

Polysiloxanes, especially silicone rubber, find use in the most widely differing fields of technology and medicine. Silicone rubber has a high oxygen permeability, for which reason this material would also be expected to be suitable for the manufacture of contact lenses. However, silicone rubber is a hydrophobic material and therefore the use of that material as a contact lens material has hitherto posed problems. Various processes are known for hydrophilising this material (EP 33 754, DE-OS 3 004 685, US-PS 4 143 949 and 3 925 178, French Published Specification 2 407 232 and German Auslegeschrift 2 353 495).

There is already known from DE-OS 3 004 685 a process for hydrophilising contact lenses made from silicone rubber, in which the surface of the silicone rubber is provided with a hydrophilic surface layer. This process comprises two steps. In a first step of the process, the silicone rubber is reacted with an oligomeric, SiH-group-containing siloxane in the presence of a catalyst (equilibration reaction) and, in a second step of the process, the equilibrated silicone rubber is subjected either to a reaction with an aqueous base or to a silane addition reaction with compounds containing C=C double bonds. By these means, a silicone rubber is obtained that has good oxygen permeability and the surface layer of which has been made hydrophilic but does not exhibit any increased tendency to form deposits in spite of the high hydrophilicity.

By contrast, the problem of the invention is to provide a moulded silicone rubber article by means of a process that is an improvement over those known hydrophilising processes inasmuch as only one process step, namely only the equilibration reaction, need be carried out in order to make the surface of the moulded silicone rubber

article hydrophilic.

This problem is solved by the features recited in claim 1. The subclaims characterise developments of the invention.

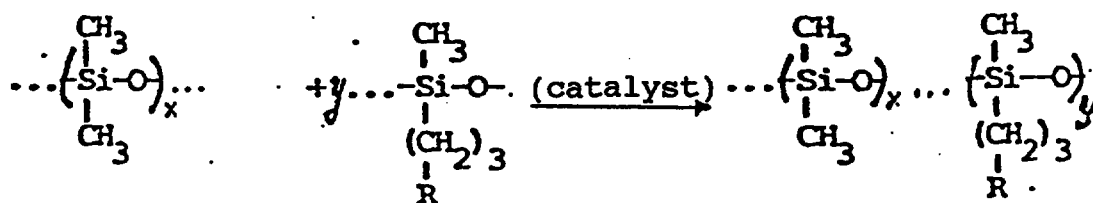
By means of the invention, there is provided a moulded silicone rubber article that has at its surface a hydrophilic composition that can be obtained by a one-step equilibration reaction. The equilibration uses as starting materials special organosiloxanes synthesised by reacting SiH-group-containing siloxanes with allyl compounds that contain protected OH groups, in the presence of catalyst, especially H_2PtCl_6 , and optionally hydrolysing the reaction product subsequently. Procedurally, the hydrolysis can take place during the conditioning of the moulded silicone rubber article and thus does not require a separate process step. The equilibration is also carried out in the presence of a catalyst in a solvent, especially in ethers, suitable catalysts being Lewis acids, especially hexachlorocyclotriphosphazene. The resulting surface composition of the silicone rubber article is hydrophilic whilst the oxygen permeability of the silicone rubber remains unimpaired. There is also no tendency to form deposits at the surface of the silicone rubber article.

In the equilibration, siloxane mixtures of different molecular weights are brought into molecular equilibrium. As catalysts for this, protons and Lewis acids (W.J. Patnode, C.F. Wilcock, J. Am. Chem. Soc. 68, 358 (1946); D.T. Hurd, J. Am. Chem. Soc. 77, 2998 (1955); DE-PS 831 098) can be used.

The treated moulded silicone rubber articles may be polydimethylsiloxane articles that have been crosslinked

hot or cold, the cold-crosslinked materials still containing some SiH groups.

The equilibration educts used may be linear α,ω -organo-dimethylsiloxanes (1 - 4), linear trimethylsilyl-terminated organomethylsiloxanes (7 - 18), cyclic organomethylsiloxanes (20 - 24) and cyclic diorganosiloxanes (25 - 26). The equilibration reaction at the surface of the moulded silicone rubber articles proceeds according to the following reaction scheme:

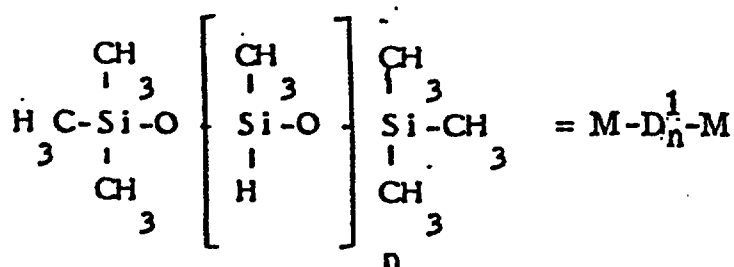


in which x is less than y and R is a hydroxyalkyl group that confers hydrophilicity and creates only a low polarity.

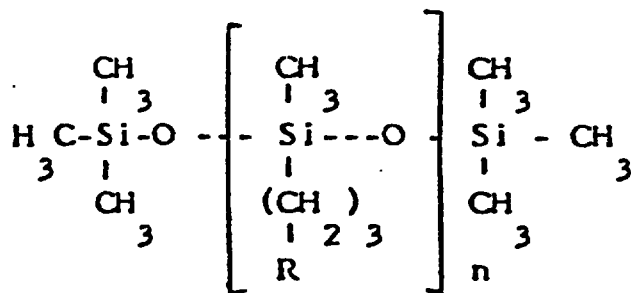
The catalysts used are preferably the Lewis acid 1,1,3,3,5,5-hexachlorocyclotriphosphazene, which gives good results, and concentrated sulfuric acid.

The following were used as linear equilibration educts: 1,3-bis(3-trimethylsilyloxypropyl)-1,1,3,3-tetramethyldisiloxane (1), 1,3-bis(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane (2) (G. Greber, S. Jäger, Makrom. Chem. 57, 150 (1962)), 3,5-bis(3-trimethylsilyloxypropyl)-1,1,1,3,5,7,7,7-octamethyltetrasiloxane, 3,5-bis(3-hydroxypropyl)-1,1,1,3,5,7,7,7-octamethyltetrasiloxane, 1,3-bis(6,7-epoxy-4-oxaheptyl)-1,1,3,3-tetramethyldisiloxane (3) (E.P. Plueddeman, G. Fanger, J. Am. Chem. Soc. 81, 2632 (1959)), 1,3-bis(6,7-dihydroxy-4-oxaheptyl)-1,1,3,3-tetramethyldisiloxane (4), the addition products of allyloxytrimethylsilane (5) and allyl

glycidyl ether (6) with polymethyl hydrogen siloxanes of different chain lengths



in which $n = 2$; 10 to 50 of the general formula

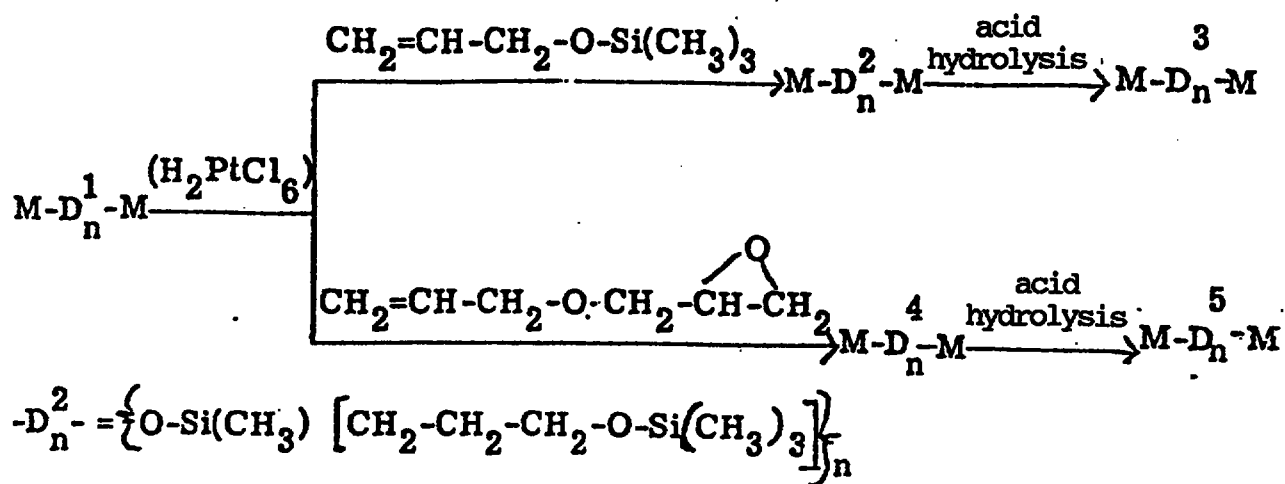


in which R is $\text{-O-Si(CH}_3)_3$; $\text{-O-CH}_2\text{-CH(CH}_2\text{O)}_2\text{-CH}_2\text{-}$

and their hydrolysis products

in which R is -OH; -O-CH₂-CH(OH)-CH₂-OH.

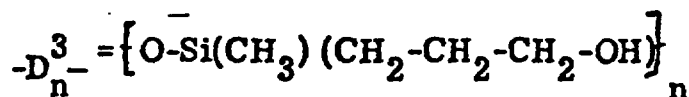
In detail, the reactions involved are the following:



$$n = 2 \text{ (7)}$$

$$n \text{ approx. } 10 \text{ (8)}$$

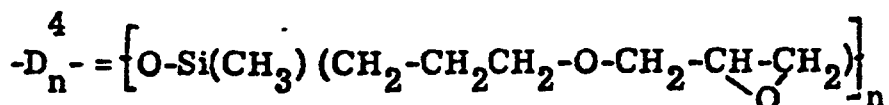
$$n \text{ approx. } 40 \text{ (9)}$$



$$n = 2 \text{ (10)}$$

$$n \text{ approx. } 10 \text{ (11)}$$

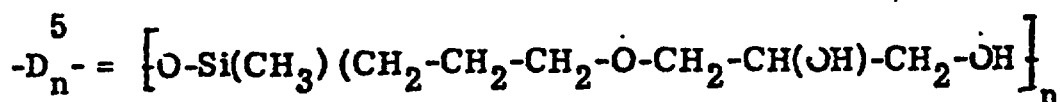
$$n \text{ approx. } 40 \text{ (12)}$$



$$n \text{ approx. } 10 \text{ (13)}$$

$$n \text{ approx. } 40 \text{ (14)}$$

$$n \text{ approx. } 50 \text{ (15)}$$

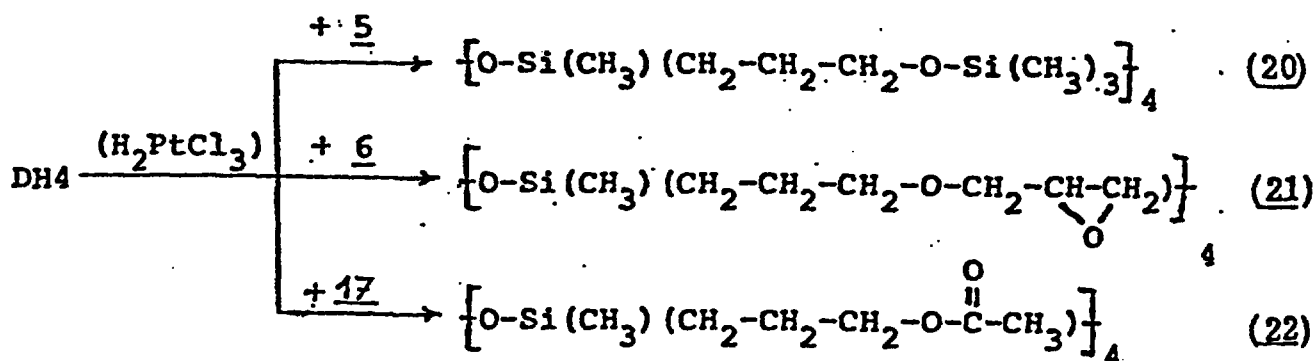


$$n \text{ approx. } 10 \text{ (16)}$$

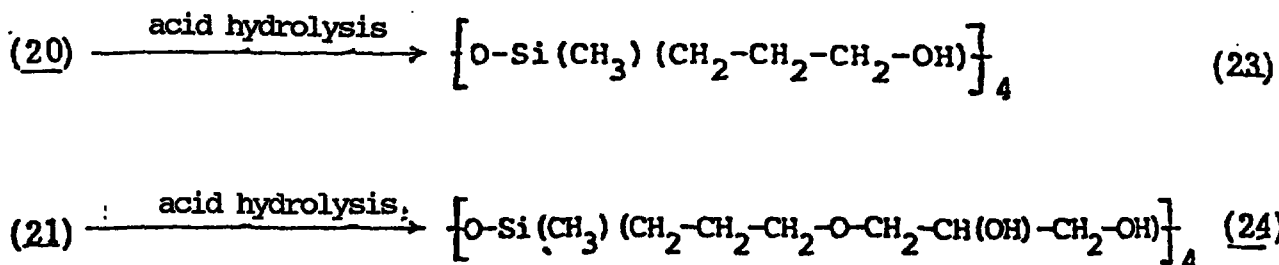
$$n \text{ approx. } 40 \text{ (17)}$$

$$n \text{ approx. } 59 \text{ (18)}$$

The starting compound used for the cyclic organomethylsiloxanes as equilibration educts was 2,4,6,8-tetramethylcyclotetrasiloxane (R.O. Sauer, W.J. Schreiber, St. D. Brewer, J. Am. Chem. Soc. 68, 962 (1946)), referred to as DH4 hereinafter. By addition of (5) or (6) or allyl acetate (19) to DH4, 2,4,6,8-tetrakis(3-trimethylsilyloxypropyl)-2,4,6,8-tetramethylcyclotetrasiloxane (20), 2,4,6,8-tetrakis(6,7-epoxy-4-oxaheptyl)-2,4,6,8-tetramethylcyclotetrasiloxane (21) and 2,4,6,8-tetrakis(3-acetoxypropyl)-2,4,6,8-tetramethylcyclotetrasiloxane (22) (M. Pflanz, unpublished scientific work, Free University of Berlin, 1983) were synthesised:



By hydrolysis of (20) and (21) 2,4,6,8-tetrakis(3-hydroxypropyl)-2,4,6,8-tetramethylcyclotetrasiloxane (23) and 2,4,6,8-tetrakis(6,7-dihydroxy-4-oxaheptyl)-2,4,6,8-tetramethylcyclotetrasiloxane (24) were synthesised:



Examples of cyclic diorganosiloxanes that can be used as equilibrating agents are 2,2,4,4,6,6,8,8-octakis(3-acetoxypropyl)cyclotetrasiloxane (25) and 2,2,4,4,6,6,8,8-octakis(3-hydroxypropyl)cyclotetrasiloxane (26). Their synthesis is described below (A. Fluthwedel, graduate work, Free University of Berlin, 1984).

Starting from SiCl_4 and 2 equivalents of allylmagnesium bromide, diallyldichlorosilane was obtained to which HBr was added under UV irradiation to form bis(3-bromopropyl)dichlorosilane. This was added dropwise at -5 to 0°C to a mixture of ice, NaHCO_3 and ether, producing 2,2,4,4,6,6,8,8-octakis(3-bromopropyl)cyclotetrasiloxane. By boiling that compound with potassium acetate in glacial acetic acid, 2,2,4,4,6,6,8,8-octakis(3-acetoxypropyl)cyclotetrasiloxane (25) was formed which, on methanolysis in the presence of sodium methanolate as transesterification catalyst, yielded 2,2,4,4,6,6,8,8-octakis(3-hydroxypropyl)cyclotetrasiloxane (26).

Diallyldichlorosilane

29 g (170 mmol) of SiCl_4 were introduced into 150 ml of anhydrous ether in a one-litre 3-necked flask equipped with reflux condenser and dropping funnel. Allylmagnesium bromide solution [prepared from 10 g (400 mmol) of magnesium and 41.5 g (34 mmol) of allyl bromide in 250 ml of anhydrous ether], filtered through glass wool, was added dropwise at room temperature, MgBrCl precipitating. After boiling for 1.5 hours under reflux and washing the residue, diallyldichlorosilane was obtained at 56°C and 16 hPa in the form of a colourless liquid in a 15 % yield.

In addition, allyltrichlorosilane (with a boiling point of 24°C at 16 hPa) was also obtained in a 15 % yield.

$^1\text{H-NMR}$ (CDCl_3): 2.1 (d, SiCH_2- , 2H), 5.2 (d, $-\text{CH}=\text{CH}^1\text{H}^2$, 1H), 5.3 (s, $\text{CH}=\text{CH}^1\text{H}^2$, 1H), 5.8 (m, $\text{CH}_2-\text{CH}=\text{CH}_2$, 1H).

Bis(3-bromopropyl)dichlorosilane

In a 100-litre quartz Erlenmeyer flask, HBr was passed into 9.5 g (50 mmol) of the above compound, cooled with ice and water, until samples taken no longer showed the NMR signals of the starting compound (40 minutes). Distillation over a 30 cm rotating band column at 98°C and 0.01 hPa yielded 14.3 g of bis(3-bromopropyl)-dichlorosilane (= 83 %) in the form of a colourless liquid.

IR (Film): 3020 cm^{-1} , ν_{CH} from $-\text{CH}_2-\text{Br}$; 2970 and 2860 cm^{-1} , ν_{CH} ; 1440 cm^{-1} , δ_{CH} ; 1410 cm^{-1} , δ_{CH} from $\text{Si}-\text{CH}_2-$; 770 and 700 cm^{-1} , from C-Br and CH_2 .

^1H -NMR (CDCl_3): 1.30 (q, $\text{Si}-\text{CH}_2-$, 2H), 2.07 (m, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$, 2H), 3.45 (t, $-\text{CH}_2-\text{Br}$, 2H).
MS: 219 (99 %, $\text{M}^+ - (\text{CH}_2)_3\text{Br}$), 177 (100 %, SiBrCl_2)

$\text{C}_6\text{H}_{12}\text{Br}_2\text{Cl}_2\text{Si}$ (343.0) calculated: C 21.01 H 3.53
found: C 20.64 H 3.62

2,2,4,4,6,6,8,8-Octakis(3-bromopropyl)cyclotetrasiloxane

A suspension 6.7 g (80 mmol) of ZnO was introduced into 55 ml of methyl acetate in a 250 ml three-necked flask equipped with condenser and dropping funnel. With stirring, 10 g (30 mmol) of the above compound, dissolved in 30 ml of methyl acetate, were added dropwise. After boiling under reflux for 2 hours, 50 ml of benzene were added. When cool, the solution was filtered with suction and washed twice with 50 ml of water each time. About 80 ml of ethanol were added to the organic phase which was then dried over Na_2SO_4 . After removing the solvent, the desired compound remained behind in the form of a highly viscous colourless oil. Yield: 13.1 g (= 22 %).

$^1\text{H-NMR}$ ($\text{CD}_3\text{-CO-CO}_3$): 0.83 (q, $\text{Si-CH}_2\text{-}$, 2H), 1.9 (m, $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{Br}$, 2H), 3.5 (t, $\text{-CH}_2\text{-Br}$, 2H).

$\text{C}_{24}\text{H}_{48}\text{Br}_8\text{O}_4\text{Si}_4$ (1120.3) calculated: C 25.02 H 4.20
found: C 23.83 H 4.17

2,2,4,4,6,6,8,8-Octakis(3-acetoxypentyl)cyclotetra-
siloxane (25)

15.3 g (13 mmol) of the above compound were added dropwise to a boiling solution of 20 g (20 mmol) of potassium acetate in 30 ml of glacial acetic acid. After boiling under reflux for 24 hours, the precipitated KBr was filtered off with suction and the glacial acetic acid was removed in vacuo. The residue was taken up in ether, the potassium acetate remaining behind. It was washed three times with 25 ml of ether each time. The combined ethereal solutions were concentrated in vacuo at room temperature, to yield the desired compound in the form of a yellowish, viscous substance. Yield 81 %.

$^1\text{H-NMR}$ ($\text{C}_2\text{D}_5\text{-OD}$): 0.66 (t, $\text{Si-CH}_2\text{-}$, 2H), 1.71 (m, $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$, 2H), 2.04 (s, -CH_3 , 3H), 4.04 (t, $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-O-}$, 2H)

MS: 884 (23 %, M^+ - $\{\text{C}_2\text{H}_5\}_3\text{-O-CO-CH}_3$)

$\text{C}_{40}\text{H}_{72}\text{O}_{20}\text{Si}_4$ (985.3) calculated: C 48.76 H 7.37
found: C 46.47 H 7.19

2,2,4,4,6,6,8,8-Octakis(3-hydroxypentyl)cyclotetra-
siloxane (26)

A solution of 0.18 g (7.8 mmol) of sodium is introduced into 20 ml of anhydrous methanol in a 100 ml three-necked flask, and a solution of 2.63 g (2.7 mmol) of the above

compound in 10 ml of anhydrous methanol is added dropwise. The methanol/methyl acetate azeotrope formed is distilled off at 58 - 62°C already during the dropwise addition. When the boiling point of pure methanol was reached, the latter was removed in vacuo. The residue was taken up in about 15 ml of water and neutralised with dilute HCl. It was concentrated to dryness. The residue was digested with ether, the ether used going into solution. The washed product was taken up in ethanol and, in so doing, freed from NaCl. After drying the solution with CaH₂ the solvent was removed in vacuo. The desired compound was obtained in the form of a colourless solid in a 74 % yield.

IR (Film): 3600-3100 cm⁻¹, ν_{CH} ; 2940, 2880 cm⁻¹, ν_{CH} ; 1440 cm⁻¹, δ_{CH} from -CH₂-; 1415, δ_{CH} from Si-CH₂-; 1150, 1010 cm⁻¹, ν_{COH} ; 1060 cm⁻¹ (Si-O-Si for cyclotetra-siloxanes, D.N. Kendall, Applied Infrared Spectroscopy, Chapman & Hall Ltd., London 1966, p. 51).

¹H-NMR (CD₃-OD): 0.64 (m, Si-CH₂-, 2H), 1.64 (m, Si-CH₂-CH₂, 2H), 3.52 (t, -CH₂-OH, 2H), 4.85 (s, -OH, 1H).

C₂₄H₅₆O₁₂Si₄ (649.0) calculated: C 44.47 H 8.70
found: C 43.08 H 7.98

Suitable solvents for the equilibration of the moulded silicone rubber articles are ethers, which must be inert towards the equilibration educts and the silicone rubber materials. The equilibration educts were dissolved in the solvent in question. After the addition of the equilibration catalyst, the moulded articles were slowly stirred in the solution at temperatures of from 80° to 110°C. After the equilibration, the moulded articles were treated further according to the equilibration educt used. If equilibration educts containing OH groups had

been used, the moulded silicone rubber articles were rinsed and dried or conditioned in physiological saline solution. If equilibration agents with protected hydroxy groups are used, the protecting groups can be split off with 5 % mineral acid following the equilibration reaction or the oxirane ring can be opened. After a 24-hour hydration, the moulded silicone rubber articles were dried or conditioned.

Experimental Section

The synthesis of the equilibration educts (1) to (4), (7), (10) and (20) and (23) is described in European Patent Application EP-A1-205 888 entitled "Modified silicone rubber and its use as a material for an optical lens and optical lenses made from that material". These educts can also be prepared in a manner analogous to that described in the following Examples.

Addition of allyl compounds to polymethyl hydrogen siloxanes

10 mmol of trimethylsilyl-terminated polymethyl hydrogen siloxane were placed in 200 ml of dioxane and the batch was heated to boiling temperature. After the addition of 2 ml of 1 % by weight H_2PtCl_6 solution in diethylene glycol dimethyl ether, the allyl compound was added dropwise, with stirring, in an amount equivalent to the $-O-Si(CH_3)_2H$ present. When the reaction mixture had been stirred under reflux for 6 hours, the solution was concentrated and the residual solvent and the unconsumed addition component were removed at 70°C and 0.1 to 0.05 hPa. Insoluble portions were subsequently removed by filtration.

α -(Trimethylsilyl)- ω -(trimethylsilyloxy)polymethyl-(3-

trimethylsilyloxypropyl)siloxane (8) (n approx. 10).

From 7.6 g (10 mmol) of polymethyl hydrogen siloxane M-D_H¹-M (n approx. 10; Baysilon oil MH 4) and 13.0 g (100 mmol) of allyloxytrimethylsilane.

Yield: 19.4 g (94.2 %); $[n]_D^{20}$: 1.4350

C₇₆H₁₉₈O₂₁Si₂₂ (2066.4) calculated: C 44.18 H 9.66
found: C 36.98 H 8.21

α -(Trimethylsilyl)- ω -(trimethylsilyloxy)poly[methyl-(3-trimethylsilyloxypropyl)siloxane] (9) (n approx. 40).

From 25.6 g (10 mmol) of polymethyl hydrogen siloxane M-D_H¹-M (n approx 40; Baysilon oil MH 15) and 52.0 g (400 mmol) of allyloxytrimethylsilane.

Yield: 73.7 g (95 %); $[n]_D^{20}$: 1.4370.

C₂₈₆H₇₃₈O₈₁Si₈₂ (7778.4) calculated: C 44.16 H 9.56
found: C 40.69 H 8.59

α -(Trimethylsilyl)- ω -(trimethylsilyloxy)poly[methyl-(6,7-epoxy-4-oxaheptyl)siloxane] (13) (n approx. 10). From 7.6 g (10 mmol) of polymethyl hydrogen siloxane M-D_H¹-M (n approx. 10; Baysilon oil MH 4) and 11.4 g (100 mmol) of allyl glycidyl ether.

Yield: 18.0 g (94.7 %); $[n]_D^{20}$: 1.4528.

C₇₆H₁₅₈O₃₁Si₁₂ (1905.2) calculated: C 47.91 H 8.36
found: C 47.41 H 8.29

α -(Trimethylsilyl)- ω -(trimethylsilyloxy)poly[methyl-(6,7-epoxy-4-oxyheptyl)siloxane] (14) (n approx. 40). From 25.6 g (10 mmol) of polymethyl hydrogen siloxane M-D_H¹-M (n approx. 40; Baysilon oil MH 15) and 45.6 g (400 mmol) of allyl glycidyl ether.

Yield: 67.1 g (94.2 %); $[n]_D^{20}$: 1.4611.

C₂₈₆H₅₇₈O₁₂₁Si₄₂ (7133.4) calculated: C 48.16 H 8.17
found: C 45.65 H 8.00

α -(Trimethylsilyl)- ω -(trimethylsilyloxy)poly[methyl-(6,7-

epoxy-4-oxaheptyl)siloxane] (15) (n approx. 50). From 31.6 g (10 mmol) of polymethyl hydrogen siloxane M-D_H¹-M (n approx. 50; Baysilon oil MH 20/30) and 57.0 g (500 mmol) of allyl glycidyl ether.

Yield: 84.4 g (95.2 %); [n]_D²⁰: 1.4622.

C ₃₅₆ H ₇₁₈ O ₁₅₁ Si ₅₂ calculated:	C 48.17	H 8.15
found:	C 44.83	H 7.94

Hydrolysis of compounds (8), (9) and (13) - (15)

5 mmol of the siloxane compounds described above were taken up in 100 ml of chloroform, 200 ml of 5 % by weight hydrochloric acid were added thereto and the batch was stirred at room temperature for 12 hours. After the addition of 200 ml of chloroform, stirring was continued for a further 30 minutes. The mixture was transferred to a separating funnel and the aqueous phase was separated off. The organic phase was washed until neutral, dried over Na₂SO₄ and concentrated in a rotary evaporator. The residual portions of solvent and trimethylsilanol or hexamethyldisiloxane were removed in vacuo at 0.1 to 0.05 hPa, the temperature being increased to 70°C towards the end of the removal operation.

α-(Trimethylsilyl)-ω-(trimethylsilyloxy)poly[methyl-(3-hydroxypropyl)siloxane] (11) (n approx. 10). From 10.3 g (5 mmol) of (8). Yield: 6.6 g (98.5 %); [n]_D²⁰: 1.4398.

C ₄₆ H ₁₁₈ O ₂₁ Si ₁₂ (1344.5) calculated:	C 41.09	H 8.85
found:	C 35.78	H 8.28

α-(Trimethylsilyl)-ω-(trimethylsilyloxy)poly[methyl-(3-hydroxypropyl)siloxane] (12) (n approx. 40). From 38.0 g (5 mmol) of compound (9). Yield 24.0 g (98.0 %); [n]_D²⁰: 1.4420.

C ₁₆₆ H ₄₁₈ O ₈₁ Si ₄₂ (4890.9) calculated:	C 40.77	H 8.61
found:	C 36.96	H 8.63

α -(Trimethylsilyl)- ω -(trimethylsilyloxy)poly[methyl-(6,7-dihydroxy-4-oxaheptyl)siloxane] (16) (n approx 10). From 9.5 g (5 mmol) of compound (13). Yield: 9.4 g (90.4 %); $[n]_D^{20}$: 1.4678.

$C_{76}H_{187}O_{41}Si_{12}$ (2085.3) calculated: C 43.77 H 8.60
found: C 38.90 H 7.33

α -(Trimethylsilyl)- ω -(trimethylsilyloxy)poly[methyl-(6,7-dihydroxy-4-oxaheptyl)siloxane] (17) (n approx. 40).

From 35.6 g (5 mmol) of compound (14). Yield: (96.0 %); $[n]_D^{20}$: 1.4755.

$C_{286}H_{658}O_{181}Si_{42}$ (7854.0) calculated: C 43.74 H 8.44
found: C 44.71 H 7.98

α -(Trimethylsilyl)- ω -(trimethylsilyloxy)poly[methyl-(6,7-dihydroxy-4-oxaheptyl)siloxane] (18) (n approx. 50).

From 44.3 g (5 mmol) of compound (15). Yield: 45.4 g (93.0 %); $[n]_D^{20}$: 1.4729.

$C_{356}H_{818}O_{201}Si_{52}$ (9776.9) calculated: C 43.73 H 8.43
found: C 41.12 H 7.70

2,4,6,8-Tetrakis(6,7-epoxy-4-oxaheptyl)-2,4,6,8-tetramethylcyclotetrasiloxane (21)

57.1 g (0.5 mol) of allyl glycidyl ether were placed in a 250 ml three-necked flask equipped with stirrer, dropping funnel, internal thermometer and condenser, and heated to 110°C. After the addition of 1 ml of a 1 % by weight H_2PtCl_6 solution in diethylene glycol dimethyl ether, 24.0 g (0.1 mol) of 2,4,6,8-tetramethylcyclotetrasiloxane were added very rapidly with vigorous stirring, the internal temperature rising to 195°C. After the addition of 2,4,6,8-tetramethylcyclotetrasiloxane, stirring was continued until the temperature of the reaction product had dropped to 130°C. Unreacted portions of allyl

glycidyl ether and 2,4,6,8-tetramethylcyclotetrasiloxane were removed by stirring the reaction mixture at 60 to 70°C under a vacuum of 0.1 hPa produced by an oil pump. The slightly yellowish crude product (77.8 %), $[n]_D^{20}$: 1.4633, was subjected to fractional vacuum distillation using a packed column. Compound (21) distilled over at about 335°C and 1 hPa in the form of a clear viscous liquid, the majority polymerising. $[n]_D^{20}$: 1.4668.

IR (Film): 3060 (m; OCH), 1110 (s; C-O-C) and 1060 cm^{-1} (vs; Si-O-Si).

MS: m/z 333 ($\text{M}-\text{C}_{14}\text{H}_{28}\text{O}_7\text{Si}_2$)⁺ (4); 318 ($\text{M}-\text{C}_{14}\text{H}_{28}\text{O}_7\text{Si}_2$, -CH₃)⁺ (4); 202 ($\text{C}_7\text{H}_{14}\text{O}_3\text{Si}_2$)⁺ (21); 101 ($\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}$)⁺ (41); 85 ($\text{C}_2\text{H}_5\text{OSi}_2$)⁺ (100).

¹H-NMR (CDCl_3): δ = 0.08 (s; Si-CH₃, 12H), 0.42 (m; Si-CH₂-, 8H), 1.50 (m; -CH₂-CH₂-CH₂-, 8H), 2.50 (q; -CH₂-CH-CH₂-O-, 4H), 2.78 (t; -CH₂-CH-CH₂-O-, 4H), 3.10 (m; -CH₂-CH-CH₂-O-, 4H), 3.34 (m; -CH₂-CH₂-O-, 4H), 3.40 (m; -O-CH₂-CH-, 4H), 3.66 (g; -O-CH₂-CH-, 4H).

$\text{C}_{28}\text{H}_{56}\text{O}_{12}\text{Si}_4$ (697.1) calculated: C 48.24 H 8.10
found: C 47.47 H 8.03

2,4,6,8-Tetrakis(6,7-dihydroxy-4-oxaheptyl)-1,4,6,8-tetramethylcyclotetrasiloxane (24).

50 ml of 5 % by weight hydrochloric acid were added to 14 g (20 mmol) of compound (21) and the mixture was stirred at room temperature for 24 hours and then transferred to a separating funnel. 100 ml of ether were added in order to accelerate the separation of the organic from the aqueous phase. After the two phases had been separated, the aqueous phase was extracted twice more with 50 ml of ether each time. The combined ethereal phases were washed with distilled water to remove the acid and were dried over Na_2SO_4 . The majority

solvent was removed in a rotary evaporator and the remainder with stirring under an oil pump vacuum of 0.3 hPa. After filtering with suction through a G-4 glass frit, compound (24) was obtained in the form of a viscous clear liquid. Yield: 14.8 g (96.2 %);

$[n]_D^{20}$: 1.4705.

IR (Film): 3450 (m; -OH), 1115 (vs; C-O-C) and 1085 cm^{-1} (vs; Si-O-Si).

MS: m/z 384 ($\text{M}-\text{C}_{14}\text{H}_{32}\text{O}_8\text{Si}_2$)⁺ (6); 369 ($\text{M}-\text{C}_{14}\text{H}_{32}\text{O}_8\text{Si}_2$, -CH₃)⁺ (8); 192 ($\text{C}_7\text{H}_{17}\text{O}_4\text{Si}$)⁺ (30); 133 ($\text{C}_6\text{H}_{13}\text{O}_3$)⁺ (100).

¹H-NMR (CDCl_3): δ = 0.08 (s; Si-CH₃, 12H), 0.50 (m; Si-CH₂-, 8H), 1.58 (m; -CH₂-CH₂-CH₂-, 8H), 3.0 (s; -CH-OH, 4H), 3.49 (d; -O-CH₂-CH, 8H), 3.54 (m; -CH₂-OH, 4H), 3.56 (m; -CH₂-OH, 8H), 3.94 (m; -CH-OH), 4H).

$\text{C}_{28}\text{H}_{64}\text{O}_{16}\text{Si}_4$ (769.6) calculated: C 43.72 H 8.39

found: C 43.30 H 8.12

2,4,6,8-Tetrakis(3-acetoxypentyl)-2,4,6,8-tetramethylcyclotetrasiloxane (22)

40 g (0.4 mol) of allyl acetate and 1 ml of 1 % by weight H_2PtCl_6 solution in diethylene glycol diethyl ether were heated to 50°C. 24 g (0.1 mol) of DH4 were then added dropwise, the temperature rising to 110°C. At the end of the addition, stirring was continued for a further 20 hours at 60°C. Subsequently, the reaction solution was distilled in vacuo, the compound (22) distilling over in the form of a viscous clear liquid at 122 to 125°C and 1.6 hPa.

Yield: 64.0 g (100 %); $[n]_D^{20}$: 1.4120.

IR (Film): 1745 (vs; $\text{C}=\text{O}$), 1080 (vs; Si-O-Si) and 805 cm^{-1} (Si-CH₃).

MS: m/z 641 (M^+) (2); 439 ($\text{M}-2\text{C}_5\text{H}_9\text{O}_2$)⁺ (81); 338 ($\text{M}-3\text{C}_5\text{H}_9\text{O}_2$)⁺ (75); 43 (CH_3OH)⁺ (100).

¹H-NMR (CCl_4): δ = 0.13 (s; Si-CH₃, 12H), 0.55 (m; Si-CH₂-, 8H), 1.60 (m; -CH₂-CH₂-CH₂-, 8H), 2.0 (s;

CH₃-CO-, 12H), 4.00 (t; -CH₂-O-, 8H).

C₂₄H₄₈O₁₂Si₄ (641.0) calculated: C 44.92 H 7.50
found: C 44.47 H 7.35

General procedure for equilibrating moulded silicone rubber articles (F 1) to (F 18)

Extracted moulded silicone rubber articles in film form that had been crosslinked hot or cold were stirred slowly in an organic ether with the equilibrating reagent and the catalyst. The solvents used, the equilibration components and their concentration, the catalyst concentration, the equilibration time and the reaction temperature are listed in the following Table 1. Table 1 contains selected examples of the preparation of hydrophilic films that have a high oxygen permeability. When the reaction was complete, the films were rinsed with ether/acetone, then stirred for 24 hours in distilled water at room temperature and subsequently dried at 80°C.

If a compound with protected OH groups (such as compound (21)) was used as equilibrating reagent, the procedure described above was followed first. After rinsing with ether/acetone, the films so treated were then rinsed briefly with distilled water and then stirred for 24 hours at room temperature with 5 % by weight hydrochloric acid, subsequently rinsed with distilled water and again hydrated for 24 hours at room temperature and then dried at 80°C.

Discussion of the results

Spectra of the linear equilibrating reagents (7) to (18)

The IR spectra of compounds (2) to (18) show the oscillations at 1260 cm⁻¹ (δ ; Si-CH₃), 1050 cm⁻¹ (ν ; Si-O-Si)

and 800 cm^{-1} (ν_{as} ; Si-CH₃) that are typical of the siloxane structure. In contrast to the starting materials, the valence oscillation band of the Si-H bond at 2170 cm^{-1} is no longer visible; instead, a larger number of bands is to be found in the range $2800 - 3000\text{ cm}^{-1}$, which can be assigned to the symmetric and asymmetric valence oscillations of the methylene group and to the symmetric valence oscillation of the methyl group. The hydrolysed addition products (11), (12), (16), (17) and (18) show the broad absorption band of the OH valence oscillations at 3400 cm^{-1} .

The ^1H -NMR spectra show the expected signals for the siloxane portion at δ approx. 0.1 ppm. The signals for the protons of the organic radicals show the expected chemical shifts.

FMIR-IR spectra of the equilibrated films

N.J. Harrick (J. Phys. Chem. 64, 1110 (1960)) and J. Fahrenfort (Spectrochem. Acta 17, 698 (1961)) describe the so-called ATR-IR recording technique (attenuated total reflection) for strongly absorbing materials. With a special sample-crystal arrangement there is a multiple reflection, the method being referred to as FMIR-IR spectroscopy (frustrated multiple internal reflection). With regard to the position of the bands, FMIR-IR spectra and transmission spectra can be compared with each other. The wave number region from 2700 to 3800 cm^{-1} was used to evaluate the equilibrated films. The nature of the surface of the samples can still be compared well here, as the depth of penetration increases only at longer wave lengths. In the $2700 - 3800\text{ cm}^{-1}$ region, the untreated films show two bands, which must be assigned to the C-H oscillations of the methyl group (ν_{s} ; 2960 cm^{-1} , ν_{as} ; 2900 cm^{-1}).

The spectra of the equilibrated films show OH valence bands of different intensities in the $3300 - 3400 \text{ cm}^{-1}$ region. Moreover, the symmetrical oscillation of the additional CH_2 fragment can be seen at about 2880 cm^{-1} . When linear siloxanes were used as equilibrating educts, the band intensities were found to be higher for the short-chain compounds - (6) than for the siloxanes (7) - (18). Of the siloxanes (7) - (18), good band intensities could be achieved only with siloxane (8). The FMIR-IR spectra of the remaining treated films were hardly different from the spectrum of the untreated sample. The greatest OH band intensities were achieved when the cyclic tetrasiloxanes were used. In this case, the films that had been equilibrated for 4 hours at 100°C and with a catalyst concentration of 1 % by weight based on the amount of siloxane used showed the most intensive increases in OH- and $-\text{CH}_2$ band intensity.

The oxygen permeability of the equilibrated silicone rubber films

The oxygen permeability of the equilibrated silicone rubber films was determined with an oxygen flux meter of the Versatae type. The oxygen permeability of the equilibrated films was not significantly different from that of an untreated film (F-0). Since the oxygen permeability of silicone rubber material depends on the thickness (F.J. Haberich, Referatesammlung der 12. Aschaffenburg Kontaktlinsentagung vom 22. bis 24. März 1979 (Collection of papers of the 12th Aschaffenburg Contact Lens Meeting from 22nd March to 24th March, 1979), page 16), in addition to oxygen permeability P , the transmissivity T and the oxygen flux J are given in Table 2. The films equilibrated with compounds (7) - (18) showed no or only slight changes in the FMIR-IR

spectra; their oxygen permeability was therefore not measured.

The contact angle of the equilibrated silicone rubber films

The contact angle is a characteristic parameter of the wettability of silicone rubber films. Untreated silicone films have contact angles of about 85°. Hydrophilic materials have contact angles smaller than 66° (Ch. F. Kreimer "KontaktlinSENchemie" (Contact Lens Chemistry), Median Verlag Heidelberg, 1980, page 84). The contact angles of the silicone rubber films selected in Table 2 all have significantly smaller values; that is, they show relatively good wettability. This is necessary for materials that are to be used for contact lenses.

The water content of the equilibrated silicone rubber films

The water content was determined by the method of G. Kossmehl, N. Klaus and H. Schäfer (Angew. Makromol. Chem. 123/124, 241 (1984)). The silicone material, hydrophilised only at the surface, has only the low water absorption that is to be expected of a silicone rubber. With two exceptions, the values for the films selected in Table 2 are less than 2 % by weight.

Suitability as a contact lens material

The synthesis of organosiloxanes with terminal OH groups and their equilibration with conventional, commercial silicone rubber films according to the process described above entailed no significant decrease in the oxygen permeability of the silicone rubber films. The values measured for the oxygen permeation permit a transport of

oxygen through the material that is more than adequate for its use as a contact lens material. The high hydrophobicity of the silicone material could be lowered by the surface modification to such an extent that the surface of the material was now hydrophilic. The values for the water content of the silicone rubber films were those also exhibited by untreated silicone material. The silicone rubber films so treated remain transparent and are most suitable as a contact lens material.

Table 1: Details of the preparation of selected silicone rubber films by equilibrating at the film surface

<u>Film</u>	<u>Equilibrating Reagent</u>	<u>Weight %</u>	<u>Solvent</u>	<u>(c) Catalyst in Weight %</u>	<u>t/h</u>	<u>t/°C</u>
<u>F 1</u>	<u>2</u>	10	EGDM ^{a)}	1.0	12	100
<u>F 2</u>	<u>2</u>	10	"-	1.0	24	100
<u>F 3</u>	<u>2</u>	10	"-	0.4	48	100
<u>F 4</u>	<u>4</u>	20	DEGDM ^{b)}	0.4	24	100
<u>F 5</u>	<u>4</u>	20	"-	0.4	2	100
<u>F 6</u>	<u>4</u>	20	"-	0.4	4	100
<u>F 7</u>	<u>23</u>	20	"-	0.4	2	100
<u>F 8</u>	<u>23</u>	20	"-	0.4	4	100
<u>F 9</u>	<u>23</u>	20	"-	0.4	24	100
<u>F 10</u>	<u>23</u>	10	"-	0.4	17	110
<u>F 11</u>	<u>23</u>	10	"-	0.4	20	110
<u>F 12</u>	<u>23</u>	10	"-	0.4	24	110
<u>F 13</u>	<u>23</u>	10	"-	0.4	48	110
<u>F 14</u>	<u>23</u>	20	"-	0.4	24	110
<u>F 15</u>	<u>23</u>	20	"-	0.4	28	110
<u>F 16</u>	<u>24</u>	5	Dioxane	1.0	1	100
<u>F 17</u>	<u>24</u>	5	"-	1.0	4	100
<u>F 18</u>	<u>24</u>	5	"-	1.0	24	100
<u>F 19</u>	<u>22</u>	50	DEGDM	0.5	48	120

a) Ethylene glycol dimethyl ether

b) Diethylene glycol dimethyl ether

c) Hexachlorocyclotriphosphazene

Table 2: Oxygen Permeability, Contact Angle and Water Content of the Equilibrated Silicone Rubber Films

Film	Film Thickness in mm	Oxygen Permeability			Contact Angle in Degrees	Water Content in % by weight
		$P \cdot 10^{11} (a)$	$T \cdot 10^9 (b)$	$J (c)$		
<u>F 0</u>						1.0
<u>F 1</u>	0.308	37.0	12.0	6.7	25	1.0
<u>F 2</u>	0.312	34.6	11.1	6.2	26	1.5
<u>F 3</u>	0.325	3308	10.4	5.8	28	0.3
<u>F 4</u>	0.255	2907	11.6	6.5	30	3.4
<u>F 5</u>	0.300	31.2	10.4	5.8	24	0.5
<u>F 6</u>	0.338	35.5	10.5	5.9	27	1.9
<u>F 7</u>	0.227	25.9	11.4	6.4	30	1.5
<u>F 8</u>	0.235	24.9	10.6	5.9	36	0.9
<u>F 9</u>	0.268	28.5	10.6	5.9	33	1.9
<u>F 10</u>	0.268	32.7	12.2	6.8	30	1.4
<u>F 11</u>	0.282	32.6	11.6	6.5	36	1.2
<u>F 12</u>	0.253	26.6	10.5	5.9	32	2.4
<u>F 13</u>	0.250	26.9	10.8	6.0	27	1.3
<u>F 14</u>	0.282	28.2	10.0	5.6	21	0.2
<u>F 15</u>	0.281	34.0	12.1	6.8	28	1.7
<u>F 16</u>					39	0.8
<u>F 17</u>					48	0.1
<u>F 18</u>					43	0.6
<u>F 19</u>	0.648	39.0	6.0	3.4	22	3.9

a) P in $\text{ml O}_2 \cdot \text{cm}^2 / \text{ml} \cdot \text{mm Hg} \cdot \text{s}$

b) T in $\text{ml O}_2 \cdot \text{cm} / \text{mm Hg} \cdot \text{s} \cdot \text{ml}$

c) J in $\text{l} / \text{cm}^2 \text{ h}$

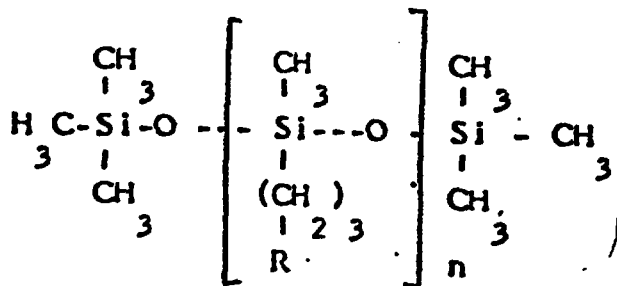
$1 \text{ mm Hg } (0^\circ \text{C}) = 1.333 \cdot 10^2 \text{ Pa}$

The silicone rubber articles, especially the contact lenses or intraocular lenses, can subsequently also be subjected to a surface treatment by plasma polymerisation with the aid of a plasma discharge. The plasma discharge is carried out in an atmosphere that contains the compounds present in the equilibration reaction. The plasma discharge can be produced with direct current or in an alternating electromagnetic field. Preferably, the plasma is discharged at a current intensity of 5 to 500 mA and at a voltage in the range of from 100 to 1000 volts. During the plasma polymerisation, there is a vacuum of 13.3 to 0.13 Pa (10^{-1} to 10^{-3} torr) in the reaction vessel.



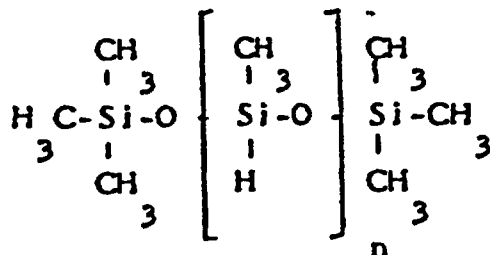
Patent Claims

1. A process for hydrophilising a moulded silicone rubber article at its surface, in which the silicone rubber at the surface of the moulded article is reacted with organosiloxanes (equilibration reaction), wherein the organosiloxanes used in the reaction have been synthesised by reacting SiH-group-containing siloxanes with allyl compounds having protected OH groups, the reaction product then optionally being hydrolysed.
2. A process according to claim 1, wherein the organosiloxanes are one or more of the following compounds: α,ω -organodimethylsiloxanes, linear trimethylsilyl-terminated organomethylsiloxanes, cyclic organomethylsiloxanes and cyclic diorganosiloxanes.
3. A process according to claim 2, wherein the linear α,ω -organodimethylsiloxanes are one or more of the following compounds: 1,3-bis(3-trimethylsilyloxypropyl)-1,1,3,3-tetramethyldisiloxane, 1,3-bis(3-hydroxypropyl)-1,1,3,3-tetramethyldisiloxane, 3,5-bis(3-trimethylsilyloxypropyl)-1,1,1,3,5,7,7,7-octamethyltetrasiloxane, 3,5-bis(3-hydroxypropyl)-1,1,1,3,5,7,7,7-octamethyltetrasiloxane, 1,3-bis(6,7-epoxy-4-oxaheptyl)-1,1,3,3-tetramethyldisiloxane, 1,3-bis(6,7-dihydroxy-4-oxaheptyl)-1,1,3,3-tetramethyldisiloxane.
4. A process according to claim 2, wherein the linear trimethylsilyl-terminated organomethylsiloxanes are addition products of the general formula



wherein R is $-\text{O}-\text{Si}(\text{CH}_3)_3$ or $-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2$

obtained from allyloxytrimethylsilane or allyl glycidyl ether and polymethylhydrogensiloxanes of different chain length and having the general formula



wherein $n = 2$ or from 10 to 50, or are hydrolysis products thereof wherein R is $-\text{OH}$ or $-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{OH}$.

5. A process according to claim 2, wherein the cyclic organomethylsiloxanes and cyclic diorganosiloxanes are one or more of the following compounds: 2,4,6,8-tetrakis(3-trimethylsilyloxypropyl)-2,4,6,8-tetramethylcyclotetrasiloxane, 2,4,6,8-tetrakis(6,7-epoxy-4-oxaheptyl)-2,4,6,8-tetramethylcyclotetrasiloxane, 2,4,6,8-tetrakis(3-acetoxypropyl)-2,4,6,8-tetramethylcyclotetrasiloxane, 2,4,6,8-tetrakis(3-hydroxypropyl)-2,4,6,8-tetramethylcyclotetrasiloxane, 2,4,6,8-tetrakis(6,7-dihydroxy-4-oxaheptyl)-2,4,6,8-tetramethylcyclotetrasiloxane, 2,2,4,4,6,6,8,8-octakis(3-acetoxypropyl)cyclotetrasiloxane and 2,2,4,4,6,6,8,8-octakis(3-hydroxypropyl)cyclotetrasiloxane.



6. A process according to any one of claims 1 to 5, wherein the equilibration reaction is carried out in the presence of a catalyst.
7. A process according to claim 6, wherein a Lewis acid or concentrated sulfuric acid is used as equilibration catalyst.
8. A process according to claim 7, wherein hexachloro-cyclotriphosphazene is used as Lewis acid.
9. A process according to any one of claims 6 to 8, wherein the equilibration reaction is carried out in an ether as solvent.
10. A process according to claim 1, wherein the SiH-group-containing siloxanes are reacted with the allyl compounds in the presence of hexachloroplatinic acid as catalyst.
11. A process according to any one of claims 1 to 10, wherein polydimethylsiloxane is used as the silicone rubber.
12. A process according to any one of claims 1 to 11, wherein the surface is subsequently treated by plasma polymerisation carried out by plasma discharge in an atmosphere which contains the compounds present in the equilibration reaction.
13. A process according to claim 12, wherein the plasma discharge takes place under direct current.
14. A process according to either claim 12 or claim 13, wherein the plasma discharge takes place in an alternat-



ing electromagnetic field.

15. A process according to any one of claims 12 to 14, wherein the plasma discharge takes place at an current of from 5 to 500 mA and at a voltage in the range of from 100 to 1000 volts.

16. A process according to any one of claims 12 to 15, wherein the plasma polymerisation is carried out in a vacuum of 13.3 - 0.13 Pa (10^{-1} to 10^{-3} torr).

17. The use of a silicone rubber article obtainable according to any one of claims 1 to 16 as an optical lens.

18. The use of a silicone rubber article obtainable according to any one of claims 1 to 16 as a contact lens.

19. The use of a silicone rubber article obtainable according to any one of claims 1 to 16 as an intraocular lens.