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 [5]. 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) and/or 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 washing glass in watery 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 reaction 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 make acid. An alkaline reaction can result when a watery 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. Leaching 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 whitens and can break off if thick enough or can form a crust of the glass surface.

On the other hand, hydroxide ions from alkaline solutions destroy bonds between the silicon 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.

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 in an abundant watery solution, aqueous solutions that have low water content can also lead to the formation of stains, whereby the leaching of glass components can have different effects. The test for stain resistance simulates the effect of weakly acidic agents with low water content (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:

When glasses contain larger amounts of slightly soluble components, such as silicon dioxide SiO_2, aluminum oxide Al_2O_3, titanium oxide TiO_2 or oxides of the rare earths in aqueous and acidic solutions, they usually resist leaching and usually also local corrosion.

If larger quantities of more readily soluble substances are present in the glass, such as alkali, earth alkali oxides, and above all the relatively readily soluble network formers like boron and phosphor oxide, then strong reactions of varying degree can be expected depending on the operating conditions. These reactions are sufficient for layer formation to 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 unaided 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 relationships so that detrimental changes during processing are not possible. The glass processor should give appropriate weight and consideration to the classifications listed in the data sheets. In order to reach a decision, the results of several test procedures may have to be considered.

Three resistance tests have been internationally standardized:

- The acid resistance test SR according to ISO 8424: 1996 [2]
- The 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/CD 13384 [1]).

2. Climatic Resistance (ISO/CD 13384)

The influence of water vapor in the air, especially under high relative humidity and high temperature, can cause a change in the glass surface in the form of a cloudy film that generally cannot be wiped off. Under normal atmospheric conditions such changes take place slowly even in sensitive glasses. This is due to a reaction with a small amount of neutral water.

An accelerated procedure is used for testing the climatic resistance of glasses. Polished uncoated glass plates are exposed to a water vapor saturated atmosphere the temperatures of which are 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 glasses are removed from the climatic chamber. The difference ΔH between the haze before and after testing is used as a measure of the resulting surface change. The measurements are conducted using a spherical hazemeter. The classifications are done based on the increase in transmission haze ΔH after a 30 hour test period.

Climatic Resistance Classes CR	**1**	**2**	**3**	**4**
Increase in Transmission	< 0.3%	≥ 0.3%	≥ 1.0%	≥ 2.0%
Haze DH		< 1.0%	< 2.0%	

Table 2-1: Classification of the 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.

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 fabrication and storing of optical glasses in class CR 1 no surface attack should be expected. The fabrication and storing of glasses in class CR 4 in which a transmission haze increase of 2% is achieved or exceeded after a 30 hour test should on the other hand 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 SCHOTT glasses are equal or better class 2. Nearly 60% fulfill class 1. For more details please refer to the data sheets. Table 2-2 shows the most sensitive SCHOTT glasses concerning CR:

	CR
KZFS12	4
N-LAK21	4
N-SK14	4
N-SK16	4

Table 2-2: Schott glasses in the highest CR class

3. Stain Resistance

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

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 PSK or LaK groups, 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: Standard Acetate 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. This change in color indicates a chemical change in the previously defined surface layer of 0.1 µm thickness insofar as the glass can form layers at all.

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

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

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.

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

More than 85% of the SCHOTT glasses are equal or better class 2. Nearly 74% fulfill class 1. For more details please refer to the data sheets. Table 3-2 shows the most sensitive SCHOTT glasses concerning FR:

	FR
SF57	5
SF66	5
N-KZFS2	4
N-SK16	4

Table 3-2: Schott glasses in the highest FR classes

4. Acid Resistance (ISO 8424:1987)

Acid resistance classifies the behavior of optical glasses that come in contact with large quantities of acidic solutions (from a practical standpoint for example, perspiration, 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 (testing is done with larger quantities of acidic solutions). The time t required to dissolve a layer with a thickness of 0.1 µm serves as a measure of the resistance to acids.

Acid resistance is denoted by a 2 or 3 digit number. The first or the first two digits indicate the acid resistance class SR. The last digit (separated by a period) tells the change in the surface visible to the unaided eye that occurs through exposure.

Two aggressive solutions are used in determining the resistance to acids.

1. A strong acid (nitric acid, c = 0.5 mol/l, pH 0.3) at 25°C is used for the more resistant glass types.

2. For glasses with less acid resistance a weakly acidic solution with a pH value of 4.6 (standard acetate) is used, also at 25°C.

This procedure 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, perspiration, cements, carbonic acid, etc.) can cause noticeable deterioration.

Class SR 5 forms the transition point between the two groups. Included in it are 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 Class SR									
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

Table 4-1: Distribution of the 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 weakly acidic solution of a given pH value at a temperature of 25C

More than 44% of the SCHOTT glasses are equal or better class 2. 35% fulfill class 1. For more details please refer to the data sheets. Table 4-2 shows the most sensitive SCHOTT glasses concerning SR:

	SR
SF66	53.4
KZFS12	53.3
LAFN7	53.3
LAKL12	53.3
N-LAK12	53.3
N-LAK7	53.3
N-SK16	53.3
N-LAK21	53.2

Table 4-2: Schott glasses in the highest SR classes

5. Alkali (ISO 10629) and Phosphate Resistance (ISO 9689)

Both test methods serve to show the resistance to aqueous alkaline solutions in excess.As concerns alkali resistance, the fact that fabrication processes that occur in water based media (for example, grinding and polishing compounds) usually become increasingly alkaline through the chemical reactions of the water and the abraded glass particles is taken into consideration. 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.

International standard ISO 9689: 1990 is available for phosphate resistance. The method takes into account the fact that the washing solutions (detergents) used to clean optical glasses 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 and phosphate resistance are denoted using two digits separated by a decimal point. The first digit lists the alkali resistance class AR or the phophsate resistance class PR, and the decimal tells the surface changes visible to the unaided eye that occur through exposure.

The alkali resistance class AR is based on the time required to remove a layer thickness of glass of 0.1 µm 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. The class distribution is shown in Table 5-1.

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

Table 5-1: Distribution 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 value of 12 (AR) and in a pentasodiumtriphosphate solution with a pH value of 10 (PR).

More than 90% of the SCHOTT glasses are equal or better AR class 2. 63% fulfill class 1. For more details please refer to the data sheets. Table 5-2 shows the most sensitive SCHOTT glasses concerning AR:

	AR
KZFS12	4.3
KZFSN4	4.3
KZFSN5	4.3
N-KZFS2	4.3
N-LAK21	4.3

Table 5-2: Schott glasses in the highest AR classes

More than 67% of the SCHOTT glasses are equal or better PR class 2. 44% fulfill class 1. For more details please refer to the data sheets. Table 5-3 shows the most sensitive SCHOTT glasses concerning PR:

	PR
KZFS12	4.3
KZFSN4	4.3
KZFSN5	4.3
LAFN7	4.3
N-FK51	4.3
N-LAK12	4.3
N-LAK21	4.3
N-LAK7	4.3
N-LAK9	4.3
N-PK51	4.3
N-PK52A	4.3
N-PSK53	4.3
SF57	4.3
N-KZFS2	4.2
SF66	4.2

Table 5-3: Schott glasses in the highest PR classes

6. Identification of Visible Surface Changes

The digit that serves to identify the visible changes in the surface behind the class listing provides the following information:

.0 no visible changes
.1 clear, but uneven surface
.2 interference colors (light selective leaching)
.3 firmly adhered, thin white layer (stronger selective leaching, cloudy surface)
.4 loosely adhering, thicker layers, for example, insoluble reaction products on the surface (this can be a projecting and/or flaking crust or a projecting surfacing; strong attack)

7. Literature

[1] ISO/CD 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

[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

[6] The properties of optical glass; H. Bach & N. Neuroth (Editors), Springer Verlag 1998

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