy silane, decyl triethoxy silane, fluorinated derivatives such as 1H,1H,2H,2H-perfluorooctyl triethoxysilane and 1H,1H,2H,2H perfluorodecyl triethoxysilane and the corresponding compounds wherein one or more of the ethoxy groups are replaced by chlorine, e.g. 1H,1H,2H,2H perfluorooctyl dimethyl chlorosilane. Mixtures of 1H,1H,2H,2H perfluoroalkyl triethoxysilanes having 8, 10 and 12 carbon atoms in the perfluoroalkyl chain may also be used.

Hydrolysis of the silicon compounds of the coating composition and subsequent cross-linking may be promoted by acid or basic conditions. It is therefore preferred that the coating composition also include an additive which shifts the pH of the composition above or below 7. Where the group X of component B is basic, it is preferred that the additive is an acid which will promote protonation of X since this is believed to promote the partition of X and the X' group of component C, at least where X' is $\text{CQ}_3\text{Z}-$. Examples of suitable acids are mineral acids such as hydrochloric and organic acids such as acetic. The amount of acid employed is not believed to be critical provided that it is sufficient to neutralise all of any base present and ensure acidic conditions. Mixtures of acids may be used.

The composition should be formed under clearly acid or basic conditions and therefore it is preferred to add the hydrolysable silicon compounds to an acidic (or basic) solution.

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Prior to application to the substrate to form the coating, the coating composition should be aged to ensure at least partial hydrolysis of the hydrolysable groups. It is particularly important that compound A be at least partially hydrolysed and it is desirable that compounds B and C are also at least partially hydrolysed so as to reduce the possibility of evaporation during the curing required to effect the formation of the crosslinked film. This ageing also improves the mechanical properties of the resulting coating. The ageing may suitably be achieved by allowing the composition to stand at room temperature for several hours. The ageing process might also be accelerated by heat but care must be taken not to induce premature crosslinking leading to the formation of insolubles. The presence of such insolubles will be seen as the formation of cloudiness in the composition. In general, ageing for 1-2 days at room temperature has been found satisfactory. If the ageing step is omitted, the coating may suffer from pinholes or other defects and this is believed to be due to the presence of excess water in the composition which has not been consumed in the hydrolysis.

The at least partially hydrolysed composition may then be applied to the substrate and cured to effect or complete crosslinking. While the substrate may consist of any suitable material whose surface is required to be made non-wetting, the invention is particularly applicable to the treatment of nozzle plates of ink jet print heads. Thus, materials to which the coating may be applied include, in particular, metals (including metals whose surface has been oxidised by atmospheric oxygen), glass, ceramics and synthetic plastics. The invention is particularly applicable to glass, metals and laser-ablatable plastics such as polyimides, polycarbonates, saturated polyesters eg. polyethylene terephthalate and polybutylene naphthenate, and polyether ether ketones.

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Prior to coating, it is preferred that the surface be pre-treated to clean it and, preferably, also increase its surface energy since this has been found to improve adhesion, especially of polyimide surfaces. One preferred pre-treatment for polyimides is to soak the surface in an aqueous alkaline solution, eg. for about an hour, rinse with water and then dry. The coating may then be applied in any suitable manner eg. roller coating, doctor knife coating or spraying. One preferred method is by meter bar whereby the composition is spread over the surface by means of a wire-wound bar. Preferably, the coating is applied as soon as possible after completion of the pre-treatment. The preferred wet coating thickness is 2 to 10 microns. At thicknesses below 2 microns, the coating may be incomplete and no apparent additional benefit is obtained from coatings more than 10 microns thick. Excessive thickness is preferably avoided if the coating is subsequently to be treated, e.g. by laser ablation, to remove some of it. A preferred dry thickness is 0.3 to 1 microns.

The coating is then caused or allowed to cure. Suitably, the cure is accelerated by application of heat and heating may conventionally be effected in an oven at a temperature which will depend upon the choice of the components for the composition but will generally be in the range 60°C to 100°C, preferably about 70 to 95°C. To ensure completion of the formation of the cross-linked film, cure times of several hours, eg. 3 to 24 hours are recommended. Cure may be enhanced if it is effected in an atmosphere of high humidity.

Preferably, the coating is aged prior to the heating step, e.g. by allowing it to stand at room temperature for a few minutes e.g. 5 to 30 minutes, since this has been found to

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improve the properties of the resultant film, and in particular its surface properties and the strength of bond to the substrate. It is believed that this is because the ageing permits partition or "self assembly" of the molecules whereby those carrying the group X- concentrate at the coating/substrate interface where those carrying the group X'- concentrate at the interface of the coating with the atmosphere.

By means of the invention, coatings are obtainable which are strongly bonded to the substrate and provide the desired surface properties. In particular, non-wetting coatings may be obtained which exhibit excellent non-wetting characteristics to a range of ink jet ink compositions including those based on low surface energy solvents such as alkylene glycols, polyalkylene glycols and ethers thereof and hydrocarbons. The required surface energy (mN.m^{-1}) of the coating to provide the desired non-wettability will depend upon the nature of the ink but in general will be less than 20 and preferably less than 10 for non-aqueous inks, and less than 45 and preferably less than 35 for aqueous inks. The coatings moreover are thermally stable up to temperatures as high as 200°C and resistant to abrasion. They also remain undamaged by exposure to pre- and post-ablation treatments such as cleansing with solvents such as acetone and propan-2-ol. A particularly important feature of the coatings where X- is $\text{CQ}_3\text{Z-}$ is their inertness to inks and their substantial freedom from defects.

In a modification of the invention, at least some of the Si atoms in the copolysiloxane may be replaced by tetravalent metal atoms, e.g. Zr and Ti. It is also envisaged that a minor proportion of the Si atoms may be replaced by di- or trivalent metal or metalloid atoms, e.g. B and Al.

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The invention is now illustrated but in no way limited by the following Example in which all parts are expressed by volume except where indicated otherwise.

EXAMPLE

A coating composition was prepared from the following components by first mixing the solvents and acids and then adding the silicon compounds

ethanol	30 parts
glacial acetic acid	0.9 part
hexanol	2.0 parts
hydrochloric acid (0.01 mol/dm ³)	5 parts
methyl triethoxysilane	5 parts
3-aminopropyl triethoxysilane	0.5 part
1H,1H,2H,2H perfluorooctyl triethoxysilane	0.5 part.

The solution so formed was then allowed to stand for 2 days to allow hydrolysis of the silicon compounds.

A sheet of polyimide is washed with about 1 mol/dm³ NaOH, rinsed well with water and dried by wiping with a clean room wipe and then the aged solution is applied to the surface of the sheet using a meter bar to form a wet coating approximately 4 microns thick. The coated sheet is allowed to stand for 5 minutes and then placed in a humid atmosphere in an oven at 95°C for 3 hours. The resulting coating thickness was of the order of 0.6 microns.

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An ink jet print head nozzle plate was then formed from the coated sheet by laser ablation.

The resistance of the nozzle plate to wiping was evaluated by measuring its receding meniscus velocity (RMV) in the following manner. An ink-soaked polyurethane foam pad is drawn across the non-wetting coating surface at a measured velocity. The velocity at which the ink just fails to follow the foam pad and begins to leave a trail of ink upon the non-wetting coating is taken to be the RMV. The minimum RMV for adequate wiping performance is 1.0mm sec^{-1} . The measured RMV was 2.7mm sec^{-1} . The RMV was still greater than 1.0mm sec^{-1} after six weeks' immersion in the ink, indicating a very low level of interaction between the ink and the coating. By way of comparison, prior coatings tended to turn grey after a similar immersion treatment due to adhesion of components of the ink to the coating. The ink employed in the above-mentioned tests was an ink jet printer ink comprising a colloidal dispersion of carbon black in tripropylene glycol monomethyl ether containing a polymeric dispersant.

In a further test, the coated nozzle plate was wiped 50 times with a cotton bud soaked in acetone. No visible damage was perceived.

In another test, the abrasion resistance of the coated nozzle plate was evaluated by rubbing it with a foam pad soaked in ink. The coating survived 1,100 wipes before any loss of non-wetting properties was observed. Examination showed that the loss of performance was due to scratching and not as a result of attack by or absorbance of the ink. The same coating survived over 150,000 rubs with a silicone wiper blade.

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The coating remained non-wetting after heating to 200°C and was still effective after the equivalent of more than 3 months continuous use of a printer fitted with the coated nozzle plate.

Coatings strongly bonded to the substrate were also obtained when the procedure described above was repeated but replacing the perfluorooctyl triethoxysilane with n-octyl triethoxysilane and with a mixture of perfluorooctyl triethoxysilane and n-octyl triethoxysilane.

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CLAIMS

1. A coating on a substrate to endow said substrate with a desired surface property, said coating comprising a crosslinked copolysiloxane containing X'- and X- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'-.
2. A non-wetting crosslinked copolysiloxane coating wherein said polysiloxane contains X'- and X- groups attached to different Si atoms wherein each X' has the formula CQ_3Z- where each Z is a divalent organic group and each X is a monovalent organic group reactive with a group on the substrate surface and has a higher surface tension than the group CF_3Z- .
3. A modification of the coating as claimed in claim 2 wherein in at least some of the CF_3Z- groups one or more of the fluorine atoms are replaced by hydrogen atoms.
4. A coating as claimed in claim 2 or claim 3 wherein the X'- groups are selected from the CH_3- groups, CF_3- groups and a mixture of such groups.
5. A coating as claimed in any one of claims 1 to 4 in which the Si atoms carrying the X'- groups and the Si atoms carrying the X- groups are separated by one or more siloxane layers.

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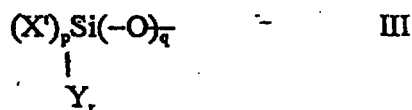
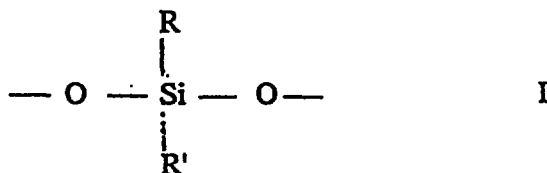
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6. A coating as claimed in claim any one of claims 1 to 5 wherein said copolysiloxane comprises the following repeating units



wherein each of R and R' is selected from monovalent hydrocarbyl groups, monovalent hydrocarbyloxy groups and -O-, each Y is an inert monovalent atom or group, l is 1 or 2, m is 1, 2 or 3, n is 0, 1 or 2, the total of l, m and n being 4; and p is 1 or 2, q is 1, 2 or 3 and r is 0, 1 or 2, the total of p, q and r being 4, provided that in at least some of the said repeating units a silicon atom is attached to at least three -O- groups.

7. A coating as claimed in claim 6 containing units of the structure I wherein at least one of R and R' is -O-.
8. A coating as claimed in claim 7 wherein in most or all of the units of structure I in which at least one of R and R' is -O-, only one of R and R' is -O-.

9. A coating as claimed in claim 6, claim 7 or claim 8 further including repeating

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units containing a polymerisable ethylenically unsaturated group attached to an Si atom.

10. A coating as claimed in any one of claims 6 to 9 wherein

each R is a lower alkyl or alkoxy group;

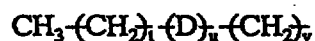
each X is selected from groups containing at least one Zerewitinoff hydrogen atom attached to a nitrogen atom;

each Y is hydrogen, a hydrocarbyl group or a hydrocarbyloxy group;

and each group X' is a group having the structure $\text{CF}_3\text{Z}-$ where Z is a divalent organic group.

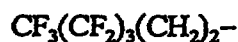
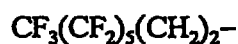
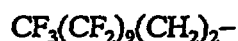
11. A modification of the coating as claimed in claim 10 wherein in at least some of the CF_3- groups, at least one of the fluorine atoms is replaced by a hydrogen atom.

12. A coating as claimed in claim 10 or claim 11 wherein each X' is selected from groups having the structure



where each A is F or CF_3 , d is a divalent atom or group, each of s, t and v is zero or a positive integer with the total of $s + t + v$ being at least one, and u is zero or one.

13. A coating as claimed in claim 12 wherein X' is selected from

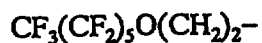


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14. A coating as claimed in any one of claims 6 to 13 wherein X contains an amine group.
15. A coating as claimed in claim 14 wherein X is aminoalkyl.
16. A coating as claimed in any one of claim 6 to 15 wherein l and p are each 1 and m and q are each 3.
17. A coating as claimed in any one of claims 6 to 16 wherein the silicon atoms of units I, II and III form from 75 to 99.1%, from 0.1 to 10% and from 0.01 to 15%, respectively, of the total number of silicon atoms in the copolysiloxane.
18. A coating as claimed in any one of claims 1 to 17 on an ink jet printer nozzle plate.
19. A coating as claimed in claim 18 which is a non-wetting coating and is on a zone of the nozzle plate surrounding a nozzle.
20. A crosslinkable film-forming coating composition for forming a coating as claimed in any one of claims 1 to 19, said composition comprising at least one hydrolysable silicon compound containing the group X' and at least one hydrolysable silicon compound

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containing the group X.

21. A composition as claimed in claim 20 further including (i) a solvent for the silicon compounds present in the composition and (ii) water.

22. A composition as claimed in claim 21 containing water in an amount of from 100 to 350 mole % of that required to effect complete hydrolysis of the hydrolysable groups.

23. A composition as claimed in claim 20, claim 21 or claim 22 comprising

- (i) at least one film-forming silicon compound A selected from those having the structure $\text{Si}(\text{R}'')_4$, $\text{RSi}(\text{R}'')_3$ and $\text{RR}'\text{Si}(\text{R}'')_2$ where each R'' is a hydrolysable group,
- (ii) at least one silicon compound B having the structure $\text{X}_l\text{SiY}_m\text{R}''_n$ where each R'' is a hydrolysable group, l is 1 or 2, m is 1, 2 or 3 and n is 1 or 2, and
- (iii) at least one silicon compound C having the structure $(\text{X}')_p\text{SiY}_q\text{R}''_r$ where each R'' is a hydrolysable group, p is 1 or 2, q is 1, 2 or 3 and r is 1 or 2, provided that at least some of the molecules contain at least three hydrolysable groups.

24. A composition as claimed in claim 23 which includes compounds having the structure $\text{RSi}(\text{R}'')_3$.

25. A composition as claimed in claim 23 or claim 24 wherein X is a basic group, said composition further including an acid.

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26. A composition as claimed in any one of claims 23 to 25 in which at least component A is in at least partially hydrolysed form.
27. A method of providing a substrate with a desired surface property which comprises forming on said surface a crosslinked copolysiloxane coating containing X- and X'- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'-.
28. A method as claimed in claim 26 which comprises applying to a substrate a crosslinkable composition of silicon compounds including a silicon compound containing the group X' and a silicon compound containing the group X and causing or allowing the said silicon compounds to crosslink.
29. A method as claimed in claim 27 or claim 28 for forming a coating on a substrate comprising applying a composition as claimed in claim 26 to a substrate and causing or allowing the components to form a crosslinked film.
30. A method as claimed in claim 28 comprising the steps of
- (i) forming a solution of the composition of claim 23 or claim 24 in a solvent therefor containing water to hydrolyse the hydrolysable groups,
 - (ii) causing or permitting at least partial hydrolysis of at least component A,
 - (iii) applying the solution obtained from step (ii) to a substrate, and

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(iv) causing and permitting the components to form a crosslinked film.

31. A method as claimed in claim 30 in which the coating obtained in step (iii) is allowed to stand before initiating step (iv).

32. A method as claimed in any one of claims 27 to 31 wherein the substrate is selected from glass, metal, ceramics and ablatable synthetic polymers.

33. A method as claimed in claim 32 wherein the substrate is selected from polyimide, polyethylene terephthalate and polybutylene naphthalate.

34. A method as claimed in any one of claims 27 to 33 wherein the substrate is an ink jet printer nozzle plate.

35. A method as claimed in claim 34 wherein the coating is applied to a zone of the nozzle plate surrounding a nozzle.

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COATING. COATING COMPOSITION AND
METHOD OF FORMING COATING

ABSTRACT

A coating on a substrate which endows the substrate with a desired surface property, the coating comprising a cross-linked polysiloxane containing X'- and X- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'-, said coating being bonded to said substrate by reaction of X- groups with substrate surface groups reactive therewith. In one embodiment a non-wetting coating is provided wherein the X'-group has the formula $\text{CF}_3\text{Z-}$ where Z is a divalent organic group or the formula $\text{CH}_3(\text{CH}_2)_t$ where t is at least 3.

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CLAIMS

1. A coating on a substrate to endow said substrate with a desired surface property, said coating comprising a crosslinked copolysiloxane containing X'- and X- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'-; the silicon atoms carrying the X groups and the silicon atoms containing the X' groups being in different siloxane layers of the coating, these layers are separated by at least one further siloxane layer; silicon atoms not attached to X or X' groups form the majority of the total number of silicon atoms in the crosslinked polysiloxane; and the coating is bonded to said substrate by reaction of X- groups with substrate surface groups reactive therewith.
2. A coating as claimed in claim 1 characterised in that the silicon atoms carrying the X groups and the silicon atoms containing the X' groups are in different siloxane layers of the coating, which layers are separated by more than one siloxane layer.
3. A non-wetting crosslinked copolysiloxane coating as claimed in claim 1 or 2 and wherein each X' has the formula CF_3Z- where each Z is a divalent organic group.
4. A coating as claimed in claim 3 wherein Z contains the group $-CH_2-CH_2-$ by which it is attached to the Si atom.
5. A coating as claimed in claim 3 or claim 4 wherein at least some of the CF_3Z- groups one or more of the fluorine atoms are replaced by hydrogen atoms.
6. A coating as claimed in claim 3, claim 4 or claim 5 wherein some or all of the X'-

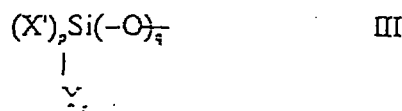
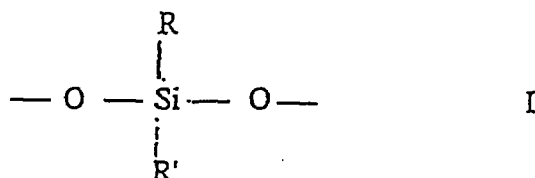
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groups are replaced by CH₃- groups.

7. A coating as claimed in any one of claims 1 to 6 wherein said copolysiloxane comprises the following repeating units



wherein each of R and R' is selected from monovalent hydrocarbyl groups, monovalent hydrocarbyloxy groups and -O-, each Y is an inert monovalent atom or group, l is 1 or 2, m is 1, 2 or 3, n is 0, 1 or 2, the total of l, m and n being 4; and p is 1 or 2, q is 1, 2 or 3 and r is 0, 1 or 2, the total of p, q and r being 4, provided that in at least some of the said repeating units a silicon atom is attached to at least three -O- groups.

8. A coating as claimed in claim 7 containing units of the structure I wherein at least one of R and R' is -O-.

9. A coating as claimed in claim 8 wherein most or all of the units of structure I in which at least one of R and R' is -O-, only one of R and R' is -O-.

10. A coating as claimed in any one of claims 7 to 9 further including repeating units containing an ethylenically unsaturated group attached to an Si atom.



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11. : A coating as claimed in any one of claims 7 to 10 wherein
each R is a lower alkyl or alkoxy group;
each X is selected from groups containing at least one Zerewitinoff hydrogen atom
attached to a nitrogen atom;
each Y is hydrogen, a hydrocarbyl group or a hydrocarbyloxy group;
and each group X' is a group having the structure $\text{CF}_3\text{Z}-$ where Z is a divalent
organic group.
12. A modification of the coating as claimed in claim 11 wherein in at least some of the
 CF_3- groups, at least one of the fluorine atoms is replaced by a hydrogen atom.
13. A coating as claimed in claim 11 or claim 12 wherein each X' is selected from groups
having the structure
- $$\text{A}_3\text{C}-(\text{CF}_2)_s-(\text{CH}_2)_t-(\text{D})_u-(\text{CH}_2)_v \text{ and}$$
- $$\text{CH}_3-(\text{CH}_2)_s-(\text{D})_u-(\text{CH}_2)_v$$
- where each A is F or CF_3 , D is a divalent atom or group, each of s, t and v is zero or a
positive integer with the total of $s + t + v$ being at least one, and u is zero or one.
14. A coating as claimed in claim 13 wherein X' is selected from
- $$\begin{aligned} &\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2- \\ &\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2- \\ &\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_2- \\ &\text{CF}_3(\text{CF}_2)_5\text{O}(\text{CH}_2)_2- \\ &\text{CH}_3(\text{CH}_2)_7- \end{aligned}$$
15. A coating as claimed in any one of claims 7 to 14 wherein X contains a primary
amine group.
16. A coating as claimed in claim 15 wherein X is aminoalkyl.



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17. A coating as claimed in any one of claims 7 to 16 wherein l and p are each 1 and m and q are each 3.
18. A coating as claimed in any one of claims 7 to 17 wherein the silicon atoms of unit I form over 50% of the total number of silicon atoms in the copolysiloxane.
19. A coating as claimed in any one of claims 7 to 18 wherein the silicon atoms of units I, II and III form from 75 to 99%, from 0.1 to 10% and from 0.01 to 15%, respectively, of the total number of silicon atoms in the copolysiloxane.
20. A coating as claimed in claim 19 wherein the silicon atoms of units II and III form from 0.4 to 3% and from 0.1 to 5%, respectively, of the total number of silicon atoms in the copolysiloxane.
21. A coating as claimed in any one of claims 1 to 20 having a thickness in the range 300 to 1000 millimicrons.
22. A coating as claimed in any one of claims 1 to 21 on a substrate selected from ablatable synthetic polymers.
23. A coating as claimed in claim 22 wherein the ablatable synthetic polymer is selected from polyimide, polycarbonate, polyethylene terephthalate, polyether ether ketone and polybutylene naphthenate.
24. A coating as claimed in any one of claims 1 to 23 on an ink jet printer nozzle plate.
25. A coating as claimed in claim 24 which is a non-wetting coating and is on a zone of the nozzle plate surrounding a nozzle.



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26. A crosslinkable film-forming coating composition for forming a coating as claimed in any one of claims 1 to 25 comprising
- (i) at least one film-forming silicon compound A selected from those having the structure $\text{Si}(\text{R}'')_4$, $\text{RSi}(\text{R}'')_3$ and $\text{RR}'\text{Si}(\text{R}'')_2$ where each R'' is a hydrolysable group,
 - (ii) at least one silicon compound B having the structure $\text{X}_l\text{SiY}_n\text{R}_m''$ where each R'' is a hydrolysable group, l is 1 or 2, m is 1, 2 or 3 and n is 1 or 2, and
 - (iii) at least one silicon compound C having the structure $(\text{X}')_p\text{SiY}_q\text{R}_r''$ where each R'' is a hydrolysable group, p is 1 or 2, q is 1, 2 or 3 and r is 1 or 2, where X and X' are as defined in claim 1, provided that at least some of the molecules contain at least three hydrolysable groups.
27. A composition as claimed in claim 26 further including (i) a solvent for the silicon compounds present in the composition and (ii) water.
28. A composition as claimed in claim 27 containing water in an amount of from 100 to 350 mole % of that required to effect complete hydrolysis of the hydrolysable groups.
29. A composition as claimed in any one of claims 26 to 28 which includes compounds having the structure $\text{RSi}(\text{R}'')_3$.
30. A composition as claimed in any one of claims 26 to 29 wherein X is a basic group, said composition further including an acid.
31. A composition as claimed in any one of claims 26 to 30 in which at least component A is in at least partially hydrolysed form.



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32. A method of providing a substrate with a desired surface property which comprises forming on said surface a crosslinked copolysiloxane coating containing X- and X'- groups attached to different Si atoms wherein the groups X'- are monovalent organic groups which provide the desired surface property and the groups X- are monovalent organic groups which are reactive with a group on the substrate surface and have a higher surface tension than the groups X'- and at least one film-forming silicon compound A selected from those having the structure $\text{Si}(\text{R}'')_4$, $\text{RSi}(\text{R}'')_3$ and $\text{RR}'\text{Si}(\text{R}'')_2$ where each R'' is a hydrolysable group, provided that some of the molecules contain at least three hydrolysable groups; and causing or allowing the said silicon compounds to crosslink to form a crosslinked copolysiloxane and the groups X- to react with the substrate surface groups reactive therewith; said at least one compound A being employable in an amount such that the silicon atoms carrying the X- groups and the silicon atoms carrying the X'- groups are in different layers of the coating, which layers are separated by at least one further siloxane layer; and the silicon atoms not attached to X- groups or X'- groups form a majority of the total number of silicon atoms in the crosslinked polysiloxane.
33. A method as claimed in claim 32 for forming a coating on a substrate comprising applying a composition as claimed in claim 26 to a substrate and causing or allowing the components to form a crosslinked film.
34. A method as claimed in claim 32 comprising the steps of
- (i) forming a solution of the composition of claim 26 in a solvent therefore containing water to hydrolyse the hydrolysable groups,
 - (ii) causing or permitting at least partial hydrolysis of at least component A,
 - (iii) applying the solution obtained from step (ii) to a substrate, and
 - (iv) causing and permitting the components to form a crosslinked film.
35. A method as claimed in claim 34 in which the coating obtained in step (iii) is allowed to stand before initiating step (iv).



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36. A method as claimed in any one of claims 32 to 35 wherein the substrate is selected from glass, metal, ceramic and ablatable synthetic polymers.
37. A method as claimed in claim 32 wherein the substrate is selected from polyimide, polyethylene terephthalate and polybutylene naphalate.
38. A method as claimed in any one of claims 32 to 37 wherein the substrate is an ink jet printer nozzle plate.
39. A method as claimed in claim 38 wherein the coating is applied to a zone of the nozzle plate surrounding a nozzle.