

Machine dishwashing of glass in private households Research results on glass damage

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Dedicated to Dr. Konrad Henkel on the occasion of his 80th birthday

Against the background of the introduction of the new, low-alkaline compact dishwashing detergents and the associated glass damage during automatic dishwashing a comparative test was carried out. Glasses of different origin and composition were subjected to a continuous dishwashing test with up to 1000 cycles which compared the highly alkaline conventional detergent with different new formulation variants of low-alkaline compact detergents obtained from the market as well as with water. While the conventional and carbonate-containing compact detergent did not cause visible corrosion, the detergent with a high disilicate content already caused serious glass damage after 50 washing cycles in the form of clouding and iridescence. These phenomena render the drinking glasses esthetically unsuitable. At the same time, on-glaze decoration of chinaware which is not resistant to machine dishwashing is protected by these last-mentioned detergents.

Details of the processes in the washed glass surface were examined by means of XPS depth profiles up to a depth of 300 nm. It could be shown that during washing with automatic dishwashing detergents of a high disilicate content silica from the wash liquor separates in a similar structure as the glass itself on the glass surface, which causes the corrosion phenomena clouding and iridescence. Active substances and constituents of the wash liquor can be incorporated in the deposited layer.

Since the new, low-alkaline compact detergents are gaining more and more importance on the market, this paper was intended to clarify the causes of increasing glass corrosion during machine dishwashing.

Maschinelles Spülen von Glas im Haushalt Forschungsergebnisse zur Vermeidung von Glasschäden

Vor dem Hintergrund der Einführung der neuen, niederalkalischen Kompaktpflege- und der dadurch in letzter Zeit beim maschinellen Spülen in der Praxis aufgetretenen Glasschäden wurde eine vergleichende Untersuchung durchgeführt. Hierbei wurden Gläser verschiedener Herkunft und Zusammensetzung mit klassischem, hochalkalischem Reiniger im Vergleich zu verschiedenen Rezepturvarianten marktgängiger niederalkalischer Kompaktreiniger und Wasser einem Dauerspültest über 1000 Zyklen unterzogen. Während der klassische und der carbonathaltige Kompaktreiniger zu keiner sichtbaren Korrosion führten, verursachte der hoch-disilicathaltige Reiniger schon nach 50 Spülgängen gravierende Glasschäden in Form von Trübungen und Irisieren. Diese Erscheinungen lassen die Trinkgläser für Zwecke der Gästebewirtung ästhetisch nicht mehr tolerierbar erscheinen. Gleichzeitig werden jedoch nicht spülmaschinenfeste Porzellanaufglasurdekore durch die letztgenannten Reiniger geschützt.

Einzelheiten der Vorgänge in der gespülten Glasoberfläche wurden durch XPS-Tiefenprofile bis in 300 nm Tiefe untersucht. Es konnte hiermit gezeigt werden, daß sich beim Spülen mit dem hoch-disilicathaltigen Reiniger aus der wäßrigen Spülflotte Kieselsäure glasartig auf der Oberfläche abscheidet, was zu den Korrosionserscheinungen Trübungen und Irisieren führt. In die abgelagerte Schicht können Wirkstoffe und Bestandteile der Reinigerflotte mit eingelagert werden.

Da die neuen, niederalkalischen Kompaktreiniger im Markt immer mehr an Bedeutung gewinnen, sollte die vorliegende Arbeit zur Klarheit über die Ursachen der Glaskorrosion beim maschinellen Geschirrspülen beitragen.

1. Introduction

Like the washing machine, dishwashing machines make a major contribution to saving work in the household. Although dishwashing machines have been on the market for more than 30 years, the number of dishwashing machines used in households is still growing continuously. In Germany, the proportion in the former Western part at present is approximately 43 % and in the former Eastern part 4 %. The average value for Europe is approximately 28 % with relative growth rates of approximately 10 %/a.

The consumer expects dishes washed in the dishwashing machine first of all to be clean and shining. For a good cleaning result, detergent, rinse aid and regenerating salt are required. Apart from a good cleaning result, the corrosion resistance of the washed dishes is highly important for the consumer. According to consumer studies, glass corrosion is the most common complaint with respect to corrosion in machine dishwashing. In particular the introduction of the new low-alkaline "compact detergents" has led to corrosion phenomena which have irritated both the consumers and the glass industry. Therefore, this paper will present the relationship between different detergent formulations and the

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corrosion phenomena occurring during machine dishwashing; it is based on an extensive comparative study.

By means of surface-analytical tests (XPS depth profiles), the corrosive effect of different detergent types on glasses will be demonstrated.

2. Detergent

2.1 Tasks and function

The detergent is the most important element in machine dishwashing. Its most important tasks are:

- removal of soil from the dishes,
- dispersing the soil in the dishwashing solution,
- complexing the residual water hardness and the hardness ions from food remains to prevent deposits on the washed dishes and machine parts,
- maximum possible protection of all the parts which are cleaned in the dishwashing machine.

During many years the composition of automatic dishwashing detergents only experienced insignificant changes. However, for reasons of environmental and consumer protection numerous new developments have been introduced in the last five years. Some of them have attained considerable commercial significance. These new products influence the corrosion of different materials during washing in the household dishwashing machine in different ways. For example, at the beginning of 1991 a new generation of phosphate-free and low-alkaline dishwashing detergents was introduced, also called "compact detergents". The corrosive metasilicate was replaced by lower alkaline constituents such as disilicates and/or carbonates, thus increasing consumer safety. Environmental pollution is also reduced by substituting citrate for triphosphate in the builder system and active oxygen for active chlorine in the bleaching system.

2.2 Composition

Automatic dishwashing detergents consist of up to five functional components:

- alkalinity carriers,
- complexing agents,
- bleaching components,
- biological active substances, i.e. enzymes,
- wetting agents.

Table 1 shows a comparison of the two different detergent generations. The conventional detergents contain phosphates as complexing and dispersing agents in order to bind the water hardness. The alkalinity carriers mainly consist of highly alkaline metasilicates, which adjust a pH value of 12 to 13 in a 1% solution. The bleaching component comes from the salts of the trichloroisocyanuric acid; they form hypochlorite when dissolved in water. Throughout Europe the conventional detergents are largely similar with respect to their composition. However, in the USA the less alkaline disilicates are used instead of the highly alkaline metasilicates.

Opinions differ strongly as to the optimal formulation basis for low-alkaline "compact detergents". Some products available on the market are formulated exclusively with the complexing agent citrate. Other manufacturers use a combination of citrate with polycarboxylate, sometimes adding phosphonate as a further dispersing agent. Apart from these there are products with high quantities of tripolyphosphate instead of citrate.

A comparable variety of combinations is used for the alkalinity carrier systems of the new detergent generation. There are systems which contain exclusively disilicates or exclusively carbonates or a combination of both. Disilicates are dried water glasses (hydrated sodium silicates with a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of about 2:1). Carbonates are sodium carbonate and bicarbonate. The alkalinity carriers determine the pH value. In most of the products of the new detergent generation the pH value is between 9 and 11.

The low-alkaline detergents were launched into the market at the end of 1990. This new segment has experienced a particularly positive development in German-speaking countries. Meanwhile the new detergents have also gained a considerable share in the European market and their importance is growing continuously. Correspondingly, the importance of the conventional products decreases, and in a few years' time they will have disappeared completely from the German market, not least for reasons of consumer and environmental protection.

3. Tests

3.1 Application tests

In the application tests the cleaning performance and the prevention of lime deposits on the washed dishes are most important. Furthermore, the interaction of the formulation with the dishes during the washing process is also an important test and quality criterion. Therefore, during each development process for a new cleaner, a large variety of different materials, e.g. glass, porcelain, stainless steel, silver and plastic, are examined thoroughly with respect to their behavior in the dishwashing machine.

3.2 Corrosion tests

The corrosion tests are used to investigate the behavior of dishes towards new detergent formulations as well as to examine detergents on the market with respect to advertised properties and to increase one's own knowledge. The tests also provide useful arguments when dealing with customer complaints about the corrosion of washed dishes. Furthermore, the results from corrosion tests help to optimize the current production.

3.3 Overview of corrosion test methods

The German standard DIN 50275 [1] defines a process for testing the behavior of dishes in household dishwash-

Table 1. Comparison of conventional with low-alkaline formulations for detergents

conventional formulations composition in wt%	ingredients	low-alkaline formulations composition in wt%															
30 to 70 metasilicate/disilicate 0 to 10 soda ash	alkalinity carriers	<table border="0"> <tr> <td>{</td> <td>soda ash</td> <td>0 to 40</td> </tr> <tr> <td></td> <td>bicarbonate</td> <td>0 to 40</td> </tr> <tr> <td></td> <td>disilicate</td> <td>0 to 40</td> </tr> </table>	{	soda ash	0 to 40		bicarbonate	0 to 40		disilicate	0 to 40						
{	soda ash	0 to 40															
	bicarbonate	0 to 40															
	disilicate	0 to 40															
15 to 40 tripolyphosphate	<table border="0"> <tr> <td>{</td> <td>sequestering agents</td> <td>+ dispersing agents</td> </tr> </table>	{	sequestering agents	+ dispersing agents	<table border="0"> <tr> <td>{</td> <td>citrate</td> <td>0 to 45</td> </tr> <tr> <td></td> <td>phosphonate</td> <td>0 to 5</td> </tr> <tr> <td></td> <td>polycarboxylate</td> <td>0 to 15</td> </tr> <tr> <td></td> <td>tripolyphosphate</td> <td>0 to 50</td> </tr> </table>	{	citrate	0 to 45		phosphonate	0 to 5		polycarboxylate	0 to 15		tripolyphosphate	0 to 50
{	sequestering agents	+ dispersing agents															
{	citrate	0 to 45															
	phosphonate	0 to 5															
	polycarboxylate	0 to 15															
	tripolyphosphate	0 to 50															
0 to 2 active chlorine carrier	bleaching agents +	active oxygen carrier															
–	bleach activator	TAED															
–	wetting agents	surfactants															
–	bioactive agents	enzymes															
–	additives	{															
<0.5 paraffin oil		fragrance	<0.5														
		paraffin oil	<0.5														
		silverware protection aid	0 to 5														
12 to 13	pH value (1% solution)	9 to 11															

ing machines; however, at present it is only available as a draft. Within the framework of the European standards, this standard is planned to be developed and published as EN (European standard) [2]. Conflicting opinions of the individual member states about the incorporation of a short test (table 2, Ceram Research) into the EN have so far prevented a consensus. RAL-RG 604 [3] describes a method for testing the suitability of cutlery for dishwashing machines. The Ceram Research Institute, Stoke-on-Trent (UK), has developed an immersion test which examines the resistance of porcelain decorations to machine detergents [4]. The Henkel method resulted from the practical product development and is suitable for all materials commonly used in private households. The test method used by Henkel has to a large extent already been published [5 to 7] and is partially also used by other test institutes.

An overview of the known test methods for the determination of dishwashing machine resistance of household dishes as well as the detailed test conditions are listed in tables 2 and 3 [8]. A comparison of the test conditions shows the most important differences:

- In the DIN method [1] the temperature in the cleaning step is only 60°C. This is not practice-related since almost every European type dishwashing machine is equipped at least with a 65°C program.
- The Henkel method in addition defines the water quantity per washing cycle and the load of soil in the dishwashing solution. This soil is dosed automatically at the beginning of the cleaning cycle (after the prewash cycle) and corresponds to the quantity of food remains which is to be expected in a fully loaded dishwashing machine. After each wash program the door is kept open for 30 min for the wash load to cool down and get dry.

Table 2. Overview of methods: corrosion tests of washed dishes in the household dishwashing machine

method	application
DIN 50 275 (draft, June 1985) ¹⁾ [1] – dynamic corrosion test of tableware in household dishwashing machines	every kind of tableware
RAL-RG 604 (June 1983) – dynamic test of dishwasher safety of cutlery	cutlery
Ceram research ²⁾ – Static immersion test for the determination of the resistance of glazes to alkaline detergent attack (March 1990)	porcelain
dynamic test of Henkel KGaA [4]	every kind of tableware

¹⁾ Still in discussion by CEN. ²⁾ British Ceram Research, Ltd., Stoke-on-Trent (UK).

Up to 1000 washing cycles are defined for all corrosion tests. According to consumer statistics this corresponds to an average life of 5 to 8 years.

After 50, 125, 250, 375, 500, 625, 750 and finally 1000 washing cycles the wash load is being evaluated for damages and optical changes, where a scoring of 0 means no change, 1 and 2 means minor acceptable changes and 3 and 4 means heavy, esthetically not acceptable damages.

4. Glass damage

4.1 General aspects

Glass accounts for the largest proportion of dishes cleaned in dishwashing machines. In spite of its chemical

Table 3. Conditions for corrosion tests

parameter	RAL-RG 604 [3] (continuous test)	DIN 50 275 (draft) ³⁾ [1]	Henkel test method
temperature in °C			
– cleaning	65	60	65
– rinsing	68	65	65
amount of water	–	8 l per fill	5 l per fill
residual water hardness	–	0 to 1 °d	3 to 4 °d
detergent			
– amount in g	30	30	30
– type	DIN 44 990 ⁴⁾ [8]	DIN 44 990 ⁴⁾ [8]	different types of detergent + water
soil	–	–	50 g liquid soil
washing cycles	1000	1000	1000

³⁾ Still in discussion by CEN. ⁴⁾ Replaced by IEC 436 reference detergent formula A [9].

resistance, in the course of time glass can already be attacked by pure water or aqueous solutions [10]. Therefore, possible changes in the glass surface due to machine dishwashing were soon recognized.

The following corrosion damage can occur:

- scratches and chated spots caused by scouring two glasses against each other,
- scratch, pin-prick and fluff-like variations,
- cracks,
- streaks,
- clouding (irreversible, over the whole surface, on one side, symmetric, ring-shaped),
- iridescence,
- strange odour,
- stickiness.

4.2 Mechanical glass damage

Mechanical damage to glasses is either due to the manufacturing process or to the arrangement in the crockery basket of the dishwashing machine, i.e. it is not influenced by the dishwashing detergent used. This damage appears in the form of scratches and chated spots due to the friction between adjacent glasses, enhanced by the temperature change. Furthermore, there can be scratch, pin-prick and fluff-like variations of the surface resulting from the manufacturing process, which are aggravated by repeated washing. These phenomena have already been described in detail in several publications [6, 7, 10 to 12]. Streaks hint at irregularities in the glass melting process, i.e. the glass composition was not melted and mixed correctly.

4.3 Corrosion due to the dishwashing process

4.3.1 Clouding

Although glass is considered as a chemically resistant substance, it is corroded by acid and caustic solutions and even attacked by pure water. This effect is enhanced

by high temperatures. Depending on the conditions in the dishwashing solution, e.g. pH value, type and quantity of dissolved ions, there are different types of corrosion. In the acid to neutral pH range, there is mostly gelation in the glass surface [13 and 14] and leaching of alkali ions. In the alkaline pH range in addition the silicate structure is destroyed by the hydrolytic cleavage of Si–O–Si bonds by means of OH[–] ions. Scanning electron micrographs reveal that the highly siliceous glass surface resulting after leaching of the alkali ions from the glass structure is porous, with holes of 1 µm in diameter [15]. The scattered light can lead to a turbid appearance of these surfaces. Glass surfaces washed with highly alkaline detergents usually appear as optically intact because of the homogeneous surface removal. An uneven temperature distribution at the glass surface during glass production or cooling can lead to the diffusion of alkali ions from the warmer regions into the colder areas of the glass surface. This occurs for example during round smelting of a glass at the edge or the subsequent attachment of a handle or a stem. A massive base can also lead to an inhomogeneous temperature distribution during cooling and thus to alkali diffusion in the glass surface. Although these surfaces appear to be optically perfect after the manufacturing process, washing in the dishwashing machine can cause characteristic clouding in areas of high alkali ion concentration. In the case of round-smelted top edges or attached stems, clouding is mostly symmetric and ring-shaped. Clouding can also occur over larger more or less regular areas which can be structured and are presumably due to the temperature regulation during the production or cooling process. Figure 1 shows an example of this type of glass damage.

4.3.2 Iridescence

This phenomenon has been known for a long time, but it has only started to gain importance in the past three years, in particular after introduction of the new “com-

compact detergent" generation. In this case the surface develops a nacrous appearance where either brownish, golden, greenish or bluish tones can predominate. It is assumed that this phenomenon is caused by the formation of thin layers with different refraction. For a long time the reason for this interference effect could not definitely be explained. On the one hand, it was assumed to be a corrosion effect, where glass constituents are leached from the surface, producing layers with different refractive indices. On the other hand, the phenomenon could be due to the deposition of constituents of the wash liquor on the glass surface resulting in the same effect. An example of a glass with a multicolored iridescence is shown in figure 2.

4.3.3 Results of corrosion tests

A comparative corrosion test over 1000 dishwashing cycles was carried out under the conditions represented in table 3 (Henkel method) with dishwashing detergents of different compositions obtained from the market. The test was carried out with a conventional detergent according to table 1 as well as three representatives of the new low-alkaline compact detergent generation. One of these compact detergents was formulated on the basis of carbonates, the second on the basis of disilicates and the third on the basis of disilicate/carbonate mixtures. As a reference, the so-called "water value" was also determined (without detergent and soil). The tested samples were soda-lime-silica glasses, potassium crystal as well as lead crystal glasses (>24 % PbO) of different suppliers which were known to be relatively dishwashing-resistant. Figures 3 and 4 show the clouding effects for the above-listed glasses and the iridescence after 125 washing cycles in the form of bar diagrams. Only the disilicate-containing detergent already shows clear effects, which could be observed with the naked eye and, thus, would be considered esthetically unacceptable⁵⁾.

The final result after 1000 washing cycles is represented in figures 5 and 6. The water value and the carbonate-containing detergent showed hardly any corrosion effects. However, the disilicate-containing products caused extremely strong, unacceptable clouding and iridescence. The glasses are optically unacceptable.

4.3.4 Corrosion in relation to the water value

It is now interesting to compare the detergents in their effect on further dishes, with particular emphasis on delicate porcelain on-glaze decorations, which were also included in the comparative corrosion test. It should be mentioned that dishwashing just with hot water already causes a considerable corrosion attack on delicate on-glaze decorated china. Therefore, the "net effect" of the

⁵⁾ The evaluation of the washed tableware was performed under defined light conditions in a black cabinet. Damages, which were visible outside the black cabinet, were scored with 3 or 4 and would be for the purpose of guest entertaining esthetically unacceptable. Beginning changes, which were only visible in the black cabinet, were scored with 1 or 2.

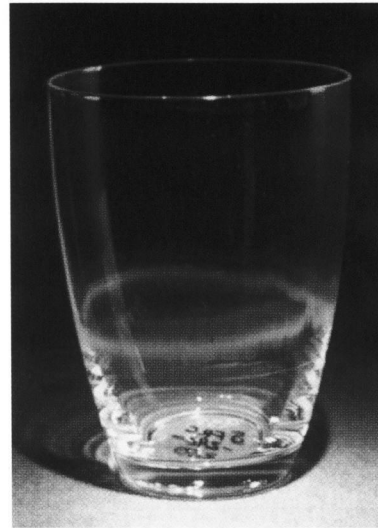


Figure 1. Symmetric clouding.



Figure 2. Iridescence.

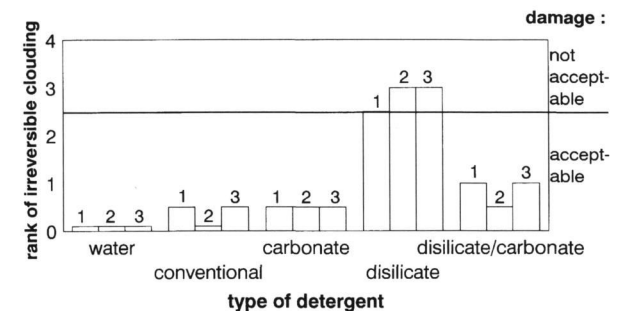


Figure 3. Clouding effects of different detergents on three glass samples after 125 washing cycles; 1: soda-lime-silica glass, 2: potassium crystal glass, 3: lead crystal glass.

detergents independent of the corrosive effect caused by the hydrolytic power of hot water alone is of great interest to the product development of automatic dishwash-

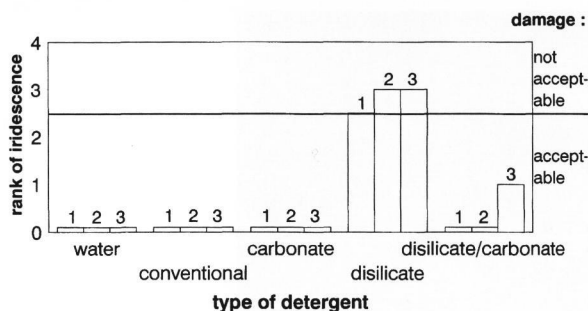


Figure 4. Iridescence of three glass samples after 125 washing cycles with different detergents; 1: soda-lime-silica glass, 2: potassium crystal glass, 3: lead crystal glass.

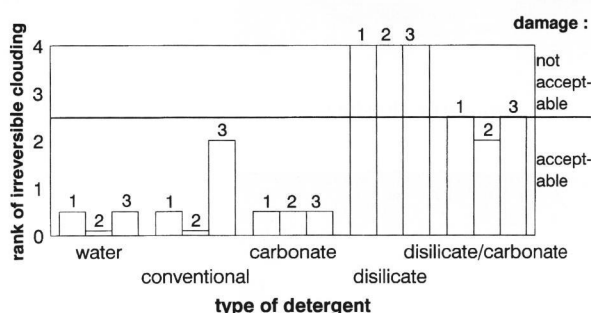


Figure 5. Clouding effects of different detergents on three glass samples after 1000 washing cycles; 1: soda-lime-silica glass, 2: potassium crystal glass, 3: lead crystal glass.

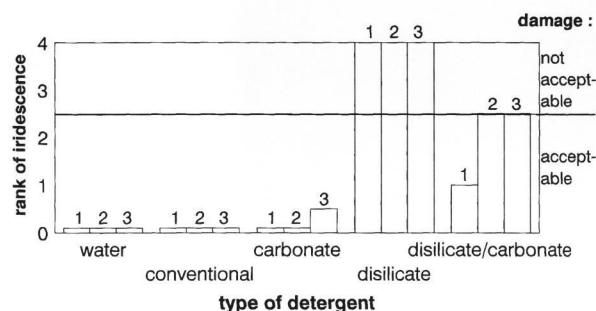


Figure 6. Iridescence of three glass samples after 1000 washing cycles with different detergents; 1: soda-lime-silica glass, 2: potassium crystal glass, 3: lead crystal glass.

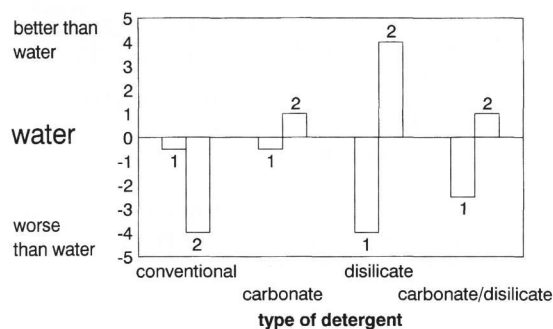


Figure 7. Corrosion of glasses and delicate on-glaze decorated china washed with different detergents in relation to the water value; 1: glasses, 2: delicate on-glaze decorated china.

Table 4. Conditions for the XPS measurement

device	ESCALAB 220 (Fisons, East Grinstead (UK))
pressure	$\approx 1.2 \cdot 10^{-7}$ mbar (after argon introduction)
area	$(500 \times 500) \mu\text{m}^2$
time	≈ 5 min
measuring parameters	15 keV, 20 mA, magnesium anode
sputtering parameters	3 keV, 10 000 μm
sputtering time	60 min

ing detergent formulations. In figure 7, the results of the corrosion test with different detergent types for glasses and delicate on-glaze decorated china are displayed not in relation to the initial value of unwashed dishes, but to the corrosion effects caused just by the hot water.

The carbonate-containing detergent shows no additional influence on the removal of pigments from delicate porcelain decorations. Its behavior is comparable to that of pure water. The conventional detergent produces less favorable results on porcelain. Detergents with a high disilicate content show a more favorable corrosion pattern, i.e. their corrosion effect on porcelain decorations is contrary to that on glass. However, in practice this is only of minor importance since most porcelain manufacturers offer decorations which are resistant to machine dishwashing. This leads to the conclusion that corrosion protection of delicate on-glaze decorated china which is actually not resistant to machine dishwashing can only be achieved at the expense of increased glass corrosion.

4.4 Surface-analytical tests

4.4.1 Silicon content on non-silicate surfaces

Surface-analytical tests were carried out for the further clarification of the observed effects. First it was to be clarified whether the effects observed with the disilicate-containing detergents are deposits or dissolution phenomena. For this purpose, non-silicate materials (plexiglass and stainless steel) were washed 500 and 625 times, respectively, with disilicate-containing detergents and examined for silicon by means of XPS. The result shows that compared to the initial value of unwashed material both in the case of plexiglass and of the stainless steel blade there is a significant enrichment of silicon compounds in the surface. This indicates a deposition of silicon compounds from the dishwashing solution onto the washed surfaces.

4.4.2 XPS depth profiles

Samples of a lead crystal glass of high quality were taken from the corrosion tests shown in figures 3 to 6 and XPS depth profiles were prepared to determine the element

distribution in the glass surface (table 4). In the sample washed 1000 times with the disilicate-containing compact detergent even at a depth of approximately 2000 nm the basic composition of the glass could not be determined. Therefore, a glass which was taken out after 50 cycles was examined by XPS. The depth profiles of lead, sodium and potassium for the glass samples that are unwashed, washed with water, conventional detergent and carbonate-containing detergent (in each case 1000 cycles) as well as with disilicate-containing detergent (50 cycles) are shown in figures 8 to 10. Figure 8 reveals that the lead content in the surface remains rather comparable with the first samples, while in the case of the disilicate-containing detergent appreciable lead quantities are only found from approximately 200 nm of depth; at approximately 280 nm the value approaches that of unwashed glass. On account of the results with the various other samples which were washed 1000 times it can be excluded that lead from a depth >20 nm is removed from the surface by the dishwashing process. Thus, the sample washed with the disilicate-containing detergent must be coated with a SiO₂-containing surface layer which grows with every washing cycle, finally leading to the previously mentioned refraction effects.

The dishwashing process has the strongest influence on the sodium content of the glass (figure 9). Of the examined glasses, the glass washed with the conventional detergent resembles the unwashed glass since here – as mentioned above – alkali ions are leached out and the silicate-based matrix substance of the glass is dissolved due to the high alkalinity. The carbonate-containing detergent leads to stronger leaching of sodium, up to a depth of approximately 120 nm. The disilicate-containing compact detergent also leads to the leaching of sodium from the base mass; however, there is no additional incorporation of sodium from the solution into the surface coating. Strong leaching of sodium was observed in the glass washed with water (depths of >300 nm); however, this does not cause optical problems.

In the case of the depth profiles for potassium (figure 10), the leaching is considerably less pronounced than with sodium. The conventional detergent resembles the unwashed glass. Unlike sodium, with pure water even after 1000 washing cycles, potassium is not completely leached from the glass surface. The surface content of potassium reaches the lowest value in the glass washed with the disilicate-containing detergent because of the formation of the surface coating, although a potassium diffusion from the base mass into the surface coating can be observed up to a depth of 100 nm.

In the depth profile of the lead crystal glass washed with the disilicate-containing detergent impurities like nitrogen, magnesium and aluminum could be identified additionally. Figure 11 shows this depth profile at first without these incorporated impurities. Worth mentioning is the continuous transition of silicon and oxygen contents in the surface coming from the base material to the surface coating. Apparently a glass structure similar

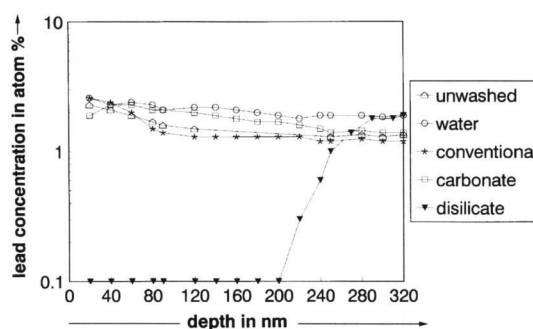


Figure 8. XPS depth profiles for lead of a lead crystal glass, washed with different detergents.

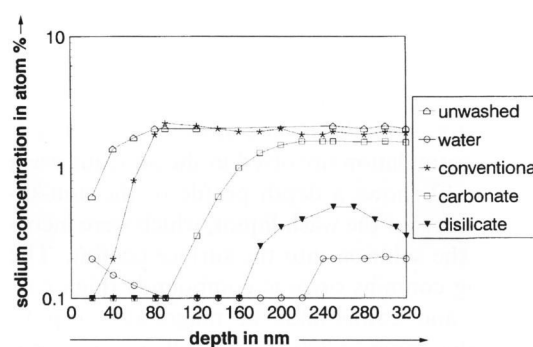


Figure 9. XPS depth profiles for sodium of a lead crystal glass, washed with different detergents.

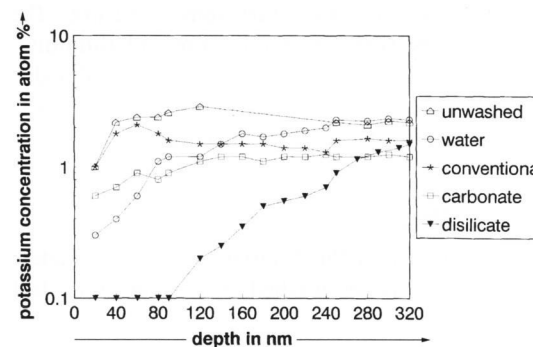


Figure 10. XPS depth profiles for potassium of a lead crystal glass, washed with different detergents.

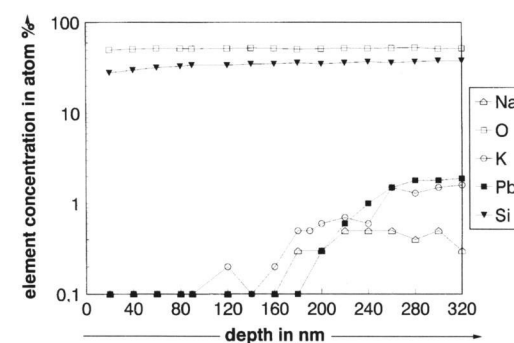


Figure 11. XPS depth profiles for different main elements of the basic composition of lead crystal glass, washed 50 times with the disilicate-containing detergent.

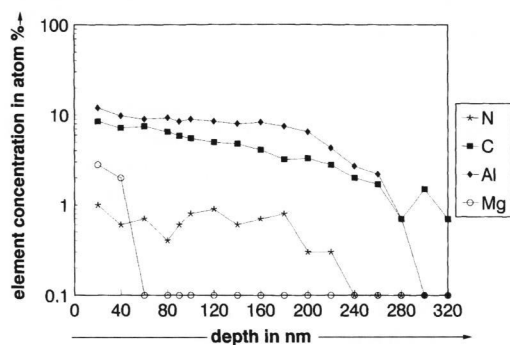


Figure 12. XPS depth profiles for different elements incorporated from the washing liquor into lead crystal glass with the disilicate-containing detergent.

to that of the basic substance is being formed during the dishwashing process by the silicate-based components of the detergent formulation dissolved in the aqueous wash liquor. Figure 12 shows a depth profile of the non-siliceous constituents of the wash liquor, which were incorporated from the solution into the surface coating. The surface coating contains organic compounds (high carbon content) and compounds of magnesium (up to ≈ 50 nm), of aluminum (≈ 320 nm) as well as of nitrogen (up to 320 nm). The nitrogen compound could stem from organic nitrogen heterocycles, which were probably added to the examined disilicate-containing product to protect silverware against tarnishing during the dishwashing process [15]. The magnesium and aluminum compounds are layer silicates (due to X-ray powder diffraction analyses of insoluble residues) which were possibly formulated into the product as additives.

4.5 Weight losses

The average weight loss for different glasses was determined on the test glasses washed in the described test program up to 1000 cycles.

As was expected, the weight loss is with 600 mg higher in the case of the conventional detergent because of the degradation of the silicate-based glass framework due to the high alkalinity of the wash liquor. The values for water and the carbonate-containing detergent are clearly lower (58 and 140 mg, respectively). The lowest weight loss is achieved with the disilicate-containing de-

tergent (32 mg). Apparently, the removal of material is almost compensated by the formation of the surface coating during the dishwashing process.

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