

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 (H₂O) 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.

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

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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.

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 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.).



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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 $0.1 \mu\text{m}$ (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]

2. Climatic Resistance

Climatic resistance describes the behavior of optical glass at high relative humidity and high 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 spherical hazemeter. The classification done based on the increase of transmittance haze ΔH after a 30-hour test period. Table 1 lists the climatic resistance classes.

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Climatic Resistance Class CR	1	2	3	4
Increase in haze ΔH	<0.3%	$\geq 0.3\%$ <1.0%	$\geq 1.0\%$ <2.0%	$\geq 2.0\%$

Tab. 1: Classification of optical glass 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 show no visible attacks after being exposed to climatic change for 30 hours. Under normal humidity conditions during the fabrication and storing of optical glasses in class CR 1, no surface attack can 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 manufactured and stored with caution because these glasses are highly sensitive to environmental influences.

When storing optical polished elements, we recommend the application of protective coatings and/or assuring that relative humidity is 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. Please refer to the individual data sheets for the specific CR class of the other glasses.

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

Tab. 2: Optical glass from SCHOTT in the climatic resistance class CR 4.

3. Stain Resistance

The test procedure provides information on possible changes in the glass surface (stain formation) under the influence of slightly 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 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 previously determined on reference samples. A brown-blue change in color indicates a chemical change in the surface layer of 0.1 μm thickness insofar as the glass is able to form layers. Table 3. lists the stain resistance classes.

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Stain resistance class FR	0	1	2	3	4	5
Test solution	I	I	I	I	II	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

Tab. 3: Classification of optical glass 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 contains all glasses that show 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 show the slowest color formation and glasses in class FR 5 the fastest color formation.

4. Acid Resistance ISO 8424 (1996)

Acid resistance describes the behavior of optical glass that comes in contact with larger quantities of acidic solutions (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 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 acid resistance. The layer thickness is calculated from the weight loss per surface area and the density of the glass.

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

Glasses in classification FR 5 show color change in less than 12 minutes. These glasses must be handled 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 4 shows these most sensitive glasses with respect to staining.

Glass type	FR
N-SK16	4
N-KZFS2	4
SF57/SF57HTultra	5

Tab. 4: Optical glass from SCHOTT in the stain resistance classes FR 4 and 5.

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 includes 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 5.

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

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
Time [h]	>100	10–100	1–10	0.1–1	<0.1	>10	1–10	0.1–1

Tab. 5: 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.

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 6 shows these most sensitive glasses with respect to acid resistance.

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

Tab. 6: Optical glasses from SCHOTT in the acid resistance class SR 53.

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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 glass 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.

Phosphate resistance describes the behavior of optical glass during cleaning with washing solutions (detergents). 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.

Both 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 phosphate resistance class PR, and the decimal indicates the visible surface change that occurs as a result of exposure. The last digit is enumerated in chapter 6.

The alkali resistance class AR indicates the time needed to remove a 0.1 μm layer thickness of glass in an alkaline solution (sodium hydroxide, $c = 0.01 \text{ mol/l}$, $\text{pH} = 12$) at 50°C .

The phosphate resistance class PR indicates the time needed to remove a 0.1 μm layer thickness of glass in an alkaline phosphate containing solution (pentasodiumtriphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$, $c = 0.01 \text{ mol/l}$, $\text{pH} = 10$) 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 7 lists the alkali and phosphate resistance classes.

Alkali Resistance Class AR	1	2	3	4
Phosphate Resistance Class PR				
Time [h]	>4	1–4	0.25–1	<0.25

Tab. 7: Classification of the optical glass 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).

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 8 shows these most sensitive glass types with respect to alkali resistance.

Glass Type	AR
N-LAK21	4.3
N-KZFS2	4.3
P-PK53	4.3

Tab. 8: Optical glasses from SCHOTT in the alkali resistance class AR 4.

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Approximately 70 % of the optical glasses from SCHOTT are equal or better in their phosphate resistance than class PR 2 and more than 40 % fulfill class PR 1. Approximately 15 % are in class PR 4. Table 9 shows these most sensitive glass types with respect to phosphate resistance.

Glass Type	PR
N-KZFS2	4.2
N-FK51A	4.3
N-FK58	4.3
N-PK51	4.3
N-PK52A	4.3
N-PSK53A	4.3
SF57	4.3
SF57HTultra	4.3
N-LAK7	4.3
N-LAK9	4.3
N-LAK12	4.3
N-LAK21	4.3
LAFN7	4.3

Tab. 9: Optical glass from SCHOTT in the phosphate resistance class PR 4.

6. Identification of Visible Surface Changes

Changes in the surface of the exposed samples are evaluated qualitatively with the naked eye. The definition of the digits behind the classification 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: adhere loosely thick layer, such as insoluble, friable surface deposits (may be cracked and/or peelable surface, surface crust, or cracked surface; strong attack)

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7. Cleaning recommendations

The following chapter discusses some recommendations on cleaning of polished optical glasses.

Dirt on optical surfaces can be slurry particles from polishing, loose dust particle from the environment, salt from finger prints or inorganic stains like lime precipitation and organic stains from solvents, packaging or others.

In general, powder free gloves or finger cots should be used when touching an optical surface. Fingerprints are slightly acidic forming stains difficult to remove. Remove dust or loosely held particles first to avoid scratching during cleaning. Use a dust free blower (dry nitrogen, or CO₂ blower).

Cleaning of optical glasses after polishing is very important to prevent imprints and/or discoloration. Dirt sticking to the surface can lead to problems in subsequent process steps or limiting coating adhesion (especially organics).

Dependent on glass and solvent, either mobile ions are dissolved out of the glass network (porous glass remains = opaque surface) or the complete network is dissolved (clear surface, unless salts from solution remain). Hydroxy solutions or fluorine containing detergents are mainly known to destroy the network. Some organic detergents can release a small amount of F that can also destroy Si-O-Si-bonds.

Water as a solvent at neutral or acidic pH is forming soft silica gel layers on surfaces of polished silica containing glasses. Polished fluorophosphate and phosphate glasses are hygroscopic. Long water exposure of polished surfaces and even humid atmosphere for storing should be prevented.

Cleaning agents usually should be neutral in pH value especially for glasses with low acid or alkaline resistance. Elevated temperatures usually increase the reaction speed if the pH is not neutral.

De-ionized water can have a pH <7 and therefore can react acidic on optical glass surfaces.

If glass parts cannot be cleaned directly after polishing they should be transported/stored in a water tank until cleaning to prevent sticking of the polishing particles. The pH of the water tank should be at pH 7 or slightly alkaline. If slurry particles dry out at the surface the attraction forces between the particles and the surface will increase and make them harder to remove.

Slightly alkaline solutions can help to lift slurry particles from the surface. Especially cerium oxide slurry particles will be repelled from the glass surface at pH >7 and can be easily removed by ultrasonic cleaning or recirculation flow. Even sensitive glasses can be cleaned in most cases by dipping them in weakly alkaline solutions (~ pH = 7.5). Then the glass can be rinsed-off and cleaned with organic solvents.

Organic solvents vaporize at room temperature, therefore they are useful for dissolving certain material and substances. Organic solvents need to be applied with great care, because they can also lead to stains on the surface depending on the glass chemistry.

Solvents can be broadly classified in two categories: polar and non-polar. Acetone is an organic solvent with a high polarity. Isopropanol is a solvent with a much lower dielectric constant. Benzene would be an example for a non-polar solvent.

Certain glasses types are sensitive towards polar organic solvents. Organic solvents do not evaporate without traces on surfaces with a high polarity. Even on typical silicate glasses, acetone and some other alcohols remain adsorbed on the surface, leading to white stains with clearly visible rims in the shape of the initial droplet. For silicates, iso-propanol and higher alcohols can be used for water removal, however, for fluorophosphates and phosphates all organics should be tested prior to use.

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There exist many industrial cleaners, some of them even tested on different glass chemistries. However, most cleaners are tested on silicate glasses only. Further, they are optimized for fast and efficient cleaning, which in the end means they are relatively aggressive.

Chemically sensitive optical glasses with cleaned and dried polished optical surface should be stored in a desiccator with desiccant or coated shortly after polishing.

8. Literature

[1] "The Chemical Durability of Optical Glass: Testing Methods", W. Heimerl, A. Peters, 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, 1996

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

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



Advanced Optics
SCHOTT North America, Inc.
400 York Avenue
Duryea, PA 18642
USA
Phone +1 570/457-7485
Fax +1 570/457-7330
info.optics@us.schott.com

www.us.schott.com/advanced_optics

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