Effect of modifiers addition and surface treatment on hydrolytic resistance of soda-lime silicate glass

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Introduction :

Soda - Lime glass is the most widely used glass for glass containers. In glass manufactures, the several types of defect have been found and one of the most common is weathering or blooming. The occurrence of weathering dues to many reasons, such as the structure of the glass, weather conditions during storage especially in the rainy season. Humidity which is very high and temperature cycle from day to night promote the blooming defect.

The glass weathering can be described as the attack of humidity on the glass surface. The basic reaction is an ion exchange process between hydrogen ions in absorbed water on the surface and alkali ions in glass. Afterwards CO_2 and SO_2 in the atmosphere react with the leached alkaline ions. Consequently, a small crystal coating will be formed on the surface. If this process occurs continuously, the coated crystal cannot be wiped out. The important mechanism of this process is the alkaline leaching. Therefore, the evaluation of the amount of alkali leaching is able to determine the trend of the weathering.

In this study, the morphology and chemical composition of the bloom defect area of the commercial glass were examined by Scanning Electron Microscope (SEM-EDX) and Energy-Dispersive X-ray . The effects of the addition zirconium dioxide, zinc oxide and the surface treatment by sulfur dioxide gas on hydrolytic resistance were evaluated by determining the amount of alkali leached out by water as solvent in accordance with ISO 719 testing standard. The effectiveness of $NaHSO_4$ used as a source of sulfur dioxide gas was evaluated by X-rays fluorescence (XRF). The colors of all glass samples and the transmittance were inspected in L*a*b* system by UV-VIS spectrophotometer for comparison with a commercial glass in order to determine the feasibility of its use in the glass container manufacture.

Objective :

To study the effects of Zirconium dioxide, Zinc oxide addition in glass batches and the surface treatment on hydrolytic resistance of soda-lime silicate glass.

Material and Methods :

The experimental works were consisted 2 parts. First part covered the original and modified glass samples preparations and characterization. The second part is the evaluation of hydrolytic resistance property in accordance with ISO 719.

Chemical composition Analysis: dolomite and weathered glass surface
By XRF and EDX
Glass formula reformulation
By glass calculation program
Original glass (D0)
Addition of dolomite: 6.20,12.20,18.20%wt (D1,D2,D3)
Melting and Annealing: Heat up to 900 °C (rate 10°C/min) hold 30 min
Heat up to 1550 °C (rate 10°C /min) Soak 2 h, annealing 570 °C 1 h
Hydrolytic resistance test
Selected formula : Lowest amount of Na_2O

Selected formula : D3 with dolomite
Glass Formula reformulation
By glass calculation program
Replacing Al_2O_3 with ZrO_2: 0.25% , 0.50 %, 0.10% DZr1, DZr2 and DZr3
Addition of ZnO: 1%,2%,3% DZn1, DZn2 and DZn3
Without Additive Ds
Melting and Annealing
Without Surface treatment by SO_2 DZr1, DZr2 and DZr3
Without Surface treatment by SO_2 DZn1, DZn2 and DZn3
Surface treatment by SO_2 Ds
Hydrolytic resistance test

Table 1: Glass Compositions (original and modified)

Raw material (wt.%)	D0	D1	D2	D3	DZr1 ,DZr2 ,DZr3	DZn1, DZn2 ,DZn3
Sand				60.635		
Soda ash				18.000		
Sodium sulfate				0.700		
Sodium nitrate				0.540		
Antimony				0.055		
Limestone	18.950	12.750	6.750	0.750	0.750	0.750
*Dolomite	-	6.200	12.200	18.200	18.200	18.200
Alumina	1.115	1.115	1.115	1.115	0.865, 0.615, 0.115	1.115
*Zirconium dioxide	-	-	-	-	0.250,0.500,1.000	-
*Zinc oxide	0.005	0.005	0.005	0.005	0.005	1.005, 2.005, 3.005
Total	100	100	100	100	100	100

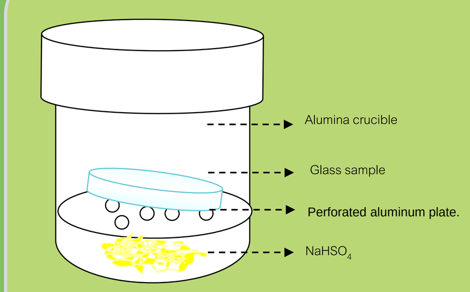

Fig 1: An alumina crucible contain $NaHSO_4$, which is a source of SO_2 gas

Dehydration at 315°C

$$2NaHSO_4 \longrightarrow Na_2S_2O_7 + H2O$$

Cracking at 460°C

$$Na_2S_2O_7 \longrightarrow Na_2SO_4 + SO_3$$

Substituted dolomite formulas were selected as lowest leaching volume of Na. Then the selected formulas (D3) were developed by adding ZrO_2 and ZnO. And the surface of D3 was treated by sulfur dioxide gas in the annealing process. An alumina crucible contained with sodiumhydrogensulfate ($NaHSO_4$), and SO_2 gas was produced while combustion process at 315 °C to 460°C

Hydrolytic resistance ISO 719 procedure

Glass sample
Glass particle preparation crushing and sieving particle size 300-500 μm
Glass particle 2 g.
Keep for 60 min in 50 ml de-ionized water at 98°C
25 ml of the obtained solution is titrated against 0.01 mol/l HCl solution
The volume of HCl needed for neutralization is recorded.
classified hydrolytic resistance grade

Results :

Table 2 : Chemical composition of dolomite by XRF

Composition (wt%)	Dolomite
CaO	31.40
MgO	19.98
SiO_2	3.04
Al_2O_3	0.26
Fe_2O_3	0.15
K_2O	0.08
Na_2O	-
TOT	100

Table 3 : Chemical composition of $NaHSO_4$ by XRF

Composition (wt%)	Before burn out	first time burn out	Second time burn out
Na_2O	17.84	23.58	25.93
SO_3	82.16	76.42	74.07
TOT	100	100	100

SO_3 which was produced from NaHSO4 at the first time was 5.74%, but at the second burning, SO_3 was occurred only 2.35%,

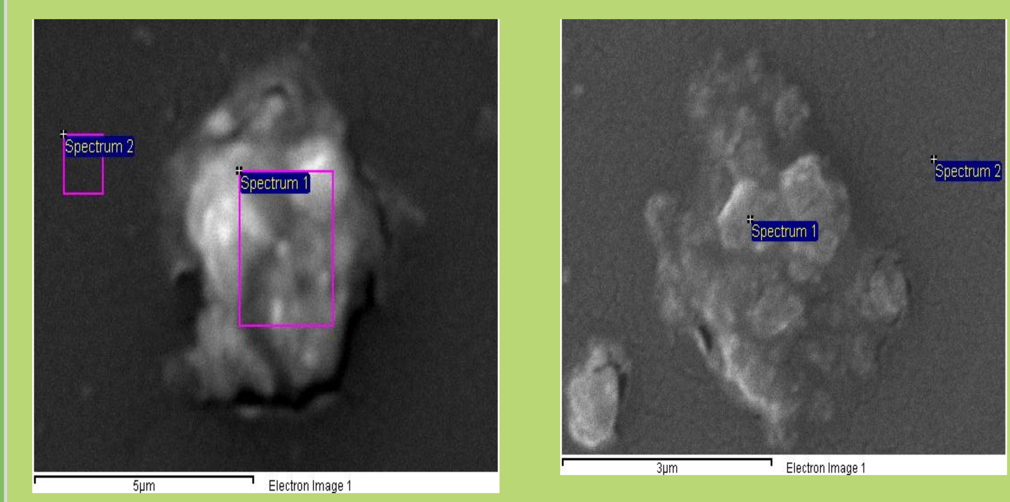

Fig 2. SEM micrographs of crystalline deposits observed on a weathered glass surface

Table 4 : Chemical composition of crystalline deposits are monitored by EDX

Composition%	A		B	
	Spectrum 1	Spectrum 2	Spectrum 1	Spectrum 2
O	53.11	51.63	57.72	54.67
Na	6.59	4.49	7.02	7.64
Mg	0.28	0.22	-	-
Al	1.87	0.75	2.94	0.74
Si	29.29	34.55	25.72	30.52
K	0.58	0.40	1.08	-
Ca	8.13	7.51	5.52	6.43
Cl	0.16	-	-	-
Total	100	100	100	100

SEM-EDX images were revealed the evidence of the crystalline deposits. That composed of Na and Ca form inner glass.

Table 5 : CIE Lab Color Analysis and %transmittance

sample	L*	a*	b*	T, %
D0	94.30	- 0.77	0.79	86.04
D3	95.69	- 0.40	0.78	89.31
DZr3	95.06	- 0.61	1.18	87.84
DZn2	95.70	- 0.47	0.84	89.43
Ds	95.59	- 0.43	0.84	89.07

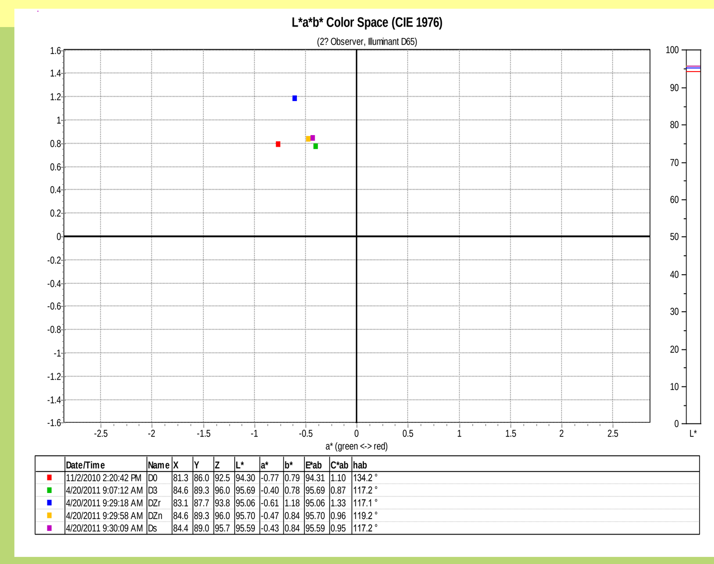

Fig 3. Results of CIE L*a*b* color analysis

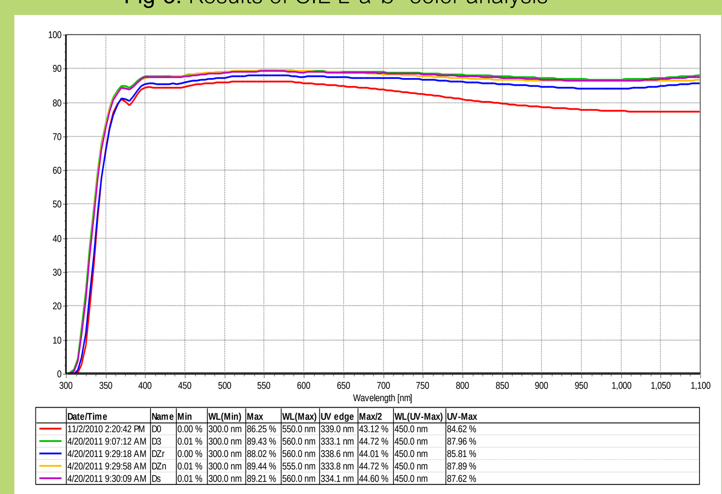

Figure 4 : The spectral transmittance of glass samples by UV –Vis Spectrophotometer .

All reformulated glasses were more transparent than the original glass. In addition, the reformulated glasses were clearer and confirmed by the color values of a* and b* that were close to an origin point than the original glass. The origin point represents the ideal white spot.

Table 6 : The volume of 0.01 mol/l HCl solution used for neutralization was recorded and classified by ISO 719

Sample	0.01M HCl needed to neutralize extracted basic oxides, ml/ 1 g. of glass	Hydrolytic resistance Class
D0	0.53	HGB3
D1	0.45	HGB3
D2	0.43	HGB3
D3	0.41	HGB3
DZr1	0.34	HGB3
DZr2	0.30	HGB3
DZr3	0.26	HGB3
DZn1	0.30	HGB3
DZn2	0.24	HGB3
DZn3	0.32	HGB3
Ds	0.20	HGB2

The sodium ions were leached in water at 98°C. From table 5. The reformulated glasses were leached lest than the original glass. The Ds sample was classified as grade 2 hydrolytic resistance glass. Decreasing of Na volume trends to increase the weathering durability.

Conclusion :

The SEM-EDX analyses of the crystalline deposits on the commercial glass surface evidenced the presence of Na and Ca crystals. This show that the lower leaching out of alkali may lead to a reduction of the blooming. The reformulated glass by substitution lime with dolomite about 18.20 **(wt.%)** , adding zirconium dioxide 0.1 **(wt.%)** and adding zinc oxide **(wt.%)** improved the hydrolytic resistance. The ZrO_2/SiO_2 substitution ,Mg/Ca substitution strengthened the silicate network and therefore increased hydrolytic resistance. The transparency of all reformulated glass were the same comparing to the original glass.

The glass surface treated by sulfur dioxide had the lowest volume of alkali leaching as a result of the SO_2 bonded with leached Na from glass. This type of deposit can be cleaned and removed by water which means the first alkali leaching from the surface are removed as well, so the amount of alkali near the surface is reduced. The $NaHSO_4$ which was used as the source of SO_2 is very efficient at the first time. However, The limitation of this method were the usage cycle of $NaHSO_4$, and the addition process for removing the coated crystals that occurred after annealing.

Further studies should be carried out to increase of the hydrolytic resistance class and more specific analysis method will be added, such as keeping glass sample in weathering chamber. Then surface microstructure will be examined by SEM, LEEM and PEEM techniques.

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