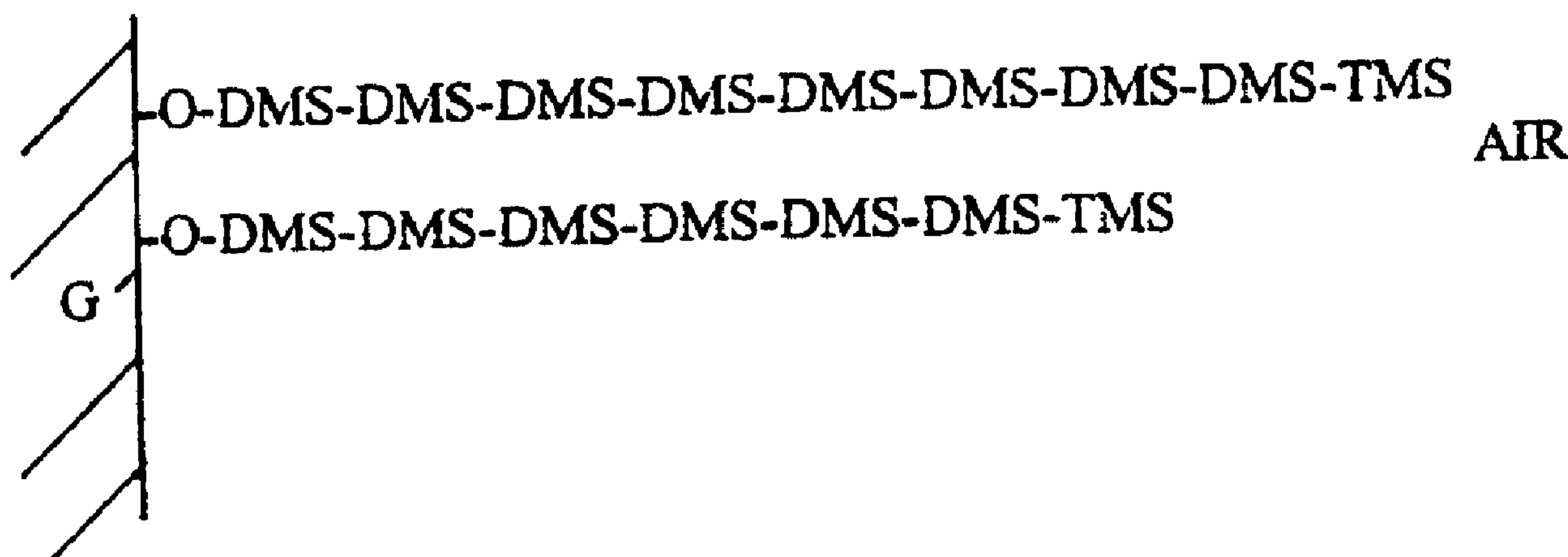




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(72) Inventeur/Inventor:  
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(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : FILM DE SILICONE COIFFEE ET SON PROCEDE D'OBTENTION  
(54) Title: CAPPED SILICONE FILM AND METHOD OF MANUFACTURE THEREOF



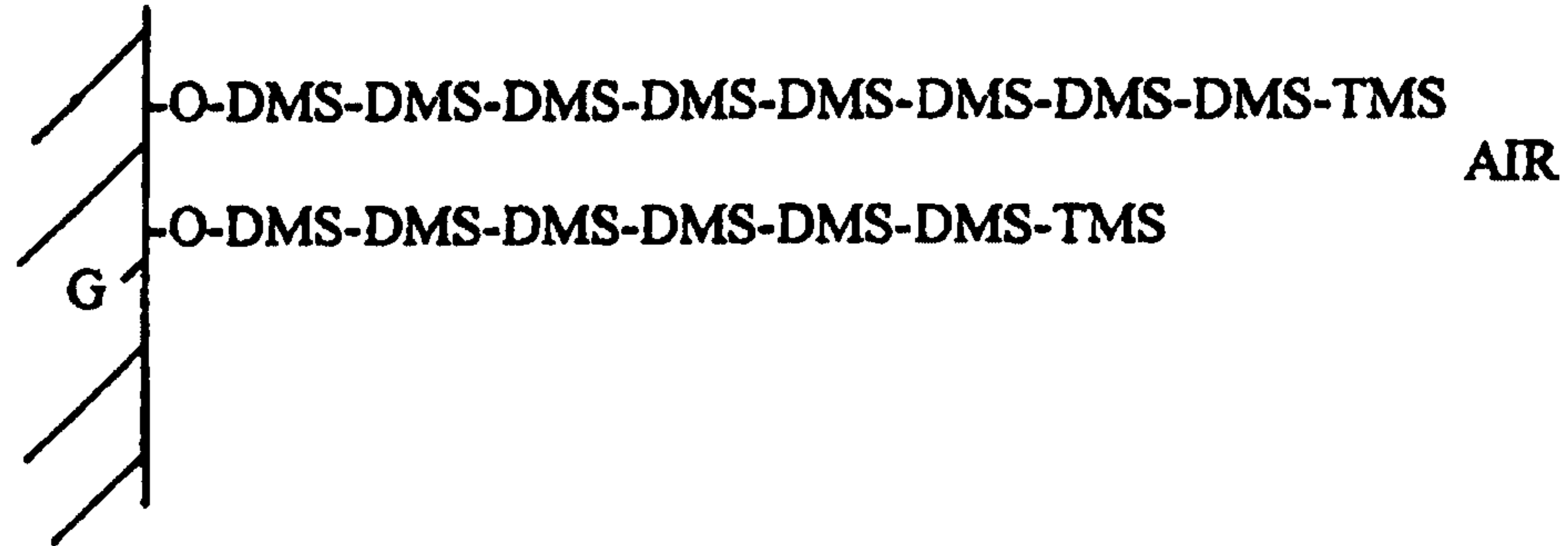
(57) **Abrégé/Abstract:**

A silicone film is attached to a surface by chemical bonding. The silicone film consists of chains of siloxane groups, each chain terminating in an end molecule which is either an ester, an ether, or a halogen. The end molecule is allowed to react with water to produce an OH group. The surface is then contacted with a capping agent which reacts with the OH group to produce a new end group which improves the properties of the film.



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|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |           |                                                                                                                                                                                                                                                                                                                                                                                                                                                              |
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| <b>(51) International Patent Classification <sup>6</sup> :</b><br><b>B05D 1/36, 3/10, B32B 17/06, 17/10</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | <b>A1</b> | <b>(11) International Publication Number:</b> <b>WO 00/25938</b><br><b>(43) International Publication Date:</b> 11 May 2000 (11.05.00)                                                                                                                                                                                                                                                                                                                       |
| <b>(21) International Application Number:</b> PCT/US99/01939<br><b>(22) International Filing Date:</b> 29 January 1999 (29.01.99)<br><b>(30) Priority Data:</b><br>09/185,202      3 November 1998 (03.11.98)      US<br><br><b>(71) Applicant (for all designated States except US):</b> DIA-MON-FUSION INTERNATIONAL, INC. [US/US]; 33012 Calle Perfecto, San Juan Capistrano, CA 92675 (US).<br><br><b>(72) Inventor; and</b><br><b>(75) Inventor/Applicant (for US only):</b> HAYDEN, Don [US/US]; 13755 Skyline Boulevard, Los Gatos, CA 95030 (US).<br><br><b>(74) Agent:</b> MYERS, Richard, L.; Myers, Dawes & Andras, 6th floor, 650 Town Center Drive, Costa Mesa, CA 92626 (US).         |           | <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> CAPPED SILICONE FILM AND METHOD OF MANUFACTURE THEREOF<br><br><div style="text-align: center;">  </div><br><b>(57) Abstract</b><br><p>A silicone film is attached to a surface by chemical bonding. The silicone film consists of chains of siloxane groups, each chain terminating in an end molecule which is either an ester, an ether, or a halogen. The end molecule is allowed to react with water to produce an OH group. The surface is then contacted with a capping agent which reacts with the OH group to produce a new end group which improves the properties of the film.</p> |           |                                                                                                                                                                                                                                                                                                                                                                                                                                                              |

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## CAPPED SILICONE FILM AND METHOD OF MANUFACTURE THEREOF

### Field of the Invention

This invention relates to the art of manufacturing silicone films.

More particularly, this invention relates to a method of manufacturing silicone films for coating surfaces containing OH or nitrogen hydrogen bonds.

In a further and more specific aspect, the instant invention concerns an improved method of manufacturing a water-repellent silicone film for coating glass and other surfaces.

### Description of the Prior Art

Various methods exist for manufacturing easily cleanable, water repellent glass products, including shower doors, windshields, glass entry doors and glass partitions in restaurants. Two such methods are disclosed in U.S. Patents no 5,415,927 to Hirayama et al. and 4,263,350 to Valimont.

In another method currently in use, the glass is coated with a film consisting of chains of silicone molecules, with each chain chemically bound at one end to the surface of the glass. Each chain contains from dozens to hundreds of dimethylsiloxane (DMS) units and is terminated at its free end by either a hydroxyl (OH) group or a chlorine attached to a silicon, which soon reacts with water vapor in the air to produce OH groups. This existing film is in use on a number of glass products as well as other silica-containing products such as granite, porcelain, earthenware and stoneware, and for the most part, has performed satisfactorily. However, the water-repellence of the film is limited to some extent by the presence of

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the terminal OH groups, which are highly water-attracting.

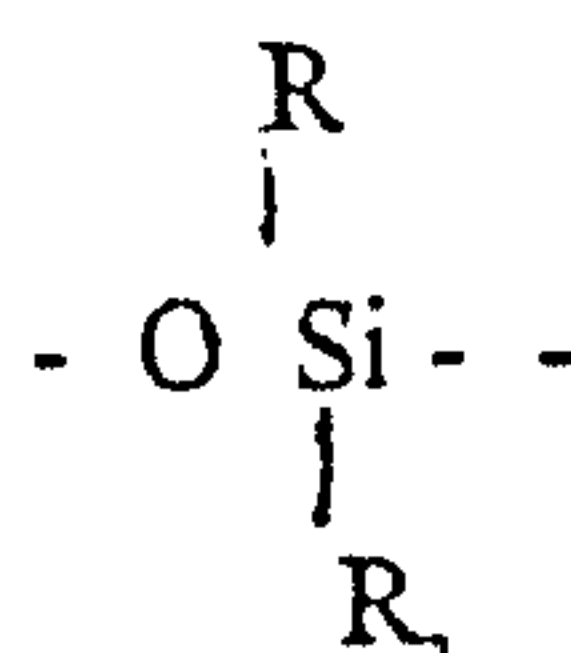
Accordingly, it is an object of the present invention to improve the water-resistance of silicone films on glass, and to provide a support film for chemically active substances.

Another object of the invention is to produce a family of silicone films for treating a variety of products such as the silica-containing products previously mentioned as well as organic substances including paper, cotton, nylon, leather, and wood, in order to improve the surface properties of those products.

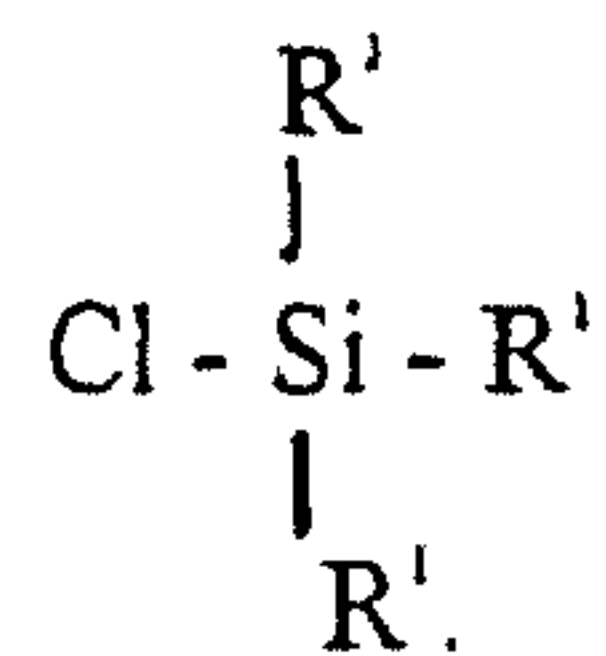
## SUMMARY OF THE INVENTION

Briefly, to achieve the desired objects of the instant invention in accordance with the preferred embodiments thereof, a silicone film is attached to a surface by chemical bonding. The silicone film consists of chains of siloxane groups, each chain terminating in an end molecule which is either an ester, an ether, or a halogen. The end molecule is allowed to react with water in the surrounding air to produce an OH group. The surface is then contacted with a capping agent which reacts with the OH group to produce a new end group which improves the properties of the film.

The specific improvement in properties will depend on the siloxane groups used, as well as the composition of the capping agent. In general, the siloxane groups have the formula



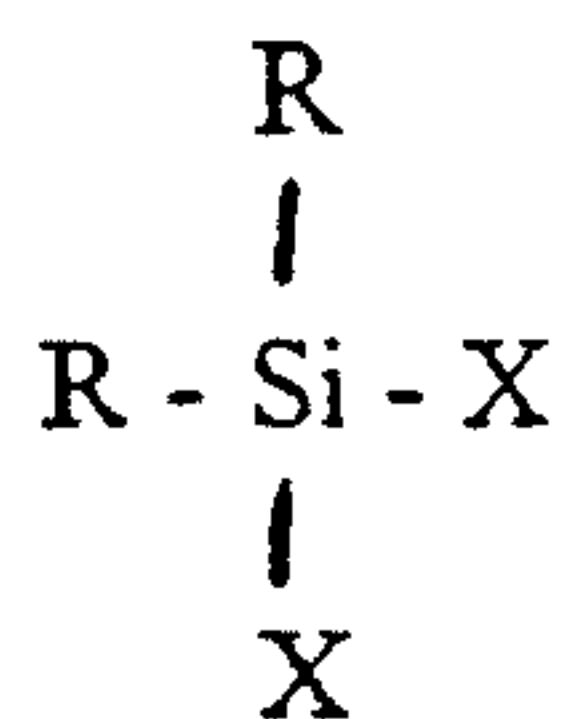
and the capping agent has the formula



For water-repellent applications, R consists of nonpolar groups, and R<sup>1</sup> consists of at least one inert group and a reactive group. . For non-water-repellent applications, R consists of polar groups. In other applications, R<sup>1</sup> could consist of chemically active groups, enabling the surface to be used as a solid state ion exchanger or an attachment point for chemically bound enzymes, chelating agents, dyes, chemical indicators or other substances.

In one aspect, the invention provides a process for treating a surface of a substrate G containing OH or nitrogen hydrogen bonds and surrounded by air, the process including the steps of:

- (a) moistening the surface with water;
- (b) contacting the surface with silane groups having the formula

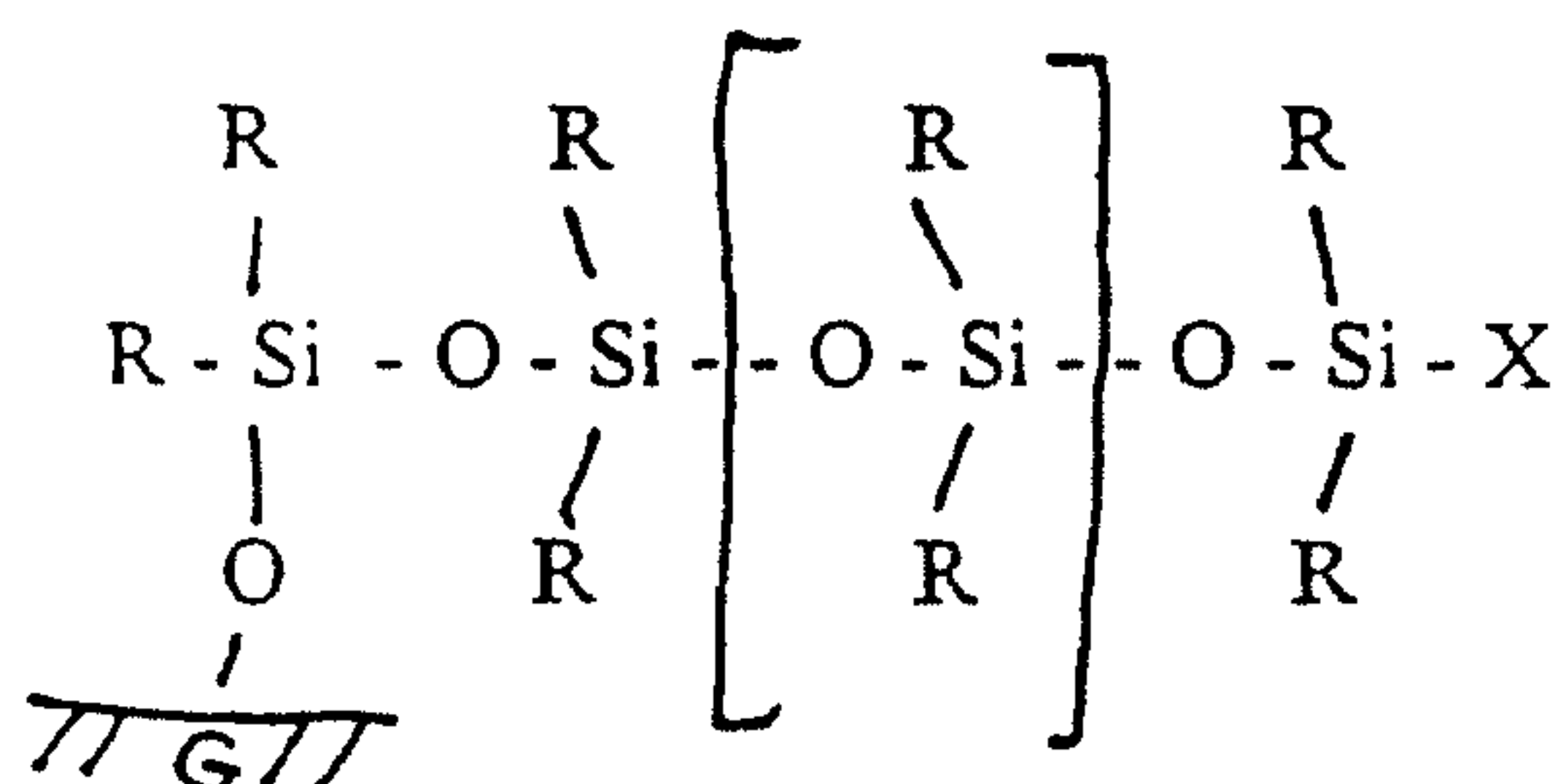


wherein

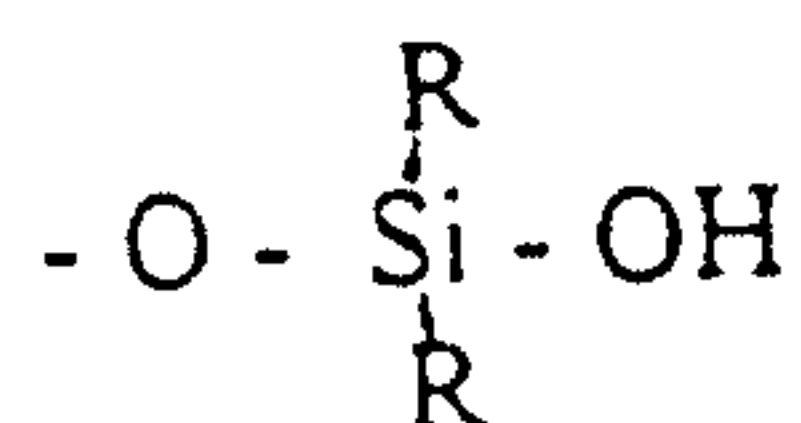
R represents polar or nonpolar groups including hydrocarbons or halogenated hydrocarbons, and

X is selected from the group consisting of esters, ethers, and halogens;

(c) allowing the silane groups to react with the OH or nitrogen hydrogen bonds and water at the surface to create a film formed of chains having the formula

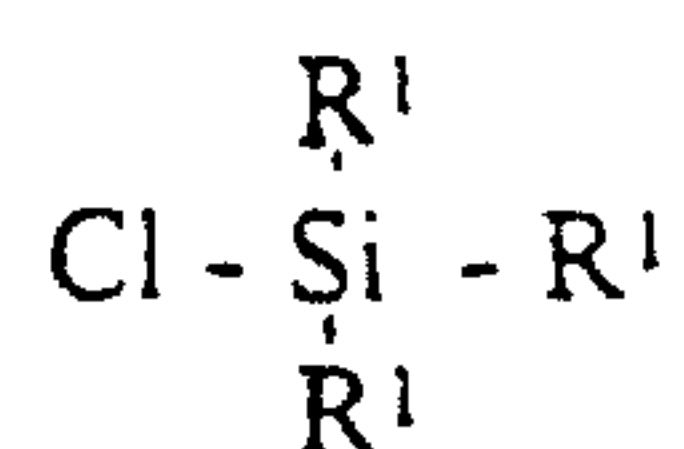


(d) allowing the X atom at the end of the chain to react with water to produce a molecule having the structure



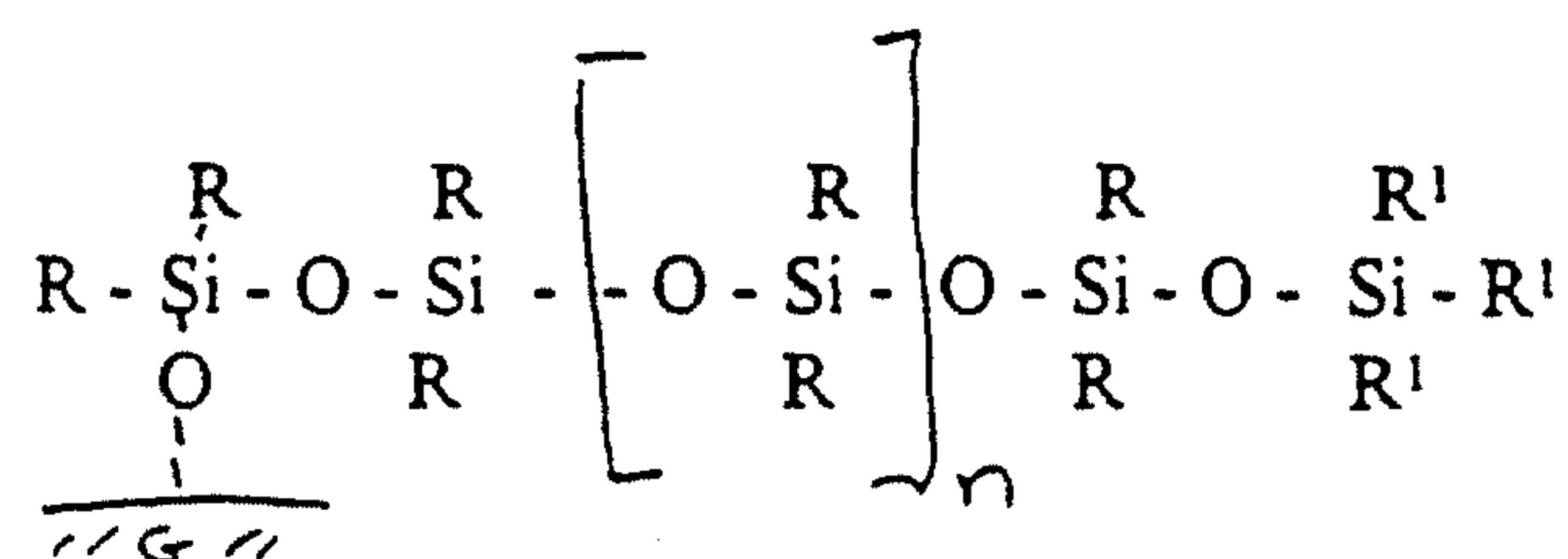
at the end of the chain; and

(e) contacting the surface with a capping agent having the formula



wherein  $\text{R}^1$  includes at least one of an inert group and a reactive group.

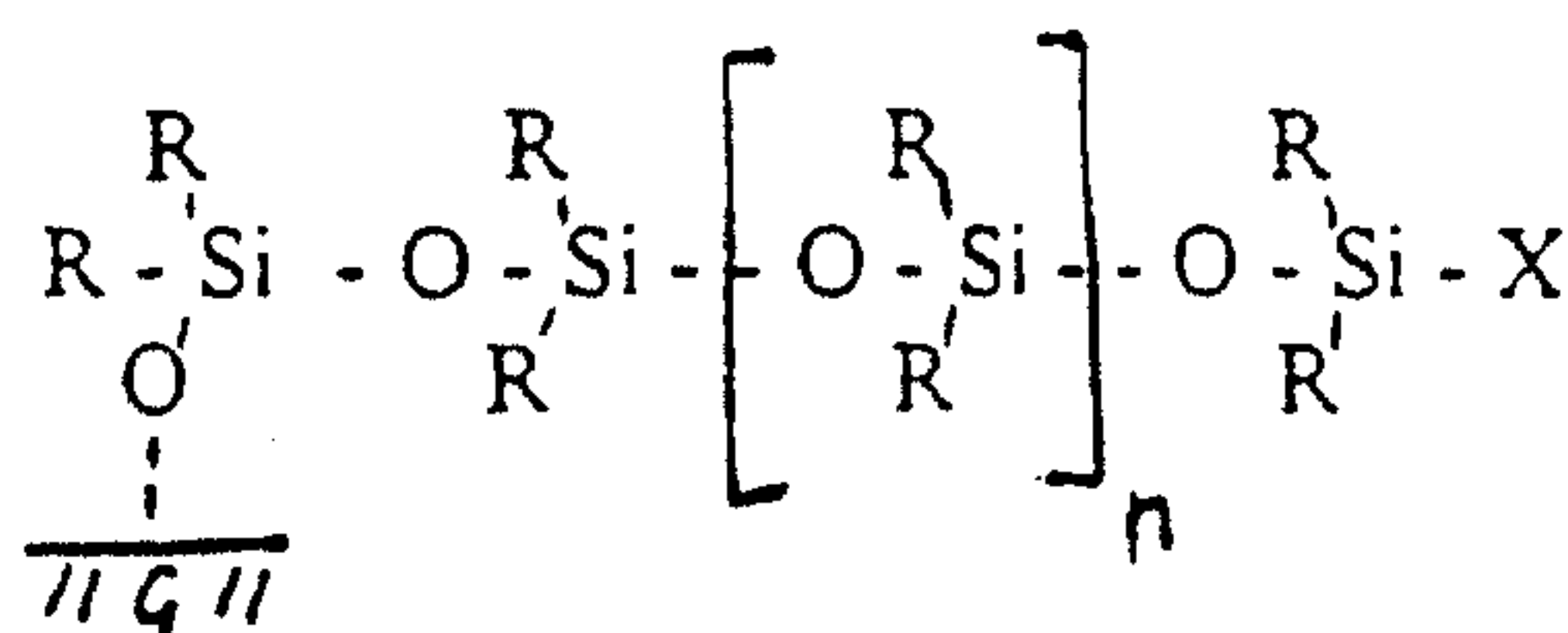
(f) allowing the capping agent to react with the molecule to result in a chain having the formula



In another aspect, the new end molecule serves as a solid state ion exchanger or attachment point for a chemically bound enzyme, a chelating agent, a dye, or a chemical indicator.

In another aspect, the invention provides a process for manufacturing water-resistant glass G in an environment including air, comprising the steps of:

- (a) coating the glass with a somewhat water-resistant film formed of chains having the formula



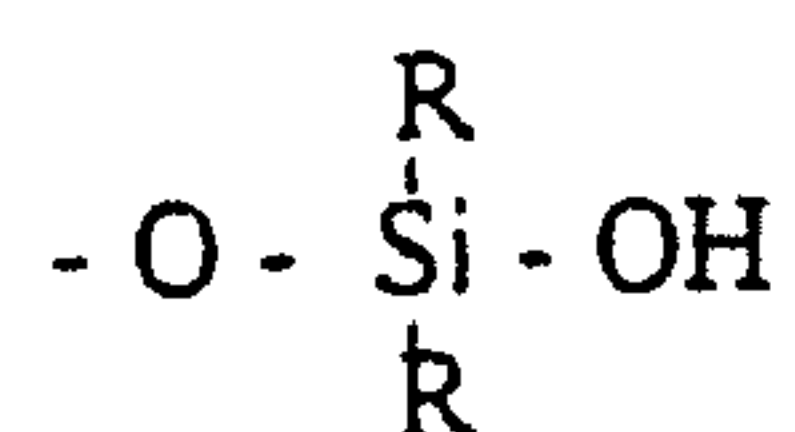
wherein

R consists of nonpolar group,

X is selected from a group consisting of esters, ethers and halogens,

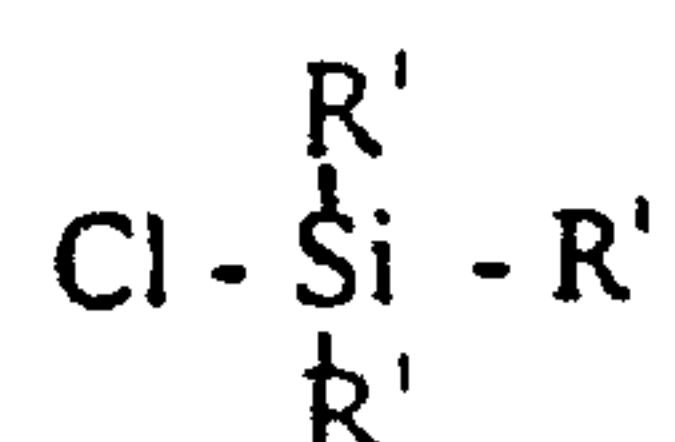
the film being chemically bonded with the glass;

(b) allowing the X atom at the end of the chain to react with water to produce a molecule having the structure



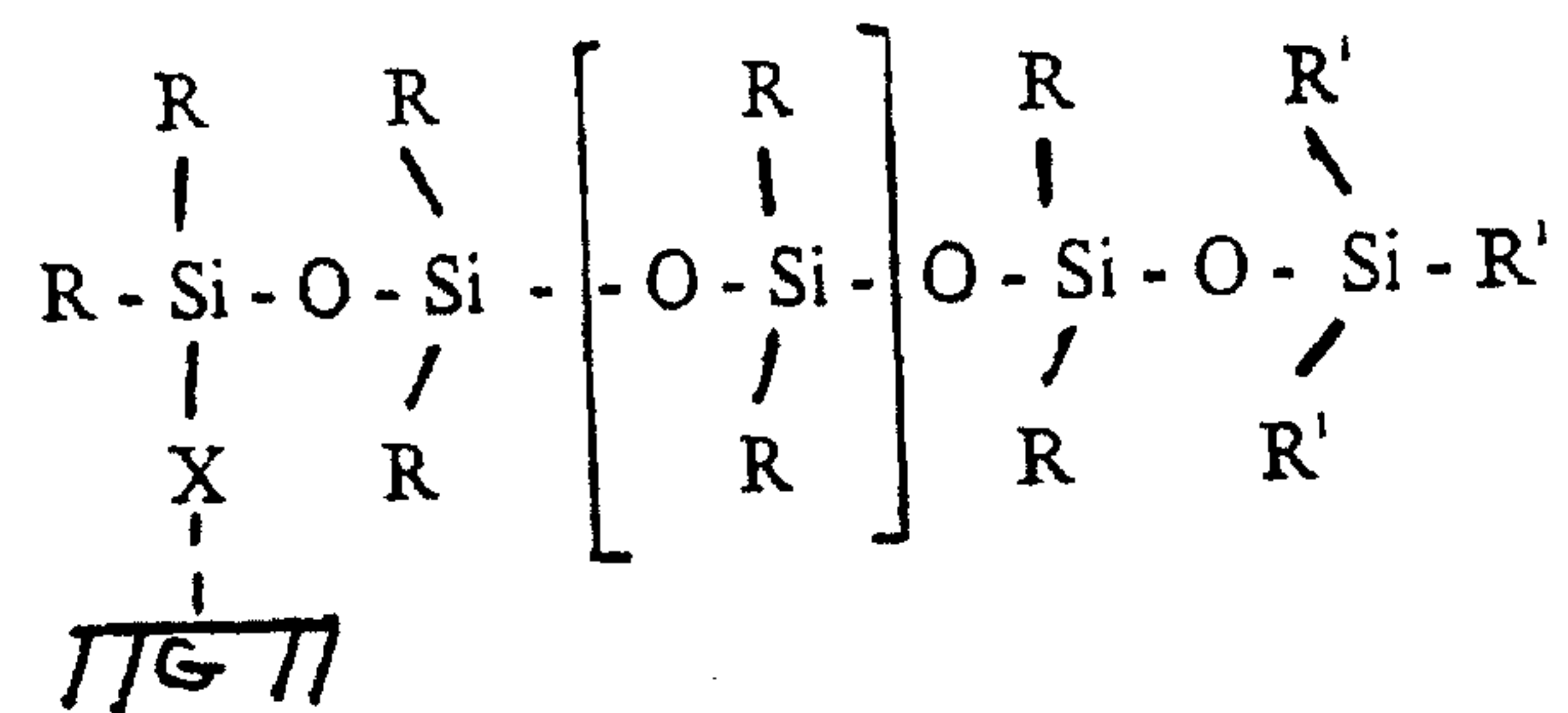
at the end of the chain; and

(c) contacting the surface with a capping agent having the formula



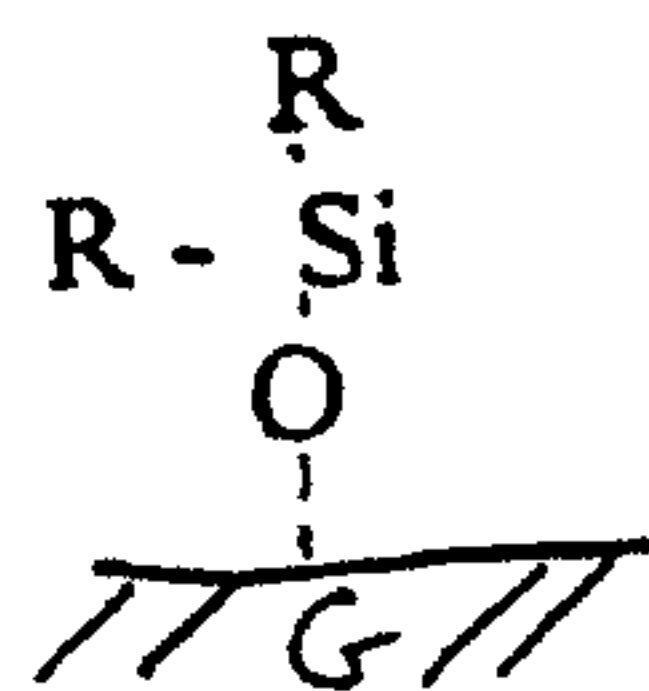
wherein R<sup>1</sup> consists of an inert group; and

(d) allowing the capping agent to react with the molecule to result in a highly water-resistant film formed from chains having the formula



In another aspect, the invention provides a process of manufacturing a water-resistant film for protecting a surface G containing OH or nitrogen hydrogen bonds wherein the process comprises the step of coating glass with a polymer having

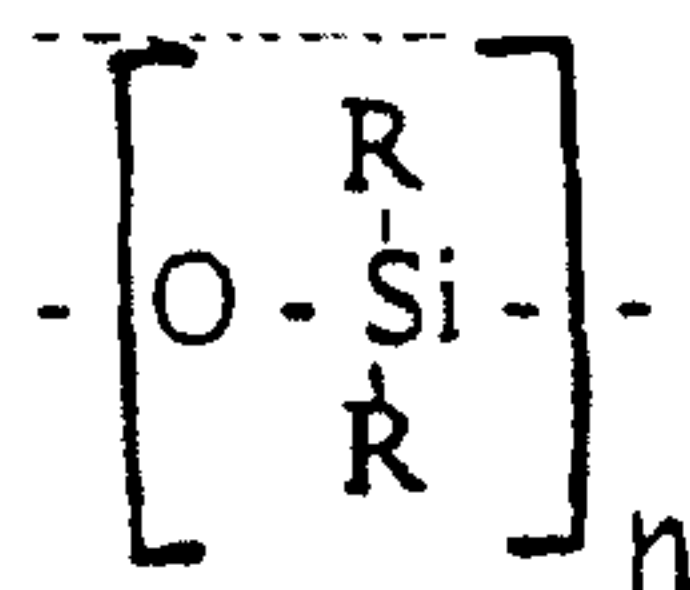
- (i) an anchor group having the formula



wherein

R consists of nonpolar groups, and

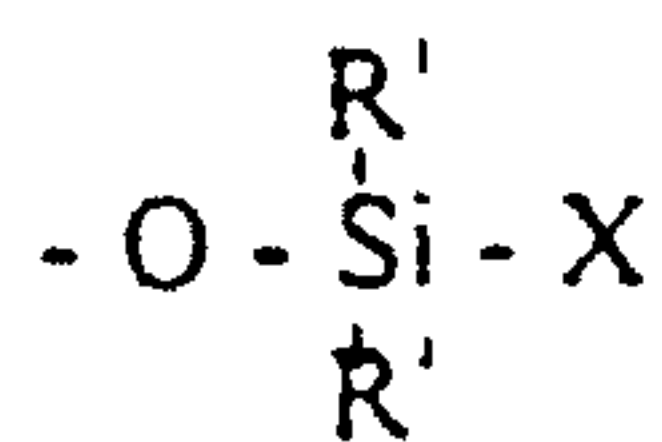
- (ii) a chain of siloxane groups, the chain having a first end and a second end, the first end of the chain being chemically bound to the silicon



molecule of the anchor group, the chain having the formula

, and

- (iii) a terminal group of molecules chemically bound to the second end of the chain, the terminal group having the formula



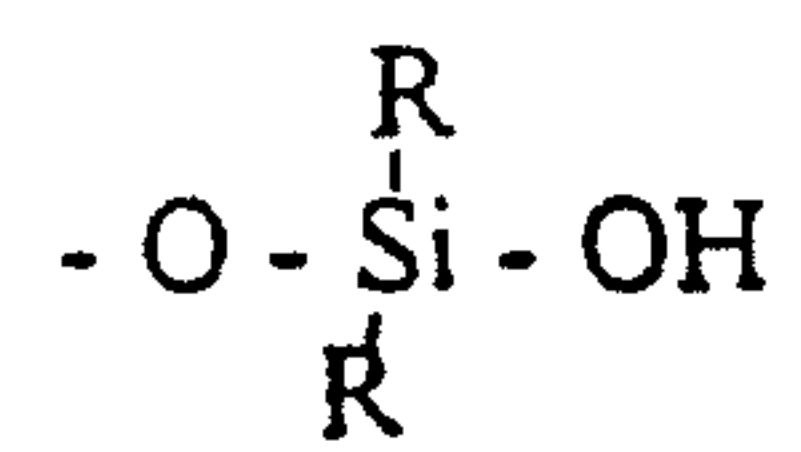
wherein

R<sup>1</sup> consists of inert groups, and

X is selected from the group consisting of esters, ethers and

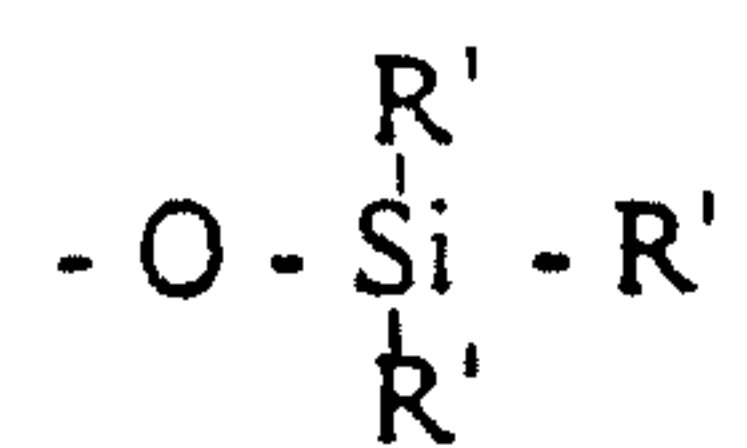
halogens, the improvement comprising the steps of

- (a) allowing the X atom of the terminal group to react with water to produce a new terminal group having the formula



; and

(b) replacing the new terminal group with a final terminal group having the structure



wherein R' consists of inert groups.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The foregoing and further and more specific objects and advantages of the instant invention will become readily apparent to those skilled in the art from the following detailed description of the preferred embodiments thereof taken in conjunction with the drawings in which:

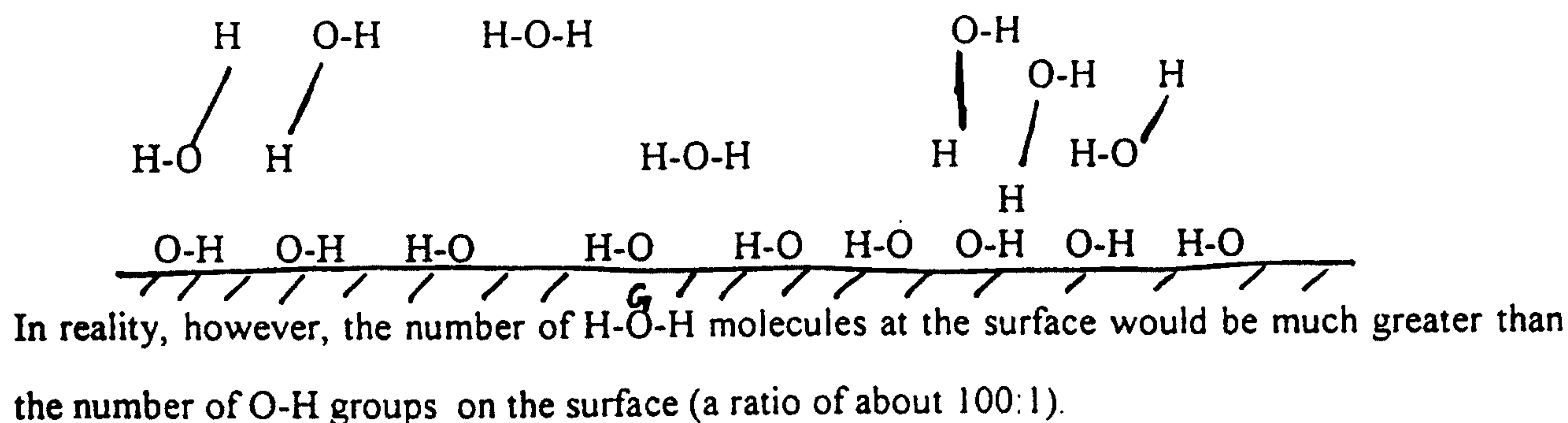
FIG. 1 is a diagrammatic representation of a surface coated with a prior art water-repellent film; and

FIG. 2 is a diagrammatic representation of a surface coated with a water-repellent film manufactured using the process of the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

Turning now to the drawings, attention is first directed to FIG. 1, which shows a surface G which has been treated with a water-repellent film using a prior art process. In the most widely-used application of the process, the surface G is glass, but the process may actually be used to treat any surface containing OH or nitrogen hydrogen bonds, such as silica-containing surfaces including granite, porcelain, earthenware and stoneware, as well as organic substances including cotton, paper, nylon, leather and others. The film comprises chains of dimethylsiloxane (DMS) groups. Each chain is chemically bonded at one end to an oxygen (O) molecule, which in turn is chemically bonded to the surface G. The opposite end of each chain includes either a hydroxyl (OH) group or a chlorine attached to silicone, which will soon react with water vapor in the surrounding air to produce an OH group.

The process by which the film of FIG. 1 is created is as follows. Initially, the surface G is moistened. The moistened surface can be represented as shown in simplified form below:



Next, the surface is treated with dimethyldichlorosilane using Portable Vapor machines which may be adapted to fixed site chambers for large volume operations, or by using a wipe-on

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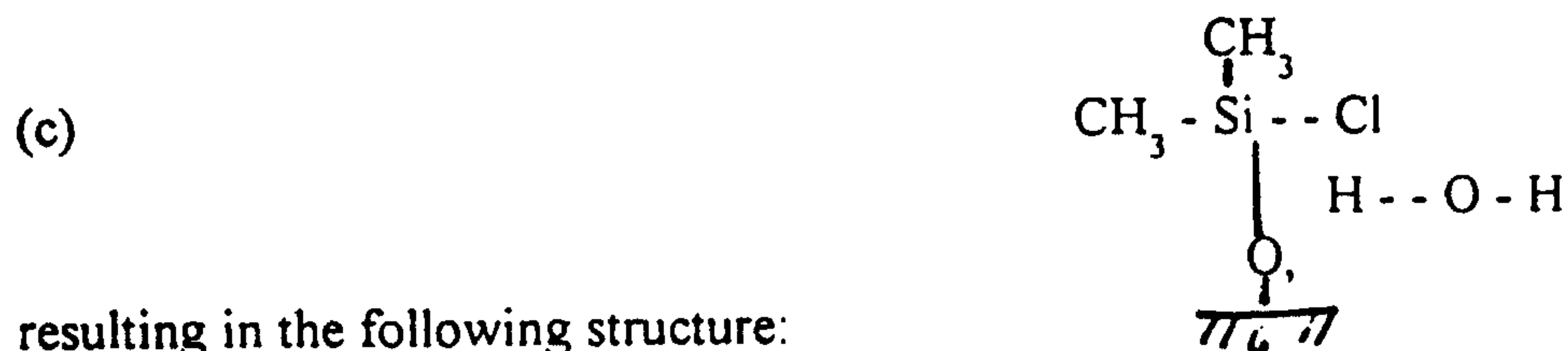
method or a dipping or spraying procedure. Where necessary, cyclohexylamine is used as a primer to ensure sufficient moisture for the chemical reaction to take place. After the dimethyldichlorosilane has been applied, a dimethyldichlorosilane molecule approaches an O-H group at the surface, as shown below:



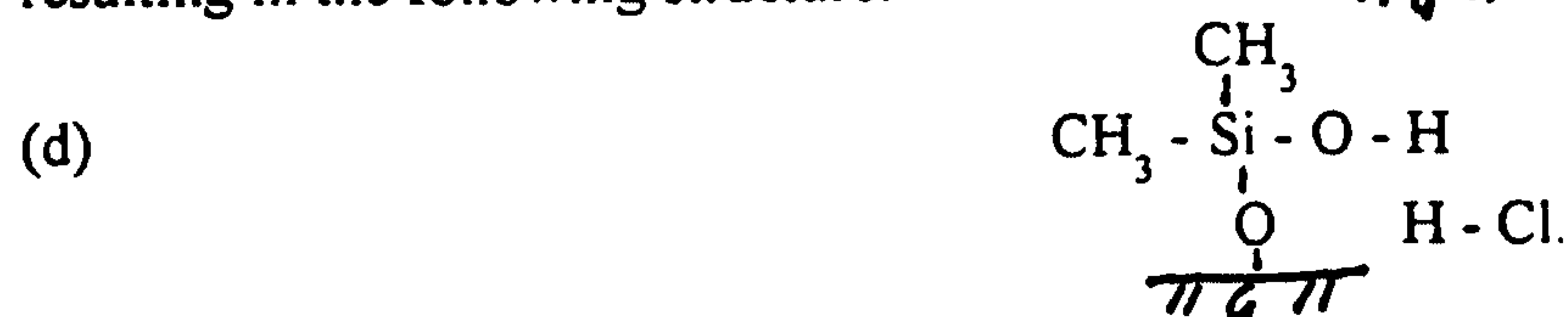
The ensuing reaction results in an anchor molecule which will chemically bond the film to the surface G, as shown below:



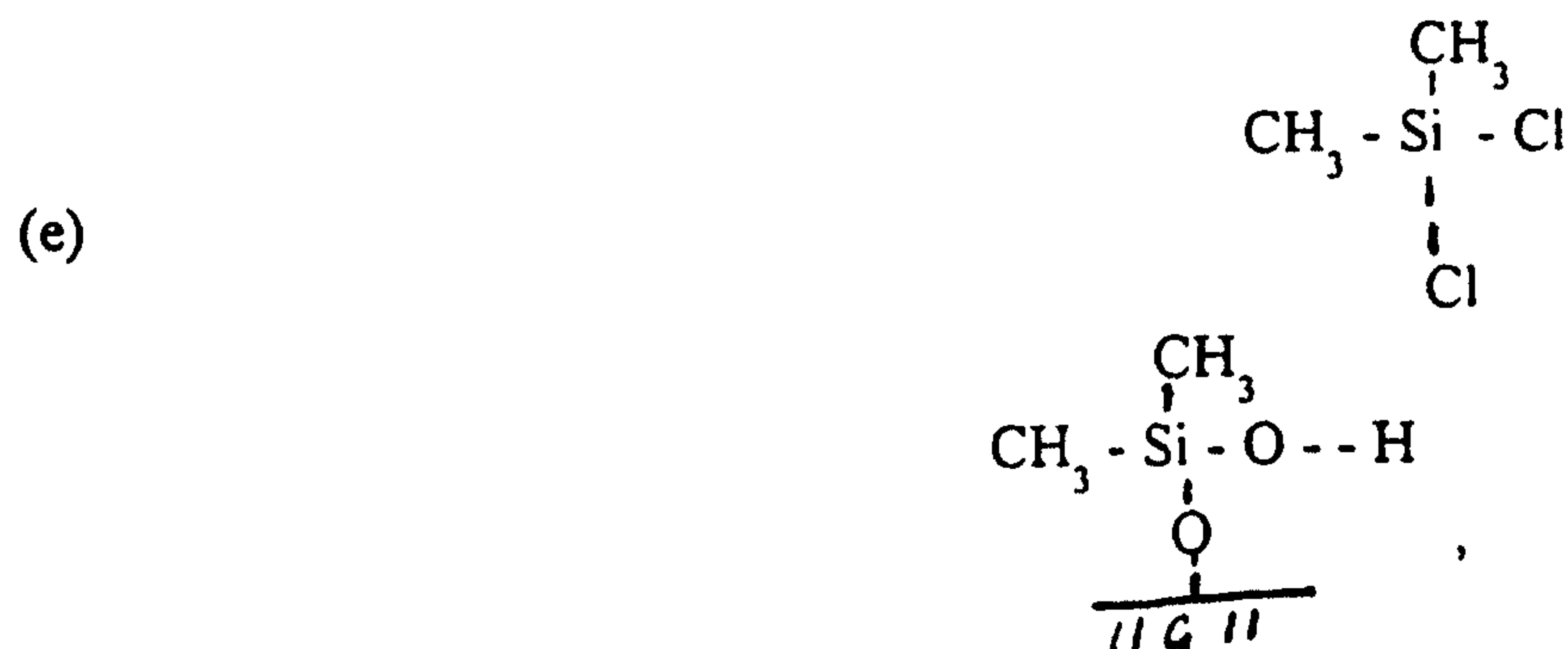
The Si - Cl bond then reacts with water absorbed on the surface G as follows:



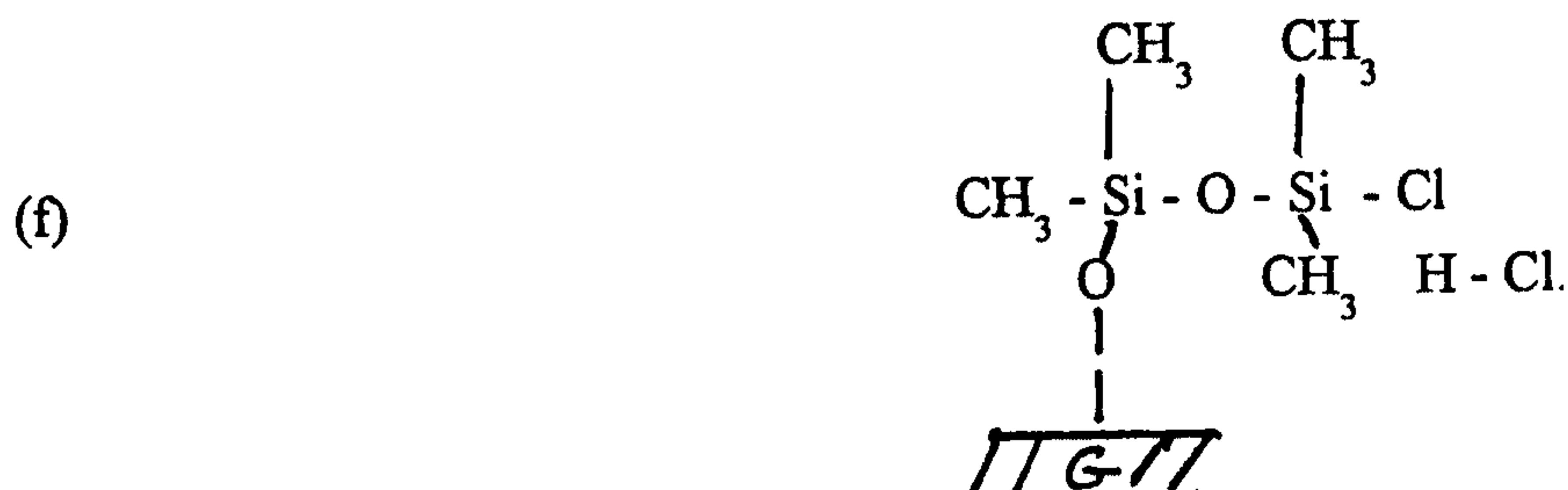
resulting in the following structure:



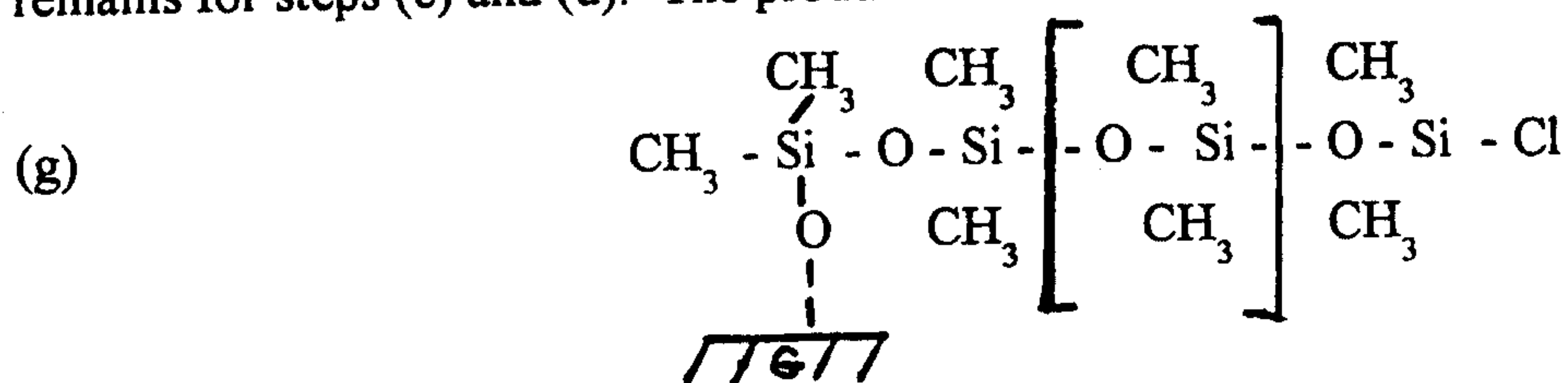
This structure then reacts with a DMS molecule as follows:



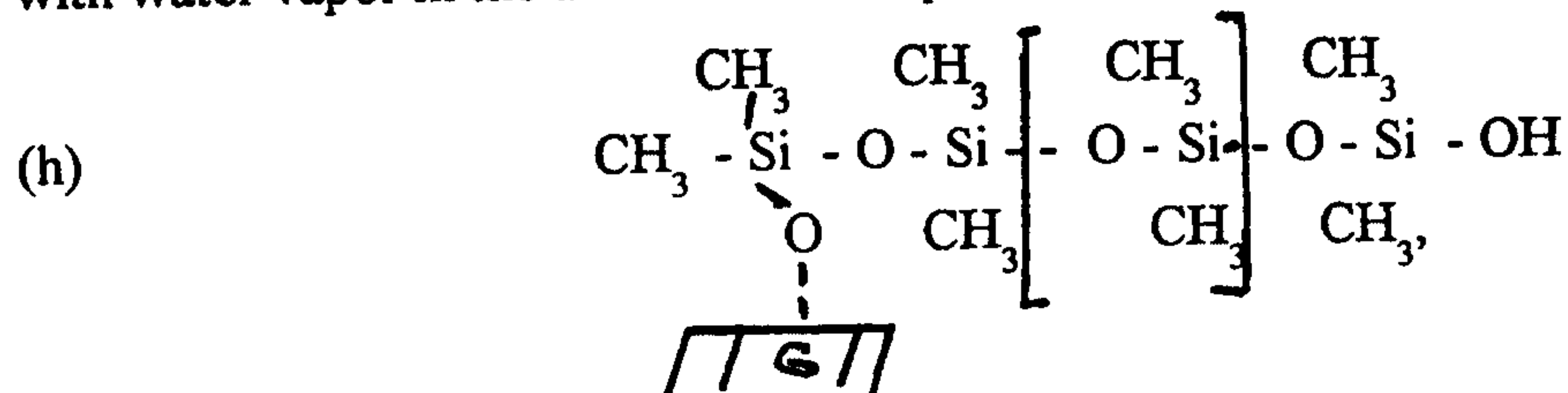
resulting in the molecule shown below:



The process of steps (c) - (f) above is repeated about 100 times until no more water remains for steps (c) and (d). The product has the formula:

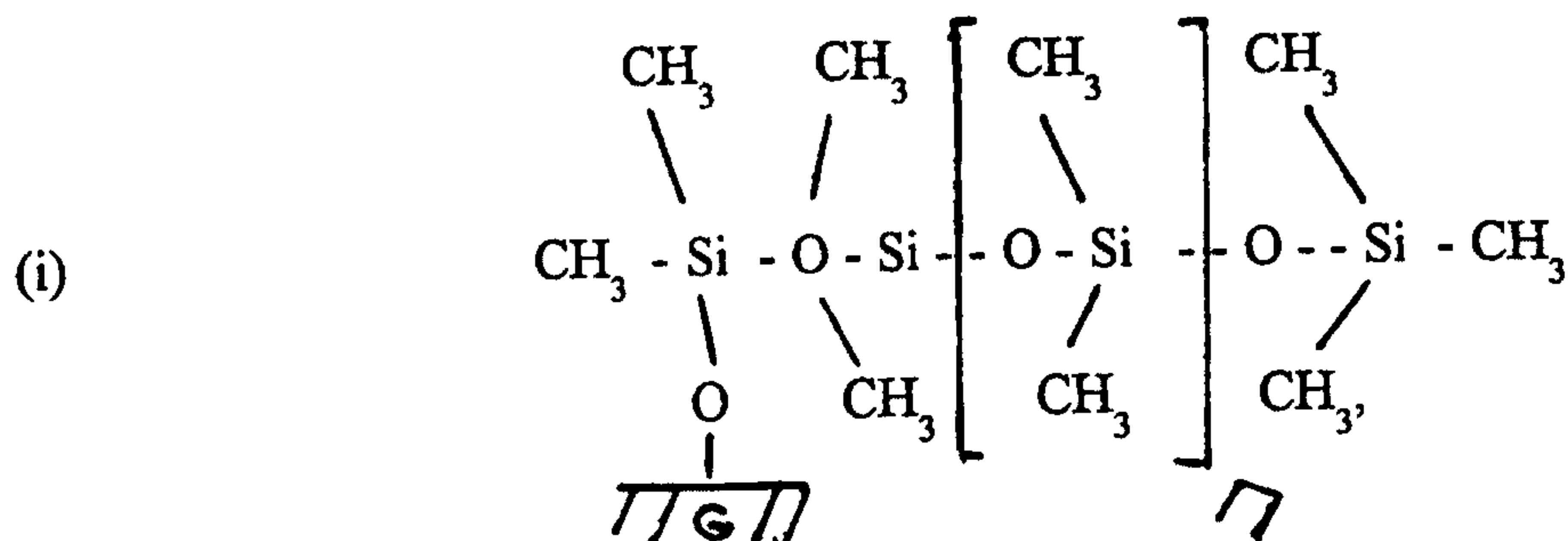


where n is around 100 or more. The groups in the brackets are highly water repellent. However, the chlorine atom at the end of the chain slowly reacts over several hours with water vapor in the air to result in a product having the formula:



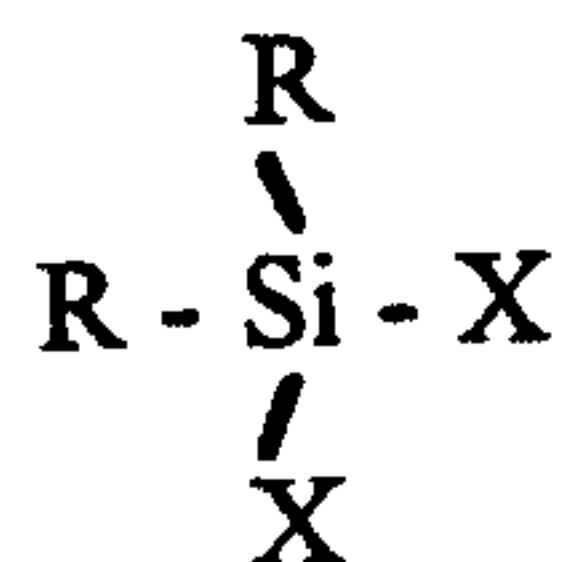
which is equivalent to the structure shown in FIG. 1. The Si - O - H group at the end of this final product is water-attracting, thus reducing the overall water repellence of the entire film, and creating a site for undesirable chemical reactions.

In the improved process of the instant invention, a surface coated with the above film is then treated with trimethylchlorosilane, which reacts with the OH group at the end of the DMS chain to produce trimethylchlorosiloxane (TMS). The final product is a film having the formula:

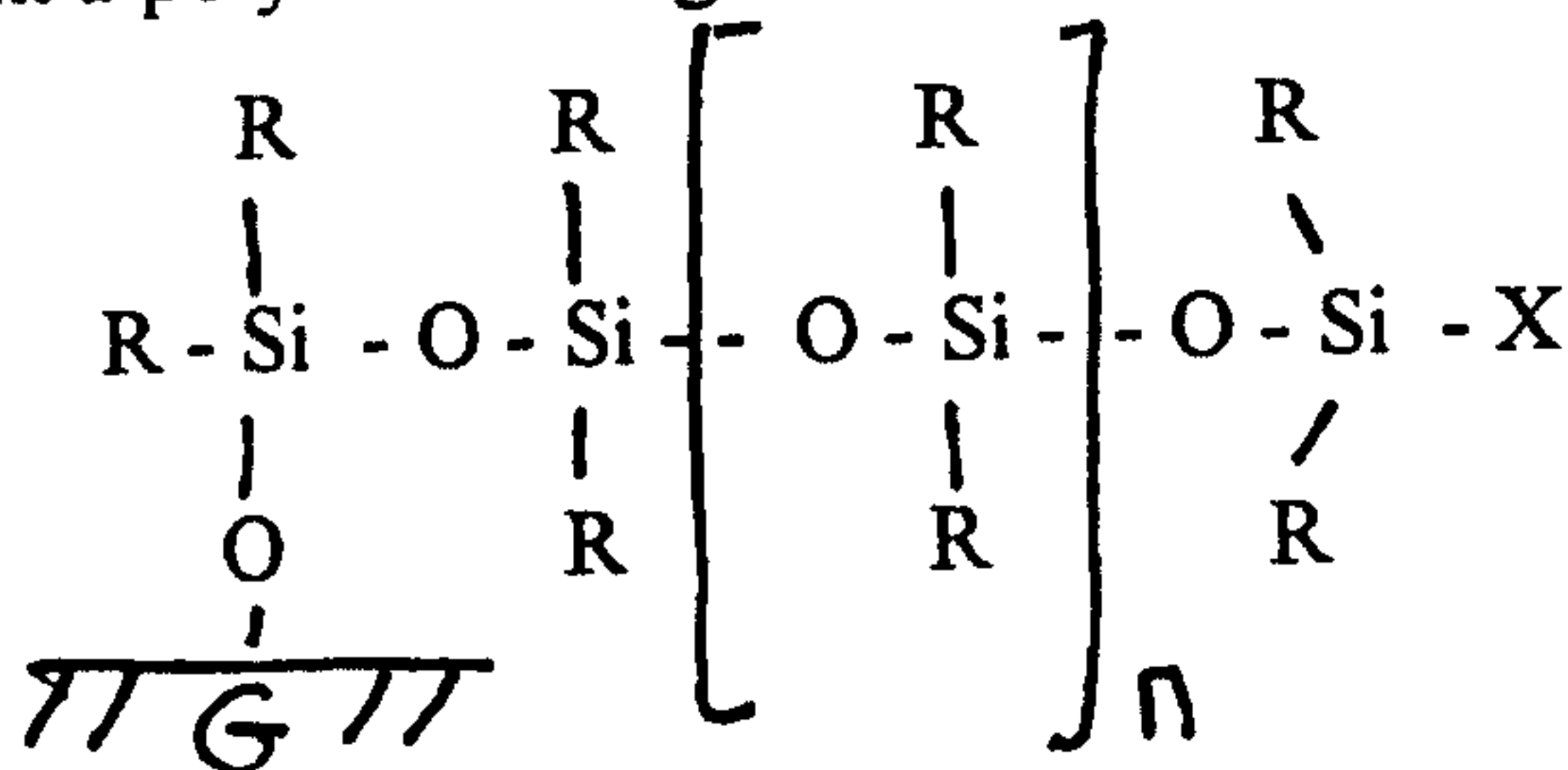


which is equivalent to the structure shown in FIG. 2. Because the TMS group at the end of the chain is chemically inert, the water-resistance of the film is much greater than that of the prior art film.

The silicone film produced by the process of steps (a)-(i) above is one specific example of the invention, intended for water-repellent applications. In a more general case, the moistened surface G is first contacted with silane groups having the formula



wherein R represents polar or nonpolar groups including hydrocarbons or halogenated hydrocarbons, and X is selected from the group consisting of esters, ethers, and halogens. The silane groups then react with the OH or nitrogen hydrogen bonds and water at the surface G to chemically bond the film to the surface G, in a process analogous to step (b) above. A series of reactions analogous to those shown in steps (b) - (f) above results in a polymer having the formula:



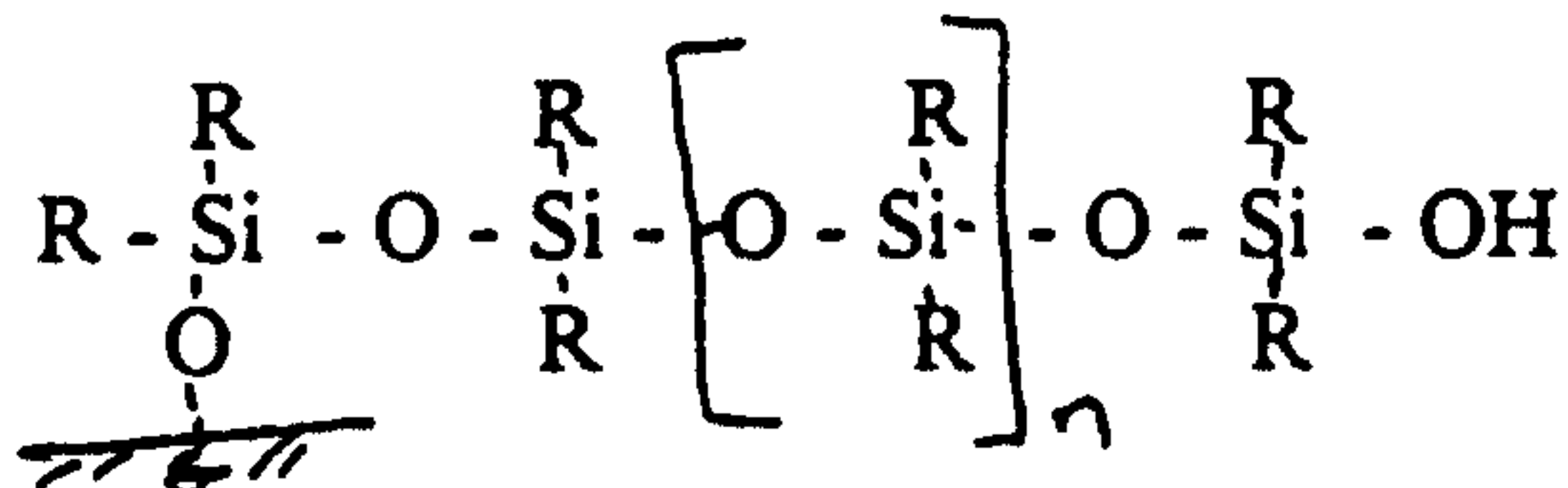
where n is around 100 or more. The X atom at the end of the chain then reacts with

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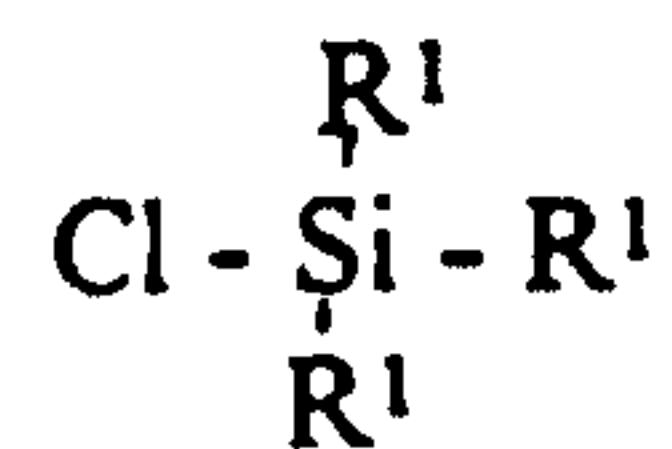
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water vapor

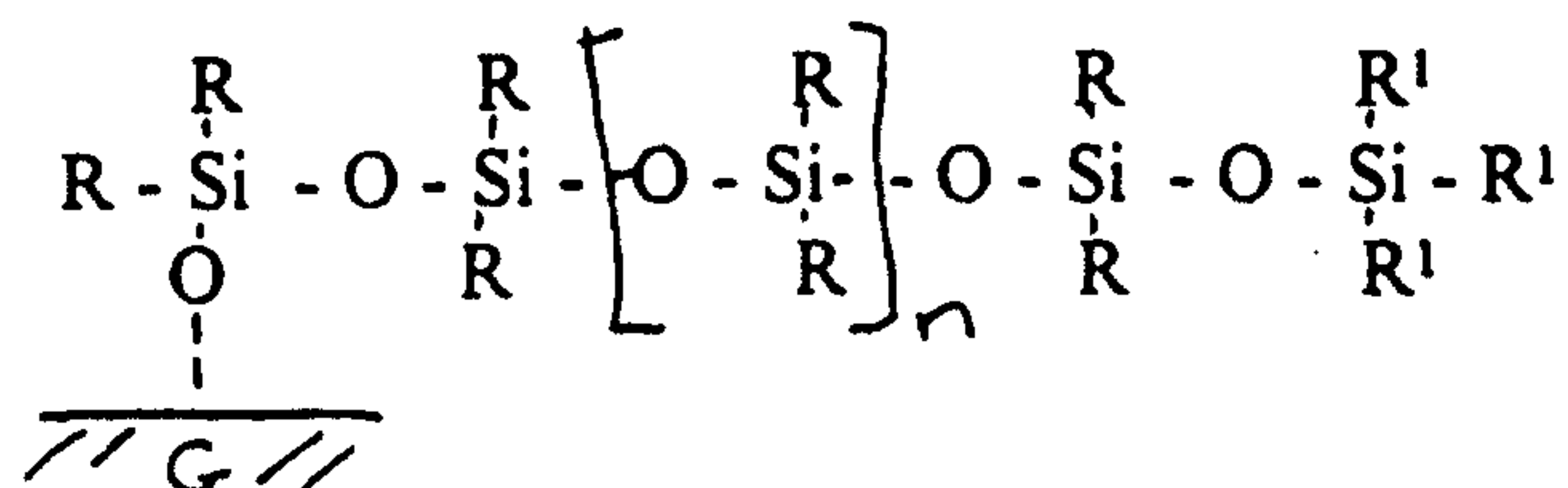
in the surrounding air resulting in a molecule having the formula:



The surface is then contacted with a capping agent having the formula:



where R<sup>1</sup> may include any combination of inert and reactive groups. The capping agent reacts with the OH group at the end of the chain, resulting finally in a chain having the formula:



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The properties of the film manufactured using this process will depend on the choice of R and R' and to a lesser extent, X. Choosing X from the chloro group gives the lowest material cost and gives a faster reaction time, while esters and ethers are less reactive but produce less troublesome coproducts and require different processing conditions.

In general, for water repellent applications, R consists of nonpolar groups and R' consists of chemically inert groups. If R consists of approximately 50% methyl groups and 50% phenyl groups, the abrasion-resistance of the film is improved. The abrasion-resistance of the film can also be improved by connecting the DMS chains with methyltrichlorosilane (which causes branched chains and additional ends). The methyltrichlorosilane would cause the chains to be tied together in a three-dimensional structure, which would resist abrasion better than a two-dimensional

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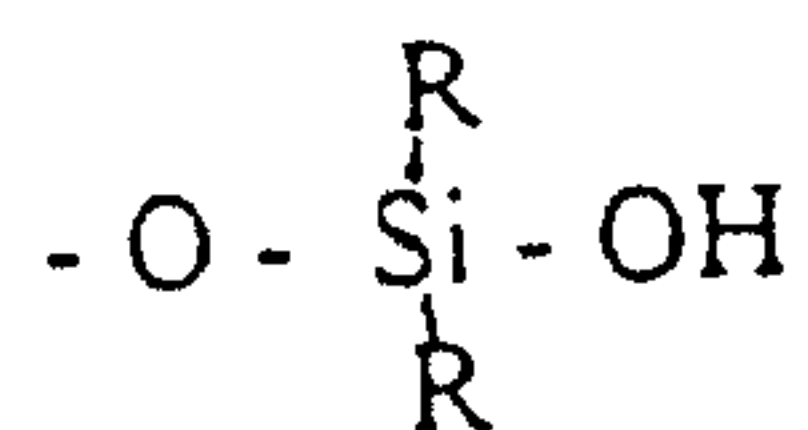
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structure.

For non-water repellent applications, R consists of polar groups. If R' is selected from chemically reactive groups, the end molecule can provide an attachment point for enzymes, chelating agents, ion exchange elements, chemical indicators and other substances.

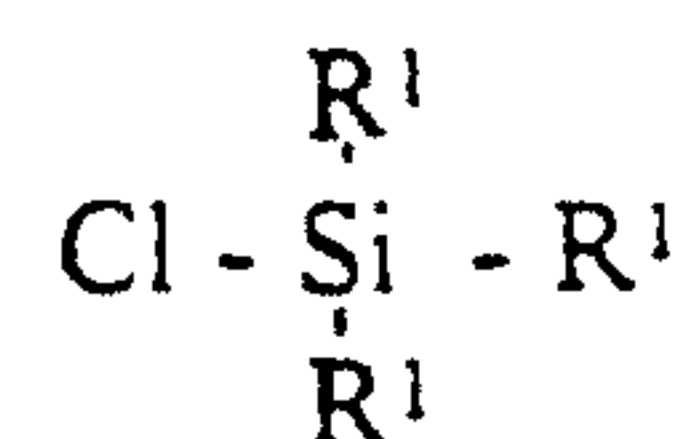
Various other modifications and variations to the embodiments herein chosen for purposes of illustration will readily occur to those skilled in the art. To the extent that such variations and modifications do not depart from the spirit of the invention, they are intended to be included within the scope thereof which is assessed only by a fair interpretation of the following claims.





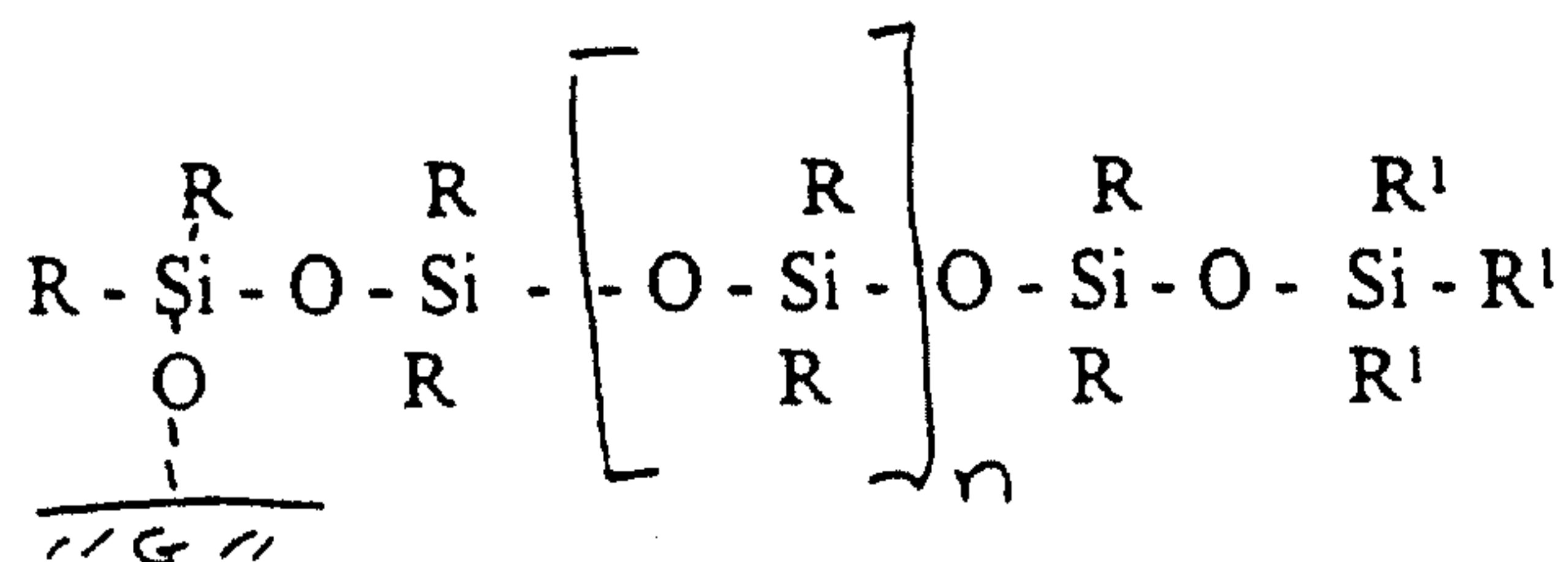
at the end of the chain; and

(e) contacting the surface with a capping agent having the formula



wherein  $\text{R}^1$  includes at least one of an inert group and a reactive group.

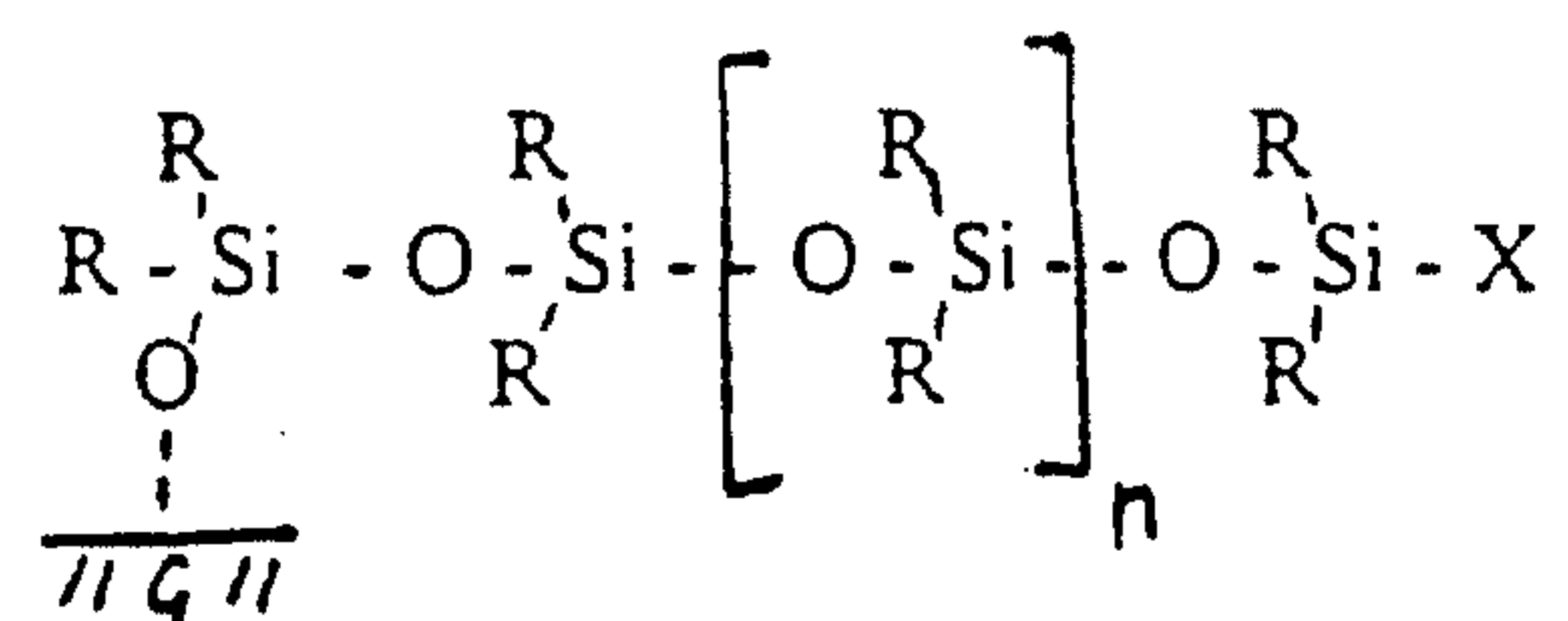
(f) allowing the capping agent to react with the molecule to result in a chain having the formula



2. The process according to Claim 1, Wherein the substrate G includes silica molecules.
3. The process according to Claim 2, wherein the substrate G is formed from a material selected from the group consisting of glass, ceramics and silica-containing minerals.
4. The process according to Claim 1, wherein the substrate G includes organic molecules.

5. The process according to Claim 1, wherein R is methyl.
6. The process according to Claim 1, wherein R is selected from the group consisting of phenyl, ethyl, methyl, butyl, amyl, and larger alkyl groups.
7. The process according to Claim 1, wherein R consists of 50% methyl groups and 50% phenyl groups, resulting in improved abrasion resistance of the film.
8. The process according to Claim 1, wherein R consists of polar groups.
9. The process according to Claim 1, where in R consists of nonpolar groups.
10. The process according to Claim 1, where in R<sup>1</sup> consists of chemically inert groups.
11. The process according to Claim 1, where in R<sup>1</sup> consists of chemically reactive groups.
12. The process according to Claim 1, wherein the step of contacting the surface with silane groups comprises chemically depositing the silane groups on the surface using a vapor machine.
13. The process according to Claim 1, wherein the step of contacting the surface with silane groups comprises a wipe-on method.
14. The process according to Claim 1, wherein the step of contacting the surface with silane groups comprises a dipping or spraying procedure.
15. The process according to Claim 1, wherein the step of moistening the surface comprises a step of priming the surface with cyclohexylamine.
16. A process for manufacturing water-resistant glass G in an environment including air, comprising the steps of:

- (a) coating the glass with a film formed of chains having the formula



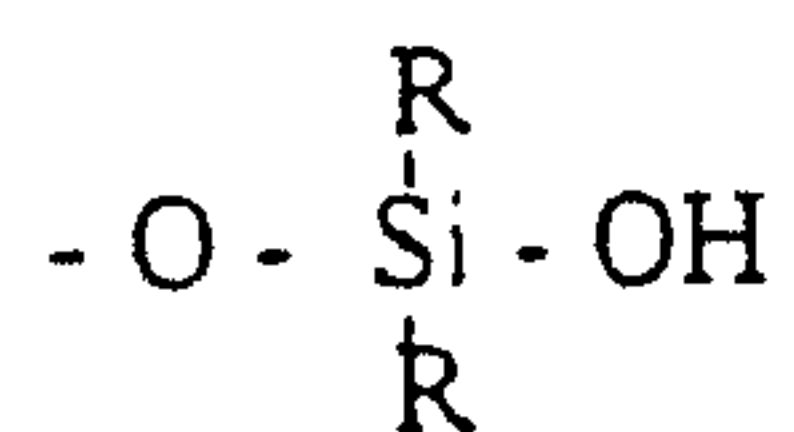
wherein

R consists of nonpolar group,

X is selected from a group consisting of esters, ethers and halogens,

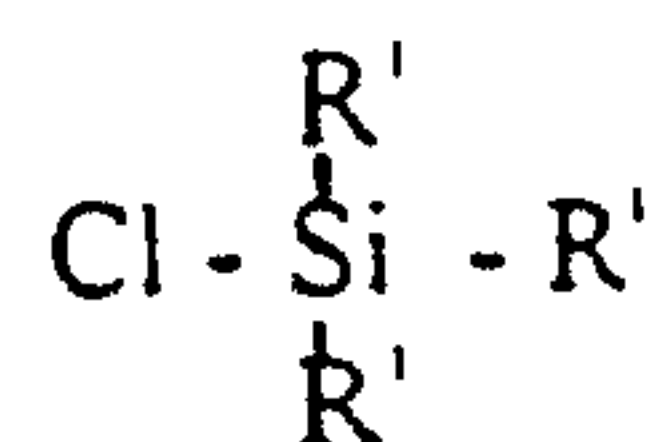
the film being chemically bonded with the glass;

- (b) allowing the X atom at the end of the chain to react with water to produce a molecule having the structure



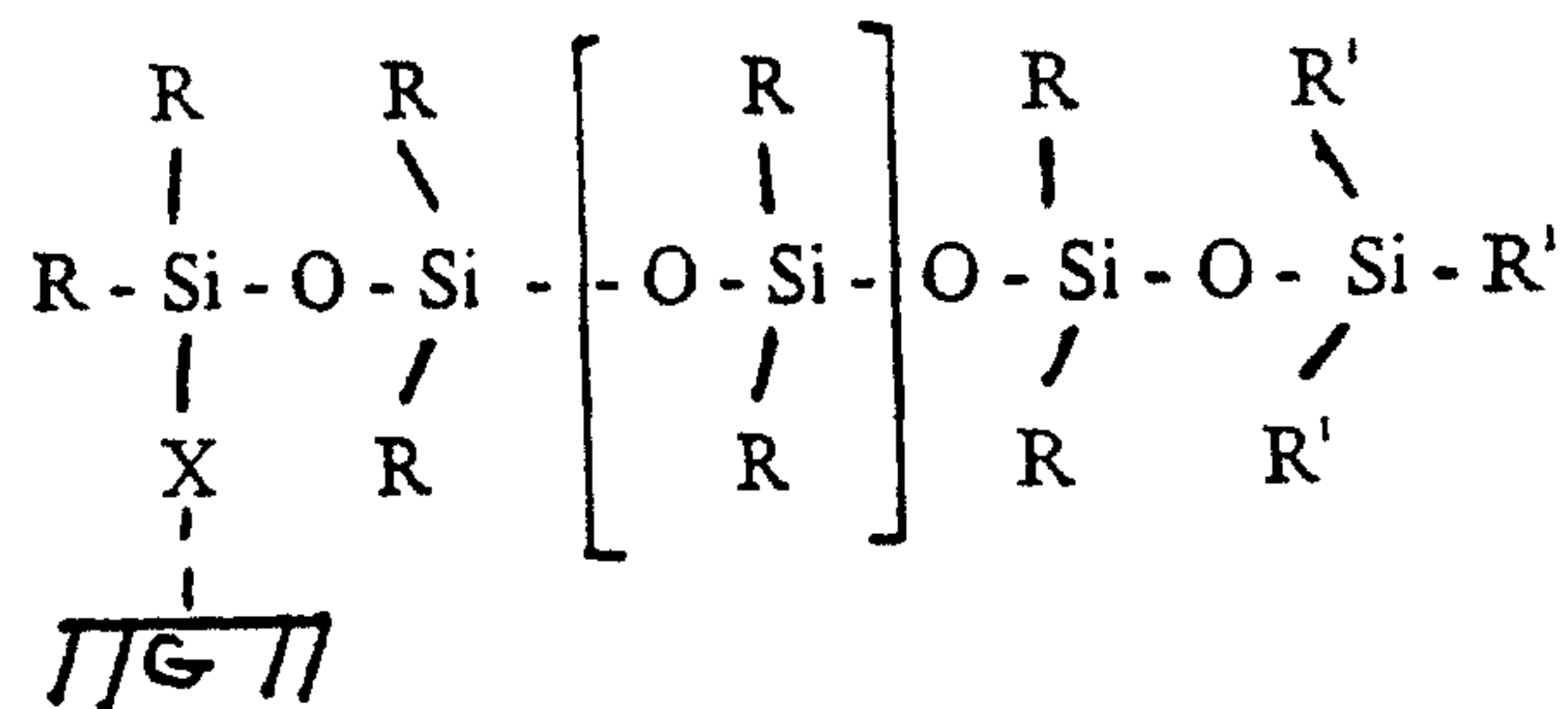
at the end of the chain; and

- (c) contacting the surface with a capping agent having the formula

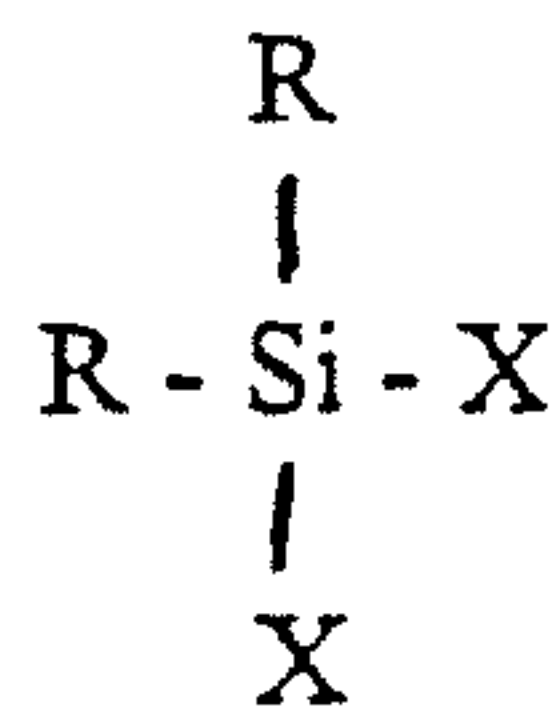


wherein R<sup>1</sup> consists of an inert group; and

- (d) allowing the capping agent to react with the molecule to result in a highly water-resistant film formed from chains having the formula



17. The process according to Claim 16, wherein the film comprises chains of dimethylsiloxane.
18. The process according to Claim 16, wherein the capping agent is trimethylchlorosilane.
19. The process according to Claim 16, wherein R is selected from the group consisting of phenyl, ethyl, methyl, butyl, amyl and larger alkyl groups.
20. The method according to Claim 16, wherein R comprises approximately 50% methyl groups and 50% phenyl groups, resulting in improved abrasion-resistance of the highly water-resistant film.
21. A process for treating a surface of a substrate G containing OH or nitrogen hydrogen bonds and surrounded by air, the process including the steps of:
  - (a) moistening the surface with water;
  - (b) contacting the surface with silane groups having the formula

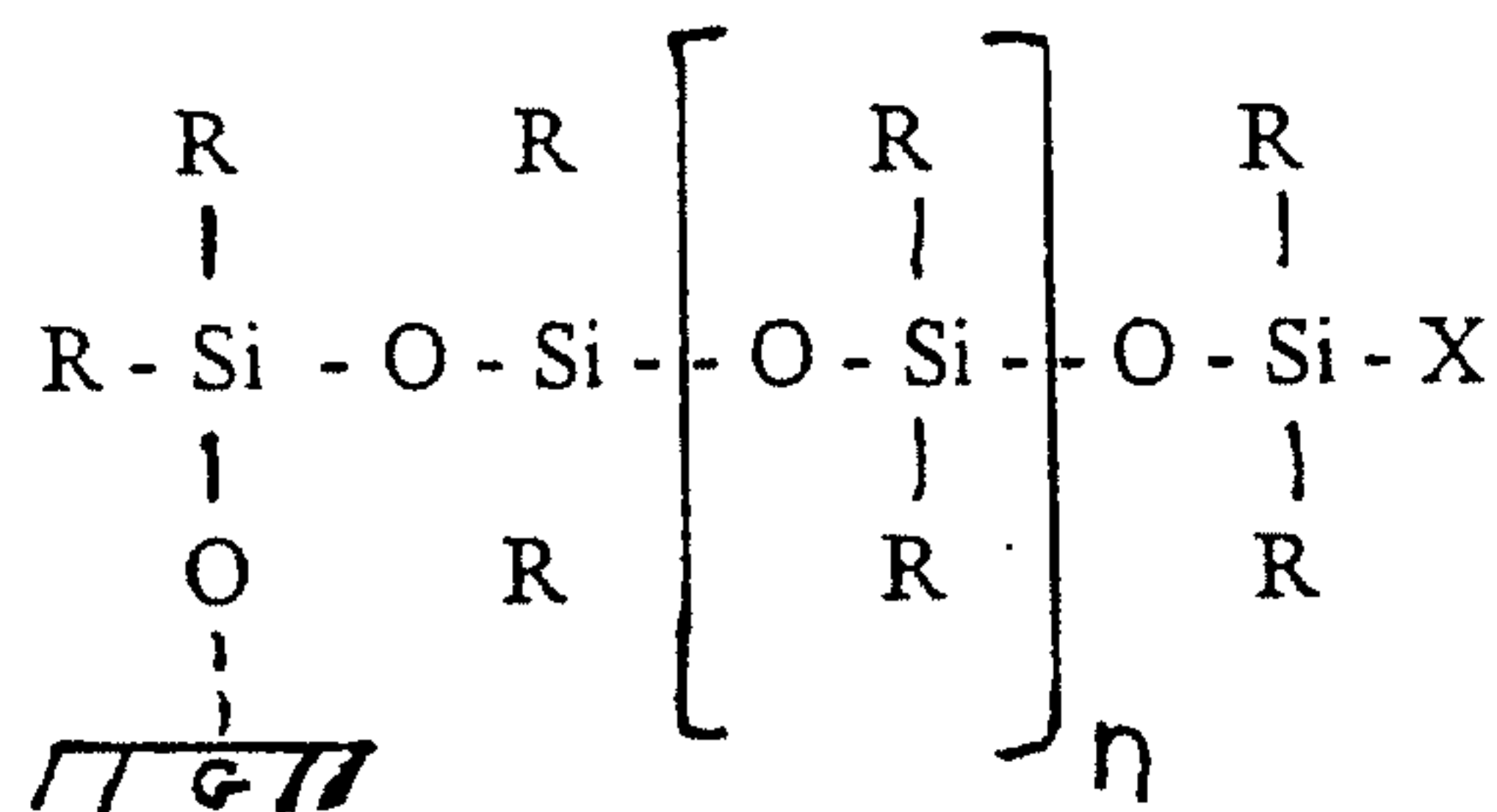


wherein

R consists of a polar group, and

X is selected from a group consisting of esters, ethers and halogens;

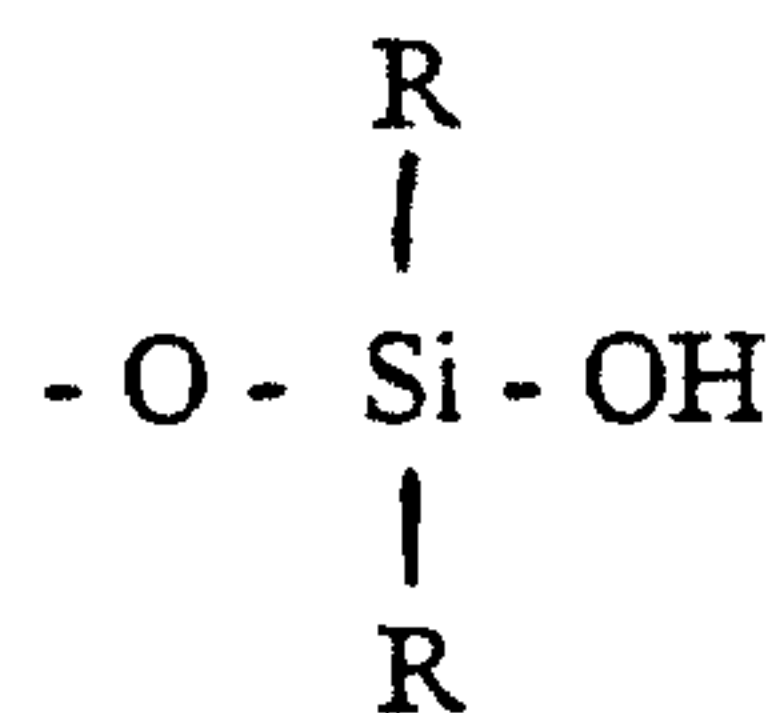
(c) allowing the silane group to react with the OH or nitrogen hydrogen bonds and water at the surface to create a film formed of chains having the formula



wherein

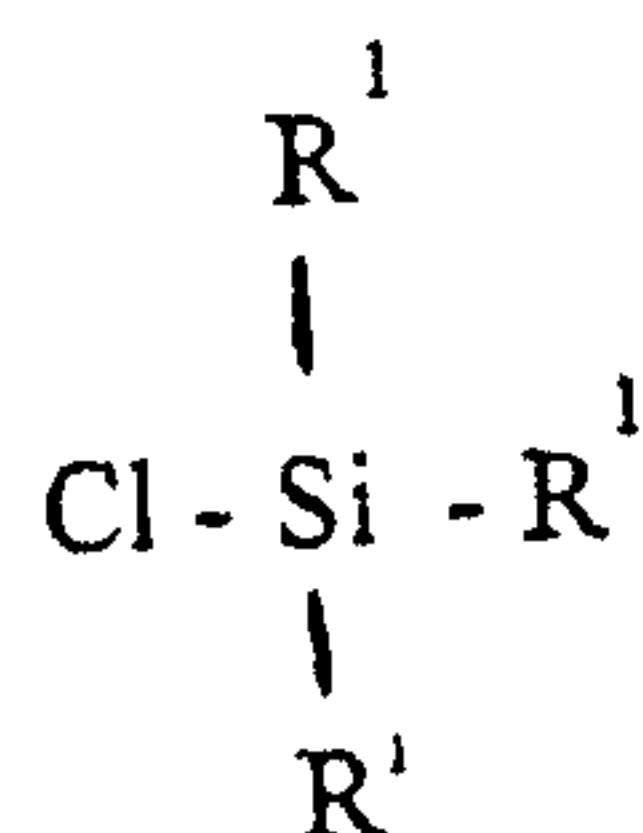
the film is chemically bonded to the surface;

(d) allowing the X atom at the end of the chain to react with water in the surrounding air to produce a molecule having the structure



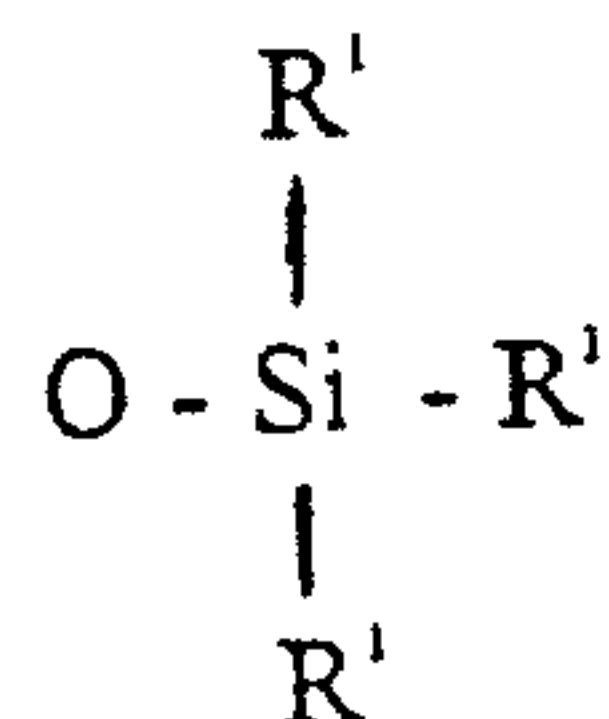
at the end of the chain; and

(e) contacting the surface with a capping agent having the formula



wherein  $\text{R}^1$  consists of a chemically active groups and

(f) allowing the capping agent to react with the molecule to result in a new end molecule having the formula



wherein the new end molecule serves as a solid state ion exchanger or attachment point for a chemically bound enzyme, a chelating agent, a dye, or a chemical indicator.

22. The process according to Claim 21, wherein the substrate G includes silica molecules.

23. The process according to Claim 22, wherein the substrate G is formed from a

material selected from the group consisting of glass, ceramics, and silica-containing minerals.

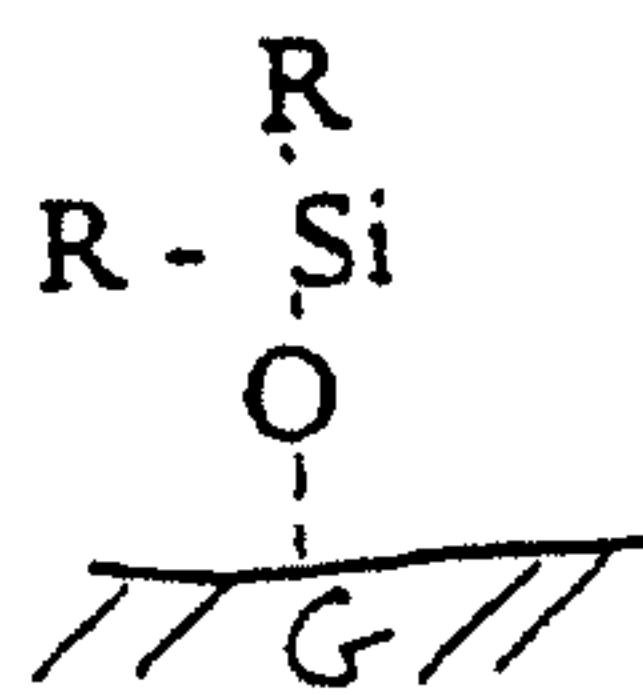
24. The process according to Claim 21, wherein the substrate G includes organic molecules.

25. The process according to Claim 21, wherein R is methyl.

26. The process according to Claim 21, wherein the film consists of chains of dimethylsiloxane.

27. In a process of manufacturing a water-resistant film for protecting a surface G containing OH or nitrogen hydrogen bonds wherein the process comprises the step of coating glass with a polymer having

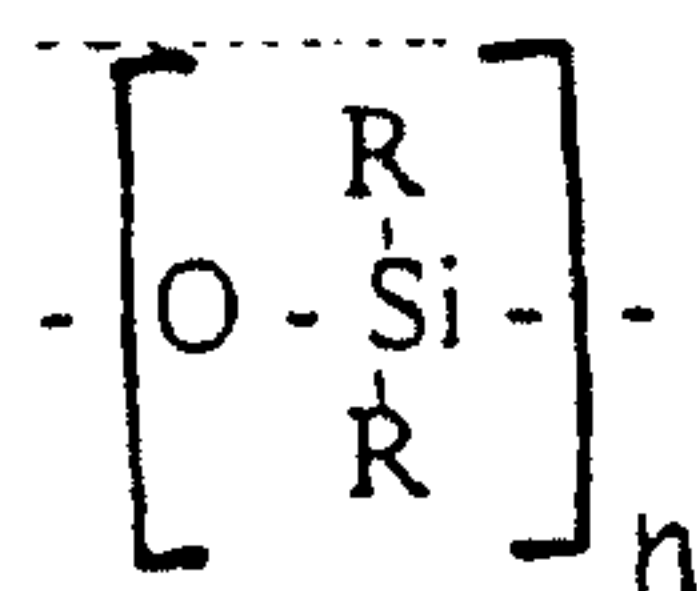
(i) an anchor group having the formula



wherein

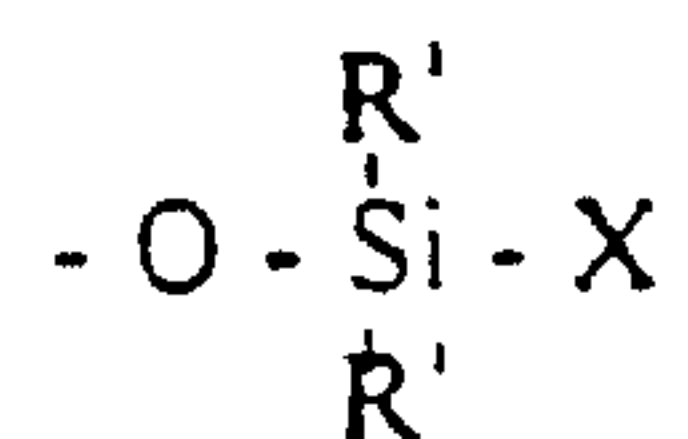
R consists of nonpolar groups, and

(ii) a chain of siloxane groups, the chain having a first end and a second end, the first end of the chain being chemically bound to the silicon molecule of the anchor group, the chain having the formula



, and

(iii) a terminal group of molecules chemically bound to the second end of the chain, the terminal group having the formula

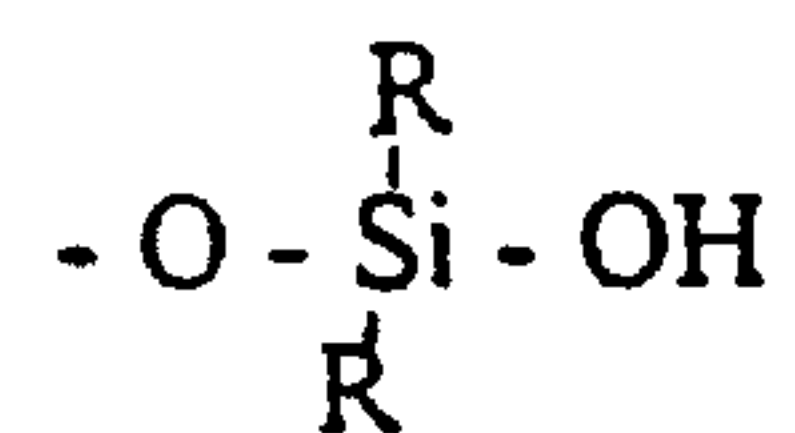


wherein

R<sup>1</sup> consists of inert groups, and

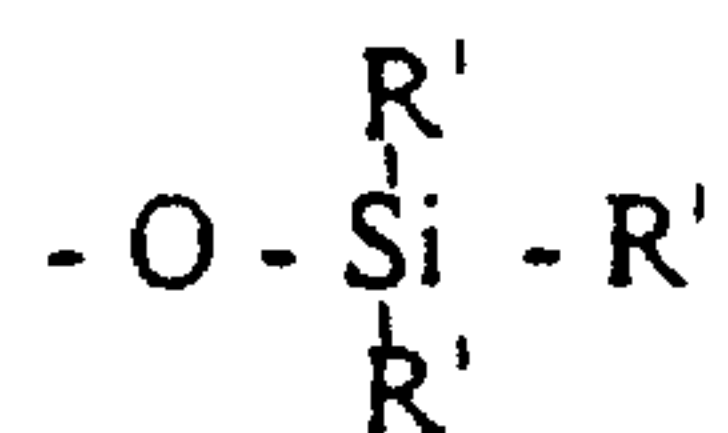
X is selected from the group consisting of esters, ethers and halogens, the improvement comprising the steps of

(a) allowing the X atom of the terminal group to react with water to produce a new terminal group having the formula



; and

(b) replacing the new terminal group with a final terminal group having the structure



wherein R<sup>1</sup> consists of inert groups.

28. The improvement according to Claim 27, wherein the siloxane groups consist of dimethylsiloxane groups.

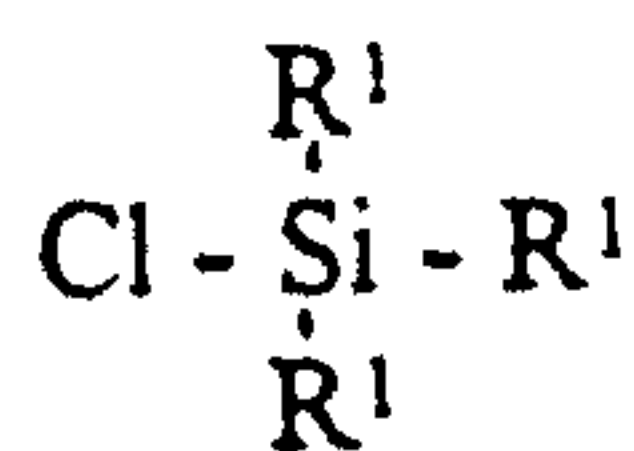
29. The improvement according to Claim 28, wherein the final terminal group consists of a trimethylsiloxane group.

30. The improvement according to Claim 27, wherein R<sup>1</sup> is the same as R.

31. The improvement according to Claim 27, wherein R is selected from the group consisting of phenyl, ethyl, methyl, butyl, amyl, and larger alkyl groups.

32. The improvement according to Claim 27, wherein the step (b) of replacing the new terminal group comprises the substeps of:

(i) contacting the surface with a capping agent having the formula



; and

(ii) allowing the capping agent to react with the new terminal group to result in an inert final terminal group.

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