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José Alonso , José A. Gómez-Pedrero , Juan A. Quiroga
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Ophthalmic Materials

1.1 Introduction

The physical, chemical, and optical properties of a modern ophthalmic lens are the result of the combination of three elements: the material the lens is made with, the geometry of the lens surfaces, and the coatings that may have been deposited on these surfaces. Therefore, it seems proper to start the study of ophthalmic lenses by summarizing the main characteristics of the ophthalmic materials. As customary, we will describe two families of ophthalmic materials: glasses and plastics (or polymers). Understanding the main properties and characteristics of ophthalmic materials is important for the practitioner in order to guide the users through the selection of the material that best fits their needs, and to instruct them on the proper care that should be provided to their lenses to achieve the best possible compensation for their visual problems.

We begin our study of materials with a brief review of glass and glass manufacturing history. We will review the development of the different types of glasses, from the common silica glass (the classical "crown" glass) to the more exotic rare-earth glasses that appeared as a result of the extensive research carried out in the years before the beginning of the Second World War and throughout the whole duration of this conflict. The main optical, mechanical, and chemical properties of glass will be reviewed in the next section, where important concepts such as dispersion, hardness, chromatic aberrations, etc. will be introduced. The next two sections of the chapter will be devoted to ophthalmic plastics, materials that have reached the preponderance in the ophthalmic industry. We will follow the same scheme, describing first the history of ophthalmic plastics and then their main properties. We will finish the chapter with some guidelines for the proper selection of ophthalmic materials according to the needs of the user.

1.2 History of Glass and Glass Manufacturing

Under the denomination of *glass,* we refer to a number of amorphous substances composed mainly of silica and other inorganic oxides which present the same properties as those of an undercooled liquid [1]. In nature, we can find glasses produced as a result of different phenomena. Most natural glasses are of volcanic origin and they are produced when the

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molten ingredients of the glass, after being mixed up in a volcanic chamber, are expelled to the outside as part of the magma, and then slowly cooled until glass is formed. This kind of natural glass, known as *obsidian*, has been employed by numerous civilizations in the manufacturing of jewelry and other objects such as the obsidian mirror, crafted by Aztec artisans, that can be found in the collection of Museum of the Americas in Madrid [2]. The impact of lightning on a beach or sandy surface may also give rise to a kind of natural glass known as *fulgurite*.

Although glass is produced in nature in the rather extreme conditions described earlier, it was possible to make glass with the technology available to mankind in the Bronze Age. Indeed, the first written account of glass discovery is due to Pliny the Elder [3] who attributed this invention to chance when a group of Phoenician natron merchants (or nitre according to Rasmussen [4]), moored on a beach, used this product in lieu of stones for supporting the cauldrons used to cook their food. When the merchants started the fire, the three fundamental ingredients of the glass, namely the silica coming from the sand and the sodium and calcium oxides obtained through the decomposition of the natron were mixed up and heated together, resulting in the appearance of streams of molten glass [3, 4]. In 1920 William L. Monroe attempted to prove the feasibility of a casual glass discovery in the way described by Pliny, with mixed results [4].

Legends aside, it is beyond doubt that glass was manufactured in the Near East throughout the Bronze Age. Glass objects such as beads have been discovered both in Syria and Egypt, dated around 2500 BCE [4], and a glass manufacturing industry flourished in Egypt around 1500 BCE. It is no coincidence that the origins of glass can be traced back to the era when the first metallurgic industry appeared. Indeed, current historiography suggests that glass may have been obtained as a byproduct of the metallurgical procedure employed to manufacture bronze objects [4]. An alternative hypothesis points out the origin of glass as an evolution of the techniques employed to produce glazing coatings for ceramic objects [4]. According to this theory, the origin of glass can be found in the type of ceramic (known as *faience*) that is obtained when a clay object is covered with sand before heating it in the kiln, so the resulting pottery appears coated by a glossy surface. The evolution of this technique, known by the Egyptians and Sumerians, may have given rise to the production of glass when the proper components [4] were melted for the first time in a furnace.

There is evidence of glass usage in the ancient World by the Roman, Indian, and Chinese [3, 5, 6] cultures. In China, glass production is documented in the fifth century BCE, presenting in its composition higher amounts of lead and barium than the glass produced in the Middle East [7]. In Roman culture, the technique of glass manufacturing was imported from the Hellenistic kingdoms around the late Republican era and it was highly developed both in output and quality in the early Roman Empire. Proof of the degree of sophistication in Roman glass-making technology is the production of transparent glass through a careful selection of sands in order to avoid glass impurities due to metallic oxides or, alternatively, by using bleachers such as antimony [8]. Transparent glass is a necessary step in order to produce optical glass but, unfortunately, most Roman glass-making knowledge was lost at the end of the Empire, so the appearance of optical glass in Europe had to wait more than a

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millennium. Roman glass manufacturing was not only focused on the inner market; indeed glass accounted for a significant part of Roman exports through the so called Silk Road, as evidenced by the discovery of Roman glass artifacts in Afghanistan, India, and China.

As stated before, at the end of the Roman empire glass production declined, as shown by the archeological evidence [9]. However, by the beginning of the first millennium CE, the new production technique of glass blowing appeared in Germany [5], leading to the development of the great glass manufacturing centers in Murano, an island of Venice, and in the region of Bohemia in the modern-day Czech Republic. At the end of the Middle Ages highly skilled glass manufacturing techniques were achieved, as is well demonstrated by the beauty of the magnificent windows that decorate the churches and cathedrals of this period. Through the middle ages, some differences in glass composition can be found between the glasses produced in Northern Europe, which usually present a higher amount of potash, than those produced in Southern Europe [10] made mainly from soda. And, finally, it is in the Middle Ages with the invention of spectacles that we find the first examples of optical glasses in history. Technically, an optical glass can be defined as a transparent glass with such a degree of homogeneity that it can be considered a homogeneous and isotropic optical medium [11] suitable to be employed in the production of lenses.

The early centuries of the modern age are marked by both technical and scientific discoveries in the field of optical glass making. Among the first, a new kind of glass known as “flint glass” or “flint crystal” was produced from the silica rich in lead oxides that comes from flint, hence its name. Flint glass presented a higher refractive index than the existing lime-soda or “crown” glass and it was highly appreciated in the manufacturing of vessels and other “crystal” objects following its discovery by Ravenscroft in 1672 [11]. By the same time, Newton formulated a theory on light dispersion [12], the fact that light of different wavelengths propagates at different speeds within the same medium. A consequence of light dispersion is the appearance of colored borders in the images produced by any optical system formed by refractive lenses, a phenomenon that is known as *chromatic aberration*. It was easily proved that flint glasses presented more dispersion than crown ones, and that this fact could be advantageously used to reduce chromatic aberration by a proper combination of a crown and a flint lens in the so-called achromatic doublet developed around 1750.

The coming of the Industrial Revolution at the beginning of nineteenth century brought with it a rupture with the traditional ways in which objects and materials were produced. This change, which affected glass making, led to the mass production of glass with higher quality than before. One of the first milestones in this process was the method devised by Guinand and Fraunhofer [13] around 1814 for removing bubbles by stirring the molten glass before cooling. Another crucial finding by Faraday in 1829 [14] was the use of platinum crucibles with better endurance against chemical attack by the molten glass. By mid-century the basic industrial glass-making process was definitively established and it can be summarized in three major operations: batching, melting, and forming [1]. In the first process, the glass components are selected and processed in order to avoid impurities, such as Fe_2O_3. Afterward, the ingredients are mixed and heated in a melting pot until

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molten glass is formed. Finally, the glass is cooled and a forming process (cutting, pressing, or casting) is carried out to obtain the final product [1].

Until 1880 there were only two available glass types: crown and flint. Crown glasses are low-index glasses with reduced dispersion, while flint glasses are just the opposite; they usually present a high index with great dispersion. It is in this year that Schott and Abbe [11] started a research program aimed at the production of high refractive index glasses with low dispersion in order to widen the range of available options for the optical designer. Their efforts culminated in the discovery of a whole family of barium-oxide glasses, which can be regarded as "high-index crowns," allowing the design of improved optical systems such as Celor or Dagor photographic lenses. This process of a scientific and systematic search of new glasses pioneered by Schott and Abbe was continued throughout the twentieth century, particularly in the interwar years by the effort of scientists like G. W. Morey and C. W. Frederik of Kodak Research Laboratories [11] who worked on the development of high-index and low-dispersion glasses using oxides of heavy atomic elements, especially rare earths such as lanthanum and thorium, embedded in a borate glass. The development of these rare-earth glasses was enhanced in the Second World War when more than 125,000 pounds (around 62,500 kilograms) of rare-earth glasses were produced in the United States [11]. With the use of rare-earth oxides, the refractive index can be as high as 1.9 while keeping the dispersion relatively low. Ultimately, both barium oxide and rare-earth glasses reached the ophthalmic industry by the last half of the twentieth century.

1.3 Glass Properties

As any other material, glass has a number of distinctive properties. Foremost of them are the optical ones, but there are also other important mechanical and chemical characteristics that must be known in order to understand properly the behavior of glass as an ophthalmic material. Thus, we are going to give first a brief summary of glass composition and, afterward, we will focus on the main optical properties: refractive index, dispersion, and transmittance. We will finish this section with a short description of relevant nonoptical properties.

1.3.1 Composition

Glass composition is not unique. In fact, different mixtures and proportions of materials lead to glasses with distinct properties. In general, glass is formed by the mixture of inorganic components [1]. For example, a typical crown glass (lime-sode glass) is formed [1] by 71.5% of silica (SiO_2) as the main ingredient, together with 14% of NaO_2, which comes from sodium carbonate Na_2CO_3 (soda), 13% of CaO (lime) and a lesser amount (about 1.5%) of Al_2O_3 (alumina). The role of each of these basic components is precisely defined. NaO_2 is employed to reduce the melting point of glass, while lime improves the chemical resistance and enhances glass formation, and alumina adds durability to the glass. Other additive widely employed in the glass industry is boric oxide, B_2O_3, which reduces viscosity and melting temperature, and forms the family of borate glasses [1].

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Apart from the basic components, other substances can be added to the glass to alter its properties. For instance, it has been known since the discovery of flint glasses by Ravenscroft in the seventeenth century, that the addition of lead oxide, PbO, increases the refractive index and dispersion of the resulting glass. As mentioned previously, in the nineteenth century, Schott researched thoroughly in order to find new glass components such as barium oxide, BaO, obtaining in this way the barium-oxide glasses which present a higher refractive index than crown ones but lower dispersion than flints [1]. Another example of index changing substances are the rare-earth oxides, such as lanthanum or thorium, employed in high refractive index glasses [1, 11]. But not only can the refractive index be varied using additives, other properties such as color and transmittance can be altered in a significant way just by adding small amounts of metal oxides to the molten glass. This is why an accurate control of impurities is of paramount importance in the manufacturing process of glass. For more details of glass composition we refer to the specialized literature, particularly the works of Musikant [1] and Twyman [11].

1.3.2 Refractive Index and Dispersion

The glasses employed by the ophthalmic industry are homogeneous and isotropic, so their optical properties are the same everywhere within the medium and do not depend on the direction of light propagation. Thus, for a given wavelength, the refractive index, n, is a constant defined as the ratio between the speed of light a vacuum and within the material [15]. As the former is always larger than the latter, the refractive index is a number larger than one. Its value, for most optical glasses, is between $n = 1.5$ and $n = 2$.

In ophthalmic optics the importance of the refractive index is that, as we will see in the following chapters, this magnitude relates the optical properties of an ophthalmic lens, namely refractive and prismatic power, with the lens geometry, particularly curvature and thickness. An example of this relation is given by the following equation:

$$P = (n-1)\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \equiv (n-1)K, \tag{1.1}$$

which relates the power of a thin lens, P, and the radius of curvature, R_1 and R_2, of the two lens surfaces through the refractive index, n. By combining the geometrical factor of equation (1.1) in a single magnitude K, we can easily see that different combinations of materials and geometries may result in the same power. Indeed, as a rule of thumb, the higher the refractive index, the flatter the lens surfaces, as shown in the following example.

Example 1 A convex-plane lens made in crown glass BK7 (refractive index $n_A = 1.523$) has a curvature radius for the first surface $R_{1A} = 85$ mm. Calculate the curvature radius of the anterior surface for another convex-plane lens with equivalent power made in an extra-dense flint glass ($n_B = 1.7506$) using equation (1.1).

As those lenses are convex-plane ones, the curvature radius of the second surface is $R_2 = \infty$ for both. Therefore, for the crown lens the geometrical factor is $K_A = 1000/85 - 1/\infty = 11.77$ D and, consequently, the power of this lens is $P_A = (1.523 - 1) \times 11.77 = 6.15$ D.

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As we want the flint lens to have the same power, then its geometrical factor must be $K_B = P_B/(n_B - 1) = 6.15/(1.7506 - 1) = 8.20$ D and the resulting curvature radius for the first surface can be easily computed as $R_{1B} = 122$ mm. Thus, the high-index lens presents a flatter convex surface whilst maintaining the same power.

Dispersion is the dependence of the refractive index of a medium with the wavelength. The refraction index establishes the link between the optical and geometrical properties of a lens. As a consequence, the presence of chromatic dispersion will result in a blurring of the image and the appearance of rainbow-like fringes at the border of the objects located in the periphery of the lens field of view. This effect is known as chromatic aberration [15]. As the correction of chromatic aberration is not possible with a single lens, it constitutes an unavoidable feature of ophthalmic lenses. Another important consequence of dispersion is that the wavelength for which the refractive index has been measured should be specified when referring to this index. The usual convention in optics establishes that when a refractive index is given without explicit information about the wavelength, it is assumed that it corresponds to Fraunhofer's spectral d line ($\lambda_d = 587.56$ nm).

Figure 1.1 shows the dispersion curves of four common glasses, where we can see that refractive index varies smoothly with the wavelength. Several analytical functions such as Cauchy's or Selmeier's formulas have been devised that provide an analytical approximation to these dispersion plots. However, the overall dispersion of a given material is usually characterized by a single parameter known as the Abbe number, which is defined as:

$$\nu_d = \frac{n_d - 1}{n_F - n_C} \tag{1.2}$$

where n_d, n_C, and n_F are the values of the refractive index measured at the wavelengths corresponding to Fraunhofer's spectral lines d ($\lambda_d = 587.56$ nm), C ($\lambda_C = 656.28$ nm), and F ($\lambda_F = 486.13$ nm), respectively, being the difference $n_F - n_C$ the *principal dispersion* [1] of the glass. Notice that the lines C and F are located, respectively, at the red and blue extremes of the visible spectrum, while the d line is placed about in the middle. The bigger

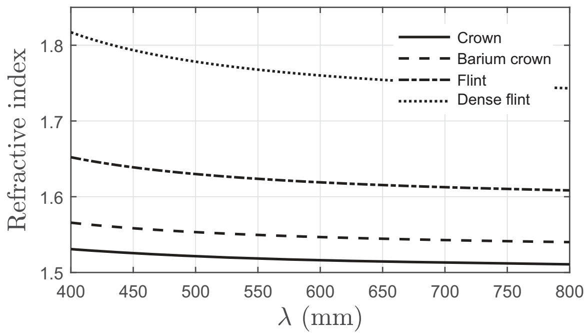

Figure 1.1 Variation of refractive index against wavelength for several glass types.

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the value of the Abbe number, the smaller the material dispersion. Ideally, a material with no dispersion would have $n_F = n_C$ and then an Abbe number $\nu_d = \infty$, according to equation (1.2).

The value of the Abbe number allows to distinguish between "crown" and "flint" (i.e. low- and high-dispersive) glasses. In general, a crown (low-dispersive) glass would be a glass whose Abbe number is greater than 50 and, conversely, a flint glass would have an Abbe number lower than this value. Note that this classification applies only to the material dispersion, not to the composition, so a glass with intermediate properties such as a barium oxide can be flint or crown depending on the value of the Abbe number (see, for example, Figure 1.1). As a rule of thumb, the larger the refractive index n_d of a material, the larger the dispersion (smaller Abbe number) as is shown in the so-called Abbe diagram [16]. However, the reader must be cautious about this rule. It is neither a law nor a fact; it is just a tendency.

As a consequence of dispersion, the optical properties of a lens are wavelength-dependent through the refractive index. For example, by combining equation (1.1) with the definition of the Abbe number (1.2), we get the following expression for the lens power variation between the two extrema of the visible spectrum

$$P_F - P_C = \frac{P_d}{\nu_d}, \tag{1.3}$$

which characterizes the so-called longitudinal chromatic aberration of a lens. As it is stated in this equation, the difference of lens power between the blue and red wavelengths is inversely proportional to the Abbe number, so the bigger the dispersion the greater the chromatic aberration. Equation (1.3) summarizes one of the main drawbacks of using high refractive index materials: as they are usually more dispersive than low-index glasses, they have a bigger chromatic aberration. As a consequence, a user of lenses with a high refractive index would perceive a greater loss of sharpness through the whole image field. As the user looks through points closer to the periphery of the lens, the effect of the chromatic aberration is the appearance of colored borders in high-contrast objects. This manifestation of the chromatic aberration is called *transverse chromatic aberration* (TCA), and is given by

$$TCA = \frac{|yP_d|}{\nu_d}, \tag{1.4}$$

where y is the distance from the optical center to the point the user is looking through.

1.3.3 Transmittance

One of the most important optical properties of a glass is transmittance. The amount of energy per unit of time carried by light is known as radiant flux. The amount of radiant flux per wavelength is *spectral* radiant flux. Let us consider now a block of glass limited by two plane surfaces, and a certain amount of radiant energy incident on one of the planes. In these conditions, the ratio between the emergent and incident radiant flux is transmittance

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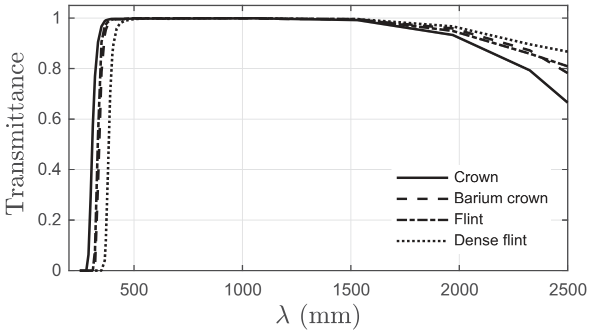

Figure 1.2 Spectral transmittance for several common glass types considering a glass thickness of 10 mm.

(see Chapter 11 for a more precise definition of transmittance). It is worth noting that transmittance should be specified for a given thickness of glass. For optical glasses an important magnitude is spectral transmittance, defined as

$$T(\lambda) = \frac{\Phi_t(\lambda)}{\Phi_i(\lambda)}, \tag{1.5}$$

where $\Phi_t(\lambda)$ is the transmitted and $\Phi_i(\lambda)$ the incident radiant flux. This magnitude is of interest not only for the visible region of the electromagnetic spectrum but also for the UV and infrared regions. Of particular interest is the behavior of spectral transmittance at the UV region. As the radiation from this part of the spectrum is potentially harmful to the eye, UV blocking is an important property of ophthalmic materials (see Chapter 11 for further details).

As can be seen in Figure 1.2, where we have plotted the spectral transmittance for the four characteristic glass types also represented in Figure 1.1, the spectral transmittance decreases abruptly in the UV region. This allows for the definition of a magnitude known as the UV cutoff wavelength λ_{UV} for which spectral transmittance reaches the value $T(\lambda_{UV}) = 0.05$ (which means that only 5% of the incident radiation is transmitted). For the glass types represented in Figure 1.2, this cutoff wavelength has a value comprised between 290 nm for the crown to 370 nm for the dense flint glasses. This means that most glasses block, at least, part of the UVA and UVB bands of ultraviolet radiation.

1.3.4 Mechanical Properties

Regarding the mechanical properties of ophthalmic glass, three main questions arise: would the material be safer enough against sudden impacts? Would it be rigid enough to withstand mechanical strain from the frame? Would it be hard enough to prevent the appearance of surface damage? These issues are addressed by manufacturing standards in which recommended values for the mechanical properties are given, as well as the tests that must be carried out to measure those properties.

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In regard to the *impact resistance*, in the United States, the Title 21 of the Code of Federal Regulations requires that all lenses must be impact-resistant except when the practitioner rules otherwise attending to the specific requirements of a particular patient (chapter I, subchapter H, part 801, see [17]). According to this standard, the impact test consists of dropping a steel ball of 5/8 inch (15.87 mm) diameter and 0.56 ounce (15.87 g) of weight from a height of 50 inches (1.270 m) upon the horizontal surface of the lens, with additional provisions on the impact point location, lens support, etc. To pass the test the lens must not fracture, so the code specifies the particular conditions that hold when a lens is considered fractured [17]. In the European Union, according to the norm EN165 [18], the lenses classified as "individual protective equipment" (such as the sunglasses according to the European Directive 89/686/ CEE) must stand an impact test described in the Norm EN166 [19], which consists of throwing a ball of 22 mm of diameter and 43 g with a required speed of 5.1 m/s against the lens surface. Similar to the Code of Federal Regulations, Norm EN166 [19] specifies in which circumstances the lens has failed the test.

The international standard that specifies the mechanical properties for uncut finished ophthalmic lenses is the ISO 14889:1997 [20]. According to this standard, an uncut finished lens should be able to pass a strength test consisting of the application of a constant load of 100 ± 2 N for 10 ± 2 seconds with a speed not exceeding 400 mm per min. The lens must pass the test without breaking or showing permanent deformation. The European Union requires that all ophthalmic lenses must fulfill the provisions of ISO 14889:1997, while in the United States this is not mandatory, although the adherence to this standard is considered a "good practice" by the Food and Drug Administration. In the EU, sunglasses, as they are considered "individual protective equipment," must pass the more exhaustive strength test described in the European Norm EN166 [19], as it must be passed by any other eye-protection equipment such as laser protection goggles and so on. Similar provisions for safety lenses are required by the Occupational Safety and Health Administration (OSHA) of the Federal Government of the United States under Title 29 of the Code of Federal Regulations 1910.133, which requires that these lenses must comply with the standard ANSI Z87.1-2010 "USA Standard for Occupational and Educational Eye and Face Protection."

Mechanical *resistance to abrasion* by ophthalmic lens surfaces is regulated by the international standard ISO-8980-5:2005, which defines abrasion resistance as the ability of the lens surface to resist the appearing of surface defects such as scratches in the normal daily use. The standard consists in the application of 25 cycles of abrasion with a mechanical tool wrapped with a folded cheesecloth. The lenses pass the test when no apparent scratches appear to the naked eye using an illuminating system described in the norm.

Therefore, there are three mechanical properties of interest when studying glasses applied to ophthalmic lenses: impact resistance or fracture toughness, tensile strength, and hardness. Glasses naturally have high compressive strength, but not so good tensile strength. For example, fused silica glass has a tensile strength of 49.6 MPa, which means that it is susceptible to breaking under a sudden impact. To overcome this problem, glass

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can be thermally or chemically treated in order to increase its toughness in a process known as tempering. Another relevant fact regarding glass resistance is that, although glass can sustain relatively high amounts of compressive strength, on occasions it can break under a smaller load if there are surface defects (such as scratches). This fact must be taken into account in the mounting process, particularly when mounting glass lenses in metallic frames, which can exercise bigger loads than plastic ones. In order to avoid this fracture under compressive load, the practitioner must take care in polishing the lens edges before mounting and checking, using a polariscope, that no important tensions appear due to the pressure of the mount over the lens. Regarding hardness, silica glass has a Knoop hardness coefficient of around 500 kg/mm^2, which is relatively high. For high-index glasses this magnitude is usually bigger, making them more prone to present surface defects.

Finally, another mechanical property to be considered is the density, which, generally, grows with the refractive index due to the use of heavy atoms such as lead or rare-earth elements in the composition of high-index glasses. For crown glasses, the density is roughly 2.2 g/cm^3, while for glasses like barium oxide Ba_2O the density is near to 3.5 g/cm^3, reaching the extreme values of 6.19 g/cm^3 for some high-index glasses, such as the P-SF68 produced by Schott Company [16]. Although there is no exact correlation between density and mass because the volume of a lens is highly dependent on the curvature radius, in general, the usage of denser glasses tends to result in heavier lenses.

1.3.5 Chemical Properties of Glass

The chemical properties of interest in ophthalmic optics are climatic resistance, staining resistance, and resistance to acid or alkali attacks. The first property can be defined as the ability of the glass to conserve its transmittance when suffering extreme temperature and humidity changes. The exposure to high degrees of humidity and abrupt temperature changes may result in the deterioration of the transmissive properties of the glass surfaces, manifested as a loss of transmittance. In general, the glasses employed in the ophthalmic industry are among the most weather resistant, and the standard ISO 8980-3:2005 only specifies weather resistance test for lenses with coated surfaces.

Staining is an optical effect caused by the formation of a coating due to chemical reactions between glass components, particularly alkali or alkali earth oxides, and water or water vapor. As a consequence of this coating, an interference pattern is formed that can be visible in some orientations by the user or by external observers. The glass manufacturers classify their glasses according to their degree of resistance to staining by the implementation of a test that consists of the submersion of glass in a diluted acid solution and the measurement of the time necessary for the development of the interference pattern. Similar tests are employed for establishing resistance to acid and alkali solutions.

A chemical property that is actually specified in the standard ISO 14889:1997 is flammability. According to the norm, flammability is tested by placing a rod heated to $650 \pm 20°$ C on the surface of the lens to be tested for 5 s. The lens passes the test if it does not show

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