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Influence of glass dealkalization on the quality of adhesion of bonded materials

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The aim of this paper is to determine the effect of dealkalization of the glass surface on the quality of adhesion of bonded parts to the glass. Most of the available studies on glass dealkalization tend to focus only on the properties of the glass itself and the processes taking place in the surface layers of the glass. However, in practice focused on adhesion, the cleanliness of the glass surface is an important factor, which is influenced, among other things, by dealkalization. In this work, the influence of the use of gaseous SO_2 in the furnace on the composition of the glass surface and on the resulting adhesion is assessed. Regarding the deterioration of the adhesion quality between the glass treated with SO_2 gas and the adhesion promoter, the cleaning efficiency of the glass surface was further tested, according to the results of the cross-cut test.

INTRODUCTION

The production of flat glass by the float process was created by Pilkington in cooperation with Ford. The process includes a continuous melting furnace and continuous rolling of the glass ribbon. In the furnace, the glass floats on a layer of molten tin, thus obtaining a completely smooth surface. It follows from this system that the float glass has an air-side and a tin-side [1, 2, 3].

Glass has many advantageous properties, including high hardness, chemical resistance, compression strength and more [4, 5]. However, the glass surface is prone to scratches, for example, due to microscopic defects that are present on the glass surface and cannot be prevented. These can be micro-cracks or micro-scratches that come from the process of glass production, its processing or from handling and use [6, 7, 8, 9]. For this reason, it is appropriate to improve the mechanical properties of the glass by using some treatment. These can be chemical or thermal strengthening treatment processes. A more effective way is the chemical treatment of glass [10, 11, 12, 13]. Typically, the ion exchange process is performed by applying a salt spray to the glass [14, 15].

Float glass without any treatment usually shows a higher surface roughness compared to the treated glass surface. The use of a cleaning medium affects which specific elements are leached from the glass. Different chemicals react differently with the surface layers of glass. For example, when the glass is exposed to water, the surface area changes. A generally accepted mechanism is the ion exchange between sodium ions from the glass and hydrogen ions from the water. The used cleaning medium further interacts with ions on the glass surface and the formation of appropriate compounds occurs [16, 17].

As mentioned above, the glass dealkalization process is commonly used during the float glass manufacturing process [18, 17]. For example, gaseous SO_2 or SO_3 is used to strengthen the glass surface chemically [10]. During the treatment, the float glass is exposed to a SO_2 atmosphere, the temperature being close to the glass transition temperature [18, 19]. As a result of the interaction, mobile alkali ions are depleted and a silicon-rich surface layer is formed [20, 21]. The overall effect of the treatment greatly depends on the input composition, the structure of the glass network and the conditions of gas application [18, 22].

To apply different materials to glass and to create a strong adhesion, it is necessary to prepare the surface of the glued materials. Cleaners or activators are used for degreasing and general preparation of the glass surface. Due to the requirement to join materials that are difficult to glue, such as glass with plastics or metals, it is also necessary to treat the surface with an adhesion promoter. These substances are specific based on the composition of the treated material and enable or improve the quality of the joint [23, 24, 25, 26].

EXPERIMENTAL

Materials

Float glass samples measuring 40 × 40 cm were used for experimental purposes. It was a soda-lime-silica glass from a commercial manufacturer, and it was possible to distinguish between tin- and air-sides of the glass sheets. Betaprime™ 5500 was used as an adhesion promoter for testing purposes. It is a one-step substance, and its further specification is given in Tab. 1.

Tab. 1. Specification of the adhesion promoter Betaprime™ 5500 [27]

Name	Betaprime™ 5500
Color	black
Type	polyisocyanates
Density [g/cm³] (ISO 845)	0.901 – 1
Solid content [%]	35 – 40
Open time [h]	0.05 – 72
Processing Temperature [°C]	10 – 40

Demi water, detergent solution, isopropyl alcohol, and acetic acid were used to treat the glass surface for cleaning. These substances were selected based on used cleaners in glass automotive practice. The acetic acid solution was used at 8%, the 2% detergent solution was made by mixing Jar Professional kitchen degreaser with water, the isopropanol was 90%, and the demi water was used cold at 20 °C and warm at 50 °C. The purity of demi water was set at 20 mS/cm. The temperature of the hot demi water was chosen according to the common parameters that are used in the washing machine when washing glass before other manufacturing processes, such as lamination [26].

Methods

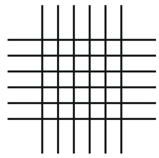
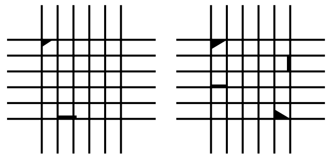
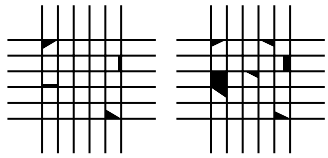
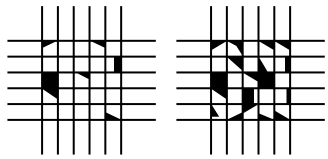
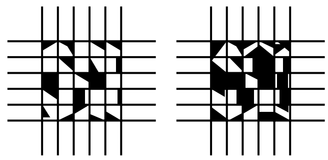
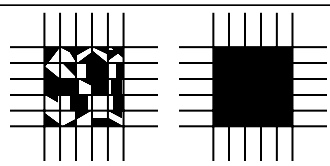
A laboratory furnace with the possibility of applying a gaseous medium was chosen to simulate the actual tempering process. This gas was SO_2, which was metered into the furnace for a defined time at a pressure of 0.7 bar.

X-Ray Fluorescence (XRF) analysis was chosen for composition analysis. Swabbing for this analysis was performed using pure pulp folded to a size of 3 × 3 cm. Strokes were made on the surface of the glass in a total of fourteen rows, always in one direction and only once in each row.

The first series of samples was glass swabs before and after the application of SO_2 gas. In total, there were ten pieces, five pieces of original glass were wiped from the air- and tin-side, and another five pieces of glass exposed to SO_2 gas were also wiped from the air- and tin-side. The temperature in the furnace was set at 650 °C, which corresponds to the temperature in the real glass tempering process. The glass was laid according to the real procedure with the tin-side down. The applied SO_2 gas was metered in for 1 minute at a pressure of 0.7 bar.

The second series of tests focused on the effectiveness of individual cleaners and the subsequent effect on adhesion. A total of 36 samples were prepared for this purpose, using 12 pieces of glass without any SO_2 gas, 12 pieces were exposed to SO_2 in a 650 °C oven for 1 minute, and the remaining 12 glasses were exposed for 5 minutes. Each group was further divided so that 2 pieces of glass were used for each treatment. These treatment methods included no cleaning, cleaning with pulp soaked in 8% acetic acid solution, in 2% detergent solution, in 90% isopropyl alcohol, in demi water at 20 °C and 20 mS/cm purity, and in demi water at 55 °C and 20 mS/cm purity. Both sides of the glass were treated. The glasses thus cleaned were left for 2 hours to evaporate the remaining cleaners. The Betaprime™ 5500 adhesion promoter was then applied to each glass using a foam applicator. The chemical was allowed to cure according to the manufacturer's recommendations [27]. After 24 hours, a cross-cut test according to ISO 2409:2020 [28] was performed to determine the purity

Tab. 2. Cross-cut test rating category and illustrative result representation [28]

ISO Class no. and description	Illustrative illustration of a grid and surface damage
ISO Class 0 No damaged area.	
ISO Class 1 Damaged area <5%.	
ISO Class 2 Damaged area >5%, but <15%.	
ISO Class 3 Damaged area >15%, but <35%.	
ISO Class 4 Damaged area >35%, but <65%.	
ISO Class 5 Damaged area >65%.	

of the surface, respectively its adhesive properties. The test was performed on both sides of the glass, i.e., on the tin-side and the air-side. The final evaluation of this adhesion test was according to Tab. 2.

The third series of tests was aimed at confirming the effectiveness of washing glass samples in warm demi water. For this purpose, XRF analysis was used, which analyzed swabs from 3 pieces of glass before washing and from 3 pieces of glass after washing in demi water at a temperature of 55 °C and a purity of 20 mS/cm. Smears were made from each glass in the same way as in the previous cases.

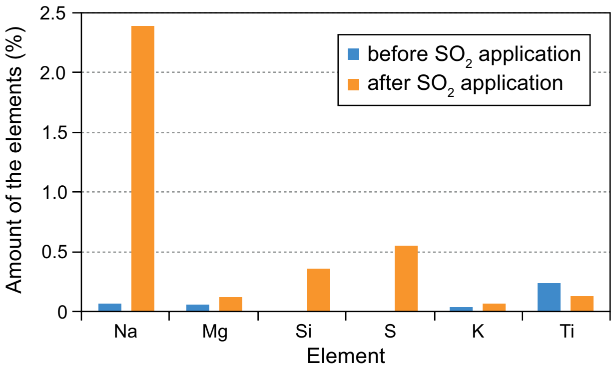


Fig. 1. Results of XRF analysis of elemental composition of smears from glass samples (average content of elements from the tin-side of the glass before and after SO_2 application)

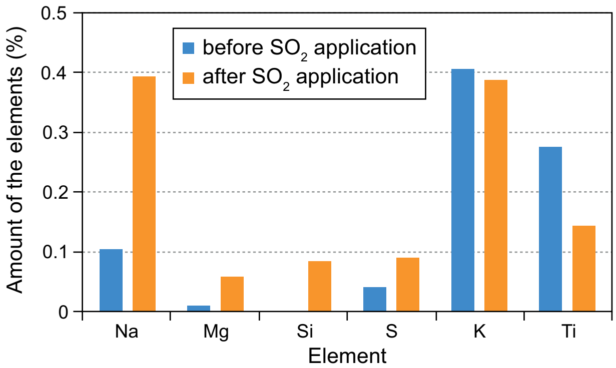


Fig. 2. Results of XRF analysis of elemental composition of smears from glass samples (average content of elements from the air-side of the glass before and after SO_2 application)

Tab. 3. Results of XRF analysis of the elemental composition of smears from glass samples in weight percent that were obtained by subtracting the reference pure pulp composition from the pulp after wiping the glass surface. The analysis was focused on swabs from the tin-side of the glass before the application of SO_2 gas and after the application of SO_2 gas. The gas was applied for 1 minute at a pressure of 0.7 bar in an oven with a set temperature of 650 °C

Element	Quantity of elements – tin-side									
	samples before SO_2 application					samples after SO_2 application				
	OB1	OB2	OB3	OB4	OB5	OA6	OA7	OA8	OA9	OA10
Na	0.070	0.043	0.097	0.061	0.071	3.265	1.471	2.678	1.501	3.036
Mg	0.059	0.085	0.026	0.055	0.070	0.089	0.157	0.090	0.141	0.124
Si	0.000	0.000	0.000	0.000	0.000	0.510	0.296	0.475	0.230	0.304
S	0.000	0.000	0.000	0.000	0.000	0.833	0.358	0.789	0.544	0.230
K	0.038	0.041	0.036	0.044	0.041	0.062	0.057	0.049	0.063	0.098
Ti	0.298	0.312	0.027	0.230	0.349	0.361	0.201	0.038	0.000	0.015

Tab. 4. Results of XRF analysis of elemental composition of smears from glass samples in weight percent that were obtained by subtracting the reference pure pulp composition from the pulp after wiping the glass surface. The analysis was focused on swabs from the air-side of the glass before the application of SO_2 gas and after the application of SO_2 gas. The gas was applied for 1 minute at a pressure of 0.7 bar in an oven with a set temperature of 650 °C

Element	Content of elements – air-side									
	samples before SO_2 application					samples after SO_2 application				
	IB1	IB2	IB3	IB4	IB5	IA6	IA7	IA8	IA9	IA10
Na	0.112	0.098	0.123	0.118	0.070	0.300	0.460	0.403	0.371	0.423
Mg	0.007	0.016	0.013	0.009	0.010	0.060	0.041	0.058	0.087	0.047
Si	0.000	0.000	0.000	0.000	0.000	0.059	0.105	0.097	0.061	0.099
S	0.033	0.040	0.047	0.050	0.038	0.048	0.108	0.060	0.122	0.110
K	0.453	0.421	0.302	0.368	0.480	0.426	0.416	0.415	0.305	0.369
Ti	0.431	0.103	0.399	0.204	0.236	0.127	0.063	0.002	0.307	0.219

RESULTS

The results of the first series of experiments are summarized in Table 3 and Table 4. The contents of the elements in the swabs analyzed by XRF analysis are given here. For better comparability, the average values of the content of individual identified elements are shown in the figures (Fig. 1 and Fig. 2).

The output of the second series of tests is Table 5 containing the results of the cross-cut test. According to ISO 2409:2020 [28], the rating ranges from ISO Class 0, which depicts no damage, to ISO Class 5, which means surface damage greater than 65% (Table 2). The worse the adhesion, the higher the rating class.

The last series of tests, which was focused on eva-luating the effectiveness of washing with warm demi water with a temperature of 55 °C and a purity of 20 mS/cm. The results of the smear from the tin-side of the glass are in Table 6, and for better emphasis, the average results were also processed into a graphic form (Figure 3). The contents of the elements from the air-side are summarized in Table 7 and a graphical representation of the change in the contents of the elements is shown (Figure 4).

DISCUSSION

It has been found that when SO_2 gas is applied to glass placed in a furnace, a layer creates on its surface, which appears to be a blue haze. This deposit consists mainly of sodium sulfate, which is formed during

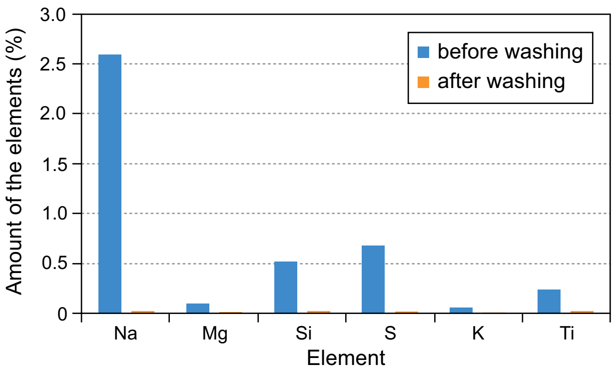


Fig. 3. Results of XRF analysis of elemental composition of smears from glass samples (average content of elements from the tin-side of the glass before and after washing with warm demi water 55 °C and cleanliness 20 mS/cm)

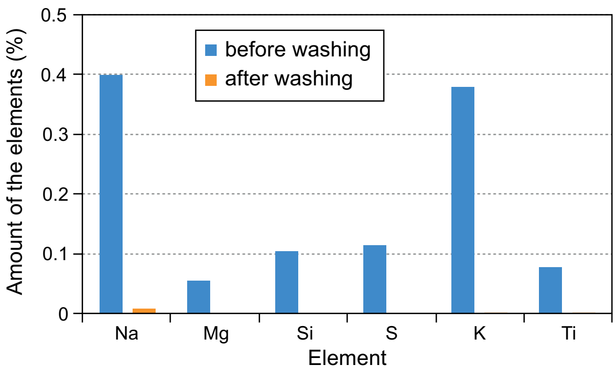


Fig. 4. Results of XRF analysis of elemental composition of smears from glass samples (average content of elements from the air-side of the glass before and after washing with warm demi water 55 °C and cleanliness 20 mS/cm)

Tab. 5. Results of testing the effectiveness of individual methods of glass surface treatment from the tin-side (samples marked with the letter "O") and from the air-side (samples marked with the letter "I") according to ISO 2409:2020 [28]. For a better clarity of the results, the values are color-coded

Sample		no cleaning	cleaned with				
			8% acetic acid solution	2% detergent solution	90% isopropyl alcohol	demi water 20 °C, 20 mS/cm	demi water 55 °C, 20 mS/cm
Original glass	O1	3	2	3	1	3	0
	O2	1	2	3	2	2	0
	I1	3	3	3	3	4	0
	I2	4	2	4	3	4	0
SO_2 treated glass for 1 min, 0.7 bar	O3	3	5	5	2	3	0
	O4	1	4	5	3	3	0
	I3	4	5	5	3	3	0
	I4	5	5	5	3	4	0
SO_2 treated glass for 5 min, 0.7 bar	O5	5	5	5	3	2	0
	O6	4	5	5	3	3	0
	I5	5	5	5	4	4	1
	I6	5	5	4	3	2	0

dealkalization of the glass surface by the reaction of SO_2 or SO_3 for strengthening the glass surface and increasing its resistance to mechanical damage [10, 18, 19, 20, 21].

According to the results of the XRF analysis, the largest increase in the content of sodium, sulfur and silicon was observed. A similar trend was observed on both sides of the glass, i.e., on the tin-side and on the air-side. From the point of view of comparing the number of elements on the individual sides of the glass before the start of the experiment, it can be said that the quantitative representation was higher on the air-side. After the application of SO_2 under defined conditions, the trend was the opposite, i.e., a larger number of elements identified by XRF analysis was on the tin-side. This can probably be explained by how the glasses were placed in the test furnace and how the used gaseous medium flowed. However, this trend was also observed in conclusion of some publications [20] [17] [29].

When the gas was applied for a longer test time of 5 minutes, a more extensive blue haze was observed, which formed on the surface of the glass. The dose and exposure time of gaseous SO_2 therefore affect the amount of deposits on the glass surface. This was also confirmed by a cross-cut test according to the ISO [28] standard, from the results of which it can be deduced that a longer exposure time, and therefore a larger gas dose, worsens the adhesion. The principle of adhesion deterioration is probably a change in the density of the adhesion promoter. This could be because the solvents contained in it dissolve the contaminants on the glass surface, which changes the physical properties of the adhesive promoter. A change in density leads to a different curing process. This different process can negatively affect the quality of the adhesive forces. Alternatively, it can be assumed that the adhesion promoter could form weaker bonds to the deposited layer, which, however, is only weakly bound to the substrate to the glass surface. Thus, when a force is applied, for example during a cross-cut test, a breakage occurs between the glass surface and the sodium sulfate contaminants.

The effectiveness of individual cleaners also depends on the amount of SO_2 used. The most effective way of all the tested methods to treat glass to improve adhesion properties was to use warm demi water at 55 °C. The purity of the demi water used was determined to be 20 mS/cm. According to [30] [31], this fact is due to the solubility of sulfates, which rises in demi water with temperature and the maximum solubility is around 33 °C, above this temperature is a gradual decrease in solubility, but the effectiveness of this method remains still preserved. The principle of the effect of washing with warm demi water is to remove a significant amount of contaminants from the glass surface. The decrease in the amount of residues was evaluated according to the results of XRF analysis. The quantitative decrease for most elements reached more than 96 % to 100 %. In this series of tests, the input amount of elements was higher on the tin-side. However, the decrease in residues was similar for both tested sides of the glass.

CONCLUSIONS

The aim of all experiments performed in this work was to verify the effect of gaseous SO_2 on the glass surface concerning its purity and the overall effect on adhesion properties. The purpose was to simulate the conditions that are realistic in production practice, i.e., when processing glass by tempering, strengthening its surface by the dealkalization process and the subsequent impact on gluing technology, in which adhesion is a key property determining quality. By using SO_2, a layer of dealkalization process products is formed on the glass surface. This layer negatively affects the quality of

Tab. 6. Results of XRF analysis of elemental composition of smears from glass samples in weight percent that were obtained by subtracting the reference pure pulp composition from the pulp after wiping the glass surface. The analysis was focused on swabs from the tin-side of the glass before the washing and after the washing with warm demi water 55 °C and cleanliness 20 mS/cm

Element	Content of elements – tin-side					
	samples before washing			samples after washing		
	OBW1	OBW2	OBW3	OAW4	OAW5	OAW6
Na	3.168	3.005	1.632	0.013	0.009	0.011
Mg	0.112	0.085	0.089	0.000	0.000	0.000
Si	0.498	0.301	0.752	0.005	0.001	0.001
S	0.743	0.427	0.865	0.000	0.003	0.001
K	0.037	0.065	0.058	0.000	0.000	0.000
Ti	0.238	0.310	0.163	0.006	0.010	0.003

Tab. 7. Results of XRF analysis of elemental composition of smears from glass samples in weight percent that were obtained by subtracting the reference pure pulp composition from the pulp after wiping the glass surface. The analysis was focused on swabs from the air-side of the glass before the washing and after the washing with warm demi water 55 °C and cleanliness 20 mS/cm

Element	Content of elements – air-side					
	samples before washing			samples after washing		
	IBW1	IBW2	IBW3	IAW4	IAW5	IAW6
Na	0.357	0.418	0.426	0.003	0.010	0.008
Mg	0.058	0.036	0.068	0.000	0.000	0.001
Si	0.073	0.135	0.106	0.000	0.005	0.000
S	0.113	0.098	0.131	0.000	0.000	0.000
K	0.403	0.394	0.342	0.001	0.000	0.000
Ti	0.055	0.109	0.065	0.002	0.003	0.000

adhesion. After the application of an adhesion promoter to the glass surface, its density probably changes by the fact that the solvents dissolve the surface contamination formed mainly by sulfates. By changing the density, the properties of the chemical change and this also affects the curing process of the promoter, during which bonds to the substrate are formed. According to the results of the cross-cut test, it can be stated that the use of gaseous SO_2 in the float glass production or in the bending of the glass and subsequent insufficient cleaning of the glass surface leads to adhesion failure, which is unacceptable in practice. Therefore, proper cleaning of the glass surface before the application of any adhesives and adhesion promoters must be an integral part of the process. Of the tested cleaning methods, the best results were obtained in the case of warm demi water. According to further analyzes, the cleaning effect of demi water with a temperature of 55 °C and a purity of 20 mS/cm was demonstrated quantitatively by XRF analysis. The benefit of this work is especially for production practice, where other materials are glued to the glass surface, which is used, for example, in the automotive glass industry. The dealkalization of the glass surface is an integral part of the glass improvement process, but subsequent effective cleaning is important so that it does not have a negative effect on other subsequent operations.

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