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(54) Title: SURFACE TREATMENT OF RIGID GAS PERMEABLE CONTACT LENSES

(57) Abstract: The present invention provides an optically clear, hydrophilic coating upon the surface of a rigid gas permeable contact lens by treating the surface of the contact lens with a strong caustic agent and subsequently sonicating the lens in an aqueous solution containing a surface-protective agent.

SURFACE TREATMENT OF RIGID GAS PERMEABLE CONTACT LENSES

FIELD OF THE INVENTION

The present invention is directed toward surface treatment of rigid, gas permeable contact lenses. More specifically, the present invention provides an optically clear, hydrophilic coating upon the surface of a rigid, gas permeable lens by subjecting the surface of the lens to a strong base followed by treatment with a dilute aqueous solution comprising a silicate salt, silicic acid, colloidal silicon dioxide, or combinations thereof. The invention is also directed to a buffered, sterile solution containing a soluble silicate that can be used to both treat and store a rigid, gas permeable contact lens.

BACKGROUND

Early hard contact lenses were produced from polymethyl methacrylate (PMMA) or cellulose acetate butyrate (CAB). Later rigid, gas permeable (RGP) contact lenses formed of silicone-containing copolymers were introduced, offering various advantages over PMMA and CAB lenses, particularly increased oxygen permeability. The original silicone-containing RGP lenses were based on copolymers of a silicone-containing monomer and methyl methacrylate.

In general, oxygen permeability has often been increased in hard or rigid gas permeable contact lenses by the addition of silicone and/or fluorine-containing materials. Examples of such materials include fluorosilicone acrylate and fluorocarbon.

Contact lenses made from silicone-containing materials have been investigated for a number of years. Such materials can generally be subdivided into two major classes, namely hydrogels and non-hydrogels. Non-hydrogels do not absorb appreciable amounts of water, whereas hydrogels can absorb and retain water in an equilibrium state. Regardless of their water content, both non-hydrogel and hydrogel silicone contact lenses tend to have relatively hydrophobic, non-wettable surfaces.

To achieve a wettable surface of a silicone-containing material, hydrophilic monomers are typically added. While this improves the wettability, addition of the hydrophilic monomer will decrease oxygen permeability.

Those skilled in the art have long recognized the need for modifying the surface of such silicone contact lenses so that they are compatible with the eye. It is known that increased hydrophilicity of the contact lens surface improves the wettability of the contact lenses. This in turn is associated with improved wear comfort of contact lenses. Additionally, the surface of the lens can affect the lens's susceptibility to deposition, particularly protein and lipid deposition from the tear fluid during lens wear. Accumulated deposition can cause eye discomfort or even inflammation. In the case of extended wear lenses, the surface is especially important since extended wear lens must be designed for high standards of comfort over an extended period of time, without requiring daily removal of the lens before sleep. Thus, the regimen for the use of extended wear lenses would not provide a daily period of time for the eye to recover from any discomfort or other possible adverse effects of lens wear.

The patent literature has disclosed various surface treatments for rendering the surface of silicone lenses more hydrophilic and more wettable, including changing the chemistry of the surface layer, coating the surface, and compounding the polymer with additives that subsequently diffuse to the surface.

A type of chemical surface modification that has been disclosed in the patent literature involves the introduction of functional groups absent in the parent polymer by the grafting or immobilization of molecules, oligomers, or polymers onto a surface. Grafting or immobilization typically involves, first, the formation of a grafting site which may comprise the formation of a radical by means of chemical reactions, UV irradiation, ionizing radiation, plasma treatment, or the like. The next step is the reaction of the species to be grafted or immobilized with the active site. Surface grafting typically involves the propagation of the reaction to form an anchored chain, wherein competing solution and interfacial reactions occur. Surface crosslinking may occur.

Coating a lens usually involves adhesion of a surface layer onto the substrate being coated. The coated layer can be relatively thick and its physical characteristics can be significantly different than those of the substrate. For coatings that involve high-energy species, for example, evaporation, sputtering, plasma polymerization, the initial stages of the treatment can involve a surface treatment.

Non-plasma techniques for forming a coating have been disclosed. For example, U.S. Patent No. 3,814,051 to Lewison discloses vacuum bonding a uniform hydrophilic quartz surface to a contact lens by vaporizing quartz, namely silicon dioxide, within a high vacuum chamber. The coating of contact lenses by dipping, swabbing, spraying or other mechanical means has been disclosed in U.S. Patents No. 3,637,416 and 3,708,416 to Misch et al. The latter patents disclose a chemical process in which a coupling film-forming organic silicon compound, a vinyl trichlorosilane, is applied to a silicone surface, followed by a silica or silica gel deposit formed by contact with a silicon halide such as tetrachlorosilane or with a silicic ester, more particularly a tetraalkoxysilane. Solutions of such compounds can also be applied in a single step to a contact lens by dipping or the like. In U.S. Patent No. 3,708,225, Misch et al. states that the capabilities of such solutions can be enhanced by incorporating a small amount of colloidal silica, preferably about 1 to 5 percent, whereby the solutions tend to thicken and become easier to apply, further facilitating the buildup of a silica or silica gel deposit.

U.S. Patent No. 3,350,216 to McVannel et al. discloses rendering a rubber contact lens hydrophilic by dipping the lens into a solution of a titanate having the formula $Ti(OR)_4$ wherein R is an alkyl group containing 2 to 4 carbon atoms.

Although such surface treatments have been disclosed for modifying the surface properties of silicone contact lenses, the results have been problematic or of questionable commercial viability. For example, U.S. Patent No. 5,080,924 to Kamel et al. states that although exposing the surface of an object to plasma discharge with oxygen is known to enhance the wettability or hydrophilicity of such surface, such treatment is only temporary.

It is desirable to provide a rigid, gas permeable contact lens with an optically clear, hydrophilic surface coating that will not only exhibit improved wettability, but which will generally allow the use of a silicone contact lens in the human eye, preferably for an extended period of time. It is highly desirable to provide a rigid, gas permeable contact lens with a surface that is hydrophilic and also highly permeable to oxygen. Such a surface treated lens would be comfortable to wear in actual use and would allow for the extended wear of the lens without irritation or other adverse effects to the cornea.

It would be desirable if such a surface treated lens were a commercially viable product capable of economic manufacture.

SUMMARY OF THE INVENTION

The present invention is directed to a rigid, gas permeable contact lens having a silicate-containing coating and a method of manufacturing the same, which coating is hydrophilic and resistant to protein and lipid deposition.

In the preferred embodiment of the invention, the method comprises treating the lens first with a strong base and then with a silicon-containing aqueous solution comprising a silicate salt, silicic acid, and/or colloidal silicon-dioxide. Treatment can be achieved after the lens has been lathed. The lens is submerged in the base followed by ultrasonication of the lens in a surface-protective, silica-containing or silica-producing aqueous solution (the term solution is broadly meant true solutions as well as colloidal particles in solution, which colloids may be formed by supersaturated solutions).

DETAILED DESCRIPTION OF THE INVENTION

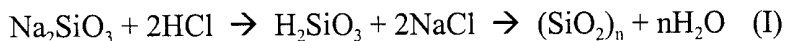
As mentioned above, the present invention is directed toward the surface treatment of a rigid, gas permeable contact lenses to improve comfort and wettability. The surface of the lens is first treated with a strong caustic solution. A silicate-containing coating is then formed, preferably by ultrasonication of the lens in a silica-containing solution.

As mentioned above, therefore, the present invention is directed to the manufacture of a hydrophilic surface coating on a rigid, gas permeable contact lens. The surface coating is durable and renders the lens wettable. The surface coating allows the lens to be comfortably worn for extended periods of time. In particular, the invention is directed to treatment with a silicon-containing aqueous solution of the lens following surface modification by a strong base. It is desired that the contact lens be sufficiently coated the hydrophilic silicate-coating such that little of the surface is hydrophobic and sufficiently distanced from eye tissue.

It has previously been discovered that if a silicon-containing solution contains, for example, a silicate salt, the free acid thereof, or a colloidal silicon dioxide (including precursors thereof), the coating is durable and hydrophilicity of the surface uniform.

Commercially soluble silicates include silicate salts. A preferred silicate is the alkali metal silicate having the general formula $M_2O \cdot mSiO_2 \cdot nH_2O$, where M is an alkali metal, preferably Na (sodium), and m and n is the number of moles of SiO_2 (silica) and H_2O , respectively, per mole of M_2O . The distribution of silicate species in aqueous sodium silicate solutions has long been of interest, and it is presently believed that silicate solutions contain a complex mixture of silicate anions in dynamic equilibrium. The composition of commercial alkali silicates is typically described by the weight ratio of SiO_2 to M_2O . These materials are usually manufactured as glasses that dissolve in water to form viscous, alkaline solutions. The ratio of SiO_2 to M_2O in commercial sodium silicate products typically varies from 0.5 to 4.0. A common form of soluble silicate, sometimes called waterglass, has a ratio of 3.2. Lower ratios of M_2O are preferred for use in this invention, for example, the sodium silicate coating a SiO_2 to M_2O ratio of 2.9 commercially available as Solution K from PQ Corp.

Silicate solutions, particularly sodium silicate solutions are preferred for use in the present invention. The pH of the silicate solution used to treat the silicone hydrogel lens is suitably around pH 7, preferably between about 6 to 8. Since sodium silicates are commercially available in alkaline form for increased solubility, a sodium silicate solution may be formed by neutralizing, by means of acidifying an alkaline solution of the silicate, for example, by changing the pH from about 10-11 to about 8. As a result of lowering the pH, the solution becomes potentially silica-containing according to the following equation (I):



In accordance with the above equation, it is apparent that silicic acid can also be used to form silica. Thus, silicates and silicic acid are considered herein to be precursors of a silica-containing compound, silica or a polymer $(SiO_2)_n$ thereof, or in other words, a

colloidal silica that can protect the lens surface. Without wishing to be bound by theory, it is believed that the presence of silica in the solutions, especially if in saturate or supersaturated, prevents the silicate in the lens coating from leaving the coating and entering the solution.

A colloidal silica or silicon dioxide material may be employed directly as a silica-containing material. Such materials are commercially available under various trade designations, including Cab-O-Sil® (Cabot Company), Santocel® (Monsanto), Ludox® (DuPont), and the like.

To form the coating of the present invention, lenses to be coated are immersed in the silicon-containing solution described above and the immersed lenses are exposed to an energy source that promotes adherence of the coating to the lens surface. Energy is provided in a form that minimizes heating of the solution. Temperatures are preferably maintained below the level where lens deformation may occur. Ultrasonication is a method ideally suited to this purpose. Ultrasonication is a well-known dispersal/disruption technique that uses mechanical vibrations to create pressure waves in fluids. This in turn forms millions of microscopic bubbles (cavities) which expand during negative pressure excursions and implode violently during positive pressure excursions. This cavitation produces a powerful shearing action and causes the molecules in the liquid to become intensely agitated. The agitated silicon-containing molecules in the solution used in the method of this invention collide with the lens surface and become attached thereto, forming a silicate-containing coating.

To illustrate this process, ultrasonication may be accomplished with equipment such as the High Intensity Ultrasonic Processor Model CP-300 (20 kHz) and Probe Model V1A, both from Cole-Parmer. When employing this equipment in the coating method of this invention, the solution is "pulsed" for short period of times. The duration of treatment is not narrowly critical, although times within the range from about 1 to 10 minutes are desirable, and treatments performed in the following examples lasted about 5 minutes. Temperature of the solution does increase during ultrasonication. However, temperatures typically do not exceed about 50 to 60°C. Heating may accelerate and

promote the precipitation of silica onto the lens, but (as noted above) excessive heating will detrimentally effect the lens.

Without wishing to be bound by theory, it is theorized that the silicate coating in the final product has sufficient silicate content to provide the desired surface properties, such as wettability and deposition resistance, and yet sufficient polymer content to provide durability. The chemistry of the silicate film in the product is not completely made of silicate and some of the original polymer material may remain in modified form.

In order to form a silicate-containing coating on the rigid, gas permeable lens surface, the lens is initially treated by soaking in a strong base. Any commercially available base may do. Concentrations of the base may range from 6N to 14N. A preferred base is sodium hydroxide and the preferred concentration is 10N.

Manufacture of the lens. The method of this invention is generally applicable to any rigid, gas permeable lens. Preferably, the lens is a silicone-containing material. A particularly preferred material is disclosed in United States Patent No. 4,780,515. Regarding these latter materials, it would be desirable to further increase oxygen permeability. One way to do that is to reduce methacrylic acid (or wetting monomer) content of the monomer mix used to prepare the lens. However, reducing methacrylic acid content causes surface properties to deteriorate. Adding the silicate-containing coating of the invention has been found to overcome the effects caused by the reduced methacrylic acid content and to produce lenses having improved comfort and wettability.

RGP contact lens materials are usually provided in the form of rods, buttons, or lens blanks, which are subsequently machined into contact lenses having desired lens surfaces. It is typical to lathe a button to provide a contact lens having the desired thickness and anterior/posterior lens surfaces.

Subsequent to lathing, the lens is subjected to surface treatment by immersing the lens in a caustic solution. The caustic solution serves to clean the surface and possibly cleave any remaining ester groups. Other vigorous conditions such as acid and peroxides do not perform as well as the bases.

Since the coating is dependent on a number of variables, the optimal variables for obtaining the desired or optimal coating may require some adjustment. If one parameter

is adjusted, a compensatory adjustment of one or more other parameters may be appropriate, so that some routine trial and error experiments and iterations thereof may be necessary in order to achieved the coating according to the present invention. However, such adjustment of process parameters, in light of the present disclosure and the state of the art, should not involve undue experimentation. As indicated above, general relationships among process parameters are known by the skilled artisan, and the art of surface treatment has become well developed in recent years. The Examples below provide the Applicants' best mode for forming the coating on a rigid, gas permeable lens.

EXAMPLE 1

This Example illustrates the preparation of a silicon-containing solution according to the present invention. The ingredients listed in Table 1 below were employed in preparing the solution.

TABLE 1

Ingredient	mg/gm	% w/w
Sodium Silicate, K grade (a 31.7% solution from PQ Corporation)	1.25	0.0396**
Boric Acid	8.5	0.850
Sodium Borate	0.9	0.090
Sodium Chloride	4.5	0.450
Hydrochloric Acid, 1N	4.5	0.450
Sodium Hydroxide, 1N	As needed*	pH 7.1 - 7.4
Purified Water q.s. to	1.0 gm	100 %

*As needed to adjust pH.

**based on dry weight

Into an appropriate stainless steel vessel, equipped with agitation, purified water was formed a first solution as follows. Water was added in an amount equivalent to 80% of the total water volume, and agitation was initiated and maintained throughout the processing of the batch. In the order listed were added and dissolved the batch quantities

of sodium chloride, boric acid, and sodium borate. The solution was mixed for a minimum of 10 minutes to ensure complete dissolution. In a separate container, a second solution was formed as follows. stock solution of sodium silicate was prepared at a concentration of 0.396% in purified water equivalent to 10% of the total water volume. The solution was filtered through a 0.45 μ m filter. The filtered sodium silicate stock solution was then added to the first solution. The hydrochloric acid (1N) was slowly added to this solution, and the pH was adjusted, if necessary, with additional 1N Hydrochloric Acid or 1N Sodium Hydroxide solution. The remaining purified water was added to bring the batch to 100% of volume. The final product should have a pH at 25° C of 7.0 - 7.4, an osmolality of 270 - 330 mOsm/Kg , and visual clarity (colorless to clear pale yellow).

EXAMPLE 2

Using the general procedure described in United States Patent 4,780,515, contact lens material was prepared from a monomer mix having the components shown below in Table 2. The mix also contained 0.054 percent by weight of Vazo-52 thermal initiator, 0.17 percent by weight of Vazo-64 thermal initiator, and 0.00979 percent by weight of tinting agent. The material was cast in the form of rods and the rods were cut into blanks. Wafers with a diameter of 12.7 mm and a thickness of 0.25 mm were cut from blanks and both surfaces polished to an optical finish using a polishing powder dispersed in deionized water and stored in a clean glass vial under deionized water until use.

TABLE 2

Component	Weight %
N-vinyl-2-pyrrolidone	5
Neopentyl glycol dimethacrylate	8
Bis(1,1,1,3,3,3-hexafluoroisopropyl) itaconate	42
3-methacryloxypropyltris(trimethylsiloxy)silane	30.8
Pentacontamethyl- α,ω -bis-(4-methacryloxybutyl)-pentacosasiloxane (M ₂ D ₂₅)	11.2

EXAMPLE 3

Wafers prepared as described in Example 2 were subjected to immersion in 10N NaOH. Samples of the base-treated lenses were then immersed in 0.125% of sodium silicate and pulsed sonicated for 5 minutes. The wafer was then sequentially treated and analyzed for the durability of the coating.

Dynamic contact angle (DCA) measurements were made with hydrated, polished wafers utilizing a Cahn Instruments DCA 322. Wafers were dipped in the test solution 7 times at an average rate of 225 microns per second. All tests were run at room temperature. A computer assisted mathematical analysis of the data yields a graph of contact angle plotted against the vertical position on the wafer. The average Advancing and Receding contact angles were obtained from the graph.

Advancing and receding measurements were recorded prior to any surface treatment. After these initial measurements were taken, the wafer was then subjected to 10N sodium hydroxide and then immersion/sonication in the solution prepared in Example 1. Measurements were taken. The treated wafer was then rinsed with borate buffered saline (BBS). Measurements were taken. The treated wafer was then rubbed on each side for 10 seconds and rinsed with BBS. Measurements were taken. The results are shown below in Table 3.

TABLE 3

Wafer Sample	Advancing Contact Angle	Receding Contact Angle
Untreated	98	42
Surface Treated	74	15
Surface Treated, Rinsed	76	15
Surface Treated, Rubbed and Rinsed	85	40

Both the Advancing and Receding Contact Angles generally decrease for the wafers which have been surface treated. The wafers that have been surface treatment

have fairly equivalent Advancing Contact Angles, which may indicate that the surface treatment is durable.

EXAMPLE 4

A wafer of the same material as the previous example was first submerged in 10N sodium hydroxide. DCA measurements were taken. The wafer was then surface treated by immersion/sonication with the solution from Example 1.

TABLE 4

Wafer Sample	Advancing Contact Angle	Receding Contact Angle
Base Treated	66	16
Base Treated, immersion/sonication	39	34

The Advancing and Receding Contact Angles both decrease with complete treatment which indicates that it is the silicate coating, not the base treatment, which lowers the Contact Angle.

Many other modifications and variations of the present invention are possible in light of the teachings herein. It is therefore understood that, within the scope of the claims, the present invention can be practiced other than as herein specifically described.

CLAIMS:

1. A method for treating the surface of a rigid gas permeable contact lens comprising the following steps:

- (a) surface treating the lens with a caustic agent;
- (b) immersing the lens in an aqueous composition comprising a surface-protective agent that comprises silica or a precursor thereof; and
- (c) sonicating said aqueous solution containing said lens.

2. The method of claim 1, wherein the aqueous composition comprises greater than 90 percent by weight water and the surface-protective agent is selected from the group consisting of a silicate salt, silicic acid, colloidal silica, and combinations thereof.

3. The method of claim 1, wherein sonicating said aqueous solution also elevates the temperature of said solution.

4. The method of claim 1, wherein said caustic agent is a base.

5. The method of claim 4, wherein said base is 10N sodium hydroxide.

6. The method of claim 1 wherein the lens is a silicone-containing rigid gas permeable contact lens.

7. A method for treating the surface of a rigid gas permeable contact lens comprising the following steps:

- (a) subjecting the surface of said lens to a caustic agent;
- (b) subsequently immersing the surface reduced lens in an aqueous solution comprising greater than 90 percent by weight water and 0.03 to 3.0 percent by

weight of a surface-protective agent selected from the group consisting of a silicate salt, silicic acid, colloidal silica, and combinations thereof, and

(c) sonicating said immersed lens of (b) for a period of 1 to 10 minutes.

8. The method of claim 6, wherein said period of time for sonicating said immersed lens is preferably about 5 minutes.

9. A rigid gas permeable contact lens including a hydrophilic surface, wherein said surface is obtained by the sequential steps of:

(a) subjecting the surface of the lens to a caustic agent to produce a pretreated surface,

(b) subsequently immersing and sonicating said pretreated lens in an aqueous solution comprising greater than 90 percent by weight water and 0.03 to 3.0 percent of a surface-protective agent selected from the group consisting of a silicate salt, silicic acid, colloidal silica, and combinations thereof while heating the solution.

10. The composition of claim 8 further comprising an effective amount of a buffering agent.

11. The composition of claim 8, comprising 93 to 99% by weight water.

12. The composition of claim 8, wherein the osmolality adjusting agent comprises an ophthalmologically suitable salt selected from the group consisting of an alkali metal or alkaline earth metal halide salt.

13. A rigid, gas permeable contact lens including a hydrophilic surface, wherein said surface is obtained by submerging said lens in a caustic agent followed by immersion of said lens in an aqueous solution comprising greater than 90 percent by weight water and 0.03 to 3.0 percent of a surface-protective agent selected from the

group consisting of a silicate salt, silicic acid, colloidal silica, and combinations thereof while sonicating the solution.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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US CL : 427/164, 600, 601; 351/160H

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/164, 600, 601; 351/160H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

BRS search terms: silicate; silicic acid, colloidal silica, contact lens, immersion, dipping, ultrasonic, sonicating, hydrophilic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,936,703 A (MIYAZAKI et al) 10 August 1999, whole document.	1-13
Y	US 3,732,620 A (MISCH et al) 15 May 1973, col. 5-8.	1-13
Y,P	US 6,099,852 A (JEN) 08 August 2000, whole document.	1-13
Y	US 5,475,074 A (MATSUOKA et al) 12 December 1995, col. 12, lines 5-12.	1-13
Y	US 5,143,750 A (YAMAGATA et al) 01 September 1992, col. 3, lines 9-32.	1-13
Y	US 4,131,696 A (COVINGTON) 26 December 1978, col. 3, lines 40-45.	10, 12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* & * document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,127,423 A (RANKIN) 28 November 1978, col. 3, lines 1-35.	2, 7, 9, 13