

## AMENDED SPECIFICATION

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## PATENT SPECIFICATION

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## (54) METHOD FOR RENDERING SILICONE RUBBER SURFACES HYDROPHILIC

(71) We, AGFA-GEVAERT AKTIENGESELLSCHAFT, a body corporate recognised under German Law, of Leverkusen, 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 performed, to be particularly described in and by the following statement:—

This invention relates to a method for rendering hydrophilic a silicone rubber surface, for example, a silicone rubber surface on a contact lens.

The surfaces of many synthetic materials cannot be wetted. For example, the hydrophobic character of silicone rubbers presents an obstacle to the use of these materials for contact lenses, although other properties of the materials are of advantage for the purpose.

It is an object of the invention to provide a method by means of which the surfaces of articles made of silicone rubbers can be rendered hydrophilic, without any noticeable adverse effect on advantageous properties of the rubber.

The present invention provides a method for rendering a silicone rubber surface of a body hydrophilic, wherein the surface is exposed to low energy radiation comprising gaseous ions and electrons produced by establishing glow discharge conditions in a gaseous atmosphere 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  $60^{\circ}\text{C}$  during its exposure to the low-energy radiation.

The low energy radiation utilised in accordance with the present invention is in

marked contradistinction with the high energy radiation previously proposed for use in, for example, cross-linking silicone and other plastics materials, or in the so-called "cold welding" of organopolysiloxanes, where energies of up to and exceeding 1 MeV are employed.

The activated gaseous ions used in accordance with the present invention may be derived from for example, oxygen and/or nitrogen, carbon dioxide, or an inert gas such as, for example, argon. The ions are produced by means of a glow discharge which will also result, of course, in electron bombardment of the surface that is to be hydrophilised.

Advantageously, an organic compound is also caused to react with the silicone rubber surface, and optionally also with any gas present.

An especially preferred form of the method of the invention will now be described for the purposes of illustration:—

The body bearing the surface that is to be rendered hydrophilic is situated on an electrode of a gas discharge device. Ions are produced from the gas within the device by applying a direct voltage or an alternating voltage, advantageously in the range of from 400 volts to 10 kV, more especially at least 0.5 kV to the electrodes of the device. The temperature of the surface that is to be rendered hydrophilic advantageously lies in the range of from  $20$  and  $60^{\circ}\text{C}$  during the glow discharge.

With regard to the gaseous atmosphere, this may consist of oxygen, nitrogen, or a mixture of these gases. It is of particular advantage to use a carbon dioxide atmosphere

when no additional organic compound is used, and to use an atmosphere comprising an inert gas, for example, argon, when an additional organic compound is used.

5 In operation, the gases are ionised by means of the applied voltage and the resulting active species (ions and electrons) impinge on the silicone rubber surface that is to be treated, whereupon the molecular chains of the poly-  
10 meric material are split up on the surface layer and interact with the active residual gases. Atoms or groups of atoms which produce hydrophilic character are thereby incorporated into the remaining polymer structure of the surface layer.

15 Reaction between an added organic compound and the silicone rubber surface takes place under the influence of the ionised gas and electrons. Advantageously, an organic  
20 compound is used which has a double bond and a terminal functional group.

25 Unsaturated carboxylic acids, for example, acrylic acid and crotonic acid, and their homologues, have proved to be suitable and advantageous.

30 The physical application of the organic compound to the silicone rubber surface, prior to its exposure to the low energy radiation, may be effected by immersing the body bearing the surface into a volume of the compound in question. A quantity of the compound diffuses into the surface layer and remains thereon after the body is taken out prior to exposure.

35 It is also possible to apply the organic compound by rubbing it into the surface that is to be rendered hydrophilic, or by rolling it into a surface layer of the material, prior to vulcanisation, of the body bearing the surface in question.

40 A proportion of the embedded organic material will, in general, be unaffected by the discharge and the retention of such a material may be undesirable for certain articles, for example, contact lenses. Accordingly after  
45 exposure of the surface to the discharge, any residual organic compound remaining in the surface is advantageously removed again by placing the body in water. The residues remaining may also be removed by means of  
50 evaporation, for example, at a high temperature.

55 By means of this method, neither the transparency nor the surface fit of the articles subjected to the process are altered to any degree. Apart from the fact that they can be wetted with liquids, improved adhesion of adhesives is obtained with surfaces treated according to the method of the invention. After  
60 treatment according to the invention, materials which hitherto could not easily be joined together in this manner, can be joined to one another in a simple manner by glueing.

65 A method in accordance with the invention will now be described, by way of example,

with reference to the accompanying drawing, which shows a diagrammatic view of an apparatus which is used for the execution of the method.

Referring to the drawing, the gas inside a vessel 1 is removed by means of a pump 2 until a pressure in the range of from about  $10^{-1}$  to about  $10^{-3}$  Torr is obtained. A valve 3 serves to control the supply of gas into the vessel 1. Inside the vessel 1 there are two electrodes 4 and 5, which are electrically insulated by means of sleeves 4a and 5a from the floor 1a of the vessel. Situated on the electrode 4 is the body 6 that is to have its silicone rubber surface rendered hydrophilic.

70 A glow discharge is produced by applying a suitable direct or alternating voltage of between 500 v. and 10 kv. the residual gases in the vessel 1 are ionised and the ions impinge on the material 6 on the electrode 4. It will be appreciated that electrons will also result from the action of the ionising voltage. Air, oxygen, nitrogen or carbon dioxide may for example serve as the gas to fill the vessel. When the activated gaseous ions meet the surface of the body 6, the molecular chains of the polymer are split up and interact with the activated residual gases. Atoms or groups of atoms which produce hydrophilic character are thereby built into the remaining polymer structure. The use of carbon dioxide as residual gas has proved particularly favourable. The wetting effect achieved by means of the method described is so marked that with contact angle measurement values even as good as that of silicate glass, or better, have been obtained. For example, for an untreated sample, contact angles of  $115^\circ$  are typical, whilst for the treated sample they are only of the order of  $20^\circ$ . It is important to stay within certain temperature limits, and a temperature range of from about  $20^\circ$  to about  $60^\circ$  C has proved most advantageous.

105 It has proved to be especially advantageous for the gaseous atmosphere to contain a proportion of water vapour, which will of course always be the case with unpurified gases.

110 An advantageous modification of the described method consists of the use of organic compounds which can react with the substrate material 6 under the influence of the ionised gases. Subsidiary reactions on the one hand between the ionised gases and the substrate material, and on the other hand between the ionised gases and the organic compounds to be incorporated may also occur. The main effect, however, is substantially brought about by the much higher concentration of the organic compounds.

115 The organic compounds considered here are preferably those which have a double bond and also a terminal functional group.

120 The advantage of these substances stem from their relatively low vapour pressure, as a result of which the risk of premature evap- 130

oration during processing is avoided. Unsaturated carboxylic acids have proved to be very suitable organic compounds for the purpose. Acrylic acid, crotonic acid, and their homologues are cited here as examples.

For preliminary treatment, the substrate material may be immersed in the corresponding organic substance. After being taken out, the substrate is rubbed down and in the dry state is placed in the vessel 1 of the apparatus. The amount of substance diffused into the substrate material is quite sufficient to obtain a good hydrophilic surface. Quantitative conversion of the organic substances introduced into the substrate material does not take place during exposure to the gaseous ions and, for physiological reasons, it is desirable for them to be washed out after processing, by lengthy immersion in water.

Instead of effecting the introduction of suitable organic compounds into the substrate material by immersion, the compounds can be rubbed into the surface or rolled into a surface layer of the initial material which is not yet vulcanised. Advantageously, the organic compound is applied to the surface by being vapourised without decomposition in the presence of the substrate material. Preferably, such vapourisation is effected in the treatment vessel 1.

In order to avoid the possibility of subsidiary reactions with the residual gas when using additional organic compounds, it is of particular advantage to use an inert gas such as argon as residual gas in the vessel 1.

The effect obtained with the method described is a surface effect, in which the duration and magnitude of the applied voltage determine the depth of penetration.

Neither the transparency nor the surface fit of the substrates introduced into the vessel 1 are altered to any significant degree by the method described. The hydrophilic character of the surface is not diminished even after long storage, and is not affected by mechanical stress arising, for example, from cleaning or rubbing.

It will be appreciated that various modifications can be made to the described apparatus. Thus, for example, the shape of the vessel and the position of the electrodes may be different.

The following Examples when read with reference to the accompanying drawing will further illustrate the invention:

#### Example 1.

A silicone elastomer acid under the trade-name Sigel 2000 by the Wacker Chemie Co. of Munich, Germany, in the form of a plane slab of 20 mm diameter and 3 mm thickness was placed on the metal electrode 4. The slab was fastened by its rim to the metal electrode, which extended beyond the slab along its whole periphery. The opposite electrode

5 was arranged at a distance of 10 cm from the first electrode.

The reaction vessel 1 was then evacuated down to a pressure of  $10^{-1}$  Torr. As soon as this pressure was reached the needle valve 3 was opened and air was admitted to the vessel to maintain the pressure during the subsequent treatment at a constant level. A voltage of 400 V (direct current, arrangement of poles immaterial) was then applied to the electrode and a glow discharge resulted. The current flowing between the electrodes was then set to 0.5 mA per  $\text{cm}^2$  by adjustment of the operating voltage. After a treatment time of 60 seconds the surface of the specimen had reached a temperature of about  $35^\circ\text{C}$ . It is to be noted that at the commencement of the treatment the reaction vessel and specimen were at a temperature of about  $20^\circ\text{C}$ .

After the indicated treatment time the voltage was turned off and the specimen was removed after blowing air through the reaction vessel. The specimen was then stored for 3 days in the open air at room temperature. After applying a drop of water of 0.05 ml the contact angle was found to be  $30^\circ$ . The contact angle of the untreated specimen had been  $105^\circ$ .

The hydrophilic property conferred on the surface by the method described in Example 1 was unaffected up to a temperature of  $80^\circ\text{C}$ . Also, the hydrophilic surface remained intact for a period of 12 months during which the specimen was observed.

#### Example 2.

The same type of silicone elastomer as in Example 1 was situated on an electrode 4 in the same manner as described in that Example. However, prior to bringing the silicone into the reaction vessel the specimen was immersed for 5 minutes in a solution of 10% by weight monomeric methacrylic acid hydroxyethylester, 10% by weight of butanol and 80% by weight of ethyl alcohol. After removing the specimen from the solution the excess liquid was removed by centrifuging.

The reaction vessel was then several times rinsed with argon of a high degree of purity and evacuated. The pressure was then adjusted to  $5 \times 10^{-2}$  Torr.

A voltage of 800 V was then applied resulting in a spontaneous glow discharge. By adjustment of the voltage the current was set for a value of 2 mA/ $\text{cm}^2$ . After a treatment time of about 30 seconds the operation was discontinued. The specimen at that point had reached a temperature of about  $50^\circ\text{C}$ . After removal of the specimen from the reaction it was extracted for 2 days in alcohol.

There was thus obtained a hydrophilic surface exhibiting a contact angle of  $20^\circ$ . These properties of the surface were constant to a temperature of  $90^\circ\text{C}$ . The specimen was of

a durable quality, optically transparent and of a high abrasion resistance.

In general a treatment time may be used of from a few seconds up to a few hours. The actual treatment time depends on the discharge current and the kinetic energy of the bombarding discharge particles.

#### WHAT WE CLAIM IS:—

1. A method for rendering a silicone rubber surface of a body hydrophilic, wherein the surface is exposed to low energy radiation comprising gaseous ions and electrons produced by establishing glow discharge conditions in a gaseous atmosphere 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  $60^{\circ}\text{C}$  during its exposure to the low-energy radiation.
2. A method as claimed in claim 1, wherein the temperature of the said surface is maintained in the range of from  $20^{\circ}$  to  $60^{\circ}\text{C}$  during said exposure.
3. A method as claimed in claim 1 or claim 2, wherein the glow discharge is produced by a voltage in the range of from 400 volts to 10 kv.
4. A method as claimed in claim 3, wherein the glow discharge is produced by a voltage in the range of from 400 to 800 volts.
5. A method as claimed in claim 3, wherein the voltage is at least 0.5 kv.
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 said electrode is an anode.
8. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises oxygen.
9. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises nitrogen.
10. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises a mixture of oxygen and nitrogen.
11. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises carbon dioxide.
12. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises an inert gas.
13. A method as claimed in claim 12, wherein the atmosphere comprises argon.
14. A method as claimed in any one of claims 1 to 13, wherein the gaseous atmosphere contains a proportion of water vapour.
15. A method as claimed in any one of claims 1 to 14, wherein an organic compound is applied to the silicone rubber surface and

caused to react therewith under the influence of the ions and electrons.

16. A method as claimed in claim 15, wherein the organic compound is one having a double bond and a terminal functional group.

17. A method as claimed in claim 16, wherein the organic compound comprises an unsaturated carboxylic acid.

18. A method as claimed in claim 17, wherein the acid comprises acrylic acid, crotonic acid, or a homologue thereof.

19. A method as claimed in any one of claims 15 to 18, wherein the application of the organic compound to the surface is effected by temporarily immersing the substrate body bearing the surface in a quantity of the compound.

20. A method as claimed in any one of claims 15 to 18, wherein the application of the organic compound to the surface is effected by rubbing the compound into the surface.

21. A method as claimed in any one of claims 15 to 18, wherein the application of the organic compound to the surface is effected by rolling the compound into a surface layer of the substrate body prior to vulcanisation of the silicone rubber.

22. A method as claimed in any one of claims 15 to 18, wherein the organic compound is applied to the surface by being vapourised without decomposition in the presence of the substrate body bearing the surface that is to be rendered hydrophilic.

23. A method as claimed in claim 22, wherein the vapourisation is effected in the vessel in which the glow discharge conditions are to be established.

24. A method as claimed in any one of claims 15 to 23, wherein unreacted organic material is removed from the hydrophilised surface resulting from said exposure to ions and electrons.

25. A method as claimed in claim 24, wherein the said removal is effected by immersing in water the substrate body bearing the hydrophilised surface.

26. A method as claimed in claim 24, wherein the removal is effected by evaporating the residual organic material.

27. A method for rendering a silicone rubber surface hydrophilic, conducted substantially as described herein with reference to the accompanying drawing.

28. A body having a silicone rubber surface that has been rendered hydrophilic by a method as claimed in any one of claims 1 to 27.

29. A body as claimed in claim 28, which is a contact lens.

a durable quality, optically transparent and of a high abrasion resistance.

In general a treatment time may be used of from a few seconds up to a few hours. The actual treatment time depends on the discharge current and the kinetic energy of the bombarding discharge particles.

#### WHAT WE CLAIM IS:—

1. A method for rendering a silicone rubber surface of a body hydrophilic, wherein the surface is exposed to low energy radiation comprising gaseous ions and electrons produced by establishing glow discharge conditions in a gaseous atmosphere 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  $60^{\circ}\text{C}$  during its exposure to the low-energy radiation.

2. A method as claimed in claim 1, wherein the temperature of the said surface is maintained in the range of from  $20^{\circ}$  to  $60^{\circ}\text{C}$  during said exposure.

3. A method as claimed in claim 1 or claim 2, wherein the glow discharge is produced by a voltage in the range of from 400 volts to 10 kv.

4. A method as claimed in claim 3, wherein the glow discharge is produced by a voltage in the range of from 400 to 800 volts.

5. A method as claimed in claim 3, wherein the voltage is at least 0.5 kv.

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 said electrode is an anode.

8. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises oxygen.

9. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises nitrogen.

10. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises a mixture of oxygen and nitrogen.

11. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises carbon dioxide.

12. A method as claimed in any one of claims 1 to 7, wherein the gaseous atmosphere comprises an inert gas.

13. A method as claimed in claim 12, wherein the atmosphere comprises argon.

14. A method as claimed in any one of claims 1 to 13, wherein the gaseous atmosphere contains a proportion of water vapour.

15. A method as claimed in any one of claims 1 to 14, wherein an organic compound is applied to the silicone rubber surface and

caused to react therewith under the influence of the ions and electrons.

16. A method as claimed in claim 15, wherein the organic compound is one having a double bond and a terminal functional group.

17. A method as claimed in claim 16, wherein the organic compound comprises an unsaturated carboxylic acid.

18. A method as claimed in claim 17, wherein the acid comprises acrylic acid, crotonic acid, or a homologue thereof.

19. A method as claimed in any one of claims 15 to 18, wherein the application of the organic compound to the surface is effected by temporarily immersing the substrate body bearing the surface in a quantity of the compound.

20. A method as claimed in any one of claims 15 to 18, wherein the application of the organic compound to the surface is effected by rubbing the compound into the surface.

21. A method as claimed in any one of claims 15 to 18, wherein the application of the organic compound to the surface is effected by rolling the compound into a surface layer of the substrate body prior to vulcanisation of the silicone rubber.

22. A method as claimed in any one of claims 15 to 18, wherein the organic compound is applied to the surface by being vapourised without decomposition in the presence of the substrate body bearing the surface that is to be rendered hydrophilic.

23. A method as claimed in claim 22, wherein the vapourisation is effected in the vessel in which the glow discharge conditions are to be established.

24. A method as claimed in any one of claims 15 to 23, wherein unreacted organic material is removed from the hydrophilised surface resulting from said exposure to ions and electrons.

25. A method as claimed in claim 24, wherein the said removal is effected by immersing in water the substrate body bearing the hydrophilised surface.

26. A method as claimed in claim 24, wherein the removal is effected by evaporating the residual organic material.

27. A method for rendering a silicone rubber surface hydrophilic, conducted substantially as described herein with reference to the accompanying drawing.

28. A body having a silicone rubber surface that has been rendered hydrophilic by a method as claimed in any one of claims 1 to 27.

29. A body as claimed in claim 28, which is a contact lens.



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