Kirk-Othmer Encyclopedia of Chemical Technology.
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CONTACT LENSES

Contact lenses are small, hemispherical-shaped optical devices placed in contact with the transparent tissue at the front of the eye called the cornea. The capillary attraction of the liquid tear layer between the contact lens and the cornea and the partial coverage of the lens by the eyelids prevent contact lenses from being dislodged during eye movement and blinking. Contact lenses are used to correct vision deficiencies such as myopia (nearsightedness), hyperopia (farsightedness), presbyopia (loss of near focusing power with age), and astigmatism. An increasingly common use of contact lenses is to change the color of a normal eye or to improve the appearance of an eye disfigured by injury or disease. Contact lenses can also be used as therapeutic devices in the medical treatment of certain eye diseases or injuries.

The concept of a contact lens device for modifying the optical power of the eye was described by Leonardo da Vinci and later by Rene Descartes and Thomas Young. In 1823, Sir John Herschel described the application of a contact lens device specifically for the purpose of correcting vision. The first contact lens was fitted to a human eye for correction of vision in 1888. The early lenses were made of blown or molded glass and were difficult to wear. The contact lens industry began to grow after World War II when the plastic poly(methyl methacrylate) [9011-14-7] (PMMA) was found to be a suitable material for contact lenses in terms of optical properties, biocompatibility, and manufacturability. In the late 1950s a hydrogel material based on poly(2-hydroxyethyl methacrylate) [25249-16-5], poly(HEMA) was discovered. Contact lenses made with this water-containing soft plastic promised significantly improved comfort compared with the hard PMMA lenses. Poly(HEMA) lenses were used in Czechoslovakia in the 1960s; popularization of soft contact lenses in the United States occurred in the 1970s, following the 1971 introduction by Bausch & Lomb of the Soflens contact lens.

The number of contact lens wearers has grown to an estimated 24 million in the United States and 50 million worldwide. Concurrently, there has been a proliferation of contact lens manufacturers and products. The 1980s saw the widespread introduction of lens products made of more oxygen-permeable materials, ie, rigid gas-permeable (RGP) materials that made PMMA lenses virtually obsolete and high water content hydrogels that competed with HEMA-based lenses.

Research continues for materials having improved oxygen permeability, deposit resistance, and comfort. In addition, there is the search for breakthrough lens designs, such as bifocal contact lens products. The challenge for contact lens manufacturers is to capture more than a 15% share of the vision correction population, now dominated by traditional eyeglasses. Furthermore, competition includes developing new surgical techniques, eg, excimer laser refractive surgery that modifies the shape of the cornea to correct vision, potentially without the use of eyeglasses or contact lenses. Detailed information on historical and clinical aspects of contact lenses (1, 2) and overviews of refractive surgery techniques (3, 4) are available.

1. Clinical Aspects

No particular contact lens type or product is considered universally superior. In some regions of the world hard lenses dominate the market, eg, some European countries and Japan; in other regions, eg, North America and

Scandinavia, soft lenses dominate. Contact lens practitioners select their preferred type of lens using criteria other than just lens material properties. However, among soft lenses, HEMA-based lenses are prescribed most often, and among hard lenses, silicone–acrylate RGP lenses are most common.

To remain safe and efficacious on the eye, contact lenses must maintain clear and wetted surfaces, provide an adequate supply of atmospheric oxygen to and adequate expulsion of carbon dioxide from the cornea, allow adequate flow of the eye's tear fluid, and avoid excessive abrasion of the ocular surface or eyelids, all under a variety of environmental conditions. The clinical performance of a contact lens is controlled by the nature of the lens material; the lens design; the method and quality of manufacture; the lens parameters or specifications prescribed by the practitioner; and the cleaning, disinfection, and wearing procedures used by the patient.

Corneal edema occurs with almost every type of contact lens as a result of corneal hypoxia during lens wear. It is most noticeable when lenses are worn during sleep. Although corneal edema is reversible, excessive and prolonged edema can lead to changes in corneal curvature, growth of blood vessels into the central cornea across the line of sight, or vision reduction through corneal haziness. Excessive edema may predispose the cornea to abrasion, inflammation, or infection, leading to a corneal ulcer. Consequently, a primary goal of contact lens manufacturers has been to develop materials with higher oxygen permeability to reduce corneal hypoxia. For a lens 0.1 mm thick, an oxygen permeability coefficient (Dk) of approximately 100 barrer units is thought to be sufficient to produce no more corneal edema than occurs when the eyes are closed during sleep with no contact lens in place (5, 6).

All contact lenses tend to accumulate debris, deposits, and discolorations on and sometimes below the surfaces (7). The deposits are usually proteinaceous or lipid but may also be inorganic compounds and microorganisms, eg, fungi and bacteria. The source of these deposits is usually the eye itself, the tear film that bathes the surface tissues, the eyelid glands, the mucoid substance secreted by certain conjunctival cells, or the immunoglobulins secreted through the vascular system. Although regular cleaning and disinfection can control these accumulations and reduce the likelihood of clinical problems such as reduced vision, inflammation or red eye, abrasion, and infection, the deposits are considered undesirable (8, 9).

Clinical experience has shown that certain types of lens materials are more prone to deposit problems. In general, lenses with negatively charged moieties at the surface accumulate greater amounts of lysozyme, the principal tear film protein (10). The introduction and use of disposable lenses make these deposits and their clinical problems less significant.

1.1. Classification of Contact Lenses

All contact lenses can be divided according to the wearing modality. Daily wear lenses are worn during the day only, being placed on the eye in the morning and removed, cleaned, and disinfected before sleep at night. Extended wear or flexible wear lenses can be worn continuously for several days and nights, including during sleep. They have a higher oxygen transmissibility than daily wear lenses, achieved either by making the lens thinner or by making the lens from a more oxygen-permeable material.

Contact lenses can be divided further according to the type of vision deficiency for which they provide optical correction, ie, myopia, hyperopia, presbyopia, and astigmatism. A toric lens is designed to correct astigmatism; an aphakic lens is designed to correct the high amount of hyperopia created when the natural crystalline lens of the human eye is surgically removed because of a cataract. A bifocal lens or multifocal lens is designed to have at least two distinct optical segments to correct vision, usually one for distant and one for close vision. For some bifocal lenses and for all toric lenses, the lens is kept on the eye in one orientation, without rotating off axis, by designing the lens with some ballasting. This provides the optimal correction of vision. Because their orientation on the eye is not critical to optical performance, nonbifocal and nontoric lenses have rotationally symmetric optics.

Contact lenses can be subdivided further according to whether they are tinted and/or disposable and by the material from which they are formulated. In addition, contact lenses can be used medically for the treatment of certain eye diseases and injuries by providing a protective cover while the tissue heals itself or by acting as a drug delivery system; such lenses are termed therapeutic lenses, bandage lenses, or shields.

Disposable lenses and lenses used in planned replacement programs are the most recent contact lens development. Traditionally, the usable life of contact lenses has been one year or longer because of the use of various lens-cleaning procedures. Disposable lenses were introduced to avoid the inconvenience and likelihood of patient noncompliance in carrying out such cleanings. They were originally intended to be used once, for one week of continuous wear, discarded, and replaced with a new pair. Disposable lenses are now prescribed with a variety of different wearing schedules, disposal periods, and cleaning and disinfection procedures. Disposable lenses are not intrinsically different in design or material from nondisposable lenses, but are generally packaged in foil–blister packets whereas nondisposable lenses are packaged in glass vials. Although the single lens cost is lower for a disposable lens, the total cost to a patient of a disposable lens system, eg, 52 lens pairs per year, is somewhat higher than the cost for a nondisposable lens system, eg, 1–2 lens pairs per year, including solutions for cleaning and disinfecting the lenses. By necessity, disposable lenses are manufactured using cost-efficient manufacturing technology to produce the huge quantities needed for the marketplace.

It is convenient to classify lenses according to whether they are rigid (hard) or flexible (soft). Some newer materials give rise to lenses that can be termed semirigid, semisoft, and the combination soft–rigid. Hard lenses, including RGP lenses, are invariably nonhydrogels, although their surfaces are wettable on the eye. Soft lenses are usually hydrogels. One notable exception is the silicone elastomer lens that is quite flexible but is not a hydrogel.

The flexibility of a contact lens material dictates, to a large extent, the design of the lens. Hard lenses are generally 8–10 mm in diameter, cover only some of the corneal surface, and fit mostly in between the upper and lower eyelids. Soft lenses are generally 13–15 mm in diameter, cover the entire corneal surface, extend onto the white of the eye, and fit well underneath the upper and lower eyelids. Hard lenses have slightly superior optical performance on the eye, superior oxygen permeability (for some rigid materials), enhanced flow of the liquid tears and removal of ocular debris from between the lens and the cornea, and durability. In addition, hard lenses allow easier cleaning and disinfection methods for the patient in some situations. Soft lenses have considerably greater comfort when first placed on the eye and more secure positioning under the eyelids, which prevents accidental dislodgement.

2. Properties of Contact Lenses

Not every polymer can be manufactured successfully into a contact lens. Several important properties for both ocular physiology and patient handling are required of a material for a contact lens application (1, 11). In addition, the type of lens application, ie, rigid, flexible, or soft, will dictate the range and importance of the key properties.

2.1. Oxygen Permeability

The most critical factor for a contact lens is oxygen permeability. With no blood vessels, the cornea must obtain oxygen from the atmosphere; the cornea will swell and become hypoxic with poor oxygenation. A contact lens has the potential to act as an oxygen barrier to the cornea, and although the cornea is oxygenated partially from a tear pump mechanism by which air-oxygenated tears flow under the contact lens, this amount of oxygen is not sufficient to allow for wearing times longer than a day. Oxygen permeability (Dk) is an intrinsic property of the material, and oxygen transmissibility (Dk/L, where L is the lens thickness) depends on the thickness of the material. There is also a growing concern for the measurement of carbon dioxide permeability; buildup of carbon dioxide behind the lens may cause significant pH changes in the tear (12).

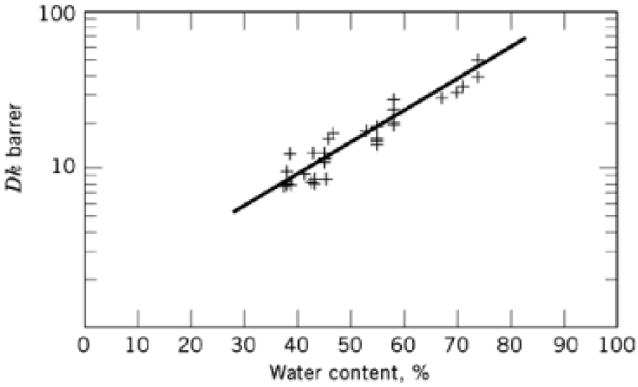


Fig. 1. Correlation of *Dk* with percent water (log-linear plot). 1 barrer $=10^{-11}$ cm^3 O_2 (at STP)·cm/(cm^2·s·mm Hg).

In the contact lens field, barrer units are typically used for the oxygen permeability coefficient (*Dk*).

$$1\ \text{barrer} = \frac{10^{-11}\ \text{cm}^3\text{O}_2\ \text{(at STP)}\cdot\text{cm}}{\text{cm}^2\cdot\text{s}\cdot\text{mm Hg}} = \frac{0.335\ \text{mmol}}{\text{m}\cdot\text{s}\cdot\text{TPa}}$$

See Barrier polymers for a discussion of permeability units.

Oxygen permeability can be measured by a variety of methods. Classical techniques such as ASTM D1434 measures the amount of oxygen transported across a polymer membrane when an infinite gradient is established (13). An alternative-method measures the oxygen volumetrically (14). The most commonly used technique is a polarographic method (15) adapted for contact lenses (16). Although several variations on the method are used, the basic principle is consistent. The lens polymer is placed over a gold electrode and immersed in a saline solution. When a potential is placed across the electrode and the solution, oxygen arriving at the gold electrode is reduced to hydroxyl and the subsequent current is measured with a sensitive ammeter. When the current at the gold electrode reaches a steady state, the current is directly related to the oxygen flux through the polymer. Oxygen permeability can be calculated as the slope of the line of the measured flux plotted against the sample thickness. Although a value can be determined from a single measurement on a calibrated system, measurement of oxygen flux for multiple thicknesses provides a more accurate value of *Dk* (17). The measurement of oxygen permeability has been frequently studied over the last several years and a number of modifications to the calculations have been made. The most significant of these is the correction for edge effects (18, 19). Because the oxygen flux is not one-dimensional through the material, some account must be made for the oxygen coming from the edges of the sample.

The physiological effect of a particular lens can be determined by measuring the increased thickness of the cornea after lens wear; studies have shown the relationship between the *Dk*/*L* of a lens and the subsequent swelling of the underlying cornea (20, 21).

Oxygen permeabilities for currently marketed hydrogel materials can be directly related to water content. Figure 1 shows the manufacturer-reported values of *Dk* and water content for marketed hydrogel materials (22). For rigid and flexible materials the *Dk* is an indirect function of siloxane content. Polydimethylsiloxane has one of the highest measured oxygen permeabilities of all tested materials. Incorporating siloxanes into a hydrophilic matrix is an important research area of contact lens manufacturers, which may lead to the development of novel experimental hydrogels that exhibit low water content but high *Dk* values.

2.2. Water Content and Refractive Index

The water content of a hydrophilic contact lens is a determinant of other properties. The relationship of water content and *Dk* is discussed above. Water content in lenses is inversely related to refractive index (23), a key property for vision correction. A lens material with a higher refractive index refracts light to a greater degree, allowing more vision correction with a thinner material. The water content of a lens is generally determined gravimetrically or inferred from the relationship to refractive index, measured with a refractometer (24).

Water content indirectly affects other lens characteristics. Water evaporation from the lens can result in a dry eye sensation and subsequent desiccative erosion of the cornea. Clinical studies have shown the incidence of corneal erosion as a result of lens desiccation to be a material-dependent and water-content-dependent phenomenon (25, 26). The nature of water and sodium ions in hydrogels has been studied primarily by nmr and thermal techniques (27, 28). An empirical relationship between water mobility in contact lens polymers and desiccative staining has been proposed (29).

2.3. Mechanical Properties

For hydrogel materials, the most important mechanical properties are strength and modulus. The modulus of a material determines relative stiffness and is generally measured under tensile conditions. A low material modulus, 0.4 MPa ($<40\ \mathrm{g/mm^2}$), handles more poorly outside the eye and possesses poor drapability; however, the material is generally more comfortable and fits well. A high modulus lens, between 1 MPa and an upper limit of approximately 2 MPa (100–200 $\mathrm{g/mm^2}$), handles much better and stands up on a fingertip, but it may irritate the conjunctiva of the eye or interact with the lid to cause discomfort. Generally, a higher modulus lens requires more parameters to fit an entire population of wearers. Modulus typically is measured using ASTM D1708 (30) modified to accommodate the smaller samples with a variety of configurations; the sample should remain in the hydrated state for an accurate value. The test can be carried through until the sample breaks and the tensile strength and elongation of the material are obtained. Naturally, the modulus is an intrinsic property and the actual lens properties depend on thickness.

The strength of a hydrophilic lens material determines how well the material survives the patient's handling, cleaning, and disinfection regimen. Materials with higher *Dk* have been found to be generally more fragile (31).

Although the strength of a lens material can be inferred from the tensile strength, the property usually measured is tear strength. Typically determined by ASTM D1938 (32), or modifications thereof, a small tear is initiated and the force required to continue the tear is measured. Tear strengths for soft contact lens applications are quite low; some marketed lenses have tear strengths under 19.6 N/m (2 g/mm). Flexible lens materials are typically elastomers and have higher moduli and significantly higher tear strengths than hydrogel materials, determined by using similar methodology.

Rigid lenses have tensile properties in the tens of MPa (thousands of $\mathrm{g/mm^2}$), which give rise to excellent vision but poorer comfort. Although tensile properties can be determined for these materials, lens performance is not as sensitive to these values as for hydrophilic lens materials.

Flexure testing has also been used to measure the strength of a RGP material (33). The strengths measured from flexure tests can be empirically related to a material's resistance to breakage during typical lens handling.

Other mechanical properties determined for RGP materials dictate their ease of processing. Glass-transition temperature (T_g), or softening temperature, also will dictate processing conditions, ie, curing, annealing, and lathing, but must be greater than eye temperature for the lens to remain rigid and maintain optics. Material hardness, measured on either the Shore or Rockwell scale, determines the capability of a material's lathing.

2.4. Light Transmittance

Contact lenses should transmit light in the visible range from 400–800 nm. The addition of tints affects light transmittance, but a majority of tinted lenses still transmit more than 85% of visible light (34). Of growing interest is the absorption of light in the ultraviolet region; there is concern about the possible relationship of the transmittance of uv light to cataracts and ocular health (35, 36). Companies have developed uv-blocking lenses that contain an additional lens component that absorbs uv light between 300 and 400 nm (37, 38). No absorber will remove 100% of uv light because leaking of absorbance into the visible region gives the lens an undesirable yellow tint. Absorbances are measured with standard spectrophotometers; techniques differ in aperture of the light beam and placement of the sample in the beam.

2.5. Wettability

Wettability dictates the biocompatibility of a contact lens material in the ocular environment. A nonwetting material will not maintain a uniform tear film between blinks. The result is a lens that is uncomfortable, provides poor vision, and has the potential for deposit formation. The most common method for wettability measurement is contact angle. Two standard methods for determining this value exist: the sessile drop technique, ie, a drop of solution is placed on the sample and the angle formed by the material surface and the leading edge of the drop is measured with a goniometer; and the captive bubble technique, ie, the sample is immersed in a solution, a bubble is captured beneath the surface, and the angle between the material and the leading edge of the air bubble is measured with a goniometer (39). A more recent technique is the measure of dynamic contact angle using the Whilhelmy plate technique (40), ie, the force of driving a sample into solution is measured to obtain the advancing contact angle, equivalent to the sessile drop value, and the force to withdraw a sample from the solution is measured to obtain the receding contact angle, equivalent to the captive bubble value (41). Contact angles have also been measured *in vivo* (42). These methods are used extensively by researchers and contact lens manufacturers, but contact angle values are not always indicative of on-eye wettability. For example, the contact angle of PMMA determined by the sessile drop technique (43) is >60, which indicates a poorly wetting surface. Yet the lens has demonstrated excellent *in vivo* wettability.

Wettability is believed to be a dynamic process involving interactions of the ocular environment and lens material (44). No method has been found to predict accurately the *in vivo* wettability of a lens material.

2.6. Deposition

Lens spoilage from tear film deposition is a common reason for lens replacement and mandates the frequent cleaning of nondisposable contact lenses. When deposits become significant, they affect vision, lens properties (45), and ocular health (46). Deposits that form on contact lenses are complex and contain proteins, lipids, and minor components such as calcium (47, 48). The mechanism of deposit formation is of research interest and draws on work in the biomedical device field (49, 50). Studies have shown that for hydrophilic lenses deposition depends on material; polymers containing a charged species show greater deposition than uncharged polymers (51, 52). Although no standardized tests exist for the measurement of deposition, each manufacturer has empirical tests to screen materials for protein or lipid deposition potential. These tests are not 100% predictive, because actual lens deposition is a function of lens type, patient tear chemistry, cleaning and disinfection regimen, and environment.

Although a variety of test methods, eg, *Dk*, modulus, and tear strength, exist to determine key properties of potential contact lens materials, a number of properties, eg, wettability and deposition, have no predictive methodology short of actual clinical experience.

3. Rigid (Hard) Lenses

Hard lenses can be defined as plastic lenses that contain no water, have moduli in excess of 5 MPa (500 g/mm^2), and have T_g well above the temperature of the ocular environment. Poly(methyl methacrylate) (PMMA) has excellent optical and mechanical properties and scratch resistance and was the first and only plastic used as a hard lens material before higher oxygen-permeable materials were developed. PMMA lenses also show excellent wetting in the ocular environment even though they are hydrophobic, eg, the contact angle is 66°.

PMMA hard lenses received wide acceptance when introduced in 1945 and thrived throughout the 1970s. The primary drawback of PMMA lenses is lack of oxygen transmissibility; the little oxygen that the cornea receives during PMMA lens wear is almost exclusively through tear exchange under the lens. During the 1980s, a series of hard lenses with higher oxygen permeability, the RGPs, were developed and introduced to the market. As a result, the popularity of PMMA lenses decreased even further.

3.1. Early RGP Lenses

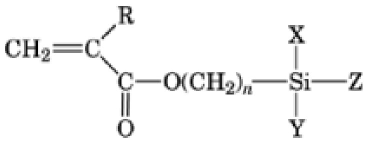
Because of poor oxygen permeability, PMMA lenses can only be worn for daily wear. To overcome the poor oxygen permeability of PMMA lenses, other rigid polymers have been investigated for contact lens application. One of the first polymer families to be successfully developed was the cellulose acetate butyrate [9004-36-8] (CAB) lenses (53, 54), which showed oxygen permeability of 10–20 barriers, approximately two orders of magnitude increase in oxygen permeability than that of PMMA lenses. However, compared with PMMA lenses, CAB lenses had a higher tendency to warp, scratch, chip, and discolor. Another class of polymers evaluated for use as a hard lens material was styrenics. Poly(*p*-*t*-butylstyrene) [26009-55-2] has a higher free volume in the three-dimensional packing, due to the bulkiness of the *t*-butyl group, giving oxygen permeability of 25 barriers; this value is considered to be high among the polymers evaluated for contact lens application in the early 1970s. Poly(*p*-*t*-butyl-styrene) was commercialized as the Airlens contact lens by Wesley-Jessen. Although possessing good flexural strength, the material showed poor scratch resistance.

3.2. Advances in RGP Materials

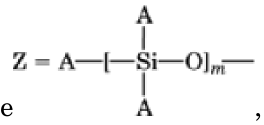
Silicone rubber is an attractive contact lens material (55) with a high oxygen permeability, resulting from the flexibility of Si–O–Si bonds. Since the mid-1970s, a tremendous amount of research-and-development work has been performed with rigid gas-permeable lens materials employing the high oxygen permeability of siloxanes. These efforts have led to the introduction of many highly oxygen-permeable hard lenses.

3.2.1. Silicone Acrylates

The development of rigid gas-permeable lens materials advanced significantly after the development of polysiloxanylalkyl acrylates and methacrylates (**1**), as a component in hard lens materials (56, 57), as claimed in a series of patents (58–62).

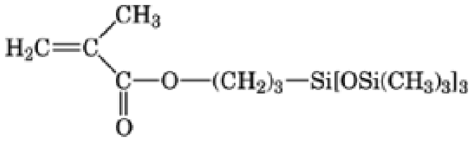


(1)

where 

$$Z = A-[-\overset{A}{\underset{A}{Si}}-O]_m-$$

, X, Y = alkyl, phenyl or Z, A = alkyl or phenyl, and $R = H$ or CH_3The simplest structure of this class of monomers, 3-(methacryloxy)propyl tris(trimethylsiloxyl)silane, [17096-07-0] (TRIS) (**2**), gives polymer with oxygen permeability >200 barrers and is particularly useful as a component for hard lens application.



(2)

Unlike a typical polysiloxane, which imparts high oxygen permeability from the flexibility of the dimethylsiloxane units, the high oxygen permeability of TRIS-containing polymers may be the result of the bulkiness of tris(trimethylsiloxy)silane units, which gives a high free volume of polymer available for oxygen transport.

The preparation of silicone acrylate–methacrylate monomers has continued with the purpose of obtaining highly oxygen-permeable hard lens materials. Bulky polysiloxanylalkyl diacrylates–dimethacrylates were modified (63, 64). Polysiloxanylalkyl acrylates–methacrylates modifications include changing the arrangements of alkyl units (65, 66) attached to the siloxane groups and making the siloxane units bulkier (67, 68). Silylmethylene methacrylates were formed by replacing siloxane units with silane units (69, 70). Acrylamide–methacrylamide analogues of polysiloxyanylalkyl acrylate–methacrylate also were prepared (71). Owing to the availability of monomers, the ease of preparation, and the excellent physical properties, acrylates–methacrylates are the favored choice for a hard lens material.

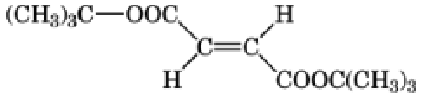
During the 1980s, unsaturated functional groups other than acrylate–methacrylate were investigated as alternative polymerizable groups to provide hard lens materials with high oxygen permeability by incorporating polysiloxanylalkyl groups. These unsaturated functional groups include vinyl (72–74), vinyl carbamate–carbonate (75), styrene (76, 77), itaconate (63), alkyne, and fumarate. Among these, alkyne- and fumarate-based systems were investigated most extensively and are described below. Because of the difference in molecular structure and the ability to polymerize, these unsaturated functionalities offer lens materials with unique morphology not achievable with acrylate systems.

3.2.2. Polyalkynes

Poly(1-trimethylsilyl)propyne (PTMSP) was prepared (78) and found to have unique properties, when compared with polyacetylene, ie, mainchain double bonds are not conjugated (79). PTMSP is colorless, soluble in common organic solvents, amorphous, and has the highest gas (including oxygen) permeability of any known polymer. The high gas permeability (oxygen permeability of approximately 10,000 barrers) is likely the consequence of a large excess free volume caused by this polymer's unique structural features (80). However, the conformational changes that cause tighter packing of silane moieties in the solid state reduce oxygen permeability. As a result, the polymer was not further evaluated as a hard lens material.

3.2.3. Polyfumarates

Because of steric hindrance, fumarates are difficult to polymerize into high molecular-weight polymers. However, it was demonstrated during the early 1980s that bulky fumarates, such as di-*t*-butyl fumarate, $C_{12}H_{20}O_4$ [7633-38-7] (**3**), can be polymerized thermally into high molecular-weight polymers (81–84).



(3)

These polymers have good optical quality as well as high oxygen permeability; their application in the optical area has been cited (85). Subsequent studies on fumarate polymerizations led to a series of interesting systems useful as hard lens materials. For example, bis(siloxanylalkyl) fumarates, which are TRIS analogues, can be polymerized–copolymerized thermally to give polymers with oxygen permeability as high as 480 barrers (86, 87), potentially higher than that of TRIS polymer. Compositions containing one dialkyl fumarate and either one bis(siloxanylalkyl) fumarate or a fluoroalkyl fumarate are also useful as hard lens materials with an oxygen permeability as high as 140 barrers (88). Fluoroalkyl fumarates copolymerized with fluoroalkyl itaconate (89) or fluoroalkyl mesoconate (90), and fumarates copolymerized with methacrylates, also give hard lens materials (91–93).

Most of the silicone-based monomers claimed useful for hard lens applications also have been evaluated as components in silicone hydrogels targeted for contact lens applications.

3.2.4. Fluoroalkyl Acrylates–Methacrylates–Itaconates–Mesoconates

Fluoroalkyl acrylates have been copolymerized with alkyl acrylates to give copolymers with increased oxygen permeability useful as a hard lens material (93). However, the principal role of fluoroalkyl acrylate–methacrylate in hard lens material has been to provide lipid resistance. To obtain a highly oxygen-permeable lens material, monomers with polysiloxane–bulky siloxane fragments are necessary. Polysiloxanes are hydrophobic and thus contact lenses manufactured from silicone monomers naturally absorb lipids from the tear fluids and exhibit serious wettability problems. Fluoropolymers have been known to have low surface energy and resist foreign materials. By incorporating fluoroalkyl acrylates–methacrylates–itaconates–mesoconates, silicone-containing hard lenses possess high oxygen permeability and better lipid resistance (60, 62, 87, 88, 94–102).

3.2.5. Other RGP Components

All hard lens materials, regardless of the oxygen permeability, must meet certain requirements, ie, the polysiloxanylalkyl monomer provides oxygen permeability and the fluoroalkyl monomer provides lipid resistance. Unlike PMMA lenses, and because of the hydrophobicity of silicones, hard lenses containing polysiloxane units need a significant amount of hydrophilic monomer to maintain sufficient wettability for patient wear. Although nonionic hydrophilic monomers are mentioned in the hard lens materials patent literature, an ionic wetting monomer, such as acrylic acid [79-10-7] or methacrylic acid [79-41-4] at 1–15%, generally is required for a silicone-based hard lens to maintain sufficient wettability; ionic monomers are cited in most hard lens material patents.

Because of high glass-transition temperatures (T_g), hard lenses are manufactured by thermal polymerization of the monomers, and thermal catalysts are a necessary part of an RGP lens formulation. One dimethacrylate or diacrylate generally is used as a cross-linker in a hard lens composition to help maintain dimensional stability. This kind of cross-linker also may affect other properties, such as mechanical strength. When a polyfluoroether-based diacrylate or dimethacrylate is used, lipid resistance and oxygen permeability improve over the common acrylic monomers (103). When a polysiloxane-based diacrylate or dimethacrylate, such as α, ω-bis(methacryloxyalkyl) polydimethylsiloxane (**4**) where $n = 1 - 10$ and $x = 1 - 200$, is used, lens material with high oxygen permeability and toughness is obtained (104).

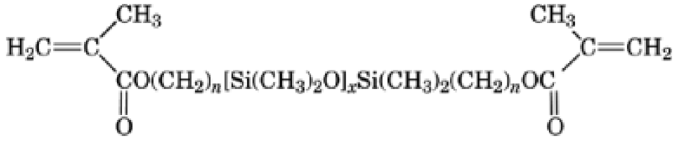
Table 1. Partial List of Rigid Gas-Permeable Lens Materials

USAN name[a]	Material composition	*Dk*, barrer[b]	Trade name	Manufacturer
airfocon	*t*-butylstryene[c]	25	Airlens	Wesley-Jessen
fluorofocon	fluoropolymer	95	Advent	3M Corp.
itafluorofocon	fluorosilicone	55	Equalens	Polymer Technology
itafocon	silicone acrylate	14	Boston II	Polymer Technology
		26	Boston IV	Polymer Technology
		32	Optacryl K	Optacryl
		54	Optacryl EXT	Optacryl
		67	Optacryl Z	Optacryl
pasifocon	silicone acrylate	49	Paraperm EW	Paragon
		92	Paraperm EW II	Paragon
siflufocon	silicone acrylate	55	Quantum I	Bausch & Lomb
		100	Quantum II	Bausch & Lomb

[a] U.S. Adopted Name Council designation for polymeric materials.

[b] 1 barrer = 10^{-11} cm^3 O_2 (at STP)·cm/s·cm^2·mm Hg.

[c] $t\text{-}C_4H_9{-}C_6H_4{-}CH{=}CH_2$ [25338-51-6]; homopolymer [9053-30-9].



$$H_2C{=}C(CH_3)C(=O)O(CH_2)_n[Si(CH_3)_2O]_xSi(CH_3)_2(CH_2)_nOC(=O)C(CH_3){=}CH_2$$

(4)

3.3. Rigid Gas-Permeable Lens Products

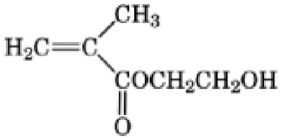
From the late 1970s to the early 1990s, a long series of RGP lens products were introduced, offering higher oxygen permeability, better wettability, and more deposit resistance. Table 1 gives a representative list of RGP products introduced to the marketplace. Depending on the method of measurement, a disagreement in published oxygen permeability values exists (6), eg, an oxygen permeability as high as 110 barrers was reached with a fluorosilicone acrylate system. Clinical results suggest that fluorosilicone acrylate hard lenses offer better deposit resistance as well as good oxygen permeability (105).

The development of rigid gas-permeable lenses resulted in tremendous growth during the 1980s. However, after replacement of most PMMA lenses with rigid gas permeables, growth of this business slowed significantly, attributed to unsatisfactory lens wettability and poor comfort. Wetting conditioning solutions have been investigated to reduce the wettability problem. Ultimately, more wettable lens materials need to be developed. The lens comfort issue may partially be resolved with the development of a variable modulus lens (106), achieved by gradually decreasing the lens modulus from the optical zone to the peripheral region.

4. Hydrogel Contact Lenses

Hydrogels are water-containing polymers, hydrophilic in nature, yet insoluble. In water, these polymers swell to an equilibrium volume and maintain their shape. The hydrophilicity of hydrogel is a result of the presence of functional groups such as $-NH_2$, $-OH$, $-COOH$, $-CONH_2$, $-CONH-$, $-SO_3H$, etc. The insolubility and stability of hydrogels are caused by the presence of a three-dimensional network. The scope, preparation, and characterization of hydrogels has been reviewed (107).

Hydrogels, ie, gelatin and agar, have been known for a long time. In the late nineteenth century, Herschel proposed the use of jelly materials on the cornea for the correction of vision (108). In 1960, the use of synthetic hydrogels for contact lenses was proposed and several U.S. patents were obtained for the invention of cross-linked hydrophilic polymers, eg, systems based on 2-hydroxethyl methacrylate [868-77-9] (HEMA) (**5**) (109–112).



$$H_2C{=}C(CH_3)\underset{\underset{\displaystyle O}{\|}}{C}OCH_2CH_2OH$$

(5)

In 1971, Bausch & Lomb received U.S. Food and Drug Administration approval for a soft contact lens based on the HEMA system and launched Soflens. The soft lens market has grown dramatically; soft lens surpassed hard lens wear by the late 1970s, accounting for about 80% of the U.S. contact lens market in the early 1990s.

Polymers used in soft contact lenses have not been limited to those derived from HEMA; other hydrophilic monomers also were explored and used. From the late 1960s through early 1970s, the primary concern among investigators was to develop proprietary formulations with higher water content and thus higher oxygen permeability.

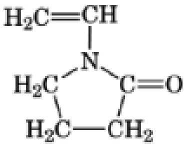
Hydrogels used for contact lens applications can be classified based on the chemical structure of hydrophilic monomers and on the water content of the hydrogel lens. These classifications are not unique because the design of hydrogels is based on the performance desired; in most cases, more than one component is used for the same or complementary purpose. In fact, some hydrophilic monomers are used in both high water and low water lenses.

The U.S. Food and Drug Administration, which has the functional authority to regulate contact lenses, classifies soft contact lens according to the water content and ionic character of the soft lens (113), ie, group I, low water ($<50\%$) nonionic; group II, high water ($>50\%$) nonionic; group III, low water ($<50\%$) ionic; and group IV, high water ($>50\%$) ionic. This classification is particularly useful for clinicians and the FDA in determining care system efficacy.

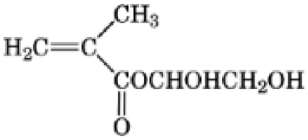
4.1. Typical Hydrogel Components

Regardless of water content, a hydrogel lens formulation consists of hydrophilic monomers, cross-linkers, and initiators. Hydrophilic monomers provide the water needed in a hydrogel, and the cross-linkers help to hold the hydrogel's shape. The initiator starts the polymerization and curing and is removed from the hydrogel after the polymerization. In addition to the above three components, a hydrogel formulation also may contain a hydrophobic monomer as a physical property modifier and a solvent to facilitate the processing.

The water content of a hydrogel depends on the hydrophilicity of the monomer, eg, cured poly(HEMA) absorbs 60% of its weight of water and thus forms a hydrogel with about 38% water content. Other hydrophilic monomers, such as *N*-vinylpyrrolidinone [88-12-0] (NVP) (**6**), and glycerol methacrylate [100-92-5] (GM) (**7**), and acrylamide monomers, such as diacetone acrylamide [2873-94-9] (DAA), have also been used to form hydrogels with higher water content.



(6)



(7)

These monomers impart hydrophilicity as a result of the presence of polar –OH and –CONH– groups. Acid-containing monomers, such as methacrylic acid [79-41-4] (MAA), and 2-acrylamido-2-methylpropanesulfonic acid [15214-89-8], provide ionic character at pH above 7.0 and contribute a large amount of water absorption.

Precursors of hydrophilic monomers, such as vinyl esters and acrylonitrile [107-13-1] have been investigated for hydrogel lens applications. Vinyl esters, eg, vinyl acetate [108-05-4], form poly(vinyl alcohol) [9002-89-5], and absorb substantial amounts of water; cured poly(vinyl alcohol) hydrogels have been claimed useful as contact lenses (114–117). Polyacrylonitrile [25014-41-9] has been hydrolyzed under different controlled conditions to form high water content hydrogel lenses with good mechanical strength resulting from hard segment domain formation during polymerization (118, 119). Research efforts on new hydrophilic monomers for high water hydrogel lenses continue into the 1990s.

Hydrophilic monomers must be cured with cross-linkers to obtain dimensionally stable hydrogels. When a methacrylate-based hydrophilic monomer, such as HEMA, is used to form hydrogel, ethylene glycol dimethacrylate [97-90-5] (EGDMA), or poly(ethylene glycol) dimethacrylates of different molecular weights are commonly used as cross-linkers. Trimethacrylates, such as trimethylolpropane trimethacrylate [3290-92-4] (TMPTMA), have also been used. When a hydrogel is formed from a methacrylate monomer and NVP, allyl methacrylate [96-65-9] (AMA) can be used as a cross-linker (120). Cross-linkers provide the required physical shapes and control some of the key mechanical properties, such as modulus and tear strength, of the hydrogels. Thus the choice and amount of a cross-linker are important in the formulation of contact lenses.

Mechanical properties of a hydrogel lens also are affected by the use of a hydrophobic monomer, such as a low alkyl methacrylate. This is particularly important when the water content of the hydrogel lens is very high. The use of these methacrylates helps preserve the required mechanical strength. Methyl methacrylate [80-62-6] (MMA) (121), isobutyl methacrylate [97-86-9] (122), and *n*-pentyl methacrylate [2849-98-1] (123) all have been used for this purpose.

Hydrogel lenses are obtained by photo or thermal polymerization of monomers in bulk or in solution. A variety of thermal and photo catalysts have been used in hydrogel formulations.

Because of the many choices of hydrophilic monomers, cross-linkers, and hydrophobic monomers, a large number of formulations have been developed and manufactured into hydrogel lenses. The water content of these hydrogel lenses ranges from about 38%, for HEMA-based lenses, to 80%, for poly(vinyl alcohol) and partially hydrolyzed acrylonitrile lenses. Table 2 gives a representative list of FDA approved hydrogel materials available to the consumer in the early 1990s.

The data in Table 2 indicate that oxygen permeability depends exclusively on water content. To increase oxygen transport to the cornea through a hydrogel lens, the lenses should either be made thinner or be fabricated from hydrophilic monomer with higher hydrophilicity, ie, HEMA-based lenses were fabricated with

Table 2. Key Properties of Select Hydrogel Lens

USAN name[a]	CAS Registry Number[b]	Composition	Water content, %	*Dk*, barrer[c]	Modulus, MPa[d]	Trade name	Manufacturer
bufilcon A[e]	[56030-52-5]	HEMA, DAA, MAA	55	17.0	0.37	Hydrocurve	Sola Barnes-Hind
crofilcon A[f]	[50450-03-8]	GM, MMA	39	8.5	1.52	CSI	Sola Barnes-Hind
etafilcon A[e]		HEMA, MAA, TMPTMA	58	24.0	0.20	Vistamarc	Vistakon
						Acuvue[g]	Vistakon
hefilcon A		HEMA, NVP, EGDMA				Softsite	Sola Barnes-Hind
hefilcon B[f]	[36425-29-3]	HEMA, NVP, EGDMA	45	13.0	0.95		Bausch & Lomb
lidofilcon A[h]		MMA, NVP, AMA	74	33.0	0.34	Sauflon	Allergan
						B&L 70	Bausch & Lomb
phemfilcon A[e]		HEMA, EEM[i], MAA	55	17.0	0.27	Durasoft	Wesley-Jessen
polymacon[f]	[25053-81-0]	HEMA, EGDMA	38	9.5	0.56	Hydron	Allergan
						Softlens	Bausch & Lomb
						SeeQuence[g]	Bausch & Lomb
tetrafilcon A[f]		HEMA, NVP, MMA, DVB[j]	43	13.0		AOSoft Aquaflex	Ciba Vision Cooper Vision
vifilcon A[e]	[35528-20-2]	HEMA, MAA, NVP, EGDMA	55	17.0		Softcon	Ciba Vision
						NewVue[g]	Ciba Vision

[a] U.S. Adapted Name Council designation of the polymeric material.
[b] Provided if available.
[c] 1 barrer = 10^{-11} cm^3 O_2 (at STP)·cm/s·cm^2·mm Hg.
[d] To convert MPa to g/mm^2, multiply by 102.
[e] FDA group IV; high protein uptake.
[f] FDA group I; low protein uptake.
[g] As disposable lens.
[h] FDA group II; low protein uptake.
[i] 2-Ethoxyethyl methacrylate [999-61-1].
[j] Divinylbenzene [1321-74-6].

a lens center thickness of 70 μm for daily wear and 35 μm for extended wear. Some hydrogel lenses, such as etafilcon, are manufactured from formulations containing an acid monomer, such as methacrylic acid, to gain higher water content. Unfortunately, the presence of methacrylate anion invites large amounts of lysozyme uptake, which reduces the water content of the lens and may affect clinical performance.

4.2. Silicone Hydrogels

Based on the success in RGP applications, polysiloxanylalkyl acrylates–methacrylates, such as TRIS, have been employed in the preparations of silicone hydrogels. These materials were used in combination with hydrophilic monomers such as HEMA and *N,N*-dimethylacrylamide [2680-03-7] to form hydrogel lenses with high oxygen permeability (16, 124–126). They also have been used with methacrylate-based prepolymers, such as those with polyurethane linkages (127, 129), to give hydrogel lenses with high oxygen permeability as well as excellent mechanical properties (128, 129).

Silicone-based monomers were prepared in different prepolymer forms, such as dimethacrylate-capped polysiloxane (**4**), and were extensively investigated for hydrogel lens applications. For example, the prepolymer of structure (**4**) formed hydrogels when copolymerized with a hydrophilic monomer such as *N,N*-dimethylacrylamide or acrylic acid (104, 130–132). Polysiloxane prepolymers can be modified to enhance wettability and physical properties of the lenses, ie, methyl groups on the siloxane units in the prepolymers, modified with hydrophilic groups, improve wettability (133, 134). The polysiloxane structures can be linked to urethane linkages before end-capping with methacrylate groups (127, 128, 135–138). When used in hydrogels, these modified prepolymers show better mechanical properties than those without modification. Polysiloxanes also can be end-capped with styrene moieties to give prepolymers that form hydrogels when copolymerized with hydrophilic monomers (139).

In addition to the silicone-based monomers–prepolymers described here, most silicone-based monomers–prepolymers claimed useful as hard lens material have been evaluated for hydrogel lens application. A majority of the efforts in preparing silicone-based hydrogels has been for increased oxygen permeability. Although silicone hydrogel lenses were claimed wettable because of moderate water contents, they have not always proven wettable in clinical testing. A possible explanation for the nonwetting is the migration of siloxane fragments to the hydrophobic air surface. In addition, lipidlike deposits are a potential problem in silicone hydrogel lenses.

4.3. Fluorohydrogels

In addition to applications in hard lenses, fluorine-based monomers, such as fluoroalkyl acrylates–methacrylates (140, 141) and fluorostyrene and fluorosulfonamide monomers (142), give hydrogel lenses after copolymerizing with hydrophilic monomers such as substituted acrylamide and NVP. In general, these hydrogels claim to have good oxygen permeability and to be useful as extended wear contact lenses (140, 141).

4.4. Miscellaneous Hydrogel Classes

Because of unique structure and flexibility in manipulating the mechanical properties, polyurethanes have been evaluated for contact lens applications. Nonsilicone polyurethane hydrogels with water contents as high as 20% were claimed to have contact lens application (143). Polyurethane interpenetrating network compositions, formed by polymerizing diacrylates in the presence of a hydrophilic polyurethane, form hydrogels and are useful as contact lenses (144–147). Prepolymers with urethane linkages or well-defined hard–soft–hard polyurethane elastomer blocks are useful in forming hydrogels with improved mechanical properties as well as good oxygen permeability (127, 128, 135–138, 148, 149).

There is great interest in developing soft lens materials that have high oxygen permeability and good wettability. Such lenses will provide patients with good comfort, high deposit resistance, and superior corneal health, particularly for extended wear applications.

The popularity of the disposable lens concept is expected to continue, and the future should bring about lenses having enhanced clinical performance combined with the convenience of disposability.

5. Flexible Nonhydrogel Lenses

5.1. Silicone–Fluorosilicone Lenses

Silicone rubber has long been considered a unique contact lens material (55), and the development of silicone rubber lenses has been reviewed in earlier editions of the *Encyclopedia*. The oxygen permeability of silicone rubber, >300 barrers, is virtually unsurpassed by any other polymeric material considered for contact lens applications.

The principal problems for silicone rubber as a viable lens material are the nonpolar nature, which gives lipid deposits and wettability problems; and the tendency to adhere to the cornea. Efforts to modify the silicone lens surface for improved wettability have achieved limited success. These efforts include grafting hydrophilic monomers, such as HEMA, GM (150), and NVP (151–153), to the lens surface and plasma treatments of finished lenses. Efforts to improve the movement of silicone lenses on the cornea with various lens designs have not been successful, and the cause of lens–cornea adherence, which is not an exclusive problem of silicone lenses, is an active area of research.

Other polysiloxane-containing polymerizable systems, such as prepolymers described earlier, also claim to have application as flexible nonhydrogel lenses (129–139, 148, 149, 154). Prepolymers containing block copolymers of polysiloxane and poly(alkylene oxide) give highly oxygen-permeable flexible lenses with good wettability (155–157). These compositions usually have some hydrophilic monomers, particularly an acid monomer, in the composition to enhance wettability. Monomers with fluoroalkyl groups, or polysiloxane prepolymers with fluoroalkyl modified siloxane side chains (158, 159), are used in addition to a wetting monomer to minimize lipidlike deposits.

5.2. Nonsilicone Flexible Lenses

To avoid wettability and lipid deposit problems associated with silicone, nonsilicone-containing elastomeric materials have been investigated as lens materials. The compositions studied have shown good oxygen permeability. For example, fluorinated telechelic polyether-based prepolymers, derived from perfluorinated poly(ethylene glycol) [25322-68-3], give lenses with good oxygen permeability and wettability after copolymerizing with some hydrophilic monomers (103, 160). These lenses, manufactured by 3M Corp., gave low overnight corneal swelling in clinical testing (161). They have been marketed as the Advent lens by Allergan, and have had limited success, because of poor comfort. Prepolymers derived from poly(alkylene oxide)s also give nonhydrogel flexible lenses with reasonable oxygen permeability as high as 70 barrers and good wettability (162–164).

6. Tinted Lenses

Contact lenses are tinted for cosmetic reasons, ie, to modify or change eye color, and for visibility, ie, to locate the lens more easily when it is out of the eye. Both rigid and hydrogel lenses can be visibility tinted. However, only hydrogel lenses are cosmetically tinted, because the rigid lens is rarely fit to cover the entire colored portion of the eye. Cosmetic tints were introduced in the early 1980s as an added feature to soft contact lenses (165). A wearer's natural eye color was combined with the tint in the lens to either enhance the existing color, ie, blue on blue, or to change the eye color, ie, a yellow-tinted lens over blue eyes results in green eyes. Tints are sufficiently dark to alter eye color, but not so dark as to affect visible light transmission adversely. Addition of tints reduces the light transmission from $>95\%$ for a clear lens to 85% for the darkest tint (166) and only slightly affects color perception (167, 168). Lenses are tinted after lens manufacture with a masking technique to provide a clear annulus around the lens periphery. Because a standard soft contact lens extends past the limbal junction and the iris, the clear annulus was required to prevent the tinted portion from being visible against the white of the eye.

In the late 1980s, a new type of cosmetic-tinted lens appeared on the market. Called an opaque tint, the lens blocks the natural color of the iris and provides a totally new color to the eye (169, 170). Brown-eyed individuals, unable to change their eye color with other tinted lenses, can now have any color eye. Doctors have expressed some concern for emmetropic wearers (require no vision correction) because the lenses are then treated as cosmetic and not therapeutic devices; cases of poor lens and eye care are cited (171, 172). The

Table 3. Dyes Approved by the FDA for Use in Contact Lenses

Color Index name	FDA names	CAS Registry Number	Color Index number
Pigment Violet #23		[6358-30-1]	51319
Pigment Blue #36	chromium–cobalt–aluminum oxide	[68187-11-1]	77343
Pigment Green #17	chromic oxide (green)	[1308-38-9]	77288
Pigment Green #7	phthalocyanine green	[1328-53-6]	74260
Iron Oxide		[977053-38-5]	77491
Pigment White #6	titanium dioxide	[13463-67-7]	77891
Vat Orange #1		[1324-11-4]	59105
Vat Brown #1		[2475-33-4]	70800
Vat Yellow #3		[82-18-8]	61725
Vat Blue #6	D&C Blue #9	[130-20-1]	69825
Vat Green #1		[128-58-5]	59825
Reactive Black #5		[17095-24-8]	20505
Reactive Blue #21		[73049-92-0]	
Reactive Orange #72		[68189-39-9]	17754
Reactive Yellow #15		[60958-41-0]	
Reactive Blue #19		[2580-78-1]	61200
Reactive Blue #4		[4499-01-8]	61205
Reactive Red #11		[12226-08-3]	
Reactive Yellow #86		[61951-86-8]	
Reactive Blue #163		[72847-56-4]	
Reactive Blue #246		[121888-69-5]	61548
Solvent Green #3	D&C Green #6	[128-80-3]	61565
Solvent Violet #13	D&C Violet #2	[81-48-1]	60725
Acid Yellow #3	D&C Yellow #10	[8004-92-0]	47005

opaque-tinted lenses are standard hydrophilic lenses that have a paste of monomer, colorant, and TiO_2 printed on the anterior surfaces in a particular pattern. A small amount of natural eye color and pattern show through to provide a realistic look. Because the tinted portion of the lenses is opaque, the optical zone of the lens must remain free of the printed pattern to prevent visibility problems. Fit and centering of these lenses are critical to provide clear vision. An alternative method of manufacture is to cast a lens containing a clear layer and TiO_2-laden layer. With proper casting and lathing of the TiO_2 layer, a lens with a clear optical zone and clear periphery surrounding an opaque ring is produced. The colorant is added to the front surface to provide the new color. Even unnatural eye shades such as violet or fluorescent colors (173) can be obtained.

Visibility tints are similar to cosmetic tints except that they are significantly lighter in intensity. Visible light transmission losses are typically 1–2%. With these tints, the lens is visible in the lens package and against a variety of surfaces, and the lens is easier to handle. The tint can be added as cosmetic tints, with a masking technique to produce a clear annulus, or the whole lens can be tinted.

6.1. Lens Colorants

Colorants used with rigid lenses are generally pigments cast into the solid matrix during polymerization. The vast majority of tints used for soft contact lenses use dyes originally developed for the textile industry, and classified according to the American Association of Textile Chemists and Colorists (AATCC). Vat, pigment, and reactive dyes are routinely used (see Dyes, reactive). Dyes approved by the FDA for use in contact lenses are listed in Table 3 (174) (see also Colorants for foods, drugs, and medical devices).

Vat dyes are water-soluble in the reduced state but extremely insoluble in the oxidized anthraquinone state (see Dyes, anthraquinone). As an example, Figure 2 shows the soluble and oxidized states for Vat Yellow

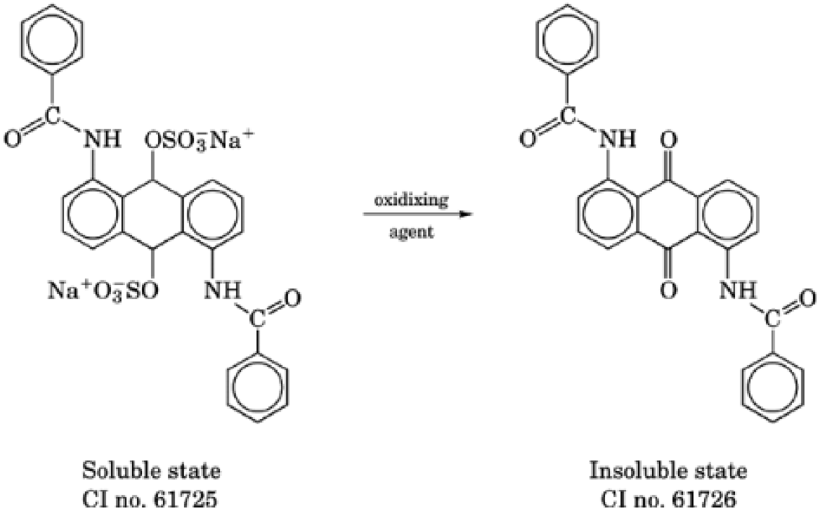


Fig. 2. Reaction of Vat Yellow #3 in contact lens manufacture.

#3, used as a yellow colorant in several lenses. The water-soluble form of the dye is allowed to diffuse into the polymer matrix for a specified amount of time. The dye is then treated with a mild oxidizing agent and the insoluble form is precipitated. The tints are extremely colorfast and stable for the life of the lens; however, the dyes are unstable in the soluble form and quite expensive.

Reactive dyes generally contain colored anthraquinones with various reactive groups attached to the nonchromophoric portions of the molecule. The reactive dyes approved by the FDA are either dichloro-*s*-triazines or sulfatoethyl sulfones, termed vinyl sulfones. Both groups react with pendent hydroxyl groups on the polymer matrix.

A recent addition to Table 3, Reactive Blue 246 differs from the other dyes and is not added to a finished lens. The dye molecule has methacrylate groups attached to an anthraquinone and is incorporated directly into the polymer matrix during polymer cure (175). This in-monomer concept has the potential to reduce dramatically the cost of visibility tinting of a contact lens.

7. Surface-Modified Lenses

The surface of a contact lens, whether rigid or soft, plays a significant role in the biocompatibility of a particular material. Wettability in the ocular environment, protein and lipid deposition, frictional comfort, and other properties all have significant surface components. Often, a polymer meeting a majority of the requirements for a contact lens application will show deficiencies at the surface. For example, the silicone lens, although possessing excellent oxygen permeability, shows poor wetting in the ocular environment and must be plasma treated to render the surface wettable.

Surface modification of a contact lens can be grouped into physical and chemical types of treatment. Physical treatments include plasma treatments with water vapor (silicone lens) and oxygen (176) and plasma polymerization for which the material surface is exposed to the plasma in the presence of a reactive monomer (177). Surfaces are also altered with exposure to uv radiation (178) or bombardment with oxides of nitrogen (179). Ion implantation (qv) of RGP plastics (180) can greatly increase the surface hardness and hence the scratch resistance without seriously affecting the transmission of light.

Chemical treatments provide a wider variety of applications, depending on the chemical functionality at the original surface and the type of functionality desired as the replacement. Most treatments replace hydrophobic and nonwetting surfaces with hydrophilic and wetting surfaces. Chemical modifications by acylation (181), esterification (182), hydroxylation (183), and treatment with organic anhydrides (184) and alkali (185) have been reported. Isocyanates have also been used as grafting links for hydrophilic coatings (186). Hydrophilic polymers can be grafted onto generally siloxane surfaces to produce a dramatic increase in wettability (187, 189).

A good example of a surface-modified lens is the Sola/Barnes-Hind Hydrocurve Elite lens, introduced in 1986. The material for the commercial Hydrocurve lens, bufilcon A [56030-52-5], contains methacrylic acid and has a high affinity for protein and subsequent deposition. The surface of the Elite lens was chemically modified with the addition of diazomethane (190) to reduce the surface charge. *In vitro* testing demonstrated a decrease in protein adsorption (191).

Although surface treatments, both physical and chemical, have demonstrated the ability to alter specific properties of contact lens surfaces, most treatments fail as a result of alteration of bulk lens properties, instability of surface treatment, or poor ocular compatibility. Research is expected to continue in the characterization and modification of contact lens surfaces.

8. Manufacture of Contact Lenses

The first usable contact lenses were produced around 1890. Glass was the only optical material available until the 1930s, and the lenses were manufactured by blowing (with or without a mold), grinding, or a combination of these processes. The radius of curvature of the contact lens surfaces was determined from a cast or impression taken of the front surface of the patient's eye. Around 1936, PMMA (Plexiglas) became available as a contact lens material. Because of its machinability at low temperatures, lathing and polishing of contact lenses with improved accuracy became possible. Molding of lenses from plastic sheets heated to conform to the shape of a cast of a patient's eye, with subsequent lathing of the prescription, also became a method of manufacturing contact lenses. Today, most contact lens materials, including xerogels, ie, hydrogels in their dry state, can be produced in a disklike form (button) that allows lathe cutting for accurate manufacture of contact lenses.

The first hydrogel poly(HEMA) lenses were manufactured using the technique of spin casting (192). The liquid monomer (containing cross-linking agents) is injected into the concave cavity of a spinning plastic mold. The centrifugal force causes the monomer to spread over the surface of the mold in a predictable, controllable manner for the particular prescription of lens being made. The formed liquid lens is then polymerized in the mold via photo curing. The resulting hardened lens can be polished or edged and is either hydrated in the mold and then released as a soft lens or released first and then hydrated. The lens undergoes extraction in hot distilled water to remove any unpolymerized monomer. The finished lens is equilibrated in normal saline (0.9% NaCl), measured, inspected, autoclaved, and packaged before shipment. Thus a spin-cast lens has its front surface (convex) formed by a mold and its back surface (concave) formed by free spinning.

Cast moldingis an increasingly used manufacturing process for both rigid gas-permeable and hydrogel contact lenses. In this process, two molds, made from a variety of plastics, are used. A female mold forms the lens front surface (convex) and a male mold forms the lens back surface (concave). The plastic molds are made from metal tools or dies that are usually stainless steel, precision lathed, and polished to the specified lens design. A variety of mold materials are used. The polymerized, hardened lens is released from the mated molds and is processed in much the same way as the spin-cast lenses described above.

Numerous variations to these manufacturing techniques exist. Some contact lenses are produced using combinations, eg, by spin casting or molding one surface and lathing the other. Other hydrogel lenses are polymerized in the mold in the hydrated state rather than in the dry state. Some lenses, eg, silicone elastomer, are molded against metal molds instead of plastic molds, similar to the reaction injection molding process.

Factors relating to the physical characteristics of the lens and to the lens cost determine the most appropriate manufacturing technique.

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