

Functional Glass Developed by Liquid Coating

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Introduction

Glass is an interesting material which is widely used in our day to day life; coatings add several functionalities to the glass to make it more useful. In general, these coatings fall into two major categories for commercial glass; Low E and specialty coatings. Low E Coatings, mostly applied using sputter deposition process, and the biggest volume in the coated glass segment, enhances the energy efficiency of glass. Specialty coatings, a growing market segment, improve the aesthetics, optics and conductive properties of the glass. From which, liquid coatings (LC) are widely used in self-cleaning glass, anti-reflection glass, anti-microbial glass, anti-UV, anti-smudge glass, anti-fog and transparent conductive glass products. They play a critical role in the specialty coating segment due to its lower cost, flexible process capabilities, and wide range of material and chemistry choices. Compared with physical vapor deposition (PVD) and chemical vapor deposition (CVD), LC demonstrates economical and simple process advantages.

Many coating application techniques, such as curtain, spray, dip, printer, and roller, can be used with liquid coatings and allows LC technology to be used in different manufacturing environments. While currently there is a variety of glass with different functional attributes within commercial glass, it is highly desirable to develop a multi-functional coated product that can survive harsh environments. In this study, the preparation and performances of anti-corrosion and anti-reflection (ACAR) glass, and anti-glare and anti-UV (AGAU) glass are reported.

1. Anti-corrosion and anti-reflection glass

The hydrolysis of glass at the coating and glass interface can destruct performance of anti-reflection (AR) coated glass. The failure mechanism may be attributed to the non-uniformity of the reactive sites of the glass surface caused by the sodium ion migration during the aging of bulk glass to surface of AR thin film.¹ It has been found there is a layer of reduced sodium concentration and increased hydrogen amount near the glass-solution interface.² When alkali ions leach from glass, it provides an avenue for water migration and creates a hydrated layer at the glass and coating interface. The more open structure in the hydrated layer of glass surface can result in a fast transfer of ions from the glass³ and could swell the coating structure.⁴ Furthermore, hydroxyl groups, OH produced by ion exchange between Na⁺ and H₂O, can boost the hydrolysis of siloxane bond and result in final damage of AR thin film. It is published knowledge that various oxides of multivalent cations may provide glass some resistance from alkaline attack mentioned within.^{5,6} One of the strategies to improve durability of AR glass is to develop anti corrosion AR glass via hybrid alkoxides. In this study, anti-corrosion AR glasses are developed by hybrid alkoxides of Si(OR)₄ and Al(s-OBu)₃, where R is CH₂CH₃ group, s-OBu is sec-butoxide, respectively.

Chemical structure of ACAR glass developed by sol-gel process

There are two basic steps in the sol-gel chemical reaction of alkoxides; these two steps are hydrolysis and condensation. Hydrolysis produces functional groups which can further condense generating three dimensional crosslinked networks.

-Hydrolysis of Si(OR)₄

Figure 1 shows the hydrolysis of tetraethyl ortho-silicate (TEOS) with an acid catalyst. SN₂ mechanisms can be used to describe the hydrolysis of TEOS.⁷ First, the electrophilicity of the Si atom is enhanced by

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the attack of a proton to the -OR group of TEOS. This proton is released from the presence of acetic acid. Now, the Si atom with more electrophilicity can be easily attacked by a water molecule and one intermediate is generated as shown in Figures 1. The further reaction of intermediate produces the hydrolyzed TEOS and releases a proton, H^+ , which can be again used as the catalyst. This is a reversible process and can be repeated to generate various hydrolyzed TEOS, such as silicic acid $Si(OH)_4$, as fully hydrolyzed TEOS.⁸ Except the reversible hydrolysis of TEOS, an esterification also exists in the process.⁹

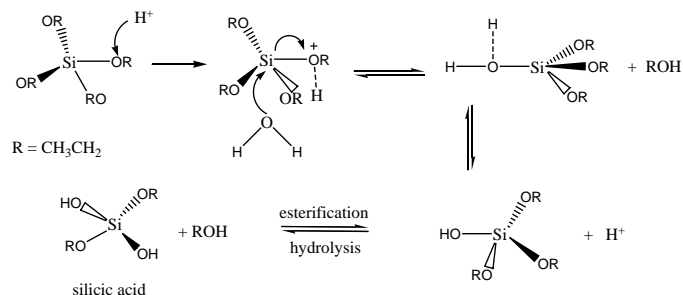


Figure 1. Hydrolysis of TEOS with acid as catalyst.

-Hydrolysis of Al(s-OBu)₃

Hydrolysis of $Al(s-OBu)_3$ also undergoes mechanism of SN_2 . Hydrolyzed $Al(s-OBu)_3$ is generated after leaving of ROH from intermediate as shown in Figure 2.

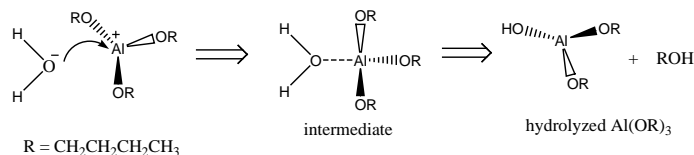


Figure 2. Hydrolysis of $Al(s-OBu)_3$.

-Condensation of $Si(OR)_4$

The hydrolyzed $Si(OR)_4$ can be further condensed via water and alcohol as shown in Figures 3. The reversible reaction is hydrolysis and alcoholysis, respectively. Initially the proton will attack oxygen atom in hydroxyl group of hydrolyzed alkoxy silane, which increases electrophilicity of Si atom, and this transition state can be easily attacked by hydroxyl group from hydrolyzed alkoxy silane molecule.

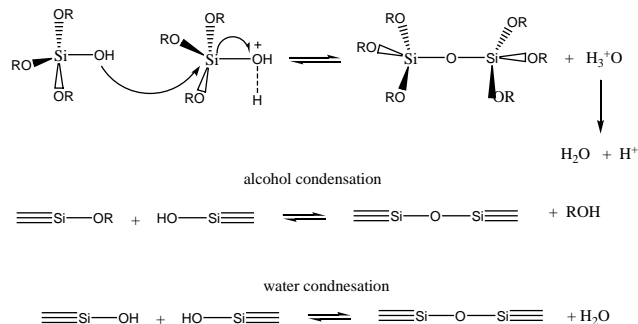


Figure 3. Condensation of hydrolyzed $Si(OR)_4$ with acid as catalyst.

-Condensation of hydrolyzed Al(s-OBu)₃

Figure 4 shows the condensation of hydrolyzed Al(s-OBu)₃. When aluminum alkoxides condensate, a double oxygen bridge forms between two aluminum atoms. A series of oligomers could be generated during the condensation. The extent of oligomerization of aluminum alkoxides depends mainly on the steric bulk of the alkoxides ligand.¹⁰

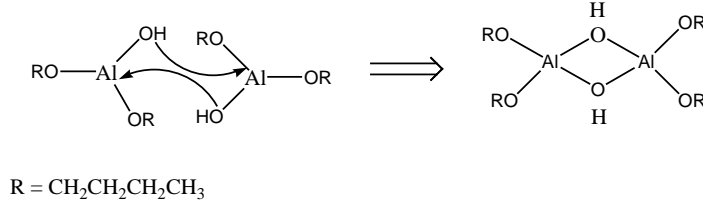


Figure 4. Condensation of hydrolyzed Al(s-OBu)₃.

Anti-corrosion mechanisms of ACAR glass made by hybrid alkoxides

-Hydrolysis of AR thin film

The hydrolysis mechanism of AR thin film can be described by Figure 5. There are many oxygen-bridging ions existing in normal soda-lime glass with no long-range order, but possible short range order. The introduction of some alkaline oxides, such as Na₂O, can hydrolyze silica-oxygen bond to form non oxygen-bridge ion as shown in Figure 5. The extra electronic charge of non-bridging oxygen ion is neutralized by alkaline ions. The presence of non-bridging oxygen ions may damage the integrity and surface properties of the glass structure, which can result in the decline of some properties of glass, such as chemical stability and mechanical strength.¹¹

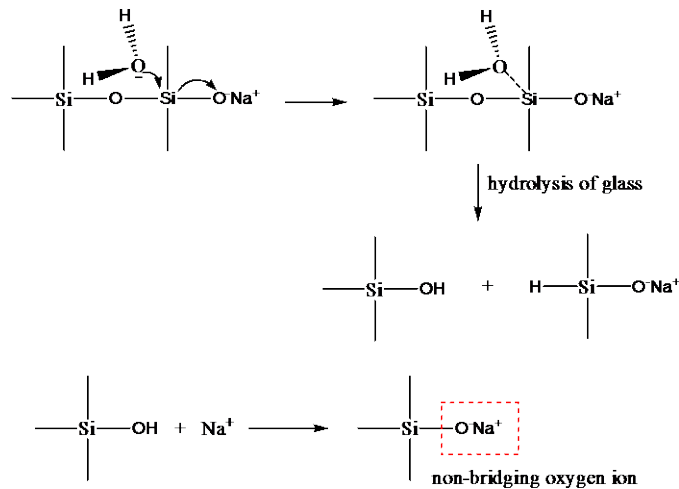


Figure 5. Hydrolysis of glass with unsymmetrical network.

-Repair mechanism of anti-corrosion AR glass made by hybrid alkoxides

Figure 6 shows the mechanism of anti-corrosion AR glass made by hybrid alkoxides of Al₂O₃ and SiO₂. Al³⁺ can exist in silica materials with two different coordinates, which is octahedral and tetrahedral, respectively. In soda-lime glass, Al³⁺ is in tetrahedral structure when ratio of Na₂O to Al₂O₃ is larger than one. Al³⁺ can catch one non-oxygen bridge ion to generate Al⁴⁺ tetrahedral structure, which connects with Si-O tetrahedral structure together and repairs the broken network. Uniform three dimension

network can enhance integrity and symmetry of glass matrix, which consequently increase chemical stability of glass.

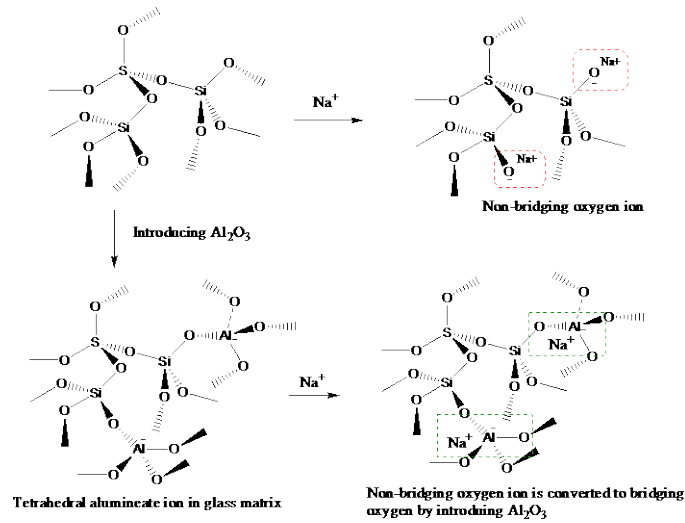


Figure 6. Durable structure of anti-corrosion AR glass made by hybrid alkoxides with $\text{Si}(\text{OR})_4$ - $\text{Al}(\text{s-OBu})_3$.

Performances of ACAR glass

Environmental durability of anti-corrosion properties is evaluated by various chamber tests with high temperature and high humidity as well as acid and base conditions. Figure 7 shows the change of $T_{qe}\%$ of ACAR versus duration within a salt fog chamber (35°C , pH: 6.5-7.0; 16 psi, humidity: 100%). It is clear that coating film on ACAR glass is very stable since there is almost no change on $T_{qe}\%$ after more than 61 days of testing.

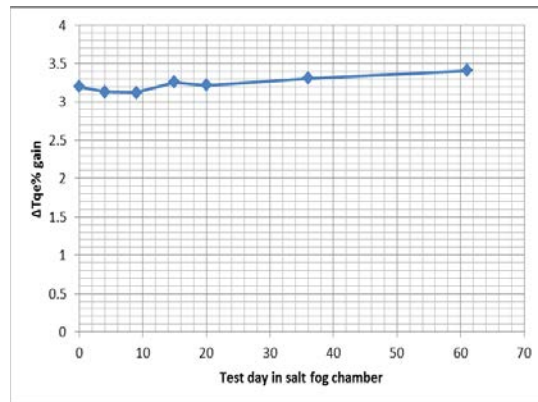


Figure 7. Change of $T_{qe}\%$ with testing time of ACAR glass in salt fog chamber.

Table 1 summarizes various performance characteristics of ACAR glass. It shows that AR glass made from hybrid alkoxides is more durable than that made by sol with only silica alkoxide. Furthermore with exception of higher transmittance and lower reflection, ACAR glass with hybrid alkoxides provides excellent adhesive, mechanical strength, and chemical stability.

Table 1. Performances of ACAR glass

Optical performance	
T _{qe} % (400 nm-1200 nm)	3.19
R% (400 nm-1200 nm)	5.03
Thickness of coated layer, nm	125
Refractive index	1.29
Surface property	
Roughness, Rm, nm	5.39
Roughness, Ra, nm	4.14
Water contact angle, degree	5.35
Adhesive and mechanical strength, ΔT_{qe} %	
Crock-meter, 750 cycles	-0.30
Tape pull	-0.40
Water boil, 100°C, 10 min	0.11
NaOH, 0.1N, 60 min	0.29
Environmental stability, ΔT_{qe} %	
CASS chamber test, 5 days	0.07
Damp heat chamber test, 10 days	-0.09
Salt fog chamber test, 61 days,	0.211

Anti-glare and anti-UV glass

Compared with anti-reflection (AR) glass, anti-glare (AG) glass demonstrates several manufacturing advantages, such as lower cost, simple process and more commercial applications. Anti-glare is mostly used in the picture frame market, but recently it is finding its presence in several other applications as well. AG glass can be used as a cover plate for laptop monitors, digital cameras, cell phones, and plasma and liquid crystal TVs.^{12,13,14} One simple method to generate AG glass is to etch the glass surface in order to generate a light scattering effect.¹⁵ However, hydroflurionic acid (HF) and NaOH are used for this process, which raises many processing concerns. HF and NaOH are extremely corrosive chemicals, which makes the process to be more safety and environmentally complex and increases the operation cost. Anti-glare surface with a “moth-eye” structure is achieved by plasma etching, but this process is also more complex and may be difficult in large scale production.¹⁶ Anti-glare surface with isotropic nanopores is also developed by monomer-corrugation,¹⁷ but the optical performance is difficult to control. However, none of those technologies previously discussed can provide anti-UV performance. More practice technology of making AG-AU glass (Anti-Glare with UV blocking attributes) is to cast polymer or inorganic thin film on the glass surface. The coating layer is composed of three parts; the first part is particles to generate scatter light, the second part is thin film to hold particles and the last part is UV absorber.^{18,19,20} Although there are many reports on AG-AR glass developed by various processes involving coating thin film, AG-AU glass with characteristics of high quality optical performances, good chemical, and durability is still a challenge.²¹

In this report, the preparation method of new type AG-AU glass is disclosed and performance of AG-AU glass is evaluated. In order to improve adhesive and abrasion strength of AG-AU glass, an interpenetrating polymer network (IPN) is introduced in the coating layer. A polysiloxane network prepared by thermal curing and a crosslinked polyacrylate network made by UV curing are two components of the IPN. The developed AG-AU glass demonstrates excellent mechanical and adhesive

strength, along with good chemical and environmental durability. In addition, the optical properties of AG-AU glass are assessed.

Interpenetrating polymer network in AG-AU glass

Interpenetrating polymer network in AG-AU glass consists of two networks, one is polyacrylate made by UV polymerization and another is polysiloxane network developed by sol-gel process.

Figure 8 shows the formation of crosslinked polyacrylate network by UV polymerization. Free radicals can be generated by irradiation of photo initiator (I-500 and I-250) with UV light and the free radical can initiate the polymerization of acrylate monomer with a crosslinking agent.²² Free radical polymerization with multiple function groups will develop the three dimension network.

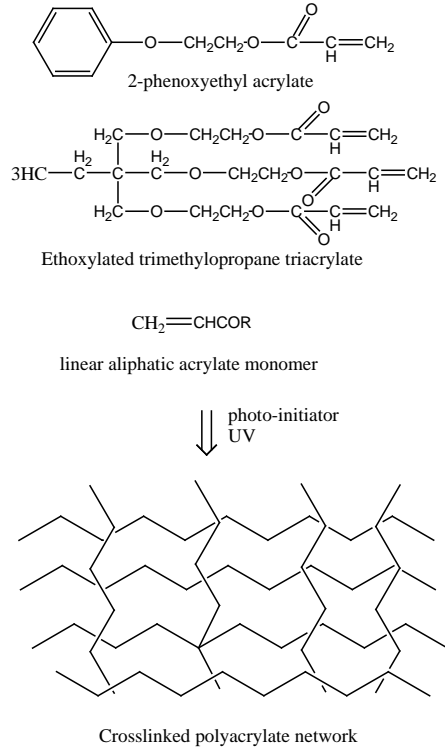


Figure 8. Crosslinked network generated by UV polymerization of monomer, oligomers and crosslinking agent.

Polysiloxane network is developed by sol-gel process involving hydrolysis and condensation of silanes as described in Figures 9 and 10.

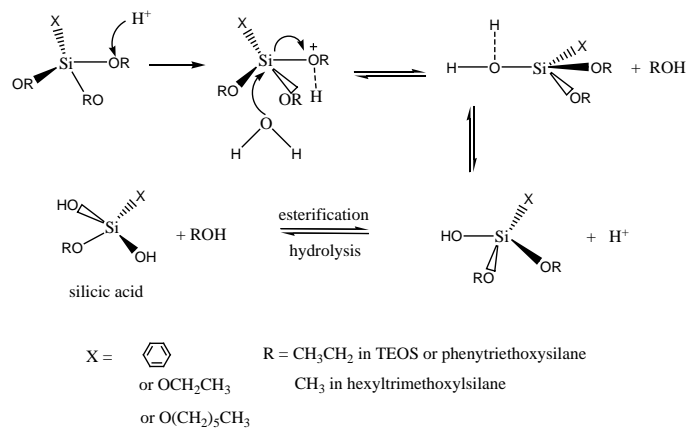


Figure 9. Hydrolysis of silanes with acid as catalyst.

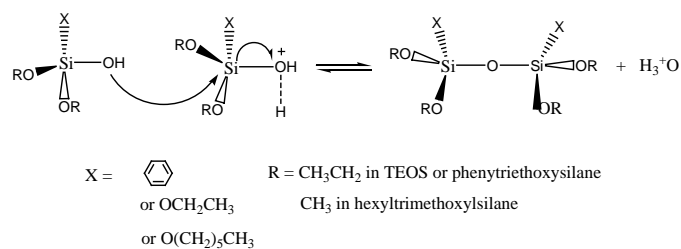


Figure 10. Condensation of hydrolyzed silanes with acid as catalyst.

In order to improve mechanical strength of the coating layer, SiO₂ nano-particle is introduced in silane solution and hydrolyzed silanes can further react with hydroxyl group on silica particle as shown in Figures 11. Stability of coating film of AG-AU can be improved by condensation among the reaction of hydrolyzed silanes, glass surface and silica particles.

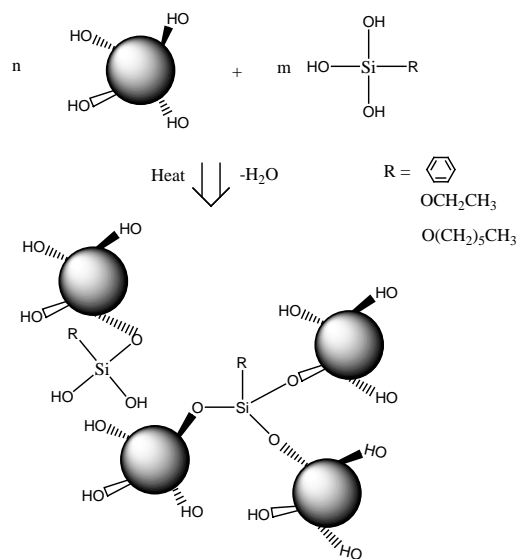


Figure 11. Condensation of hydrolyzed silanes and silica particles.

Figure 12 shows a theoretical model of the interpenetrating hybrid network developed in AG-AU thin film. Polysiloxane and polyacrylate networks are penetrating each other and silica particle is bonded with the polysiloxane network.

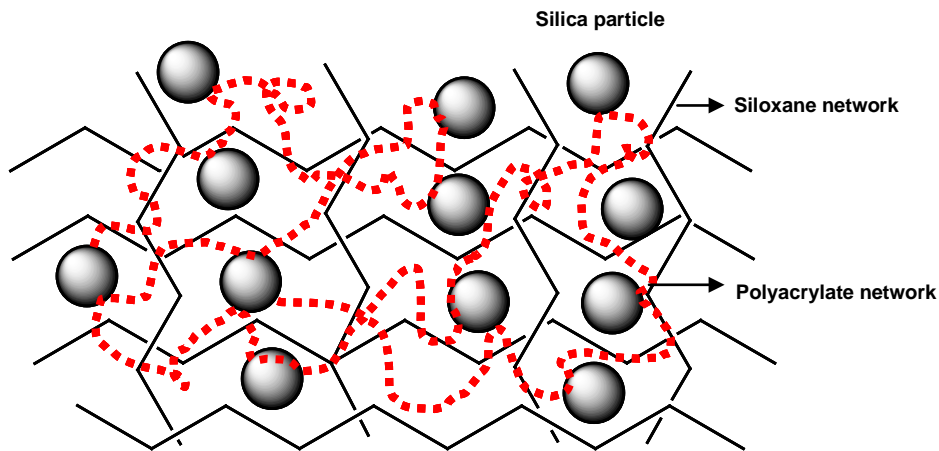


Figure 12. Schematic illustration of interpenetrating polymer network (IPN) in AG-AU coating layer.

Performances of AG-AU glass

Figure 13 shows the image and morphology of AG-AU glass measured by microscopy and profilometer, respectively. It is clear that rough surface is generated on AG-AU glass via inserted SiO_2 particles, which can provide function of anti-glare through reduced specular reflection and increased diffusive reflection.

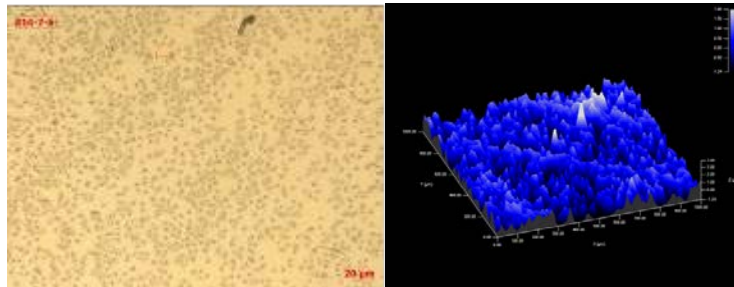


Figure 13. Microscopy (left) and morphology (right) of AG-AU glass.

Function of anti-glare is confirmed by observing image of object set in front of AG-AU glass. Figure 14 shows an image of white pencil on AG-AU. Only a small reflection of the white pencil is observed from AG-AU glass, whereas a more intense reflection is observed from the normal glass.



Figure 14. Image of a white pencil on AG-AU glass (right) and normal glass (left). The distance of color picture from AG-AU and normal glass is approximately 2 cm.

Table 2 and 3 shows various optical, chemical, mechanical and surface properties of AG-AU glass. The AG-AU glass exhibited excellent UV blocking and ant-glare properties without compromising the transmission, resolution and clarity. The UV transmission value ($T_{uv}\%$) of 0.15% suggests the blocking of 99.85% UV light through this glass. The data shown in Table 3 shows the developed AG-AU glass has excellent adhesive and mechanical strength. The performance AG-AU glass in several environmental chambers is very good with no significant change in $\Delta T_{uv}\%$, $\Delta T_{vis}\%$ or $\Delta Haze\%$.

Table 2. Optical and surface property of AGAU glass

Surface property	
Thickness, μm	5.33
Roughness, R_a , μm	0.592
Roughness, R_m , μm	0.688
Water contact angle, degree	102
Optical performance	
$T_{uv}\%$ (Transmission of UV light)	0.15
$T_{vis}\%$	89.77
R%	7.75
Haze%	6.08
Clarity%	62.07
Resolution (line/cm)	5.6

Table 3. Adhesive and mechanical strength and chamber test of ACAR glass

Test items	$\Delta T_{uv}\%$	$\Delta T_{vis}\%$	$\Delta Haze\%$
Adhesive and mechanical strength			
Tape pull	0	-0.07	1.09
Crock-meter	0	-0.06	1.15
Brush	0.08	0.09	0.09
Chemical stability			
Finger oil	0.33	-0.1	0

Windex (100%)	1.06	-0.79	1.31
Ethanol (100%)	0.22	-0.02	0.81
Acetic acid (4%)	0.7	-1.85	2.35
Ammonium solution (3%)	0.54	-0.1	-1.45
Environmental stability			
QUV, 6 days	0.04	0.14	2.94
85°C/85%, 6 days	0.09	-0.76	5.3
Freeze thaw, 6 days	0.06	-0.42	0.78

Summary

Anti-corrosion and anti-reflection (ACAR) glass had been developed by sol-gel process with introducing tetrahedral aluminate ion into polysiloxane network. Chemical stability of ACAR glass is significantly improved by reducing non-bridging oxygen ion in polysiloxane network.

Excellent adhesive and mechanical strength of ACAR glass are achieved. Anti-glare and anti-UV (AG-AU) glass with an interpenetrating polymer network (IPN) had been prepared by UV polymerization of acrylate and sol-gel process of silane. AG glass is established by inserting a spherical SiO₂ particle in coating layer with the IPN structure. Extremely low UV transmission (0.15%) is achieved by introducing a UV absorber covalently bonded with the polysiloxane network. Developed AG-AU glass displays excellent adhesive and mechanical strength as well as good chemical stability.

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