

## Examination of universal microhardness of hard reaction layers resulting from reactions of organic polymers with container glass surfaces and their use for low-friction protective layers

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Clear, highly alkaline and wear-resistant hard reaction layers are formed by direct alkaline coupling of organic polymers with functional groups, particularly high-molecular polyols, to siliceous glass surfaces having container glass compositions. As compared with untreated glass these are characterized by an increased universal hardness and an excellent scratch resistance. Formation of these layers requires a highly alkaline reaction medium, e.g. 2% NaOH, 85°C, according to the conditions of the alkaline washing process of returnable beverage bottles in the bottling plants. It can be assumed that the formation of the reaction layer is associated with the formation of highly molecular ionic polymers with 5-coordinated silicon. Results of universal microhardness measurements of the hard reaction layers which were formed with aqueous polymer dispersions (epoxy resin microdispersion; low-molecular oxidized polyethylene) are presented. The increase of plastic universal hardness in comparison with untreated glass demonstrates the enhanced wear resistance of these layers. So far layer thicknesses up to 0.3 µm could be achieved. These results suggest new approaches to develop highly efficient low-friction protective layers for returnable bottles, and after increasing the thickness of the hard reaction layer up to several micrometers, they could possibly be applied also to lightweight bottles under enhanced internal pressure as used for carbonated beverages. Universal microhardness measurements are a very useful tool in the development and most effective improvement of such novel low-friction protective coatings for container glass.

### Untersuchung der Universalmikrohärte harter Reaktionsschichten als Ergebnis von Reaktionen organischer Polymere mit Behälterglasoberflächen und ihre Anwendung für Gleitschutzschichten

Durch direkte alkalische Kopplung organischer Polymere mit funktionellen Gruppen, insbesondere hochmolekularer organischer Polyole, an silicatische Glasoberflächen mit Behälterglaszusammensetzung, bilden sich klare, hochalkalibeständige, verschleißfeste harte Reaktionsschichten, die gegenüber Glas eine erhöhte Universalmikrohärte und hervorragende Kratzfestigkeiten aufweisen. Zur Ausbildung dieser Schichten ist ein hochalkalisches Reaktionsmedium erforderlich, z.B. 2% NaOH, 85°C, entsprechend den Bedingungen der alkalischen Wäsche für Getränke-Mehrwegflaschen in Abfüllanlagen. Es wird vermutet, daß die Reaktionsschichtbildung unter Ausbildung hochmolekularer ionischer Polymere mit 5fach koordiniertem Silicium erfolgt. Es werden die Ergebnisse von Universalmikrohärteuntersuchungen an harten Reaktionsschichten vorgestellt, die mit wäßrigen Polymerdispersionen (Epoxidharz-Mikrodispersion; niedermolekulares, oxidiertes Polyethylen) abgeschieden wurden. Die Erhöhung der plastischen Universalmikrohärte gegenüber unbeschichtetem Glas demonstriert die erhöhte Verschleißfestigkeit dieser Schichten. Bisher konnten Schichtdicken bis zu 0,3 µm erreicht werden. Die Ergebnisse eröffnen neue Lösungswege zur Entwicklung hocheffizienter Gleitschutzschichten für Mehrwegflaschen. Bei Erhöhung der Schichtdicke auf einige Mikrometer werden möglicherweise auch Anwendungen für Leichtgewichtsflaschen interessant, die die bei karbonisierten Getränken unter erhöhtem Innendruck stehen. Universalmikrohärteuntersuchungen sind ein hervorragendes Hilfsmittel bei der Entwicklung und Optimierung solcher neuartigen Gleitschutzschichten für Behälterglas.

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### 1. Introduction

The use of lightweight glass containers with increased internal pressure for carbonated beverages is possible only if they are provided with low-friction protective layers of high efficiency. These layers are capable of preventing defects in practical use in order to minimize the

consumer's risk of premature bottle breaking. If economic reasons demand a reduction of the layer thickness to < 10 µm, layers having a considerably higher hardness and wear resistance in addition to a sufficiently low coefficient of friction become necessary, which could not be achieved with polymer layers under normal conditions. Using returnable bottles for which greatest possible weight reductions are also desirable, such layers further must have a high resistance against alkalis.

In an AiF research project [1] the possible use of organophosphonic acids as adhesion promoter for polymeric coatings was investigated and the fundamentals for a subsequent technological process development of

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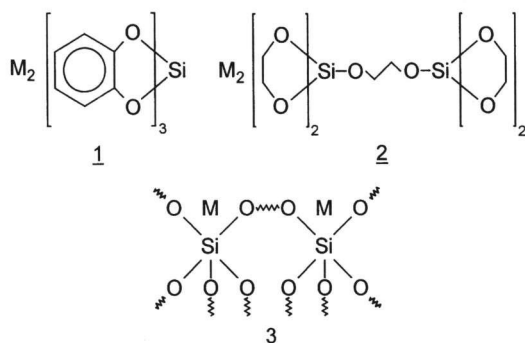
low-friction protective container glass coatings with high alkali resistance were created, now allowing a multiple bottle circulation including alkaline washing processes. Thus, it was shown that organic polymers with suitable functional groups, particularly high-molecular polyols, have the surprising capability of forming hard, wear-resistant reaction layers with an increased microhardness as compared with the original glass surface when treated in high-alkaline reaction media even without phosphonic acid adhesion promoters. This opens an entirely new access to resolve the problem of providing also lightweight containers with efficient protective coatings.

This paper discusses first results of investigations of universal microhardness of these hard reaction layers which were conducted to obtain data on mechanical properties and layer thickness. Particularly such information as gathered on elastic and permanent deformations in the course of these investigations result in conclusions which are of interest for the wear resistance assessment.

## 2. Fundamentals

### 2.1. Chemical background

Previous papers already dealt with the direct reaction of  $\text{SiO}_2$  with a coordinating ligand, e.g. silica, sand, or quartz with catechol (1,2-dihydroxy benzene) in alkaline reaction media under formation of the chemically highly resistant hexa-coordinated tris-(catecolato)-silicate 1 [2]. It was later found that an analogous reaction of sand, NaOH and ethylene glycol results in a higher-molecular, predominantly five-coordinated glycolato silicate 2 [3 to 6], which is considerably more reactive than 1. By exchanging the glycol ligands with higher-molecular diols (e.g. polyethylene glycols) high-molecular ionic polymers 3 can be obtained from 2 [5 and 6]. These compounds open up new aspects of synthesis chemistry for processing of novel, even higher-molecular organosilicates with increased coordination number of silicon.



Explanation: M = alkali metal (lithium, sodium, potassium, cesium); HO—OH: higher-molecular polyols, e.g. tetraethylene glycol, polyethylene glycol.

### 2.2. Scratch resistance

Measuring the scratch resistance is an important practical test carried out by the container glass industry to

determine the effectiveness of low-friction protective coatings on container glass. When performed on coated glass rods, it is carried out conforming to the scratch tester of the American Glass Research Inc., Butler, PA (USA), for glass bottles. For this purpose a measuring device was constructed with two glass rods arranged one above the other in a right angle with respect to each other. The glass rod attached to the lower motor-driven support is slowly moved at a steady speed against the bottom side of the stationary second glass rod fastened above it with mountable weights allowing for variable adjustment of the friction load on the rods between 0 and 48 N. When applying equal loads, the friction load exerted on the rods is considerably higher as compared to the bottles. Thus, the measured scratch resistance values of rods  $P_r$  and bottles  $P_b$  cannot be directly compared. According to [7] the approximation

$$P_b/P_r = R_b/R_r \approx 13 \quad (1)$$

is to be applied based on radii of  $R_b = 32.5$  mm and  $R_r = 2.5$  mm. To compare with the scratch behavior of cleaned uncoated glass surfaces, glass rods have been prepared by tempering at  $500^\circ\text{C}$  to remove all adsorbed organic contaminants liable to reduce friction. On these cleaned surfaces a first trace of scratch marks is clearly visible with the naked eye after loading with about 0.4 N. These scratch marks consist of many individual linear defects aligned at an angle of  $45^\circ$  to the direction of rod movement. It is postulated that the conventional layer system  $\text{SnO}_2$ /low-molecular oxidized polyethylene still predominantly used in the container glass industry does only allow the occurrence of initial defects visible to the naked eye within the area of contact on the "scratch marks" subjecting the bottles with a load of  $>250$  N ( $\approx 19$  N on glass rods).

### 2.3. Universal microhardness

Hardness measurements serve to characterize the mechanical behavior of material surfaces or coatings by characteristic values. Their application to assess the protective properties of thicker polymer layers in the range of 15 to 40  $\mu\text{m}$  on glass substrates has already been published, however in the load range  $> 100$  N [8].

Universal microhardness measurements are increasingly used for low indentation depth, e.g. when investigating hard coatings of approximately 1  $\mu\text{m}$  thickness [9 to 12]. Despite the different meaning of this universal microhardness, HU, in the physical sense still untenable formal conversions to the conventional Vickers hardness can be found even in the more recent literature [13]. Therefore, a short explanation of the various characteristic values and their mode of determination shall be given.

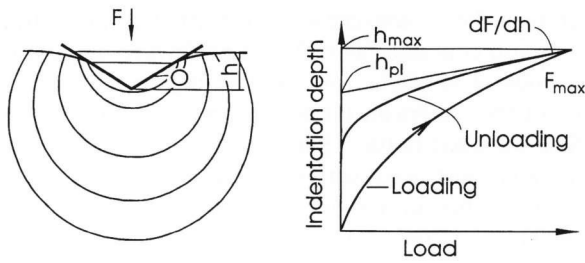


Figure 1. Schematic deformation profile beneath the Vickers pyramid and evaluation of the indentation curve as a function of load.

In measuring the universal microhardness [9] the movement of a mostly square Vickers pyramid is measured during a stepwise loading by force  $F$ . The indentation depth  $h$  gives a fictitious indentation area  $O$  based on the geometric pattern of the pyramid so that the value of the universal hardness  $HU$

$$HU = F/(c \cdot h^2) \tag{2}$$

is obtained with the form factor of the Vickers pyramid  $c = 26.43$  (figure 1). Since the indentation depth under load includes not only permanent plastic deformation but also portions of elastic deformation,  $HU$  therefore is a measure for both the inelastic and the elastic resistance of the material. Using the increase of force exerted in one experiment, the hardness as a function of indentation depth can be recorded.

Information on the elastic behavior within the range of maximum load is obtained by additional measurement of the indentation depth during unloading according to Loubet et al. [14]. For this purpose the slope of the unloading curve  $h = f(F)$  at maximum force  $(dh/dF)_{F_{max}}$  is determined. Then the value of the inelastic plastic indentation depth  $h_{pl}$  is calculated by subtraction of its elastic portion as a linear extrapolation of the apex of the unloading curve to  $F = 0$  (figure 1):

$$h_{pl} = h_{max} - F_{max} \cdot (dh/dF)_{F_{max}} \tag{3}$$

From that and considering the Poisson constant  $\nu$  a value for the elastic modulus  $E_{HU}$  can be deduced:

$$E_{HU} \equiv \frac{(1 - \nu^2) \cdot \sqrt{\pi}}{9.9 \cdot h_{pl} \cdot \left(\frac{dh}{dF}\right)_{F_{max}}} \tag{4}$$

For the maximum force from the computed plastic indentation depth  $h_{pl}$  a plastic universal hardness  $HU_{pl}$  is defined in analogy to equation (2):

$$HU_{pl} = F/(c \cdot h_{pl}^2) \tag{5}$$

It represents the resistance against permanent deformation by the indenter. By its content it corresponds to the conventional Vickers hardness.

### 2.3.1. Tip correction for low indentation depths

Deviation of the real pyramid tip from the ideal geometric form results in apparently increased values of the universal microhardness in the case of low indentation depths below  $3 \mu m$  [9 and 10]. Therefore, instead of  $h$  a corrected indentation depth  $h_{corr}$  is used for all computations in the formulas (2 to 5) [15] which is specific for the used device and depending on the measured indentation depth  $h$ :

$$h_{corr} = h^2 \cdot (1 + a \cdot h^b) \tag{6}$$

It takes into account the actually effective area of the indenter with the parameters  $a$  and  $b$ , which are experimentally adapted from measurements on homogeneous materials.

Despite the tip correction additional effects and irregularities (summarized as Indentation Size Effect (ISE)) occur in the initial range of the indentation depth  $< 0.1 \mu m$ , e.g. the influence of the surface roughness, local structural irregularities of the examined materials, a changed indentation mechanism of the actually rounded tip, but also systematic errors in the automatically predetermined zero point of indentation depth. As a consequence, the absolute hardness values in this initial range can no longer be compared with values obtained from greater indentation depths. However, characteristic values obtained with the same measuring device and the same indenter under identical conditions are comparable to those of other samples as far as identical indentation depths are concerned.

### 2.3.2. Application to coated materials

According to the rule of Bückle [10] correct hardness data of coatings can only be obtained if the indentation depth is less than  $1/10$  of the coating thickness. It means, a deformation zone approximately ten times the indentation depth develops in the material in front of the indenter (figure 1). Investigating materials with a gradient of hardness in the surface area the universal microhardness changes as a function of indentation depth. Considering the deformation zone as origin of the indentation information all derived values have always to be discussed as integral information from the entire zone – an inverse application of the well-known rule of Bückle.

A more subtle representation of the hardness modification with the indentation depth is achieved by differential evaluation of the indentation curve. In this case the relation of  $h = f(\sqrt{F})$  has proven to be of particular advantage. From the derivative  $dh/d\sqrt{F}$  a differential universal hardness  $HU_{diff}$

$$HU_{diff} \equiv \frac{1}{c} \cdot \left(\frac{dh}{d\sqrt{F}}\right)^{-2} \tag{7}$$

is defined which approaches the value of  $HU$  for homogeneous materials. It is also described in the manual and

the firmware of the measuring device of Fischer [15]. Because  $HU_{diff}$  is influenced by the differential change of distance  $dh$  only, errors resulting from measuring the indentation at lower loads, especially at the zero point, are suppressed or at least considerably reduced by using the non-linear correction according to equation (6).

Examining a homogeneous coating on a substrate as a function of the indentation depth  $h$ , the value of  $HU$  initially corresponds with the universal hardness of the coating. Exceeding a defined indentation depth of approximately  $1/10$  of coating thickness  $d$ ,  $HU$  as an integral term gradually begins to approach the hardness value of the substrate (see curves in [9 and 10]). In contrast thereto the differential hardness  $HU_{diff}$  at this point ( $\approx 1/10 \cdot d$ ) already undergoes an almost abrupt change. At least qualitatively, this differential change of hardness can be correlated to the beginning permeation of the deformation zone into the substrate at a depth of  $10 \cdot h$ , corresponding to the inversion of the rule of Bückle.

### 3. Experimental

#### 3.1. Sample material, polymeric dispersions used

Almost in all investigations, including the examination of universal microhardness, glass rods (diameter 4.3 to 5.0 mm) composed of two different container glass compositions, which were melted from bottle fragments in an inductively heated platinum crucible, were used (table 1). Glass type II conforms with the glass compositions presently used in the container glass industry and is less reactive than glass type I. For the majority of the microhardness examinations the samples were subjected to a corroding pretreatment in 2% NaOH at 85°C, for 1 h, in order to increase the reaction rate with the polymers and to improve polymeric adhesion. Out of the examined functionalized polymers and lubricants two polymeric dispersions were especially suitable to obtain hard, wear-resistant reaction layers on which the microhardness measurements were performed:

= Low-molecular, partially oxidized polyethylen (PE) TEGOGLAS RT 40 TL (Th. Goldschmidt AG, Essen (Germany)) is an aqueous PE dispersion having a solid content of approximately 23% which contains reactive groups ( $\equiv\text{COH}$ ;  $\text{COOH}$ ) and can be diluted arbitrarily down to the desired concentration for use. While performing the alkaline treatments it was found helpful to improve the PE adhesion to the glass surface by applying a thin layer of the  $\text{NH}_4$  salt of the phosphonic acid adhesion promoter 4 [CH<sub>3</sub>(CH<sub>2</sub>)<sub>19</sub>N(CH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>)<sub>2</sub>] using the dipping process prior to spray coating the PE [1]. In the samples no. 3 and 6 in table 2 the reaction with PE could also be achieved directly with a 2% NaOH solution to which 1.4% TEGOGLAS (solid content) was added.

= Epoxy resin microdispersion [16]

The dispersion was partly synthesized following the method described in [16] in collaboration with Hoechst

Table 1. Chemical composition (in wt%) of the used white glass types

	glass type I	glass type II
SiO <sub>2</sub>	71.95	71.68
Na <sub>2</sub> O	14.99	13.11
CaO	11.07	9.89
Al <sub>2</sub> O <sub>3</sub>	0.76	1.61
MgO	0.75	2.68
SO <sub>3</sub>	0.49	0.12
K <sub>2</sub> O	0.12	0.50
BaO	0.05	0.08
Fe <sub>2</sub> O <sub>3</sub>	0.076	0.071
$T_g$	552°C	562°C (calculated)

AG, Werk Kalle-Albert, Wiesbaden (Germany), because epoxy dispersions available on the market can not be diluted down to the required concentration of about 2% solid content. As shown in table 3, a certain quantity of polyoxypropyleneamine (JEFFAMINE M 2005, Texaco Inc., Houston, TX (USA)) serving as reactive lubricant is added to the two components consisting of a higher-molecular epoxy-amine adduct and a lower-molecular epoxy resin as hardener. Components A and B were mixed together in the molar ratio 1:3, e.g. only  $1/3$  of the amine adduct necessary for the complete reaction with the epoxy resin was used, so that a sufficient concentration of reactive  $\equiv\text{C}-\text{OH}$  groups (generated from epoxy groups by alkaline hydrolysis) is present.

The polymer coating was applied by spraying.

#### 3.2. Formation of the hard reaction layers

The formation of the hard reaction layers was achieved through treatment in highly alkaline solutions (2% NaOH, 85°C, >30 min) according to the conditions of the alkaline washing process in the bottling plants. The applied polymer layer of approximately 1  $\mu\text{m}$  thickness sometimes fails to undergo a complete reaction with the glass surface with the result that the hard reaction layer having formed after the alkaline treatment is often covered with a more or less soft unreacted polymer layer. Prior to the microhardness measurements this was removed from the hard reaction layer without damaging it. For performance of the microhardness investigations the samples were prepared as follows (table 2):

Sample no. 1: glass type II, untreated, not annealed (annealing did not result in a significant change of microhardness).

Sample no. 2: glass type II, epoxy resin. The glass rods were subjected to a corrosive pretreatment with NaOH and subsequently sprayed with the epoxy resin dispersion until a coherent coating was obtained. After hardening at 140°C, 1 h, a final alkaline treatment with 2% NaOH, 85°C, 2 h, was performed.



Table 2. Universal microhardness investigations: mechanical parameters of hard reaction layers with polymers on glass surfaces with container glass compositions (maximum load 10 mN)

sample no.:	1	2	3	4	5	6	7
glass type:	II	II	II	II	II	I	I
treatment:	untreated	epoxy resin	NaOH/PE	PE, without <u>4</u>	PE, with <u>4</u>	NaOH/PE	PE, with <u>4</u>
indentation depth <i>h</i> in $\mu\text{m}$ :	$0.196 \pm 0.004$	$0.164 \pm 0.007$	$0.170 \pm 0.008$	$0.189 \pm 0.011$	$0.196 \pm 0.003$	$0.182 \pm 0.010$	$0.149 \pm 0.007$
universal hardness HU in GPa:	$4.24 \pm 0.13$	$5.55 \pm 0.38$	$5.24 \pm 0.39$	$4.46 \pm 0.39$	$4.21 \pm 0.10$	$4.75 \pm 0.42$	$6.43 \pm 0.48$
plastic universal hardness HU <sub>p</sub> in GPa:	$12.8 \pm 0.3$	$24.5 \pm 1.7$	$19.4 \pm 1.7$	$15.3 \pm 0.9$	$12.9 \pm 0.3$	$16.2 \pm 0.9$	$37.5 \pm 3.2$
elastic modulus $E/(1 - \nu^2)$ in GPa:	$88 \pm 2$	$115 \pm 6$	$109 \pm 8$	$91 \pm 4$	$87 \pm 2$	$98 \pm 4$	$141 \pm 7$

Table 3. Composition (in g) of the epoxy resin microdispersion

composition of component A	component B	final composition
20.00 epoxy amine adduct (mol. weight 3320)	12.30 EPON 828, epoxy equivalent weight 190	5.10 component A
5.00 ethylene glycol monobutyl ether	85.10 ethylene glycol monobutyl ether	7.97 component B
1.94 propionic acid	0.87 $\gamma$ -glycidoxypropyltrimethoxy silane	0.42 JEFFAMINE M 2005
1.47 formic acid	1.74 ACROPAL N 060 (emulgator)	86.51 water
71.59 water		
100.00	100.01	100.00

Sample no. 3: glass type II, NaOH/PE. Glass rods pretreated with NaOH were sprayed with a diluted TEGOGLAS dispersion and then after drying at 130°C treated in an alkaline PE dispersion (2% NaOH, 1.4% solid content PE, 3 h) at 85°C. The sprayed-on PE layer remained completely intact.

Sample no. 4: glass type II, PE, without 4. Glass rods pretreated with NaOH were sprayed with a diluted TEGOGLAS dispersion and then treated with 2% NaOH, 85°C, 2 h.

Sample no. 5: glass type II, PE, with 4. same as sample no. 4, however, with additional application of a thin phosphonic acid adhesion promoter 4 prior to the PE spraying process.

Sample no. 6: glass type I, NaOH/PE. Glass rods pretreated with NaOH were treated for 3 h only in the alkaline PE dispersion. After completing the reaction no adherent unreacted PE layer remained (treatment in conformity with sample no. 3, however, without PE spraying).

Sample no. 7: glass type I, PE, with 4. Treatment same as sample no. 5.

A qualitative assessment of the formed hard reaction layers mainly was made with a stereoscopic microscope which allows a fairly good evaluation of topography and approximate layer thickness under suitable illumination utilizing an oblique angle of incidence and resulting shadow effects. Until now it was not possible, however, to find an adequate routine procedure for quantitatively measuring the layer thickness. In connection with investigations to determine bursting pressure resistance, a test sample was cut from the cylinder wall of a 0.33 l soft drink bottle that had previously been coated with epoxy resin as in sample no. 2 (table 2), and a layer thickness of approximately 0.3  $\mu\text{m}$  of the hard reaction layer was then measured with a profilometer (Tencor Instruments, Mountain View, CA (USA)) at the marginal steps of "windows" engraved in its polymeric layer before the alkaline treatment. These steps were clearly visible under the stereoscopic microscope and corresponded with the maximum layer thickness so far obtained. Even investigations conducted with a scanning electron microscope failed to provide information on the layer thickness because of the absence of distinct phase transitions between glass and reaction layer on the fracture surfaces.

Only deviations on the fracture lines occurring in the immediate superficial area might possibly indicate deviating fracture behavior in the reaction layer.

### 3.3. Experimental measuring conditions of the universal microhardness investigations

All investigations were made with the microprocessor-controlled universal hardness measuring device Fischer-scope H 100 (Fischer, Sindelfingen (Germany)).

The loading process was carried out in 30 steps from 0.4 to 10 mN (for comparative measurements to 1000 mN) which were equidistant in the scale of the square root of the load with intervals of 5 s between the individual steps of increasing load. After 10 s at constant end load the unloading followed by reversing the sequence of the loading steps.

Prior to every further measurement the indenter was cleaned by indentation in a Piacryl plate.

## 4. Results and discussion

Investigations of universal microhardness and scratch resistance were carried out on samples no. 1 to 7 (table 2) as described in sections 2.2 and 3.2.

Determination of the scratch resistance yielded results which were considerably better than those postulated for the conventional layer system SnO<sub>2</sub>/low-molecular oxidized polyethylene (see section 2.2.). Up to the extreme load of 48 N ( $\approx 625$  N on bottles) none of the examined coating systems (samples no. 2 to 7) exhibited any defects on the scratch traces even under microscopic examination and after repeated alkaline treatments meeting the conditions of alkaline washing of returnable bottles in the bottling plants (2% NaOH, 85°C, 30 min).

### 4.1. Universal microhardness investigations

The results of universal microhardness measurements under maximum load are listed in table 2. The average indentation depth under a load of 10 mN is 0.19  $\mu\text{m}$ , with sample no. 7 it is only 0.15  $\mu\text{m}$ . As an effect of the surface treatment the corrected universal microhardness HU, obtained as an average value of at least five individual series of measurements, shows a significant increase in samples no. 2, 3, and 6, and particularly no. 7, less pronounced in sample no. 4, and not in sample no. 5. Figure 2 shows the variation of HU relative to the indentation depth in samples no. 1, 2, 3, and 6. With increasing indentation depth the universal microhardness of samples no. 2 and 3, being in the immediate surface area almost twice as high, approaches the HU value for untreated glass. Figure 3 demonstrates the extremely high increase of HU up to about 15 GPa in the immediate surface area as found in sample no. 7. In these samples the greatest increase has been observed for the plastic hardness HU<sub>pl</sub> (table 2). The derived modulus of elasticity, as a measure of the reversible elastic defor-

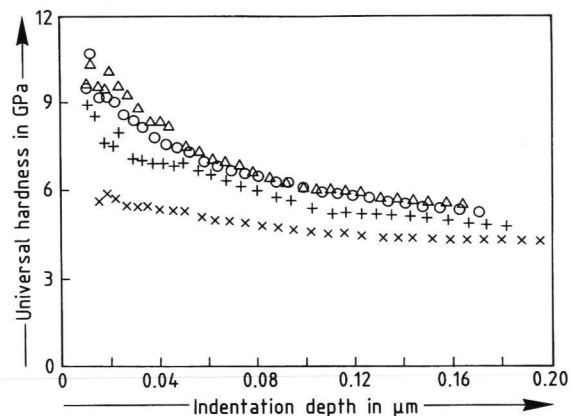


Figure 2. Universal microhardness HU as a function of indentation depth for samples no. 1 ( $\times$ ), no. 2 ( $\Delta$ ), no. 3 ( $\circ$ ) (glass type II), and no. 6 ( $+$ ) (glass type I).

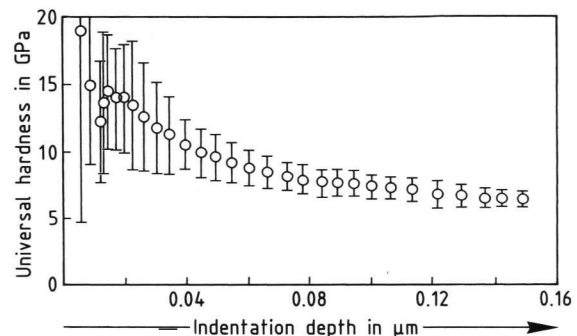


Figure 3. Universal microhardness HU as a function of indentation depth for sample no. 7 (glass type I). The marked bars represent the standard deviations.

mation behavior, also shows an increase, but to a lesser degree. Again the greatest increase is seen in sample no. 7.

For characterizing the wear resistance of a protective layer for practical applications, not only the defect or crack initiation but also the resistance against surface destruction by a loaded hard apex is assumed to be an additional characteristic value. From all deduced parameters of the microhardness investigations the plastic universal hardness HU<sub>pl</sub> represents the reciprocal value of permanent surface destruction in relation to the load and should be suitable for characterizing such wear resistance changes of the surface. The HU<sub>pl</sub> values in table 2 are presented graphically in figure 4 for the samples no. 2, 3 and 6 in comparison with the untreated glass. The standard deviations are depicted in the columns. They demonstrate a marked improvement of the plastic universal hardness by factors 1.3 to 1.9 according to the type of coating under a load of 10 mN. With sample no. 7 (not shown in figure 4) HU<sub>pl</sub> achieving a value of 37.5 GPa is even considerably higher. With increasing loads the protective effect decreases and can be neglected at 1 N (indentation depth

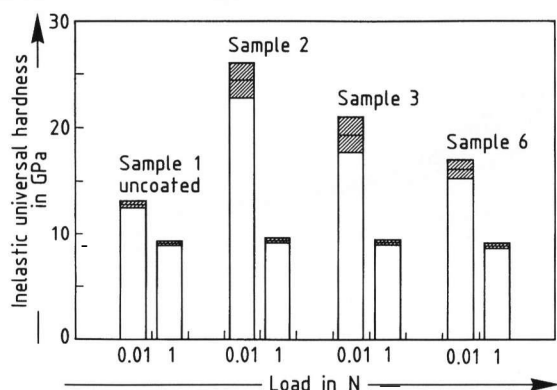


Figure 4. Plastic (inelastic) universal hardness  $H_{U_{pl}}$  for samples no. 2, 3 (glass type II), and no. 6 (glass type I) as compared with untreated glass (glass type II) at maximum loads of 0.01 and 1 N. Hatched regions of the bars show the standard deviation (table 2).

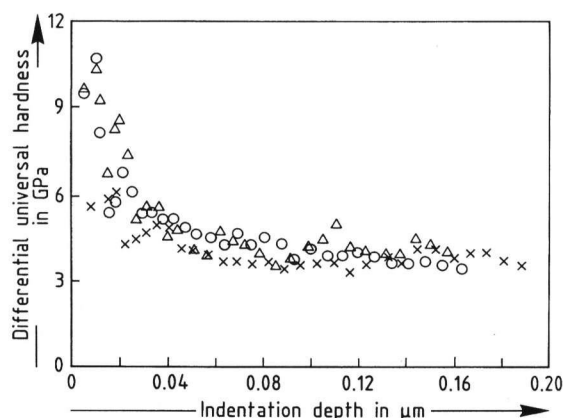


Figure 5. Differential universal hardness  $H_{U_{diff}}$  as a function of indentation depth for samples no. 1 (x), no. 2 (Δ), and no. 3 (O) of glass type II.

approximately  $3\ \mu\text{m}$ , as shown in figure 4 for comparison). It should be noted that in this load range a sharply ground diamond pyramid is, in a general view, suitable to differentiate even extremely hard surfaces. However, the more blunt and softer objects in practical applications create much lower stress at the same load, so that a coated surface will resist much higher loads as compared to evaluation by microhardness measurement.

An increased variation of the individual series of measurements was obtained in the coated samples no. 2, 3, 4, 6 and 7. A closer examination reveals that this apparently results from an alternation of softer and harder areas in the layer. Concerning sample no. 4 (no adhesion promoter 4) the increase of variation, however, is not associated with an increase of the universal hardness. This could be caused by the possibility that the areas of lower hardness have a degree of universal hardness below that of the hardness of the untreated glass (structural changes of the glass surface may be due to NaOH pretreatment). In comparison, the variation in

sample no. 5 is low. Therefore, it is to be assumed that the phosphonic acid adhesion promoter 4 facilitates a more homogeneous formation of the reaction layer with PE, without inducing greater increases in hardness.

Sample no. 7 (glass type I, treatment exactly the same as in sample no. 5) exhibits some peculiarities inasmuch as inconsistencies are found in the load curves showing a significantly higher variation and a considerably higher plastic universal hardness  $H_{U_{pl}} = 37.5 \pm 3.2\ \text{GPa}$ , the causes of which require clarification through additional investigations. This deviant result in connection with the increased portion of elastic deformation energy demonstrates the different reaction behavior of the more reactive glass type I in contrast to glass type II. This has been corroborated by results of parallel investigations with other coating systems showing that glass type I in general yields higher scratch and better wear resistance properties of the hard reaction layers as compared with the glass type II.

For a better evaluation of the depth extension of the harder layer the differential universal hardness  $H_{U_{diff}}$  in figure 5 is used. In comparison with the untreated glass the values for samples no. 2 and 3 are considerably increased in the range of an indentation depth up to  $30\ \text{nm}$  only. According to the concept of the deformation zone extension this results in a dimension of the harder layer of approximately  $0.3\ \mu\text{m}$ , which is in agreement with the results of profilometer measurements and the microscopic evaluations.

#### 4.2. Reaction mechanism of polymer coupling

In the course of the experiments the coupling of functionalized polymers or other higher-molecular compounds with container glass surfaces could be shown not only for the described epoxy resin and the low-molecular, partially oxidized polyethylene (PE) but also for a variety of other substances, such as waxes with functionalized groups, polyethylene glycol, and polyoxyalkyleneamines. While the reaction layers formed by means of polyalkoxylized substances have so far proven too brittle and insufficiently wear-resistant, excellent layer properties having a high degree of wear resistance could now be obtained with epoxy resin and PE resulting in excellent scratch resistance and increased universal microhardness. It can be assumed that the formation of this reaction layer on the glass surface associated with the formation of high-molecular ionic polymers according to 3 with 5-coordinated silicon also takes place in the reaction with high-molecular polyols like oxidized polyethylene or other OH-functionalized polymers, provided a sufficient concentration of reactive groups is present (section 2.1.). Until now no information with regard to such reactions could be found in the literature. At this time no explanation can be offered concerning the reaction mechanism for the coupling of polyoxyalkyleneamines. It is possible that reactive

$\equiv\text{C}-\text{OH}$  groups are formed through cracking of the polyether backbone in the high-alkaline reaction medium.

## 5. Summary of results

The results of microhardness investigations as presented here were derived from first attempts to obtain information on the mechanical properties and thickness of the hard reaction layers which are formed by direct alkaline coupling of organic polymers with functional groups (particularly high-molecular polyols).

A quantitative assessment of the mechanical behavior of these layers can be made by using the universal microhardness, especially the plastic universal microhardness. Surprisingly these investigations resulted in the fact that depending on the treatment parameters in the examined coated samples (except for sample no. 5) marked increases in the universal microhardness, particularly in the plastic universal microhardness (reduction of the plastic component of the deformation behavior) could be found, as compared to the untreated glass.

An increased variation of the characteristic mechanical values of the coated samples except for sample no. 5 (PE with adhesion promoter 4) suggests that reaction layers with areas of varying hardness had formed which are associated with inhomogeneities or locally varying layer thicknesses and are visible also in microscopical examination of the layers. Partly these irregularities are originated already in the spraying process.

The high values of universal microhardness, and in particular the plastic universal hardness in sample no. 7 (glass type I), are connected with the higher chemical reactivity of glass type I as compared to glass type II. The achievable hardness values depend on the glass composition, the used type of polymers, and the reaction conditions in an interrelationship which cannot be explained at this time.

Use of phosphonic acid adhesion promoter 4 in sample no. 5 seems to facilitate the formation of a more homogeneous reaction layer with PE which, however, is not combined with an increase of universal microhardness.

The layer of increased hardness of approximately  $0.3\ \mu\text{m}$  thickness resulting from the curve of differential microhardness is in agreement with the results obtained by profilometer measurements and evaluation of microscopic examinations.

The plastic universal hardness is of importance for characterizing the wear resistance of a layer. High  $\text{HU}_{\text{pl}}$  values stand for high resistance against permanent deformations under mechanical load. Apart from this other layer parameters (e.g. layer thickness, friction coefficient, surface roughness, crack initiation resistance) are also of great importance with regard to the wear resistance in practice and for changes of the mechanical strength under load.

These initial results point out that the universal microhardness investigation can serve as a very useful method for characterizing the mechanical properties of hard reaction layers on glass and as an important aid to optimize its wear resistance. Additionally it provides information on the inhomogeneity of layers through evaluation of the standard deviations. Performing such examinations, however, requires great precision in carrying out the measurements and in the sample preparation to ensure that exactly defined reaction layers are formed. For more extensive information, particularly in the sub-micrometer range, further methodical and theoretical work regarding the mechanism of the damaging process is necessary.

## 6. Final conclusions for practical applications

Highly alkaline and wear-resistant hard reaction layers are formed by direct alkaline coupling of two examined organic polymers with functional groups on reactive container glass surfaces. This results in excellent scratch resistance. Optimizing the wear resistance in such polymer layer systems, they become most suitable for the development of highly efficient low-friction protective layers for returnable bottles because the layer thickness increases with increasing duration of the alkaline washing process while the high degree of scratch resistance is maintained. The method elaborated in this context should allow further developing these layer properties with the goal to ultimately satisfy even extreme requirements that have to be met by efficient low-friction protective layers for lightweight bottles. In addition to creating an optimum degree of wear resistance of the whole layer system, this would also necessitate to increase the thickness of the hard reaction layer underneath up to a few micrometers which can be achieved by various procedures. Application of a multiple layer system (approximately  $10\ \mu\text{m}$ ) consisting of a basic layer of reactive polymers with functional groups to form the hard reaction layer and a secondary protective coating of a highly alkali and wear-resistant polymer is similarly conceivable. Considerable improvement of polymer adhesion in the initial phase of alkaline coupling with the glass surface can be achieved by use of organophosphonic acid adhesion promoters [1].

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