

PATENT SPECIFICATION

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(54) METHOD FOR INCREASING THE HYDROPHILICITY
 OF A SILICONE RUBBER SURFACE

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 AKTIENGESELLSCHAFT,
 a body corporate organised according to the
 laws of the Federal Republic of Germany, of
 Leverkusen, Federal Republic of Germany,
 do hereby declare the invention, for which
 we pray that a patent may be granted to us,
 and the method by which it is to be per-
 formed, to be particularly described in and by
 the following statement:—

The invention relates to a method for
 increasing the hydrophilicity of a surface of
 silicone rubber containing silicon dioxide as
 a filler, for example, the surface of a contact
 lens made of silicone rubber.

British Patent Specification No. 1,362,939
 discloses a method of increasing the hydro-
 philicity of a silicone rubber surface wherein
 the surface is exposed to low-energy radiation
 comprising gaseous ions and electrons pro-
 duced by establishing glow discharge condi-
 tions in a gaseous atmosphere at an ambient
 pressure in the range of from 10^{-2} to 10^{-5}
 Torr, and wherein the body bearing said
 surface is situated on an electrode of the gas
 discharge apparatus and the temperature of
 the surface does not exceed 60°C during its
 exposure to the low-energy radiation.

It is an object of the present invention to
 produce a hydrophilic surface of improved
 stability, and especially to produce a surface
 resistant to hydrolytic influences, thereby
 achieving long-lasting physiological com-
 patibility of the moulded body, for example, a
 contact lens, which has been treated.

The present invention provides a method
 for increasing the hydrophilicity of a surface
 of a silicone rubber which contains silicon
 dioxide as a filler, wherein the surface is
 exposed to low-energy radiation comprising
 gaseous ions and electrons produced by
 establishing glow discharge conditions in a
 gaseous atmosphere consisting substantially
 wholly of oxygen at an ambient pressure in
 the range of from 10^{-2} to 10^{-5} Torr, and
 wherein the body bearing said surface is
 situated on an electrode of the gas discharge
 apparatus and the temperature of the surface

does not exceed 60°C during this exposure
 to the low-energy radiation, the kinetic energy
 of the gaseous oxygen ions being such that a
 surface layer of silicon dioxide is formed com-
 prising decomposed silicone rubber and
 exposed filler.

The proportion of filler in the silicone
 rubber is preferably in the range of from 35
 to 55 per cent by weight.

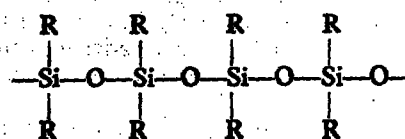
If the filler is of the "prepared" type, that
 is to say, it has been subjected to a surface
 treatment to render it hydrophobic, the hydro-
 phobic outer layer will, in general, be decom-
 posed by the exposure to low-energy radia-
 tion according to the invention so as to expose
 the silicon dioxide itself and thus to increase
 the hydrophilicity of the filler.

Preferably, the gaseous oxygen ions have
 kinetic energy greater than the bond energy
 of the Si—C bond and/or greater than the
 bond energy of the Si—O bond. It is especially
 advantageous for the gas ions to have an
 energy in the range of from 3 to 50 eV.

Advantageously, the oxygen atmosphere
 contains a proportion of water vapour, pre-
 ferably in the range of from 0.1 to 1 per cent.

Preferably, after the exposure to low-energy
 radiation, the hydrophilised silicone rubber
 surface is subjected to the action of water or
 water vapour, advantageously for at least
 twelve hours. The water is preferably at a
 temperature of at least 80°C. Especially good
 results are obtained by the action of water
 vapour on the silicone rubber surface.

The silicone rubber surface is preferably
 the surface of a moulded body comprising a
 cross-linked organopolysiloxane rubber. Linear
 organopolysiloxane rubber has the following
 partial structural formula:



in which R is an organic group, for example
 an alkyl group such as, for instance, a methyl

group; on cross-linking, the polymer chains may, for example, be joined to one another by means of oxygen bridges, so that the final moulded article may be regarded as a single giant molecule.

Preferably, the filler is a reinforcing silicon dioxide filler having a surface area of at least 50 m²/g, as measured by nitrogen adsorption according to the method described in ASTM Special Technical Bulletin No. 51 (1941), pages 95 *et seq.* Fillers of this type may be, for example, silicon dioxide obtained pyrogenically in the gas phase, silicic acid aerogels or silic acid xerogels. Generally speaking, the greater the surface area of the silicon dioxide, the better its performance as a reinforcing filler; accordingly, it is preferred according to the invention to use a silicon dioxide filler having a surface area of at least 150 m²/g, preferably at least 300 m²/g.

Silicon dioxide fillers are generally prepared before blending with silicone rubber, in order to increase the adhesion with the rubber. Compounds which may be used for such preparation include organosilicon compounds, for example, trimethylethoxysilane; treatment with this compound gives a silicon dioxide filler having trimethylsiloxy groups bound on its surface. Silicon dioxide thus treated is strongly hydrophobic, as is a silicone rubber containing such a treated filler.

In order to render the surface of the silicone rubber wettable, it is exposed according to the invention to gaseous oxygen ions, with consequent formation of a surface layer of active SiO₂. This layer consists partly of decomposed rubber, and partly of silicon dioxide filler on which any "preparation", for example a surface layer of trimethylsiloxy groups, has been decomposed. The resulting surface is not only hydrophilic but also resistant to mechanical stress and to hydrolysis.

According to Pauli, the energy of the Si—C bond is approximately 3 eV. In order to break this bond, therefore, a corresponding collision energy of the ions is necessary, which can be produced in a simple manner in a dependent or independent gas discharge.

Preferably, the silicone rubber surface is exposed to negative oxygen ions, which can interact readily with positive silicon resulting from surface decomposition of the polysiloxane. Accordingly, it is also preferable to employ a D.C. voltage, which enables such negative ions to be applied to the surface more efficiently. For the same reasons, it will be appreciated that the body bearing the surface to be treated is then advantageously situated on an anode of the gas discharge apparatus.

If the collision energy of the gaseous ions is equal to or greater than the energy of the bonds Si—C or Si—O, these bonds are broken, and organo-components separate off and can be drawn off under vacuum. Only Si and O₂

are then available as reaction components, and recombination thus occurs.

Ion energies of 3 eV or higher are advantageously used, but experience has shown that an upper limit of 50 eV is preferably not exceeded. Within this energy range a practical number of recombinations to SiO₂ is obtained. If the energy is increased beyond 50 eV, the hydrophilic properties of the surface worsen as the collision energy increases.

By means of the procedure described, the surface of the SiO₂ contained as filler in the polymer is exposed and the organopolysiloxane in between is converted to SiO₂. The effects which occur may be readily understood by reference to the structural formula given hereinbefore for linear organopolysiloxanes.

After the ion treatment, the moulded silicone rubber body is preferably subjected, as previously discussed, to the action of water, preferably for at least twelve hours, and preferably at a temperature of at least 80°C; the water is preferably in the form of water vapour.

Moulded silicone rubber bodies treated according to the invention have a durable hydrophilic surface, which is resistant to hydrolytic splitting of the Si—O bond. As an example, some portions of moulded bodies were treated in accordance with the invention whereas the remaining portions were left untreated. The bodies were then boiled in water for 5000 hours. No noticeable deterioration was observed in the hydrophilic properties of the treated areas, but the non-treated areas had become clouded and noticeably rough.

The following Example illustrates the invention:

EXAMPLE

A circular disc made of organopolysiloxane rubber crosslinked with benzoyl peroxide is 5 mm thick and has a diameter of 20 mm. The disc is placed on an electrically conductive support which lies opposite an electrically conductive plate. The support and the plate, which are about 25 cm apart, form the electrodes of a glow discharge device and are enclosed in a vessel. The vessel is evacuated; after a pressure of approximately 10⁻² Torr has been reached, it is flooded with pure oxygen. The vessel is then re-evacuated and pure oxygen is again admitted until normal pressure is reached again. It is then evacuated once again until a pressure of approximately 10⁻² Torr is reached. When a voltage is applied a glow phenomenon occurs immediately. The current density is approximately 1 mA per cm² and, after 2 minutes at this current density the treatment is discontinued. The plate pre-treated in this way is thereupon boiled in water for 24 hours. The surface then proves to be easily wettable and is resistant to mechanical stress, such as may happen for example to a contact lens as a result of rubbing with the finger-tips during cleaning. Medical

investigations show no reduction in physiological compatibility.

WHAT WE CLAIM IS:—

1. A method for increasing the hydrophilicity of a surface of a silicone rubber which contains silicon dioxide as a filler, wherein the surface is exposed to low-energy radiation comprising gaseous ions and electrons produced by establishing glow discharge conditions in a gaseous atmosphere consisting substantially wholly of oxygen at an ambient pressure in the range of from 10^{-1} to 10^{-3} Torr, and wherein the body bearing said surface is situated on an electrode of the gas discharge apparatus and the temperature of the surface does not exceed 60°C . during its exposure to the low-energy radiation, the kinetic energy of the gaseous oxygen ions being such that a surface layer of silicon dioxide is formed comprising decomposed silicone rubber and exposed filler.
2. A method as claimed in claim 1, wherein the silicone rubber contains from 35 to 55 per cent by weight of filler.
3. A method as claimed in claim 1 or claim 2, wherein the surface is exposed to gaseous oxygen ions having a kinetic energy greater than or equal to the bond energy of the Si—C bond.
4. A method as claimed in any one of claims 1 to 3, wherein the surface is exposed to gaseous oxygen ions having a kinetic energy greater than or equal to the energy of the Si—O bond.
5. A method as claimed in any one of claims 1 to 4, wherein the surface is exposed to gaseous oxygen ions having an energy in the range of from 3 to 50 eV.
6. A method as claimed in any one of claims 1 to 5, wherein the glow discharge is produced by a D.C. voltage.
7. A method as claimed in claim 6, wherein the said electrode is an anode.

8. A method as claimed in any one of claims 1 to 6, wherein the oxygen ions are negative oxygen ions.

9. A method as claimed in any one of claims 1 to 8, wherein the treatment with gaseous ions is carried out in an oxygen atmosphere containing from 0.1 to 1 per cent of water vapour.

10. A method as claimed in any one of claims 1 to 9, wherein the surface is subsequently treated with water.

11. A method as claimed in claim 10, wherein the surface is treated with water for at least 12 hours.

12. A method as claimed in claim 10 or claim 11, wherein the temperature of the water is at least 80°C .

13. A method as claimed in any one of claims 10 to 12, wherein the water is in the form of water vapour.

14. A method as claimed in any one of claims 1 to 13, wherein the silicon dioxide filler has a surface area of at least $50\text{ m}^2/\text{g}$.

15. A method as claimed in claim 14, wherein the surface area is at least $150\text{ m}^2/\text{g}$.

16. A method as claimed in claim 15, wherein the surface area is at least $300\text{ m}^2/\text{g}$.

17. A method as claimed in claim 1, carried out substantially as described in the Example herein.

18. A body having a silicone rubber surface the hydrophilicity of which has been increased by a method as claimed in any one of claims 1 to 17.

19. A body as claimed in claim 18, which is a contact lens.

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investigations show no reduction in physiological compatibility.

WHAT WE CLAIM IS:—

- 5 1. A method for increasing the hydrophilicity of a surface of a silicone rubber which contains silicon dioxide as a filler, wherein the surface is exposed to low-energy radiation comprising gaseous ions and electrons produced by establishing glow discharge conditions in a gaseous atmosphere consisting substantially wholly of oxygen at an ambient pressure in the range of from 10^{-1} to 10^{-3} Torr, and wherein the body bearing said surface is situated on an electrode of the gas discharge apparatus and the temperature of the surface does not exceed 60°C . during its exposure to the low-energy radiation, the kinetic energy of the gaseous oxygen ions being such that a surface layer of silicon dioxide is formed comprising decomposed silicone rubber and exposed filler.
- 10 2. A method as claimed in claim 1, wherein the silicone rubber contains from 35 to 55 per cent by weight of filler.
- 15 3. A method as claimed in claim 1 or claim 2, wherein the surface is exposed to gaseous oxygen ions having a kinetic energy greater than or equal to the bond energy of the Si—C bond.
- 20 4. A method as claimed in any one of claims 1 to 3, wherein the surface is exposed to gaseous oxygen ions having a kinetic energy greater than or equal to the energy of the Si—O bond.
- 25 5. A method as claimed in any one of claims 1 to 4, wherein the surface is exposed to gaseous oxygen ions having an energy in the range of from 3 to 50 eV.
- 30 6. A method as claimed in any one of claims 1 to 5, wherein the glow discharge is produced by a D.C. voltage.
- 35 7. A method as claimed in claim 6, wherein the said electrode is an anode.

8. A method as claimed in any one of claims 1 to 6, wherein the oxygen ions are negative oxygen ions. 45

9. A method as claimed in any one of claims 1 to 8, wherein the treatment with gaseous ions is carried out in an oxygen atmosphere containing from 0.1 to 1 per cent of water vapour. 50

10. A method as claimed in any one of claims 1 to 9, wherein the surface is subsequently treated with water.

11. A method as claimed in claim 10, wherein the surface is treated with water for at least 12 hours. 55

12. A method as claimed in claim 10 or claim 11, wherein the temperature of the water is at least 80°C . 60

13. A method as claimed in any one of claims 10 to 12, wherein the water is in the form of water vapour.

14. A method as claimed in any one of claims 1 to 13, wherein the silicon dioxide filler has a surface area of at least $50\text{ m}^2/\text{g}$. 65

15. A method as claimed in claim 14, wherein the surface area is at least $150\text{ m}^2/\text{g}$.

16. A method as claimed in claim 15, wherein the surface area is at least $300\text{ m}^2/\text{g}$. 70

17. A method as claimed in claim 1, carried out substantially as described in the Example herein.

18. A body having a silicone rubber surface the hydrophilicity of which has been increased by a method as claimed in any one of claims 1 to 17. 75

19. A body as claimed in claim 18, which is a contact lens.

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