Optimization and semi-automatic evaluation of a frosting process for a soda lime silicate glass based on phosphoric acid

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Abstract
Chemical glass frosting processes are widely used to create visual attractive glass surfaces. A commonly used frosting bath mainly contains ammonium bifluoride (NH₄HF₂) mixed with hydrochloric acid (HCl). The frosting process consists of several baths. Firstly, the preliminary bath to clean the object. Secondly, the frosting bath which etches the rough light scattering structure into the glass surface. Finally, the washing baths to clean the frosted object. This is where the constituents of the preceding steps accumulate and have to be filtered from the sewage. In the present contribution, phosphoric acid (H₃PO₄) was used as a substitute for HCl to reduce the amount of ammonium (NH₄⁺) and chloride (Cl⁻) dissolved in the waste water. In combination with magnesium carbonate (MgCO₃), it allows the precipitation of ammonium within the sewage as ammonium magnesium phosphate (MgNH₄PO₄). However, a trivial replacement of HCl by H₃PO₄ within the frosting process causes extensive frosting errors, such as inhomogeneous size distributions of the structures or domains that are not fully covered by these structures. By modifying the preliminary bath composition, it was possible to improve the frosting result considerably. To determine the optimal composition of the preliminary bath, a semi-automatic evaluation method has been developed. This method renders the objective comparison of the resulting surface quality possible.

KEYWORDS
automated quality control, etching, glass frosting, phosphoric acid

1 | INTRODUCTION

Chemical etching processes of glass are widely used in industry to obtain a well-defined structured surface.¹⁻³ Technical applications for wet etching using solutions based on hydrofluoric acid are in the photo voltaic industry to improve the efficiency of solar cells.⁴⁻⁵ However, other typical applications are the manufacturing of visual attractive frosted glass surfaces for light bulbs, bottles for cosmetic products or decorative objects.⁶⁻⁷

A soda lime silicate glass can be easily frosted by immersion in a hydrochloric acid (HCl) solution saturated with ammonium bifluoride (NH₄HF₂), sodium bifluoride (NaHF₂), and ammonium fluorosilicate ((NH₄)₂SiF₆).

It has long been known that the frosting effect is caused by small crystal-like structures etched in the glass surface.⁸⁻⁹
These structures originate from fluorosilicates $X\text{SiF}_6$ ($X = \text{Na}^+, \text{NH}_4^+$), crystallizing on the surface during the frosting process, and preventing further etching of the glass below the formed salt crystals.\textsuperscript{7,10} Figure 1 shows the typical surface of a chemically frosted glass. It was etched using a supersaturated solution of a commercially available salt mixture and HCl.

The shape and size of these crystal-like structures can be modified using salts such as NaHF\textsubscript{2} or (NH\textsubscript{4})\textsubscript{2}SiF\textsubscript{6} or by moving the glass within the frosting bath as discussed later. Furthermore, the intensity of the frosting effect can be adjusted by the dwell time within the frosting bath.

During the frosting process, a large amount of waste water polluted with high concentrations of F\textsuperscript{−}, NH\textsubscript{4}\textsuperscript{+}, and Cl\textsuperscript{−} is produced. While F\textsuperscript{−} can easily be separated by precipitation with Ca\textsuperscript{2+} (Equation 1), NH\textsubscript{4}\textsuperscript{+} and Cl\textsuperscript{−} remain within the solution.

$$\text{Ca(OH)}_2 + 2\text{F}^{-} \rightarrow \text{CaF}_2 + 2\text{OH}^{-} \quad (1)$$

Due to increasingly stringent waste water regulations in many regions and raising disposal costs, these pollutions should be avoided. A possible way to remove the NH\textsubscript{4}\textsuperscript{+} is to add Mg\textsuperscript{2+} and PO\textsubscript{4}\textsuperscript{3−} to the sewage to precipitate NH\textsubscript{4}\textsuperscript{+} as ammonium magnesium phosphate (Equation 2).

$$\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} \rightarrow \text{Mg} \cdot \text{NH}_4 \cdot \text{PO}_4 \downarrow \quad (2)$$

The substitution of the HCl by phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) can additionally reduce the Cl\textsuperscript{−} concentration in the sewage. A reduction of HCl can also lead to a decreased corrosive attack of the equipment used in the process.

It has already been shown that the use of substitutes like sulfuric or nitric acid for the frosting solution is possible.\textsuperscript{11-13} However, Frayret et al\textsuperscript{12} determined an influence of the solutions on the shape and size of the crystal-like structures and the frosting intensity due to an alteration of the acid. As described by Spierings,\textsuperscript{1} the addition of different acids to a HF solution also influences the etching rate of the silicate glass.

Own initial attempts in which HCl was substituted by H\textsubscript{3}PO\textsubscript{4} resulted in inhomogeneous frosting results and extensive frosting errors. These manifested themselves in the form of inhomogeneous size distributions of the structures or domains that are not fully covered by these structures. Since the HCl contributes to a clean glass surface,\textsuperscript{2} this effect may be caused by surface contaminations. Spierings\textsuperscript{1} showed that defects such as micro cracks or locally differing glass compositions have a significant influence on the HF etching process and the resulting surface morphology. Those flaws or production-related surface contaminations influence the frosting.\textsuperscript{14} Therefore, they may cause an inhomogeneous frosting result and lead to an increased scrap rate. A reduction of these defects on the frosted glass surface can be obtained by treating the glass ware in a stripping bath (referred to as preliminary bath in this study), which removes contaminations and homogenizes the surface.\textsuperscript{12} Preliminary tests confirmed the impact of its composition on the frosting quality. Therefore, an experimental program to investigate the influence of different preliminary baths on the frosting quality was developed.

An approach for evaluation of the frosting intensity exists,\textsuperscript{12} but no parameter was proposed to objectively assess the frosting quality regarding the uniformity of the surface finish. Thus, two semi-automatic evaluation methods are proposed to objectively compare the quality of the resulting surface finish.

## 2 | MATERIALS

For systematic examinations, flat glass samples with dimensions of approx. 3 × 4 cm made from commercially available glass containers were prepared. The composition of the glass used in this study, determined by means of ICP-OES, is listed in Table 1.

The solutions for the frosting process were made using H\textsubscript{3}PO\textsubscript{4} (85 wt%), HCl (31 wt%), and HF (40 wt%), and the commercially available salt mixtures LERITE SX 20 and LERITE SX 28 by SEPPIC Corp. LERITE SX 20 is a

| Oxides | SiO\textsubscript{2} | Na\textsubscript{2}O | CaO | BaO | Al\textsubscript{2}O\textsubscript{3} | MgO | K\textsubscript{2}O | Total |
|--------|----------------|----------------|-----|-----|----------------|-----|-----------|-------|
| Quantity | 71.4 | 13.2 | 7.0 | 2.4 | 2.2 | 1.6 | 1.3 | 99.1 |
mixture of \( \text{NH}_4\text{HF}_2 \) and \( \text{BaSO}_4 \) in a ratio of about 9:1, while LERITE SX 28 contains mainly \( \text{NH}_4\text{HF}_2 \) and \( \text{NaHF}_2 \) in a ratio of about 7:3 and traces of \( (\text{NH}_4)_2\text{SiF}_6 \). The exact composition could not be determined reliably by X-ray diffraction.

3 | EXPERIMENTAL METHODS

3.1 | Frosting process

In preparation of the frosting process, the tailored specimens were rinsed off with deionized water and then dried at 20°C.

The frosting process consisted of three main steps. First, the glassware was immersed in a preliminary bath for 5 seconds. The industrially used process used a diluted HCl solution as preliminary bath. However, in this study, the HCl was replaced by diluted hydrofluoric acid HF and various \( \text{H}_3\text{PO}_4-\text{NH}_4\text{HF}_2 \) mixtures.

![Figure 2](image)

**Figure 2** Examples of the examined glass samples of a test series after frosting. The positions where the microscopic image were taken are marked by red circles on the specimen in the middle sample.

![Figure 3](image)

**Figure 3** Visualization of the image processing, exemplarily shown for a glass with an inhomogeneous frosting result.

![Figure 4](image)

**Figure 4** Three exemplary evaluated images. A – good quality, B – medium quality, C – bad quality. Size distribution of masked areas of three selected pictures.
Subsequently, the glass was dipped in the 30°C warm frosting bath for 15 seconds. In preliminary tests, an effective frosting bath based on phosphoric acid was identified. It had a mixing ratio of 1.0 L phosphoric acid (35 wt%) to 2.5 kg frosting salt consisting of 66.7 wt% Lerite SX 20 and 33.3 wt% Lerite SX 28.

In the last step, the final product was cleaned using multiple hot water baths. This is where the constituents of the preceding steps accumulate and have to be filtered from the sewage.

### 3.2 Semi-automatic evaluation methods

Five samples were produced and evaluated at each variation step. Since matting errors often occur only locally or are inhomogeneously distributed over the surface, a high number of samples is preferable. As shown in Figure 2, nine microscopic images were taken of each sample.

The microscope used was a CARL ZEISS AXIOTECH 100 HD combined with an Olympus UC30 digital camera, which had a resolution of 2080 × 1544 px. The images were taken using an ocular with a 5× magnification. The scale is 0.690 μm/px (145 px ≈ 100 μm). The following analysis was done using pixel values. Higher image resolutions and larger selected image sections are advantageous for this method, but the evaluation parameters must be adjusted accordingly.

The light intensity had to be set in such a way that there was a good contrast between areas with and without crystal-like structures on the glass surfaces. Additionally, the tip of the crystal-like shapes had to appear as a bright spot. Any microscope setting leading to such results can be considered appropriate for this method. In this study, the microscope was set to differential interference contrast to obtain the desired result.

For the evaluation of the images, the program IMAGEJ was used in combination with a self-written macro-file. The pictures were converted into a 8-bit grayscale image as shown in Figure 3B. Thereafter, their contrast was optimized (Figure 3C) and the image was binarized using a brightness threshold of 50%.

#### 3.2.1 Evaluation using granulometric values

Afterward, the tip of every crystal-like shape was masked, as it can be seen in Figure 3D. However, frosting defects are clearly visible as large black areas. Subsequently, the size of the masked areas was measured and their size distribution was analyzed. The largest masked area \( A_{\text{max}} \) was used for the evaluation of the frosting process, in particular for assessing the surface quality of the matted glass. This parameter represents the area of the largest masked object in the image. The lower the value of this parameter, the better the frosting result. Very high values usually originate from nonfrosted areas or other frosting defects as shown in Figure 4.

Table 2 can be used to evaluate the frosting quality. With \( A_{\text{max}} \) values up to 500 px (238 μm²), the surface was supposed to be error-free frosting.

![Average grey values of 3 × 2 image sections of Figure 3D](image)

![SEM images show the difference in shape of the crystal-like structures resulting from movement (A) intense movement of the glass within the frosting bath in an industrial process and movement (B) less movement in a manual process. Both specimens were frosted using the HCl-based frosting processes](image)
sufficiently uniform and error-free. Specimens with $A_{\text{max}}$ values between 500 and 3000 px (238-1428 μm²) show minor frosting errors in matting, but the overall result may still be acceptable. For larger $A_{\text{max}}$ values, significant irregularities were observed.

3.2.2 | Evaluation using grey value deviations

Another method to evaluate the frosting quality is to split the binary image (Figure 3D) into horizontally $x$ and vertically $y$ sectors, and to calculate its mean grey value $G$ as visualized in Figure 5.

$G$ can be any value of $\mathbb{R}$ between 0 and 255. Then, the standard deviation of the grey values $\sigma_{\text{grey},x\times y}$ of the picture is calculated (Equation 3).

$$\sigma_{\text{grey},x\times y} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (G_i - \overline{G})^2}, \quad n = x \times y \quad (3)$$

The lower the standard deviation, the more homogeneous the distribution of brightness over the matte surface, which suggests an uniform frosting effect. The mean value of the standard deviations $\Delta\sigma_{\text{grey},x\times y}$ of a sample series is then used for the evaluation of the frosting quality.

4 | RESULTS AND DISCUSSION

Specimens that were frosted industrially were taken as a reference. Therefore, the differences to the sample

| Composition | Subjective evaluation |
|-------------|-----------------------|
| No preliminary bath | Extensive frosting defects |
| HCl 31 wt% | Extensive frosting defects |
| H₃PO₄ 35 wt% | Extensive frosting defects |
| HF 5 wt% | Uniform but weak frosting |
| HF 2.5 wt% | Uniform frosting |
| HF 1.25 wt% | Some frosting defects |
| NH₄HF₂ 35 g/L | Some frosting defects |
| NH₄HF₂ 35 g/L; H₃PO₄ 0.35 wt% | Uniform frosting |

produced manually in the laboratory had to be considered. Presumably, the movement of the specimens within the frosting bath seems to have an effect on the shape of the frosted glass surface (Figure 6). The effect becomes visible for the industrially frosted specimens at the touching edges of the pyramids. They are less clearly defined due to the formation of crater-like structures (Figure 6A). That results in a rougher surface and therefore a more intense frosting effect.

4.1 | Initial examinations of the composition of the preliminary bath

In preparation of the larger test series, various preliminary baths were tested for their basic suitability for the frosting process. In addition to phosphoric acid, various hydrofluoric acid concentrations and ammonium hydrogen fluoride solutions were tested as shown in Table 3.

Extensive frosting defects like an inhomogeneous size distribution of crystal-like structures and seemingly unfrosted areas were present when the specimen was immersed into the H₃PO₄-based frosting bath without any pretreatment.

The same behavior was found using preliminary baths made of 31 wt% HCl or 35 wt% H₃PO₄. Considerably better results could be achieved using preliminary bath consisting of hydrofluoric acid (HF), which is in accordance to Frayet et al.¹² The best results were achieved using a HF solution in a concentration range of 2.5 wt%-5.0 wt%, while specimens treated with 1.25 wt% HF still showed frosting defects and an inhomogeneous size distribution of the crystal-like structures. However, a preliminary bath consisting of 5 wt% HF only led to a weak frosting effect and relatively coarse crystal-like structures. That suggests that pretreatment with HF reduces the amount of crystallization nuclei on the surface of the glass on which the matting salts can subsequently crystallize (Figure 7).

4.2 | Systematic examinations of the composition of the preliminary bath and discussion of the evaluation methods

However, since handling liquid hydrofluoric acid was considered problematic due to safety reasons, an NH₄HF₂
solution \( (c = 32.5 \text{ g/L}) \) and a \( \text{NaHF}_2 \) solution \( (c = 32.5 \text{ g/L}) \) acidified with phosphoric acid \( (0.35 \text{ wt\%}) \) were chosen as alternatives. \( \text{NaHF}_2 \) was finally rejected because of its poor solubility.

The initial tests with these two solutions were promising and therefore the test matrix, shown in Table 4, was processed to determine the optimal mixture ratio of \( \text{NH}_4\text{HF}_2 \) and phosphoric acid. As a reference, industrially frosted specimens using the original \( \text{HCl} \)-based frosting process were utilized. Subsequently, the results were evaluated using the semi-automatic evaluation methods referred to in Section 3.2.

Tables 4–6 show the results of the tested frosting baths. For a better clarity, the results were visualized using a color palette from green to red. Thereby, a green data point represents a good frosting result, while a red data point indicates a large deviation compared to the reference value and most likely a bad frosting result. While in Table 4 the evaluation parameters mentioned in Table 2 were used as reference, the result of the industrial frosting was used in Tables 5 and 6 as the reference value for the desired frosting result.

According to these results, it becomes clear that both methods can basically divide the test matrix into good and bad frosting results. With one exception, the evaluations of the methods are in accordance with the subjective impressions of the frosting qualities. The usage of a preliminary bath consisting of \( 5 \text{ wt\%} \text{ H}_3\text{PO}_4 \) and \( 35 \text{ g/L} \text{NH}_4\text{HF}_2 \) led to a dense frosting with only a few voids, but there were distinct structures like blotches or scratches visible. These structures originate from crystal-like structures of different size distributions. Due to the structure of the described defects, both methods were not able to evaluate them correctly, with \( \sigma_{\text{grey},5\times3} \) particularly misjudging the sample.

Subjectively, the best frosting result could be achieved using a solution of \( 5 \text{ wt\%} \text{H}_3\text{PO}_4 \) and \( 35 \text{ g/L} \text{NH}_4\text{HF}_2 \) as preliminary bath, which is supported by the evaluation method using \( A_{\text{max}} \). In contrast, the grey value deviation suggests a better frosting result using a combination of \( 5 \text{ wt\%} \text{H}_3\text{PO}_4 \) and \( 20 \text{ g/L} \text{NH}_4\text{HF}_2 \). On the glasses frosted using the latter solution, isolated samples showed distinct frosting errors, which could not be detected because of their homogeneous distribution within the microscopic picture (Figure 8).

The amount of segments used for the determination of \( \sigma_{\text{grey}} \) shows a strong dependence on the image quality. Due to the microscope’s low depth of focus, even slight curvatures can lead to blurring. This leads to a sub-segmentation in certain areas and thus to a higher deviation in the grey value.

One approach to circumvent this problem could be to use the raw or grayscale images instead of the binary images. This method would introduce additional inhomogeneous distributed brightness levels, since the microscope used is prone to noticeable vignetting. A variation in the glass thickness would also introduce brightness differences. Furthermore, the use of the absolute grey value is conceivable, but only useful if the glass specimens have basically the same thickness which was not ensured in this study. In addition, the same light conditions for image acquisition have to be maintained. The effects of variable glass thickness and the vignetting can easily be seen in the overview in Figure 9.

Figure 9 shows an overview of the microscopic images taken and evaluated for two samples and the industrial reference. The frosting errors of the specimens immersed in a
preliminary bath, consisting of 10 wt% H₃PO₄ and 10 g/L NH₄HF₂, can easily be seen in Figure 9A. Figure 9B shows the specimens immersed in a preliminary bath composition consisting of 5 wt% H₃PO₄ and 20-50 g/L NH₄HF₂, which resulted in the best frosting result based on H₃PO₄. The reference frosting, based on HCl, still produces slightly better results as shown in Figure 9C. This quality difference may be caused by the preparation method of the glass used. In addition, the samples were frosted in a manual process in the laboratory.

5 | CONCLUSION

A substitution of HCl in the frosting process by H₃PO₄ is not possible without introducing frosting defects. These defects can be substantially reduced with preliminary baths containing diluted HF or a 5 wt% H₃PO₄ solution mixed with 20-50 g/L NH₄HF₂.

The optimal composition of the preliminary bath consists of 5 wt% H₃PO₄ and 30-50 g/L NH₄HF₂. However, there is still a need for optimization of the H₃PO₄-based frosting process to eliminate the remaining frosting errors. This may be achieved by focusing on the optimization of the composition of the main frosting bath.

Furthermore, it was shown that an automated evaluation process can be used to determine the frosting quality of a glass ware using microscopic images. On the one hand, the evaluation method using $A_{\text{max}}$ was the most promising, supporting the subjective impression of the frosting quality. On the other hand, the grey value deviation method required less computational effort and may be
more useful for large amounts of specimen. Nevertheless, the grey value deviation is prone to frosting errors which are homogeneously spread across the surface. It showed slight deviations to the subjective impression of the frosting quality, while the improvement trend was displayed correctly. Therefore, these methods may also be used for quality assurance processes or to evaluate further modifications in the frosting process.

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