CORROSION OF MULTICOMPONENT GLASSES BY AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS

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Transfer of glass components into solution was studied on borosilicate glass Simax and on soda-lime-silica container glass, using aqueous solutions of citrate (0.1 to 4 wt.%) and salts of several organic acids (lactic, tartaric, oxalic, ascorbic, gluconic and EDTA). The powdered samples of the glasses were extracted (for 4 to 24 hours) at 98 °C, concentrations of SiO_2 and CaO were determined in the extracts.

The results showed that neutral aqueous solutions of salts of all the organic acids in question promoted significantly the dissolution of both types of glasses as compared to dissolution in distilled water. The effect of citrate was studied in detail. Even low concentrations of citrate (0.1 wt.%) speeded up transfer of SiO_2 and of CaO into solution. In the case of soda-lime glass, the resulting SiO_2/CaO ratio in the leachates (citrate solutions) was very close to the ratio of the components in the glass, which is indicative of congruent dissolution of glass. The results obtained with both multicomponent types of glasses are in good agreement with the findings of a previous study concerned with similar effects on silica glass.

INTRODUCTION

It is known from the literature [1-8] that the presence of some organic compounds in aqueous solutions speeds up transfer of glass components into solution. Increased aggressivity was established with neutral solutions of citrate, lactate, oxalate, ascorbate, malate, gluconate, salts of ethylenediaminetetraacetic acid (EDTA) and others. Bacon and Raggon [1] ascribe the increased corrosive effects of the neutral solutions on silicate glasses mainly to the formation of soluble complex organic compounds with silicon. However, no such complex compounds have so far been described in the literature. On the other hand, a number of organic compounds are capable of forming complexes with cations of many metallic elements, some of which are components of glass (Ca, Mg, Al, Pb, Zn, Fe, etc.). For this reason other authors [2, 3] explain the higher aggressivity of these solutions towards glass by formation of soluble complexes of organic anions with the cations of metallic elements contained in glass, rather than with silicon.

A previous paper of the present authors [4] was concerned with studying the effect of neutral aqueous solutions (4 wt.%) of selected organic compounds on the corrosion of silica glass and that of pure crystalline SiO_2 (natural rock crystal). The corrosion effects were found to decrease in the sequence citrate, oxalate, lactate, disodium salt of EDTA, ascorbate, tartrate, gluconate. The rate of dissolution into all these solutions was higher than that into distilled water whose *pH* had been adjusted by NaOH to an approximately neutral value corresponding to that of the organic solutions. These results appear to bear out the assumption [1] that some type of organic silicon compound accelerating dissolution of silica glass is actually involved in the process.

Increased transfer of SiO_2 and other glass components into solutions of the given organic compounds was likewise established in the case of multicomponent glasses. Ernsberger [2] observed more extensive corrosion of soda-lime glasses by dilute EDTA solutions in an alkaline medium, and explained it by formation of soluble complex EDTA compounds with Al^{3+}, Ca^{2+} and Mg^{2+} from the surface of glass and by subsequent elimination of their stabilizing effect on the glass structure. Olsen et al. [3] found that EDTA in an alkaline medium had a similar effect on lead crystal and assumed this to be due to a complex EDTA-lead compound.

The question of the effect of organic compounds on the corrosion of glass is important in particular in connection with foodstuff and pharmaceutical container glasses. It was found [5] that for instance a 10 wt.% sodium gluconate solution attacked soda-lime and borosilicate glass faster than water and 0.8 wt.% NaCl solution. Pineiro [6] points out that the amount of SiO_2 extracted from soda-lime and borosilicate glasses increases in the sequence $H_2O <$ physiological solution

< 0.1 M borax < isotonic glucose solution < sodium gluconate.

Passl [7] noticed a more extensive aggressive effect of potassium lactate on soda-lime glass with a dealkalized surface as compared to the effect of physiological solution. Similarly, study [8] established that SiO_2 passed into a neutral solution of sodium salt of EDTA at a higher rate from pharmaceutical glass containers with a dealkalized surface, as well as from borosilicate glass.

The present paper is a continuation of previous studies [4, 8] and deals with the aggressive effects of aqueous solutions of selected organic compounds on borosilicate glass and soda-lime glass used in the manufacture of containers for foodstuffs and pharmaceuticals.

EXPERIMENTAL PART

The measurements were carried out with Simax glass (the Pyrex type) and with white container soda-lime-silica glass (the latter having the composition 73.59 SiO_2, 0.6 Al_2O_3, 8.02 CaO, 2.82 MgO, 14.89 Na_2O (wt.%)). The leaching solutions had the same compositions as in study [4], i.e. aqueous solutions of sodium citrate, tartrate, lactate, ascorbate and gluconate, potassium oxalate, disodium salt of EDTA, and the solutions of the corresponding organic acids. In most of the instances, the concentration was 4 wt.% with the exception of citrates (0.1 to 4 wt.%). The *pH* of the solutions of salts of organic acids was adjusted to neutral values by adding the corresponding organic acid or NaOH. Distilled water, and distilled water whose *pH* was adjusted with NaOH to an approximately neutral value, were used as reference leaching media.

The experimental conditions and measuring methods were also the same as those used in study [4]. The extraction was carried out on ground glass samples (grain size fraction 0.3-0.5mm) in teflon vessels (2g of glass in 50 ml solution) at 98 °C for 4 to 24 hours. The concentration of SiO_2 in the extract was determined photometrically (to ČSN 70 0527), and in the leachates where the organic compounds would interfere with the assay, use was made of the AAS method. The concentration of calcium in the leachates was determined on a flame photometer.

RESULTS AND DISCUSSION

Simax glass

The concentrations of SiO_2 in the Simax glass leachates after extracting for 6 and 24 hours are listed in table 1. The results show that compared to distilled water all of the approximately neutral solutions (*pH* 6.6 to 7.1) of salts of organic acids promoted significantly the transfer of SiO_2 into solution. In the case of solutions of organic acids with a low *pH* (1.7 to 2.3) the SiO_2 concentration in the leachates was either lower than, (citric, oxalic, gluconic acids) or comparable to, that in water (lactic acid). The only exception was the case of tartaric acid where the SiO_2 concentration was somewhat higher. The effects of the individual solutions are also demonstrated by the diagram in figure 1 showing the plot of SiO_2 concentration in the leachates after 24-hour extraction.

Table 1. Concentration of SiO_2 in solutions after leaching of borosilicate glass (Simax).
Temperature 98 °C, concentration of organic solutions 4 wt.%.

solution	initial *pH*	time of leaching (hours)	c_{SiO_2} (mg l^{-1})
distilled water	5.7	6	5.9
		24	31.7
distilled water with NaOH	6.9	6	9
		24	39.1
citrate	7.1	6	47.1
		24	239.6
citric acid	2.1	6	< 4.3
		24	14.2
tartrate	7.1	6	72.1
		24	272
tartaric acid	2.0	6	5.8
		24	61
lactate	6.8	6	67.2
		24	415
lactic acid	2.3	6	8.6
		24	32.5
gluconate	6.9	6	17.1
		24	250.3
gluconic acid	1.8	6	< 4.3
		24	16.9
ascorbate	6.7	6	14.8
		24	67.2
ascorbic acid	2.7	6	< 4.3
		24	6.6
oxalate	6.6	6	88.1
		24	224.8
oxalic acid	1.7	6	< 4.3
		24	13.9
disodium salt of EDTA	6.9	6	5.2
		24	113.6

The time dependence of SiO_2 concentration in leachates for the selected solutions is plotted in figure 2. In view of the small number of the time periods measured the relationships have a merely orientation value but nevertheless show that the rate of dissolution of

SiO_2 from glass into neutral aqueous solutions of salts of organic acids was higher than that in water (by a factor of 7 to 10). The transfer of SiO_2 into solution is already accelerated by low concentrations of organic salts in solution, as demonstrated by figure 3 where the concentration of SiO_2 in the leachate after 6 hours of extraction is plotted in terms of citrate content in the solution (from 0.1 to 4 wt.%). The relationship shows that following a rapid increase in SiO_2 concentration in the leachate, the rate of SiO_2 dissolution will slow down with increasing citrate concentration in the solution. This indicates that similarly to the case of silica glass [4], only a certain concentration of the organic compound in solution will be sufficient for removing SiO_2 from the solution by combining with the organic compound under the given conditions of extraction.

All of the results of measurements on Simax glass are in agreement with the similar measurements determining the effects of the same organic compounds on silica glass [4]. Courses similar to those with silica glass were likewise exhibited by the concentrations of SiO_2 in leachates in terms of *pH* of the citrate solution (figure 4) when compared to the citrate-free aqueous solution adjusted to the required *pH* with NaOH or HCl. In this case also, increasing *pH* of the initial citrate solution brings about more distinct increases in SiO_2 concentration in the leachate than in the instance of citrate-free solution.

The similarities in the effects of aqueous solutions of the organic compounds in question on silica glass and on multicomponent borosilicate glass Simax with a high SiO_2 content (80.6 wt.%) are indicative of identical

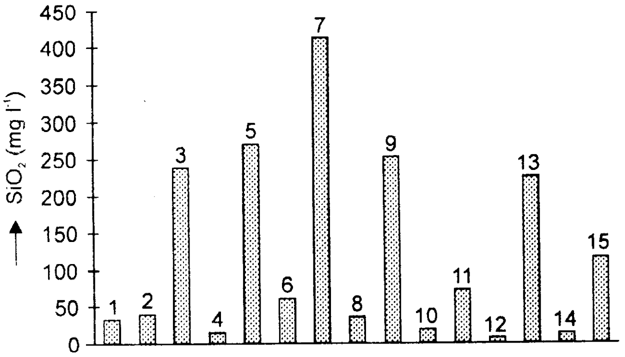

Figure 1. Concentration of SiO_2 in Simax borosilicate glass leachates. Temperature 98 °C, time of leaching 24 hours.
1 - distilled water, 2 - distilled water with NaOH (*pH* = 6.90), 3 - citrate, 4 - citric acid, 5 - tartrate, 6 - tartaric acid, 7 - lactate, 8 - lactic acid, 9 - gluconate, 10 - gluconic acid, 11 - ascorbate, 12 - ascorbic acid, 13 - oxalate, 14 - oxalic acid, 15 - disodium salt of EDTA

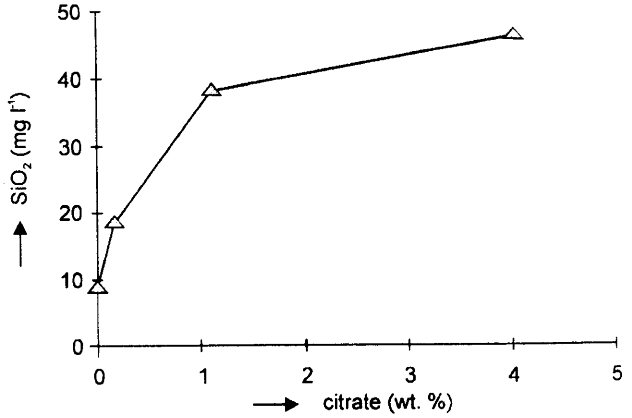

Figure 3. Concentration of SiO_2 in Simax glass leachates vs. citrate content in leaching solution.
Temperature 98 °C, time of leaching 6 hours.

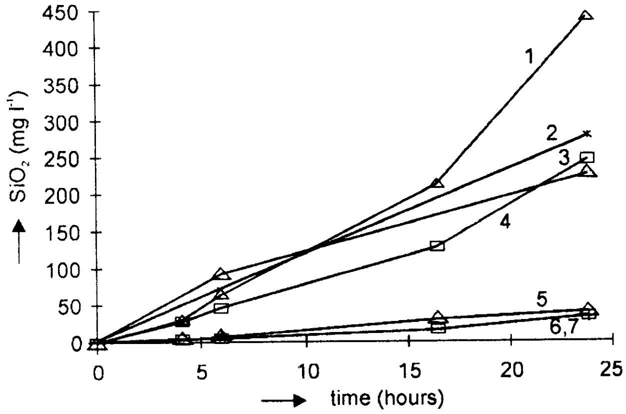

Figure 2. Concentration of SiO_2 in Simax glass leachates vs. time of leaching. Temperature 98 °C.
1 - lactate, 2 - tartrate, 3 - citrate, 4 - oxalate, 5 - distilled water with NaOH, 6 - distilled water, 7 - lactic acid

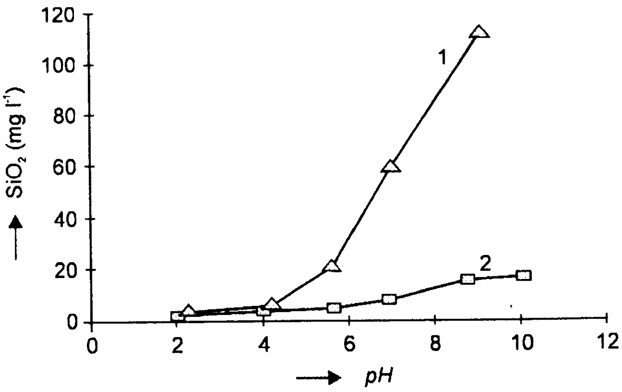

Figure 4. Concentration of SiO_2 in Simax glass leachates vs. *pH* of leaching solution.
1 - citrate, 2 - distilled water with NaOH or HCl

mechanisms responsible for speeding up corrosion of the two types of glass. The main part in the process is obviously played by formation of some type of soluble organic compound of silicon which removes SiO_2 from the solution and thus speeds up the dissolution of glass.

Soda-lime-silica glass

Citrate and citric acid solutions were selected as extracting organic solutions for white container soda-lime-silica glass. Apart from SiO_2, also CaO content was determined in the leachates. Figure 5 shows the time dependence of SiO_2 concentration in leachates into the individual solutions, and figure 6 the corresponding relationships for CaO. The results again indicate a distinct effect of citrate on increasing the contents of both SiO_2 and CaO in the leachates. The concentrations of SiO_2 in leachates into citric acid solutions were very low, at the AAS method determination limit, and are therefore not plotted in the diagram in figure 5.

In the case of soda-lime glass, the dependence of SiO_2 content in the leachate on citrate concentration in the leaching solution (figure 7) is similar to that for Simax glass and silica glass [4]. The corresponding relationship for CaO extraction, likewise plotted in figure 7, has a character also resembling that of SiO_2: already low citrate concentrations in the leaching solution (0.1 wt.%) lead to considerable increase in CaO content in the leachate, and this rate of increase tends to slow down with increasing citrate concentration.

For extraction periods of 4 and 24 hours, the calculated values of the SiO_2/CaO molar ratio in the leachates were compared with the corresponding initial ratio of the components in the glass (table 2). In water, the SiO_2/CaO ratio increases in terms of time in agreement with the generally accepted concept [9] that the initial stage of preferential leaching of CaO is followed by prevailing dissolution of the extracted surface layer rich in SiO_2. With leachates into the 4 wt.% citrate solution the SiO_2/CaO ratio does not increase in terms of time, remaining fairly constant over the range of 8.56 to 10.46, this being in good agreement with the initial SiO_2/CaO molar ratio of the glass (8.56). This is indicative of an approximately congruent dissolution of glass in the citrate solution over the time interval in question. Leachates into citrate solutions of lower concentrations (0.1 and 1 wt.%) for extraction periods of 6 hours (table 2) also show molar ratios SiO_2/CaO very close to the ratio of the components in the glass.

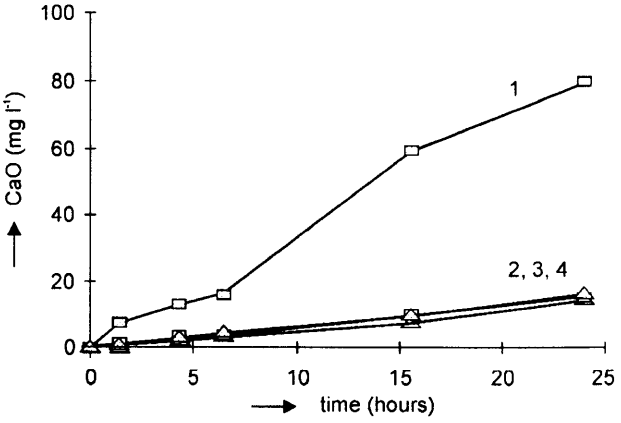

Figure 6. Concentration of CaO in soda-lime-silica glass leachates vs. time of leaching. Temperature 98 °C.
1 - citrate, 2 - distilled water, 3 - distilled water with NaOH, 4 - citric acid

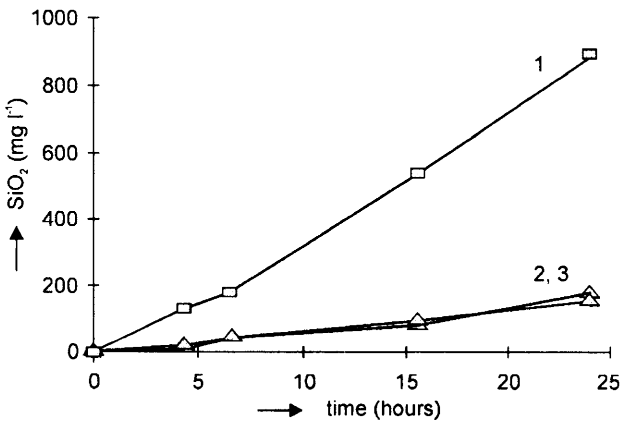

Figure 5. Concentration of SiO_2 in soda-lime-silica glass leachates vs. time of leaching. Temperature 98 °C.
1 - citrate, 2 - distilled water, 3 - distilled water with NaOH

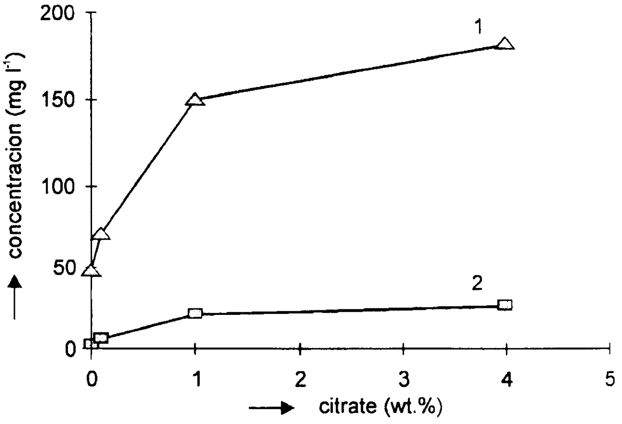

Figure 7. Concentration of SiO_2 and CaO in soda-lime-silica glass leachates vs. citrate content in leaching solution. Temperature 98 °C, time of leaching 6 hours.
1 - SiO_2, 2 - CaO

Table 2. The molar ratios of SiO_2/CaO in soda-lime-silica glass leachates.
Temperature 98 °C, SiO_2/CaO ratio for the bulk glass is 8.56.

solution	initial *pH*	time (hours)	SiO_2/CaO
distilled water	5.7	4	6.52
		6	18.34
		16	24.31
		24	27.21
distilled water with NaOH	6.9	4	7.1
		6	15.73
		16	19.13
		24	22.49
citrate (4 wt.%)	7.1	4	8.72
		6	10.46
		16	8.56
		24	10.36
citrate (0.1 wt.%)	7.0	6	8.31
citrate (1 wt.%)	7.0	6	8.7

CONCLUSION

Neutral aqueous solutions of salts of citric, lactic, tartaric, oxalic, ascorbic, gluconic and EDTA acids accelerate distinctly the dissolution of the Simax borosilicate glass as compared to distilled water. Citrate solutions, which were selected for more detailed study, were found to exhibit similar aggressive effects also on soda-lime-silica glass. Already low concentrations of citrate in solution (0.1 wt.%) resulted in a marked increase in SiO_2 and CaO concentrations in the leachate. The aggressive effect of citrate on both glasses increases at first very quickly, but gradually slows down considerably.

The concentration of SiO_2 in extracts from Simax glass increases with increasing *pH* of the citrate, the increase being more distinct than with the corresponding citrate-free aqueous solutions.

The SiO_2/CaO molar ratio of leachates from soda-lime glass into citrate solution remained fairly constant for the time of leaching employed (4 to 24 hours) and corresponded roughly to the molar ratio of the components in the glass. This indicated that the dissolution of glass was approximately congruent. In contrast to this, the SiO_2/CaO ratio in leachates into water increased in terms of time, this being in agreement with the general concept of the mechanism of corrosion by water, based on preferential extraction of CaO during the initial phases of leaching.

The results presented in this paper are in good agreement with the results of the previous study carried out on silica glass [4]. The similarity of the effects of neutral aqueous solutions of salts of the given organic acids on silica glass, Simax multicomponent glass and soda-lime glass allows to conclude that some types of soluble organic compounds of silicon are formed by the effect of neutral and alkaline aqueous solutions on silicate glasses. The process is then responsible for reducing the concentration of SiO_2 in solution and increases the difference between saturated and actual concentration, which is the driving force of dissolution of the glass matrix.

Acknowledgement

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KOROZE VÍCESLOŽKOVÝCH SKEL VODNÝMI ROZTOKY ORGANICKÝCH SLOUČENIN

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Z literatury je známo [1-8], že přítomnost některých organických sloučenin ve vodných roztocích urychluje přechod složek ze skla do roztoku. Tento poznatek byl potvrzen v předchozí práci autorů [4], kde byl sledován vliv vodných roztoků solí některých organických kyselin na rozpouštění křemenného skla a přírodního křišťálu. Předložená práce navazuje na tyto výsledky a zabývá se působením těchto roztoků na vícesložková skla: boritokřemičité sklo Simax a sodnovápenatokřemičité (bílé obalové) sklo.

Drťové vzorky skel byly louženy ve vodných roztocích (1 až 4 hmot.%) solí vybraných organických kyselin při teplotě 98 °C po dobu 4 až 24 h. Ve výluzích byla stanovena koncentrace SiO_2 (fotometricky nebo AAS) a u sodnovápenatého skla i CaO (plamenová fotometrie).

Bylo zjištěno, že neutrální vodné roztoky solí sledovaných organických kyselin (citronové, mléčné, vinné, šťavelové, askorbové glukonové a EDTA) výrazně zvyšují rozpouštění skla Simax v porovnání s destilovanou vodou (tabulka 1, obrázek 1). Z časových závislostí koncentrace SiO_2 ve výluzích do jednotlivých roztoků (obrázek 2) je zřejmé, že rychlost rozpouštění skla Simax do neutrálních roztoků solí sledovaných organických kyselin je několikanásobně (7 až 10 x) vyšší než do vody.

U roztoku citrátu, který byl vybrán pro podrobnější studium, byl zjištěn obdobný zvýšený korozní účinek také na sodnovápenatokřemičité sklo, jak je vidět z porovnání časových závislostí koncentrace SiO_2 (obrázek 5) i CaO (obrázek 6) ve výluzích do roztoku citrátu a vody. K výraznému zvýšení koncentrace SiO_2 ve výluzích z obou skel vedla již nízká koncentrace citrátu (0,1 hmot.%) v roztoku. Korozní účinek roztoku citrátu roste u obou skel (obrázky 3 a 7) s rostoucí koncentrací citrátu v roztoku z počátku velmi rychle, postupně se tento nárůst při vyšších koncentracích citrátu zpomaluje.

Koncentrace SiO_2 ve výluzích ze skla Simax roste s rostoucím *pH* roztoku, nárůst je u roztoků citrátu výraznější, než u roztoku bez citrátů se stejným *pH* (obrázek 4).

Molární poměr SiO_2/CaO ve výluzích ze sodnovápenatého skla do roztoku citrátu zůstával pro všechny měřené časy loužení (4 až 24 h) na přibližně konstantní hodnotě (tabulka 2) srovnatelné s molárním poměrem těchto složek ve skle, což svědčí o přibližně kongruentním rozpouštění skla. Molární poměr SiO_2/CaO ve výluzích do vody naproti tomu s časem vzrůstal (tabulka 2), což je v souladu s obecnými představami o mechanismu koroze skla vodou.

Výsledky práce jsou v souladu s výsledky získanými v předchozí práci [4] pro křemenné sklo. Podobnost v působení neutrálních vodných roztoků solí výše uvedených organických kyselin na křemenné sklo a vícesložková skla Simax a sodnovápenatokřemičité sklo vede k závěru o podobnosti hlavního děje, který způsobuje zvýšení koroze křemičitých skel vodnými roztoky uvedených organických sloučenin obecně. Výsledky podporují předpoklad, že u křemičitých skel dochází působením uvedených organických sloučenin v neutrálních a alkalických vodných roztocích ke vzniku rozpustné organické sloučeniny křemíku, což vede k urychlení rozpouštění skla.

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