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• A new gas permeable contact lens is produced using a solid silicone core and a plasma polymer surface. This surface is hydrophilic and impermeable to macromolecules. The surface characteristics of this lens were compared with the surface characteristics of available silicone contact lenses. We found that in contrast to our lens, the silicone contact lenses lost their hydrophilic surface with time. In addition, they are permeable to lipid dyes, eg, Sudan red.

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Silicone rubber is used in the manufacture of contact lenses either as the sole lens material or in combination with polymethylmethacrylate. Pure silicone has the advantage of being the most gas-permeable material[1] used in the manufacture of contact lenses. The respiratory needs of the human cornea are presumably best served by this material. Also, the fact that silicone can be inherently soft as a long-chain polymer and does not depend on water absorption is advantageous as visual acuity is unaffected as hydration of the contact lens on the cornea changes. Silicone does have a serious disadvantage; it is permeable to large macromolecules in the tear film, especially those that are lipid soluble.[2,3] For this reason, clinical trials with silicone contact lenses have largely been unsuccessful. Most lenses accumulate tear-film deposits on their surface that result in blurred vision, irritation, and discomfort. These deposits permeate the material and are not readily removable with cleaning.

The purpose of this study is to describe a new gas-permeable contact lens, which consists of a central core of solid silicone covered by a thin plasma polymer that is hydrophilic and impermeable to macromolecules. Surface characteristics of this type of lens will be compared with the surface characteristics of other silicone lenses.

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MATERIALS AND METHODS

Plasma Polymer Surfaced-Silicone Contact Lenses

Silicone contact lenses were obtained. Plasma polymer was then formed on the surface of the lens to a 400-A thickness. Lenses were mounted on an aluminum-holding device and placed in a bell-jar vacuum system. The bell jar was then evacuated to a vacuum of less than 10^{-3} mm Hg. The lenses were rotated between two electrode plates. Methane gas was then introduced into the system at an established flow rate. Glow discharge was obtained with a 10-kHz power source. Glow discharge was continued until the thickness monitor indicated that 400 A of methane polymer had been deposited on the surface of the contact lenses. The flow of methane gas was then stopped, and the lenses were treated with oxygen plasma.

Analysis of Surface Wettability

Three groups of silicone contact lenses were evaluated. In the first group, six lenses were subjected to our method of methane-plasma polymerization followed by treatment with oxygen plasma. Methane polymer was deposited on the lens surface for a thickness of 400 A. In the second group, six lenses were subjected by the manufacturer to surface treatment, consisting of oxygen plasma alone. In the third group, six lenses were subjected by the manufacturer to water vapor plasma.

After cleaning each lens with a physiologic saline solution, a 10-μL drop of sterile water was placed on the convex surface of the lens and the surface was photographed. The contact angle of the water was then measured five minutes after removal from the sterile water, and at 1 and 3 days, and at 1, 3, and 4 months thereafter.

Dye Penetration Test Results

A lipid soluble stain (Sudan red) was prepared in a standard manner. Six lenses from each group were placed in the dye from ten seconds to four hours. The lenses were dried with tissue paper to remove the stain from the surface of the lens and then photographed.

Four lenses of each group were placed in a water-soluble dye (sodium fluorescein) for 12 hours. After removal from this solution, they were dried with tissue paper and photographed.

Water Contact Angle of Silicone Contact Lens after Treatment by Plasma

Time After Removal of Lens From Physiologic Saline Solution	Treatment Group		
	1*	2†	3‡
5 min	26°	10°	25°
24 hr	30°	22°	98°
3 days	27°	60°	101°
1 mo	23°	65°	100°
3 mo	28°	71°	104°
4 mo	27°	70°	100°

*Consisted of six lenses treated with methane-oxygen plasma.

†Consisted of six lenses treated with oxygen plasma.

‡Consisted of six lenses treated with water-vapor plasma.

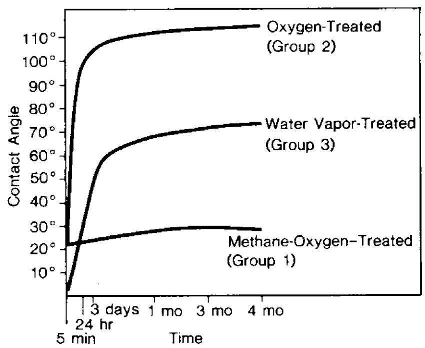

Fig 1.—Water contact angle on surface of silicone contact lenses during four-month period.

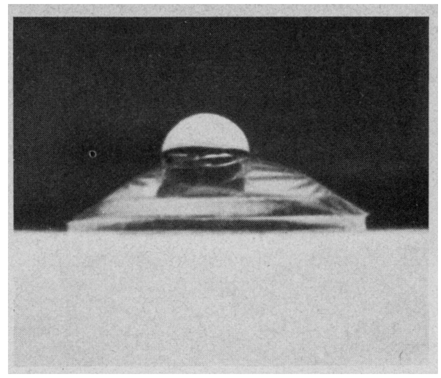

Fig 2.—Water contact angle of silicone contact lens treated by oxygen plasma 24 hours after removal from water.

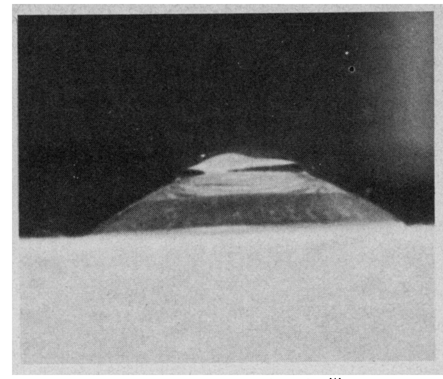

Fig 3.—Water contact angle of silicone contact lens treated by water-vapor plasma five minutes after removal from water.

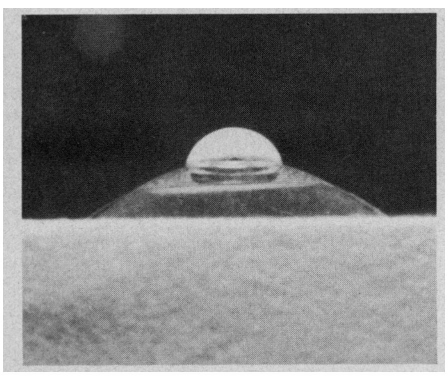

Fig 4.—Water contact angle of silicone contact lens treated by water-vapor plasma three days after removal from water.

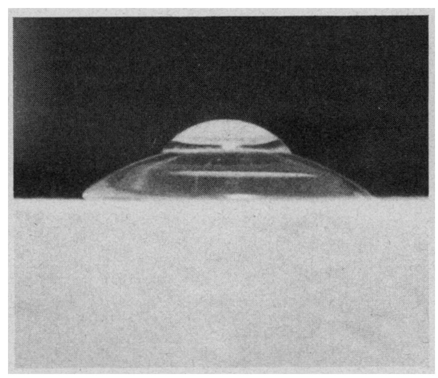

Fig 5.—Water contact angle of silicone contact lens treated by methane and oxygen plasma three days after removal from water.

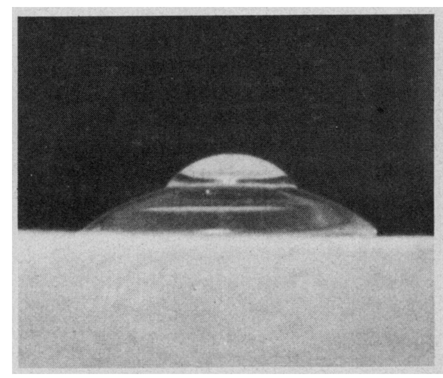

Fig 6.—Water contact angle of silicone contact lens treated by methane and oxygen plasma four months after removal from water.

RESULTS

Contact-angle measurements are given in the Table and shown in Fig 1. All lenses were initially wettable, with the water vapor-treated (group 3) lenses being the most wettable. This wettability gradually decreased over time for all but the methane plasma-treated (group 1) lenses (Figs 2 through 6).

Dye Penetration

Lipid-soluble stain rapidly penetrated (<10 s) all lenses in groups 2 and 3. Lenses treated with methane (group 1) resisted dye penetration and had less penetration after four hours than the other lenses did after 10 s (Fig 7). All lenses were resistant to penetration by water-soluble dye.

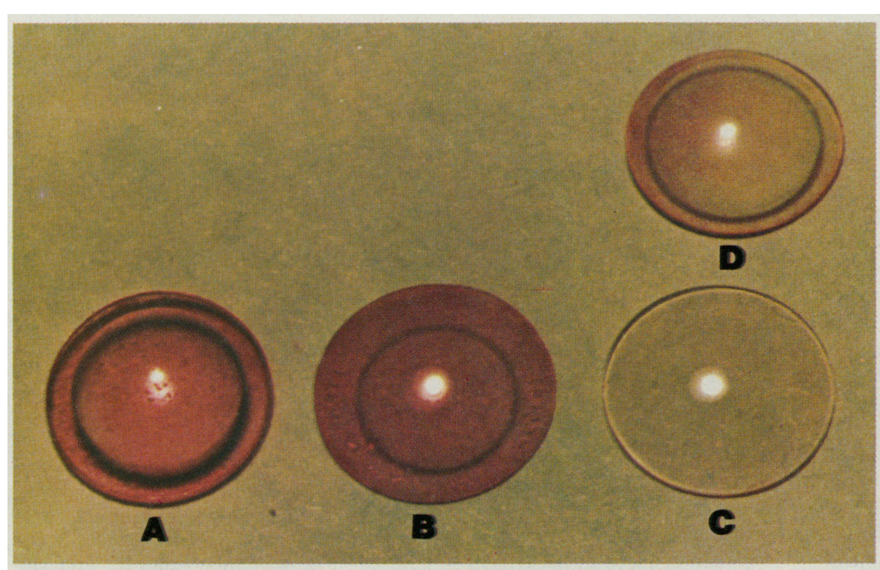

Fig 7.—Photograph of oxygen plasma-treated (A), water vapor plasma-treated (B), and methane-oxygen-treated (C) lenses 10 s after dye immersion and after four hours for methane-oxygen-treated lens (D).

COMMENT

Plasma (ionized gas) is usually formed by subjecting a gas to electric glow discharge as the gas flows into a vacuum. When a substrate, eg, silicone or polymethylmethacrylate, is exposed to plasma, a chemical reaction occurs on the surface. When oxygen or nitrogen gas is used to form plasma, the gas is merged with the polymer surface. Treatment with oxygen or water vapor incorporates hydrophilic groups on the surface of the polymer. This is an example of nonpolymer-forming plasma. When methane gas is used as the source of plasma, plasma polymer is formed and deposited on the surface of the substrate. In this case, methane acts as a monomer; it undergoes polymerization and reacts with the surface of the substrate. Methane can be used to produce a highly cross-linked polymer with a tight molecular structured network. A new type of contact lens can then be formed consisting of a central core of solid silicone, which is highly oxygen permeable, and an outer shell of plasma polymer, which is hydrophilic and deposit resistant. Plasma reactions are confined and limited to the surface of a substrate and, unlike ionization produced by penetrating radiation, the intensity of the reaction is greatest at the surface. Thus, plasma provides the ideal methods of modifying a surface of a substance without affecting the bulk properties, eg, oxygen permeability.[4]

In this study, we compared the treatment of silicone contact lenses by three different types of plasma. When we measured the wettability of the contact lenses over time, water-vapor treatment (group 3) produced the most wettable surface. However, this effect was temporary and lessened appreciably as the lenses were exposed to air. This reduction in wettability was even more pronounced in the oxygen-treated lenses (group 2); the wettability decreased rapidly after removal from the water. The methane-treated lenses remained wettable for four months. This long-term effect is important, as a contact lens on the surface of the eye is exposed to constant drying during wear. Methane treatment alone can produce a wettable surface, but it is improved by adding oxygen plasma treatment, which produced nondecaying hydrophilic surface for the following reasons.

Polymer solids have a loose molecular structure in which rotation and reorientation of molecules at the surface can take place. This is unlike the surface of a metal or ceramic in which a tight molecular structure exists. When hydrophilic groups are attached to silicone using oxygen or water vapor plasma, rotation of the hydrophilic groups into the interior of the solid and away from the surface takes place.[5] Inward rotation of hydrophilic groups on a hydrophobic polymer occurs because of the thermodynamic requirement of minimizing the interfacial tension of a solid.[5] This results in a gradual decay of the hydrophilic surface.

When the surface of a contact lens is treated with methane plasma, the carbon atoms are so tightly joined that no rotation can take place. Hydrophilic groups attached to the methane polymer are fixed in position and do not rotate. This results in a nondecaying hydrophilic surface. The thickness of the methane produced polymer is only 200 to 500 A and is less than a wavelength of light, thus, the optical properties of the lens are unaffected.

Establishing a tight barrier on the surface of a silicone contact lens has an advantage other than producing a hydrophilic surface; the lens becomes impermeable to lipids and lipoproteins. Thus, methane treatment can prevent adhesion of tear-film deposits to the lens and the lens can be immersed for hours in a lipid soluble dye with little penetration, while the same dye readily penetrates contact lenses unprotected by a barrier polymer (Fig 7). The loose molecular structure of silicone makes this material permeable to lipid-soluble materials.

Danker & Wohlk Inc, Uniondale, NY, provided 12 and Dow Corning Corp, Midland, Mich, provided six of the 18 silicone lenses used in this investigation.

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