TIE-30: Chemical properties of optical glass

1. General Information

Optical glasses acquire their properties through their chemical composition, melting process and finishing methods. In order to obtain specific optical properties, chemical compositions must often be chosen that lead to products with less than optimum chemical resistance [1]. For this reason there is a relatively large range of resistance of the different optical glasses with reference to environmental influences and chemical demands.

Water (H_2O) or rather its ionic components H^+ (hydrogen ions that make an aqueous solution acidic) or OH^- (hydroxide ions that make an aqueous solution alkaline) always play a decisive role. The pH value indicates whether the aqueous solution is neutral (values around 7), acidic (values below 7) or alkaline (values above 7). The quantity of water or of its ionic components is also significant: whether present in abundance, for example, when glass is cleaned with aqueous solutions, or whether only a little water is present, for example, from moisture in the air, perspiration, or condensation.

The pH value of solutions containing an abundance of water remains practically unchanged during reactions with glass. If only little water is present, atmospheric compounds, such as carbon dioxide from the air or, in heavily industrialized areas, sulphur dioxide can dissolve in water and lead to acidic solutions. An alkaline solution can result when a small quantity of aqueous solution is enriched by alkali ions migrating from the glass.

1.1. Layer Formation

In large quantities of neutral or acidic media, chemical processes occur in which cations from the glass (preferably alkali ions) are exchanged with the hydrogen ions from the solution. Leached layers that are also called ”silicate gel layers” because of their composition are formed over the course of time, their thickness depending on the resistance of the glass. They can be perceived by the naked eye as interference colors when their thickness exceed approximately ¼ of the wavelength of visible light. If such a layer becomes even thicker, it slowly turns white and can break off if thick enough or appears as a crust of the glass surface.

On the other hand, hydroxide ions from alkaline solutions destroy bonds between the silicon and oxygen ions that give the glass its structure. The glass is dissolved. These processes can play a role in polishing and washing operations. The data on acid, alkali, and phosphate resistance give a general impression of the chemical resistance of glass.

SCHOTT glass made of ideas

1.2. Local Corrosion and Stain Formation

A change in humidity and temperature on glass surfaces can lead to localized corrosion, which is characterized by the test for climatic resistance.

In contrast to the formation of layers when water is in abundance, reactions under very small masses of water (water in deficiency) can lead to the formation of stains, whereby additionally interactions with leached components can take place. The test for stain resistance simulates the effect of weak acidic agents with water in deficiency (breath, fingerprints, etc.).

1.3. Relationship Between Glass Composition and Chemical Resistance

The following explanations are given to allow a better understanding of the possible reactions on the surfaces of optical glass:

Glasses containing larger amounts of sparingly soluble components, such as silicon dioxide SiO_2, aluminum oxide Al_2O_3, titanium oxide TiO_2 or oxides of the rare earths, are more resistant to leaching by aqueous and acidic solutions. They usually also are more resistant to local corrosion.

If glasses, however, contain large quantities of more readily soluble substances such as alkali and possibly also alkaline earth oxides, and - above all - relatively readily soluble network formers such as boron and phosphorous oxide, then strong reactions of varying degree can be expected depending on the operating conditions. These reactions are sufficient for layer formation or removal of the glass surface.

The chemically altered depth of a layer of 0.1 µm (through removal or layer formation to the point of visibility to the naked eye) is used as the limit value for the tests for acid, alkali, phosphate and stain resistance.

These short explanations make it clear that it is impossible to adequately describe the chemical behavior of all optical glasses with a single test procedure. The processor of an optical glass must therefore have a comprehensive picture of the chemical behavior so that detrimental changes during processing are being excluded. The glass processor should give appropriate weight and consideration to the classifications listed in the optical glass data sheets. In order to reach a decision, the results of several test procedures may have to be taken into consideration.

Three resistance tests have been internationally standardized:

- Acid resistance test SR according to ISO 8424: 1996 [2]
- Alkali resistance test AR according to ISO 10629: 1996 [3]
- Phosphate resistance PR according to ISO 9689: 1990 [4]

The climatic resistance test CR is currently available as a proposed standard (ISO/DIS 13384 [5]).

2. Climatic Resistance (ISO/DIS 13384)

Climatic resistance describes the behavior of optical glasses at high relative humidity and elevated temperatures. The influence of water vapor in the air, especially under higher

humidity and temperatures, can cause a change in the glass surface in the form of a cloudy film that generally cannot be wiped off. The chemical process is a reaction with water in deficiency. Under normal atmospheric conditions such changes take place slowly even in sensitive glasses.

An accelerated procedure is used to test the climatic resistance of glasses. Polished, uncoated glass plates are exposed to a water vapor saturated atmosphere, the temperature of which is alternated between 40°C and 50°C on an hourly basis. Since the temperature increase in the glass plates follows that of the atmosphere, water condenses on the glasses during the warming phase. In the cooling phase the temperature of the atmosphere initially falls faster than that of the glass plates causing a drying of the glass surface. This is augmented by a heating source.

After an exposure time of 30 hours the glass plates are removed from the climatic chamber. The degree of weathering of the glass surface is determined by measuring the difference in haze between the weathered and the virgin specimen. The measurements are conducted using a sphere transmission haze meter. The classification is done based on the haze difference value ΔH obtained after the 30 hour test period. Table 2-1 lists the climatic resistance classes.

Table 2-1: Classification of optical glasses into climatic resistance classes CR 1 – 4 based on transmission haze increase after being subjected to a 30 hour climatic change test in the temperature range from 40°C to 50°C.

Climatic Resistance Class CR	**1**	**2**	**3**	**4**
Haze difference ΔH	< 0.3%	≥ 0.3% < 1.0%	≥ 1.0% < 2.0%	≥ 2.0%

The glasses in class CR 1 display no visible attack after being subjected to 30 hours of climatic change. In normal humidity conditions during the processing and storing of optical glasses in class CR 1 no surface attack should be expected. On the other hand, the processing and storing of optical glasses in class CR 4, in which the transmission haze increase is 2% and higher after a 30 hour test period, should be done with caution because these glasses are very sensitive to climatic influences.

For storage of optically polished elements we recommend the application of protective coatings and/or assuring that the relative humidity be kept as low as possible.

More than 80% of the optical glasses from SCHOTT are equal or better in their climatic resistance than class CR 2. Nearly 65% fulfill class CR 1. Only 5% of the glasses fall into class CR 4. These five most sensitive glasses with respect to their climatic resistance are shown in table 2-2. Please refer to the individual data sheets for the specific CR class of the other glasses.

Table 2-2: Optical glasses from SCHOTT in the climatic resistance class CR 4

Glass type	CR
N-LAK21	4
N-SK14	4
N-SK16	4
KZFS12	4
P-SK57	4

3. Stain Resistance

The test procedure gives information on possible changes in the glass surface (stain formation) under the influence of lightly acidic water (for example perspiration, acidic condensates) without evaporation.

The stain resistance says nothing about the resistance to climatic change (see climatic resistance) or highly acidic solutions (see acid resistance).

There are glasses, for example in the N-PSK or N-BAF families, that form no stains and therefore are listed in stain resistance class FR 0, although they have low acid and climatic resistance. In these cases, layers of glass are removed during the test without stain formation. Therefore it is important when evaluating the chemical behavior of optical glasses to consider all resistance test results!

The stain resistance class is determined according to the following procedure:
The plane polished glass sample to be tested is pressed onto a test cuvette, which has a spherical depression of max. 0.25 mm depth containing a few drops of a test solution.

Test solution I: Sodium Acetate Buffer pH = 4.6
Test solution II: Sodium Acetate Buffer pH = 5.6

Interference color stains develop as a result of decomposition of the surface of the glass by the test solution. The measure for classifying the glasses is the time that elapses before the first brown-blue stain occurs at a temperature of 25 °C. Changes in color correspond to certain thicknesses of the surface layer, which were determined on reference samples previously. A brown-blue change in color indicates a chemical change in the surface layer of 0.1 μm thickness insofar as the glass can form layers at all. Table 3-1. lists the stain resistance classes.

Table 3-1: Classification of optical glasses into stain resistance classes FR 0 – 5 based on the elapsed time before test solutions I or II cause brown-blue staining (layer thickness ~0.1 µm).

Stain resistance class FR	**0**	**1**	**2**	**3**	**4**	**5**
Test solution	I	I	I	I	II	I/II
Time [h]	100	100	6	1	1	0.2
Stain development	no	yes	yes	yes	yes	yes
Color change	no	yes/no	yes	yes	yes	yes

Stain resistance class FR 0 contains all glasses that exhibit virtually no interference colors, even after 100 hours of exposure to test solution I.

Glasses that display color change in less than 100 hours belong to classes FR 1–5, whereby glasses in class FR 1 exhibit the slowest color formation and glasses in class FR 5 the fastest color formation.

Glasses in classification FR 5 exhibit color change in less than 12 minutes. These glasses must be treated with particular care during processing.

More than 50% of optical glasses from SCHOTT form no stains and therefore are listed in stain resistance class FR 0. Less than 5% of the optical glasses are in stain resistance class 4 and 5. Table 3-2 shows these most sensitive glasses with respect to staining.

Table 3-2: Optical glasses from SCHOTT in the stain resistance classes FR 4 and 5

Glass type	**FR**
N-SK16	4
N-KZFS2	4
SF57	5

4. Acid Resistance (ISO 8424:1996)

Acid resistance classifies the behavior of optical glasses that come in contact with larger quantities of acidic solutions (for example, laminating substances, carbonated water, etc.). If an acidic aqueous medium reacts with a glass surface, stains can form (see stain resistance), or the glass can decompose, or both reactions can occur simultaneously. The acid resistance test provides particularly valuable information concerning dissolution of the glass. For the test, glass specimen polished on all six surfaces, are immersed in a large quantity of acidic solution. The time t required to dissolve a layer with a thickness of 0.1 µm at 25°C serves as a measure of the resistance to acids. The layer thickness is calculated from the weight loss per surface area and the density of the glass.

Two aggressive solutions are used in determining the resistance of the glasses to acids. A strong acid (nitric acid, c = 0.5 mol/l, pH 0.3) is used for the more resistant glass types, whereas glasses with less acid resistance are exposed to a weak acidic solution with a pH value of 4.6 (sodium acetate buffer).

This method, using two different solutions, is adopted to allow for the fact that some glasses cannot contain enough of the sparingly soluble substances to be able to achieve greater chemical resistance without negatively influencing the optical specification. Such glasses are therefore susceptible to damage during processing, since even weak acids with pH values of 4 - 6 (for example, carbonic acid, cements, perspiration, etc.) can cause noticeable deterioration.

Class SR 5 represents the transition point between the more acid resistant glasses SR 1 – 4 and the more acid sensitive glasses in SR 51 – 53. Class SR 5 includs glasses for which the time for removal of a layer thickness of 0.1 µm at a pH value of 0.3 is less than 0.1 h and at a pH value of 4.6 is greater than 10 hours. An overview of the classes is listed in Table 4-1.

Acid resistance is denoted by a two or three digit number. The first or the first two digits indicate the acid resistance class SR. The last digit, which is separated by a decimal point, indicates the visible surface change, that occurred through exposure. The last digit is enumerated in chapter 6.

Table 4-1: Classification of optical glasses in acid resistance classes SR 1 – 53 based on the time in which a layer thickness of 0.1 µm is removed in an acidic or weak acidic solution of a given pH value at a temperature of 25°C

Acid resistance class SR	1	2	3	4	5		51	52	53
pH Value	0.3	0.3	0.3	0.3	0.3	4.6	4.6	4.6	4.6
Time [h]	> 100	10-100	1-10	0.1-1	<0.1	>10	1-10	0.1-1	<0.1

Approximately 45% of the optical glasses from SCHOTT are equal or better in their acid resistance than class SR 2 and 35% fulfill class SR 1. Less than 10% are in class SR 53. Table 4-2 shows these most sensitive glasses with respect to acid resistance.

Table 4-2: Optical glasses from Schott in the acid resistance class SR 53

Glass Type	SR
N-LAK21	53.2
N-PSK53A	53.3
N-SK16	53.3
N-LAK7	53.3
N-LAK12	53.3
LAFN7	53.3
KZFS12	53.3

5. Alkali Resistance (ISO 10629: 1996) and Phosphate Resistance (ISO 9689: 1990)

Both test methods serve to classify the resistance of glasses to aqueous alkaline solutions in excess and use the same classification scheme.

The alkali resistance indicates the sensitivity of optical glasses in contact with warm, alkali liquids, such as cooling liquids in grinding and polishing processes. The test takes into account the fact, that through processing which occurs mostly in water based media the solution usually becomes increasingly alkaline through the chemical reactions of water with the abraded glass particles. This particularly applies when such solutions are recycled. Also taken into consideration is the fact that higher temperatures can occur as a result of the abrasion. Finally, consideration has also been paid to the fact that warm alkaline solutions are widely used in washing processes for the cleaning of polished surfaces.

The phosphate resistance describes the behavior of optical glasses during cleaning with washing solutions. The method takes into account the fact that the washing solutions (detergents) used for cleaning usually are not pure hydroxide solutions, rather they contain polyphosphates among other things. The phosphate resistance classes allow statements to be made regarding the resistance of optical glasses to such detergents.

The alkali as well as the phosphate resistance are denoted using two digits separated by a decimal point. The first digit lists the alkali resistance class AR or the phosphate resistance class PR, and the decimal indicates the visible surface change that occurs through exposure. The last digit is enumerated in chapter 6.

The alkali resistance class AR is based on the time required to remove a layer thickness of glass of 0.1 µm in an alkaline solution (sodium hydroxide, c = 0.01 mol/l, pH = 12) at a temperature of 50°C. The phosphate resistance class PR is based on the time required to remove a layer thickness of glass of 0.1 µm in an alkaline phosphate containing solution (pentasodiumtriphosphate $Na_5P_3O_{10}$, c = 0.01 mol/l, pH = 10) at a temperature of 50°C. The layer thickness is calculated from the weight loss per surface area and the density of the glass. Table 5-1 lists the alkali and phosphate resistance classes.

Table 5-1: Classification of the optical glasses in alkali resistance classes AR 1 – 4 and phosphate resistance classes PR 1 – 4 based on the time required to remove a layer thickness of 0.1 µm at a temperature of 50 °C in a caustic sodium solution with a pH value of 12 (AR) and in a pentasodiumtriphosphate solution with a pH value of 10 (PR).

Alkali Resistance Classes AR Phosphate Resistance Classes PR	**1**	**2**	**3**	**4**
Time [h]	>4	1-4	0.25-1	<0.25

Approximately 90% of the optical glasses from SCHOTT are equal or better in their alkali resistance than class AR 2. More than 60% fulfill class AR 1. Only 5% of the glasses are in class AR 4. Table 5-2 shows these most sensitive glass types with respect to alkali resistance.

Table 5-2: Optical glasses from SCHOTT in the alkali resistance class AR 4

Glass Type	**AR**
N-LAK21	4.3
N-KZFS2	4.3
KZFSN5	4.3
KZFS12	4.3
P-PK53	4.3

Approximately 70% of the optical glasses from SCHOTT are equal or better in their phosphate resistance than class PR 2 and over 40% fulfill class PR 1. Approximately 15% are in class PR 4. Table 5-3 shows these most sensitive glass types with respect to phosphate resistance.

Table 5-3: Optical glasses from SCHOTT in the phosphate resistance class PR 4

Glass Type	PR
N-KZFS2	4.2
N-FK51A	4.3
N-PK51	4.3
N-PK52A	4.3
N-PSK53	4.3
SF57	4.3
N-LAK7	4.3
N-LAK9	4.3
N-LAK12	4.3
N-LAK21	4.3
LAFN7	4.3
KZFSN4	4.3
KZFSN5	4.3
KZFS12	4.3
P-PK53	4.3

6. Identification of Visible Surface Changes

Changes in the surface of the exposed samples are qualitatively evaluated with the naked eye. The definition of the digits behind the class number for acid, alkali and phosphate resistance is as follows:

.0: no visible changes
.1: clear, but irregular surface (wavy, pockmarked, pitted)
.2: staining and/or interference colors (slight selective leaching)
.3: tenacious thin whitish layer (stronger selective leaching, a cloudy/hazy/dullish surface)
.4: loosely adhering thick layer, such as insoluble, friable surface deposit (may be cracked and/or peelable surface, surface crust, or cracked surface; strong attack)

7. Literature

[1] W. Heimerl, A. Peters: "The Chemical Durability of Optical Glass: Testing Methods" in The Physical Properties of Optical Glass, ed. by H. Bach, N. Neuroth (Springer Verlag, Berlin Heidelberg 1995,1998) pp. 229 - 244

[2] ISO 8424: Raw optical glass - Resistance to attack by aqueous acidic solutions at 25°C - Test method and classification; June 1996

[3] ISO 10629: Raw optical glass - Resistance to attack by aqueous alkaline solution at 50°C - Test method and classification; July 1996

[4] ISO 9689: Raw optical glass - Resistance to attack by aqueous alkaline phosphate-containing detergent solutions at 50°C-Testing and classification; December 1990

[5] ISO/DIS 13384: Raw optical glass - Testing of the climate resistance CR (resistance to humidity) at temperatures changing between 40°C and 50°C and classification; January 1999

For more information please contact:

Advanced Optics
SCHOTT AG
Germany
Phone: + 49 (0) 6131/66-1812
Fax: + 49 (0) 3641/2888-9047
E-mail: info.optics@schott.com
www.schott.com/advanced_optics

SCHOTT
glass made of ideas