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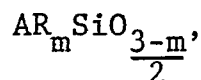
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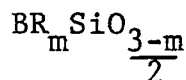
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(54) **Composition for treating carbon fibre precursors.**

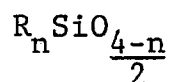
(57) A composition for treating acrylonitrile-based precursor fibres for the production of carbon fibres comprises a siloxane polymer characterised in that the siloxane polymer consists of 1 to 50 siloxane units of the general formula (a)



0 to 50 siloxane units of the general formula (b)



and 10 to 900 siloxane units of the general formula (c)



wherein R is hydrogen or a C₁₋₁₈ hydrocarbon group, A represents either certain amido groups containing organic groups or the reaction product of a silicon-bonded group -R'NH-R⁺ with one or more monoepoxides or lactones, B denotes a polyoxyalkylene group. Fibres produced by a method which includes the treatment with such compositions are superior in cosmetic appearance and strength.

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This invention relates to a composition for treating carbon fibre precursors, more specifically those precursor fibres which are acrylonitrile-based fibre. The invention also relates to the treatment of the precursor, the treated precursor fibres and the use of the composition in the manufacture of carbon fibres.

It is known that one way of obtaining carbon fibres is by thermally stabilising acrylonitrile-based fibres (referred to in the literature and hereinafter as PAN fibres) in an oxidising atmosphere, followed by carbonising the fibres in a non-oxidising atmosphere. The thermal stabilisation of the PAN fibres in an oxidising atmosphere is an exothermic reaction which may result in the local accumulation of heat, causing an uneven reaction and possibly the fusion or embrittlement of the fibres during this step. This will result in fibres which are not of a sufficiently high quality for many applications. Several solutions have been suggested to remedy these shortcomings. For example it has been suggested to impregnate the PAN fibres with organic silicone substances as lubricants prior to the thermal stabilisation step. Proposed silicone substances include dimethyl siloxane polymers, diphenyl siloxane polymers, amino-functional siloxane polymers and epoxy-functional siloxane polymers. The use of such substances, however, tends to generate a static charge on the fibres which may cause entanglement of the fibres and generation of fluff, rendering the production steps of carbon fibres difficult and producing unsatisfactory fibres. To avoid such problems it has been suggested to add antistatic substances, for example anionic or nonionic surfactants, glycerine, polyethylene glycols and polypropylene glycols. The literature suggests that the application of the antistatic materials may be done simultaneously with or subsequent to the application of the organic siloxane substances mentioned above.

The use of the most preferred organic siloxane substance, which is an aminofunctional siloxane polymer, causes some problems as this material tends to form gel particles at the treatment temperature which may be as high as 60 °C, especially in the presence of carbon dioxide, at the temperatures at which in certain processes the PAN fibres are dried, i.e. around 150 °C, or at temperatures at which they are thermally stabilised, i.e. around 250 °C. The problem results in a bath life which is unsatisfactory for pretreatment of the PAN fibres and in a substandard quality of carbon fibres.

There is therefore a need to provide a treating composition which does not gel to the extent of amino-functional siloxane polymers, but which is still as efficient in avoiding fusing, entanglement and fluffing of the fibres during production.

We have now found that if certain nitrogen-containing siloxane polymers are used, improved treating compositions for the PAN fibres are obtained.

According to the invention there is provided a composition for treating acrylonitrile-based precursor fibres for the production of carbon fibres, which comprises a siloxane polymer consisting of 1 to 50 siloxane units having the general formula (a)



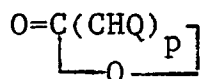
0 to 50 siloxane units of the general formula (b)



and 10 to 900 siloxane units of the general formula (c)



wherein R represents a hydrogen atom or a hydrocarbon group having up to 18 carbon atoms and n and m denote a value of from 0 to 3, A represents either (i) an amido group containing organic group of the general formula R'NQC(O)R, R'C(O)NR₂ or R'[NZ(CH₂)_a]_bNZ(CH₂)_aNZQ, wherein R' denotes a divalent hydrocarbon group having from 2 to 8 carbon atoms, Q represents an alkyl group or a hydrogen atom, each Z represents a hydrogen atom, a lower alkyl group or an RC(O)- group, at least one Z being a RC(O)- group, a is an integer of from 2 to 6 and b has a value of 0, 1 or 2, or (ii) a group which is the reaction product of a silicon-bonded group -R'NH-R⁺ wherein R⁺ denotes a hydrogen atom or a group of the formula R'NHR or R'NHR'NHR with one or more monoepoxides or lactones of the general formula

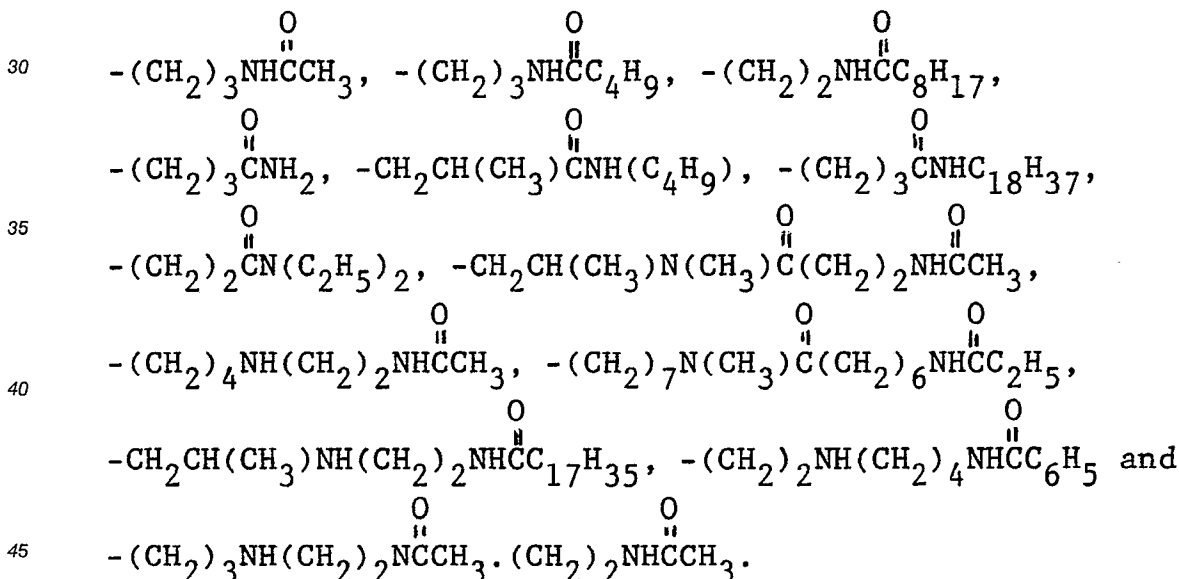


5 wherein Q is as defined above and p has a value from 2 to 7, B denotes a polyoxyalkylene group of the general formula $\text{R}'(\text{OC}_2\text{H}_4)_c(\text{OC}_3\text{H}_6)_d\text{OR}^*$ wherein R^* is a group R or a group $\text{C}(\text{O})\text{R}$, c is an integer and d is 0 or an integer.

Siloxane polymers which are useful in the compositions of the invention are generally linear siloxane polymers, although it is possible that a small amount of branching is present in the polymers. This means that in the general formulae of the siloxane units, m in units (a) and (b) preferably has a value of 1 and n in units (c) preferably has a value of 2. Only small amounts of units wherein m is 0 or n is 0 or 1 are acceptable. Preferably in no more than 2 to 5% of all siloxane units do m or n have such values. At least two siloxane units will be end-blocking units and, in the case of some branching being present in the siloxane polymer, more end-blocking units will be present. The end-blocking units may be units of the formula $\text{R}_3\text{SiO}_{\frac{1}{2}}$, $\text{AR}_2\text{SiO}_{\frac{1}{2}}$ or $\text{BR}_2\text{SiO}_{\frac{1}{2}}$. It is preferred that only two end-blocking units are present and they will both have the formula $\text{R}_3\text{SiO}_{\frac{1}{2}}$.

In siloxane polymers which are useful in the compositions of the invention each R independently denotes a hydrogen atom or a hydrocarbon group having up to 18 carbon atoms. Preferably the silicon-bonded group R is an alkyl or aryl group having up to 8 carbon atoms, for example ethyl, propyl, hexyl, cyclohexyl and phenyl, most preferably at least 80% of all silicon-bonded R groups present are methyl groups.

The group A denotes (i) an amido containing group or (ii) a group which is the reaction product of an amino group with one or more monoepoxides or lactones. In the case of (i) the silicon-bonded group A may be $\text{R}'\text{NQC}(\text{O})\text{R}$ or $\text{R}'\text{C}(\text{O})\text{NR}_2$ wherein R may be hydrogen, methyl, ethyl, butyl, octyl, octadecyl, vinyl or phenyl. Alternatively the group A may be $\text{R}'[\text{NZ}(\text{CH}_2)_a]_b\text{NZ}(\text{CH}_2)_a\text{NZQ}$, wherein Z represents hydrogen or $\text{RC}(\text{O})-$, a is an integer of from 2 to 6 and b is 0, 1 or 2. Examples of A (i) therefore are

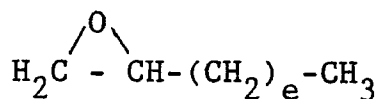


Siloxane polymers having silicon-bonded A groups of the formula $\text{-R}'\text{NQC}(\text{O})\text{R}$ may be prepared for example by reacting the corresponding amino-substituted siloxane polymer with an acid or an acid anhydride. Siloxane polymers wherein the A group has the formula $\text{-R}'\text{C}(\text{O})\text{NR}_2$ may be obtained by reaction of the corresponding carboxylic-substituted siloxane polymer with ammonia or an amine. Suitable preparative methods are known in the art and have been described for example in G.B. patent specifications Nos. 882 059, 882 061 and 1 117 043.

In the case of (ii) where A denotes the reaction product of an amine-containing substituent with either one or more monoepoxides or one or more lactones, the siloxane polymer may be obtained by reacting a siloxane polymer having a silicon-bonded group $\text{-R}'\text{NH-R}^*$, wherein R^* denotes a hydrogen atom or a group of the formula $\text{R}'\text{NHR}$ or $\text{R}'\text{NHR}'\text{NHR}$ with one or more of the reagents. The group R' preferably has from 2 to 8 carbon atoms for example propylene, isobutylene and hexylene. The group R^* may be

hydrogen or a group containing a primary or secondary amine or a diamine. Examples of the amine containing substituents are $-(CH_2)_3NH_2$, $-CH_2CH(CH_3)CH_2NH_2$, $-CH_2CH(CH_3)NH(CH_2)_2NH_2$, $-CH_2CH(CH_3)-CH_2NHCH_2CH_3$ and $-(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$.

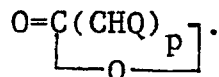
Monoepoxides employed in the preparation of the reaction product are organic compounds having one epoxy group. By the term epoxy is meant a group composed of oxirane oxygen attached to two vicinal carbon atoms. Monoepoxides which are suitable for use are those wherein the substituent of the said vicinal carbon atoms are hydrogen, hydrocarbon groups or ester or ether containing hydrocarbon groups. Preferably one of the carbon atoms has only hydrogen atoms whilst the other carbon atom has an alkyl group attached to it which may range from methyl to a linear C_{21} alkyl group. Most preferred are those monoepoxides wherein the alkyl group has from 1 to 10 carbon atoms especially from 1 to 4 carbon atoms. Examples of suitable monoepoxides are ethylene oxide, propylene oxide, butadiene monoxide, 2,3-epoxycyclopentane, substituted olefin oxides e.g. 2,3 epoxypentylbenzene, epoxy alcohols e.g. glycidol, 2,3 epoxycyclopentanol, 3,4-epoxy-6-methylcyclohexylmethane, glycidyl ethers e.g. phenyl glycidyl ether, butyl glycidyl ether or glycidyl esters e.g. glycidyl acetate. Preferred are those monoepoxides of the general formula



wherein e has a value of from 0 to 20, preferably 0 to 8, most preferably 0 to 3.

The reaction product may be prepared according to known methods. For example the two reagents may be reacted together in the presence of a low molecular weight aliphatic alcohol or in the presence of a catalytic amount of water. The reaction can be carried out at room temperature in the presence of such catalyst but is preferably carried out at increased temperatures, for example temperatures of 50°C or more. Where a primary amine group is present in the siloxane polymer two monoepoxide molecules can react with the amine. The amine groups in the reaction product may be tertiary, secondary or a mixture of those although some unreacted primary amine groups may also still be present.

The lactones which are useful in the preparation of the reaction product have the general formula



It is preferred that Q denotes hydrogen and that p has the value of from 3 to 6. Examples of suitable lactones are γ -butyrolactone and epsilon-caprolactone. The resulting reaction product has substituents which contain the group $=\text{NCO}(\text{CHQ})_p\text{OH}$ linked to a silicon atom via a divalent hydro-carbon group. The reaction is preferably carried out by heating the reactants together for example in aqueous emulsion or in solution, most preferably under reflux in e.g. methyl ethyl ketone, toluene or ethanol. The proportions of the reaction may be chosen according to the number of amino groups one desires to have converted by reaction with the lactone. It will be clear to the person skilled in the art that siloxanes which are useful for incorporation in the composition of the invention can be made not only by the reaction of e.g. polyorganosiloxanes having amine containing substituents, as described above, but equally for example by the reaction of the corresponding silanes which may later be hydrolysed or cohydrolysed with other silanes and/or siloxane polymers, e.g. cyclosiloxanes or by other known methods described in the literature.

The group B in the siloxane polymer, when present, is an oxyalkylene group linked to a silicon atom via an alkylene group. The oxyalkylene group contains oxyethylene units and optionally oxypropylene units. If both units are present it is preferred that the number of oxypropylene units is not greater than the number of oxyethylene units. The number of oxyalkylene units in each group B is preferably not more than 40. It is preferred that the value of c is from 5 to 20 and the value of d from 0 to 20, preferably 10 to 20. The alkylene group R' is preferably a dimethylene, propylene or isopropylene group. The group R^* may be a hydrogen atom, thus resulting in a hydroxyl end-blocked oxyalkylene substituent, an alkyl group or an acyl group. Oxyalkylene substituents can be linked to the siloxane polymer by any of the known methods. For example a siloxane polymer having silicon-bonded hydrogen atoms may be reacted with oxyalkylene groups having unsaturated end groups in the presence of a hydrosilylation catalyst. For example an allyl end-blocked oxyalkylene compound could be reacted giving a group R' which is a propylene unit. Examples of suitable groups B include $-(CH_2)_3(OCH_2CH_2)_{12}OC(O)CH_3$ and $-(CH_2)_3(OCH_2CH_2)_{18}(OCH_2CH-$

(CH₃)₁₈OH. The production of siloxane polymers which have both A and B substituents present may be achieved for example by the cohydrolysis of silane having oxyalkylene substituents, silanes having amine containing substituents and polyalkylcyclsiloxanes in the presence of the appropriate catalyst e.g. acid or alkali compounds, followed by the further reaction of the amino group with e.g. one or more monoepoxides of lactones.

Siloxane polymers which are useful in compositions of the invention may have up to about 1000 siloxane units in the chain. Preferably the polymers will have from 80 to 500 siloxane units, most preferably 100 to 400. It is preferred that the majority of siloxane units have the formula (c), there being up to 12% of all siloxane units those of the formulae (a) and (b) or of formula (a) alone. More preferred are those siloxane polymers where up to 5% of all siloxane units have the formula (a) or the formulae (a) or (b). It is, however, most preferred to use siloxane polymers where no siloxane units of formula (b) are present and where the amount of siloxane units of formula (a) are from 1 to 3% of all siloxane units in the polymer. In those polymers where siloxane units of both formulae (a) and (b) are present it is preferred that the number of siloxane units having the formula (a) is larger than the number of siloxane units with the formula (b).

The PAN fibres which can be treated by the compositions of the invention in order to prepare them for thermal stabilisation prior to the formation of carbon fibres, are well known in the art and contain at least 90 mole% of acrylonitrile derived units and up to 10 moles of units derived from a co-monomer component copolymerisable with acrylonitrile. Preferably the fibre contains at least 95 mole% of acrylonitrile and up to 5 mole% of units derived from the co-monomer. Examples of suitable co-monomers comprise acrylic acid, methacrylic acid, itaconic acid, allyl alcohol, methallyl alcohol, crotonic acid, acrylamide, sodium methallyl sulphate, methylmethacrylate, methylitaconate, 2-(1-hydroxyalkyl)acrylonitrile, esters of 2-(1-hydroxyalkyl)acrylate, allyl sulphonic acid, styrene sulphonic acid, vinyl pyridine and vinyl pyrrolidone.

The compositions of the invention preferably comprise a diluent or carrier for the siloxane polymer. This could be a solvent, for example chlorinated hydrocarbons, aromatic solvents or aliphatic solvents. Preferably, however, the siloxane is provided in an oil-in-water emulsion. Such emulsion preferably has a siloxane content of from 1 to 25% by weight. The emulsion preferably also contains one or more surfactants in order to stabilise it. Suitable surfactants are known in the art and include nonionic polyoxyethylene alkylphenyl phosphates, e.g. octaoxyethylene octylphenyl phosphate and decaoxyethylene dodecylphenyl phosphate, alkoxylates of aliphatic alcohols, e.g. secondary alcohols and polydiorganosiloxane polyoxyalkylene copolymers, e.g. those having a so-called rake structure where the oxyalkylene groups are pendant in the siloxane chain and those having the ABA structure where the oxyalkylene groups are located at the end of the siloxane chain. If the siloxane polymer of the composition of the invention has no groups B present the composition preferably also includes a substance which gives antistatic properties to the treated fibres. Suitable substances include glycerine, alkylene glycol having at least 6 carbon atoms, polyalkylene glycol having at least 20 carbon atoms and polyorganosiloxane polyoxyalkylene copolymers having up to 200 siloxane units in the siloxane chain. The ratio of siloxane polymer to antistatic substance may vary from 1/4 to 4/1 by weight. Preferably the ratio is from 1/2 to 2/1.

The acrylonitrile-based fibres are to be impregnated with the siloxane polymer and, if present, the antistatic substance prior to the thermal stabilisation of the fibres. This may be done by any of the methods which are known in the art. These methods include the addition of the siloxane polymer to the spinning solution and the treatment of the acrylonitrile-based fibre in its water swollen state as it is obtained by spinning. The water swollen fibre can be produced by the wet-spinning process or by the dry-spinning process wherein the extruded spinning solution is introduced into an aqueous coagulating bath. It is necessary that the siloxane polymer is incorporated into the acrylonitrile-based polymer in an amount of from 0.01% to 5% by weight of the fibre, preferably 0.05 to 3%, most preferably 0.5 to 2.5%. It is preferred that the fibre is treated in its water-swollen state by an emulsion of the siloxane polymer. The water-swollen state when the fibre is most suitable for treating with the composition of the invention is usually reached by spinning, water washing and stretching of the fibre. In order to get the best results it is preferred that the fibres have a water content of from 20 to 200% by weight, based upon the weight of the dry fibre. Treated fibres may then be dried or left wet before treating them thermally to stabilise them.

According to the invention there is also provided a method of treating PAN fibres in preparation of their thermal stabilisation which comprises treating the fibres with a composition as described above, before heating the treated fibres. The invention also provides treated PAN fibres and a method of making carbon fibres which comprises treating PAN fibres with a composition as described above.

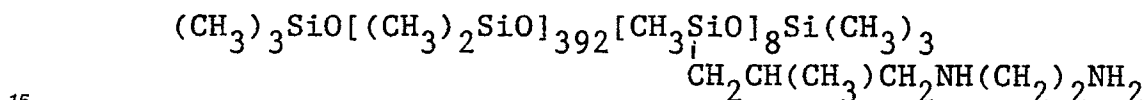
The benefits from using compositions according to the invention lies primarily in that they do not cause any gelling when exposed to elevated temperatures for an extended period. As a result carbon fibres which are produced according to the method are superior to prior art materials in cosmetic appearance. It is also important that the material with which the precursor fibres are treated should leave no residue on the fibres

before they reach the carbonisation step, which follows the thermal stabilisation, and is usually carried out at temperatures of 1000 and 1500 °C. Siloxane polymers which are used in the method of the invention have a thermal decomposition temperature which is far below the carbonisation temperature and leave no residue when thermally decomposed.

5 There now follows an example composition which illustrates the invention.

Example

A 51 flask was fitted with heating facilities, a stirrer, thermometer, nitrogen blanket and dropping funnel.
10 2.534kg of a siloxane polymer of the average formula



was loaded to the flask together with 422g of isopropanol, 169g of methanol and 50g of water. The mixture was heated to 55 to 60 °C with agitation. 165g of 1,2-epoxybutane were slowly added and the mixture was kept at 60 °C for at least 5 hours, after which volatiles were removed at 90 °C and reduced pressure. The
20 resulting polymer was then emulsified by mixing 150g of the polymer thus obtained with 30g of an ethoxylated (5 units) C14 alkyl and 60g of an ethoxylated (7 units) C14 alkyl and stirring the mixture for 10 minutes. Then 322g of water were added in three stages, with 10 minutes of mixing in between, followed by the addition of 435.5g of water with 2.5g of acetic acid under agitation.

When high modulus carbon fibres were produced by treating the polyacrylonitrile precursor fibres with
25 the emulsion of the example, an improvement in the strength of the fibres was found. Compared with a control system in which the emulsion of the example was left out, high modulus fibres were found to have a strength which was on average 0.3 GPa higher than the control fibres. When, instead of the emulsion of the example, a polydimethylsiloxane polyoxyalkylene copolymer was used no improvement in strength was observed over the control. The cosmetic appearance of the high modulus fibres was also compared with the
30 control fibres made without the emulsion of the example. Cosmetic appearance was better for the fibres treated with the emulsion compared with the control. This was confirmed by broken filament count assessment which showed that the fibres treated according to the invention had a broken filament count which was only 46% of the broken filament count for the control.

It can be seen from the above example that carbon fibres made by treating the precursor fibres with a
35 composition according to the invention show improved strength and cosmetic appearance.

Claims

1. A composition for treating acrylonitrile-based precursor fibres for the production of carbon fibres which
40 comprises a siloxane polymer characterised in that the siloxane polymer consists of 1 to 50 siloxane units having the general formula (a)



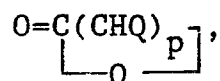
0 to 50 siloxane units of the general formula (b)



and 10 to 900 siloxane units of the general formula (c)

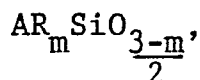


wherein R represents a hydrogen atom or a hydrocarbon group having up to 18 carbon atoms A represents either (i) an amido group containing organic group of the general formula $R'NQC(O)R$, $R'C(O)NR_2$ or $R'[NZ(CH_2)_a]_bNZ(CH_2)_aNZQ$, or (ii) a group which is the reaction product of a silicon-bonded group $-R'NH-R^+$ wherein R^+ denotes a hydrogen atom or a group of the formula $R'NHR$ or $R'NHR'NHR$ with one or more monoepoxides or lactones of the general formula

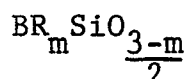


B denotes a polyoxyalkylene group of the general formula $R'(OC_2H_4)_c(OC_3H_6)_dOR^*$, R' denotes a divalent hydrocarbon group having from 2 to 8 carbon atoms, R^* is a group R or a group $C(O)R$, R^+ denotes a hydrogen atom or a group of the formula $R'NHR$ or $R'NHR'NHR$, Q represents an alkyl group or a hydrogen atom, Z represents a hydrogen atom, a lower alkyl group or an $RC(O)-$ group, at least one Z being a $RC(O)-$ group, a is an integer of from 2 to 6, b has a value of 0, 1 or 2, c is an integer and d is 0 or an integer $\bar{n}$ and $\bar{m}$ have a value of from 0 to 3 and $\bar{p}$ has a value from 2 to $\bar{7}$.

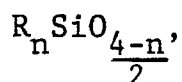
2. A composition according to Claim 1 further characterised in that the siloxane polymer is a substantially linear polymer having no more than 2 to 5% siloxane units which cause branching of the polymer, in that the siloxane polymer consists of a total of from 80 to 500 siloxane units and in that up to 12% of said units have the general formula (a) or (b).
3. A composition according to either Claim 1 or Claim 2 further characterised in that the siloxane polymer does not contain any siloxane units of the general formula (b) and in that the composition also includes a substance which imparts antistatic properties.
4. A composition according to either Claim 1 or Claim 2 further characterised in that the combined value of $\bar{c}$ and $\bar{d}$ in substituent B is not higher than 40 and in that $\bar{d}$ is not larger than $\bar{c}$.
5. A composition according to any one of the preceding claims further characterised in that it also comprises a diluent or carrier for the siloxane polymer.
6. A composition according to any one of the preceding claims further characterised in that it is in the form of an oil-in-water emulsion containing from 1 to 25% by weight of the siloxane polymer.
7. A method of treating acrylonitrile-based precursor fibres for making carbon fibres comprising applying a composition to the precursor fibres prior to heating them, characterised in that the composition comprises a siloxane polymer consisting of 1 to 50 siloxane units of the general formula (a)



0 to 50 siloxane units of the general formula (b)

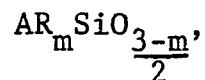


and 10 to 900 siloxane units of the general formula (c)



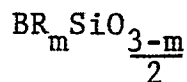
wherein R, A, B, $\bar{m}$ and $\bar{n}$ are as defined above.

8. A method according to Claim 1 further characterised in that sufficient of the composition is applied to give 0.01 to 5% by weight of the siloxane polymer based on the weight of the acrylonitrile-based precursor fibres.
- 5 9. A method according to either Claim 7 or Claim 8 further characterised in that the precursor fibre is treated with the composition when in a water swollen state having a water content of from 20 to 200%.
10. The use of a composition in the manufacture of carbon fibres characterised in that acrylonitrile-based precursor fibres are treated with a composition comprising a siloxane polymer consisting of 1 to 50 siloxane units of the general formula (a)
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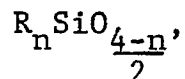
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0 to 50 siloxane units of the general formula (b)



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and 10 to 900 siloxane units of the general formula (c)



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wherein R, A, B, m and n are as defined above prior to heating the fibres.

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