ÎMBUNĂTĂȚIREA PROPRIETĂȚILOR FIZICE ŞI CHIMICE ALE PRODUSELOR RECOAPTE CAVE DIN STICLĂ, DEPOZITATE SAU AFLATE ÎN UZ▲

INCREASING PHYSICAL AND CHEMICAL PROPERTIES OF ANNEALED HOLLOW GLASSWARE AS WELL AS OF THOSE STORED AND USED

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The results of experiments on improving the chemical stability of various types of annealed commercial glassware (i.e., after their manufacture) as well as of those stored and used are analyzed and integrated. The main points of the technique developed are as follows. A fixed quantity of the reagent is introduced into the glassware at room temperature, followed by heat treatment, during which the glass surface is leached out. For the investigation, a variety of hollow glassware was used: containers (bottles, flasks, jars, etc.) from decolorized, green and brown glasses, laboratory and assorted glassware, ampoules made from medical glass, illuminating glassware made from transparent colorless and milk glasses etc. The glass surface was leached with sulfur dioxide, hydrogen chloride and fluoride, difluorodichloromethane, difluoro-chloromethane, and mixtures of gases. The reagents were fed into the glassware mainly in the gaseous state and in the form of solutions and solid substances. Thermochemical treatment of annealed hollow glassware by reagents gases was found to improve the water and acid resistance of glass by one-two orders of magnitude, mechanical strength – by 30 % thermostability and microhardness increased by 10 %.

Se analizează şi se generalizează rezultatele experimentelor pentru îmbunătățirea stabilității chimice a diferitor tipuri de produse recoapte din sticlă (adică după fasonarea lor) şi celor deja aflate la păstrare şi exploatare. Esența procedeului elaborat constă în următoarele: în interiorul produsului la temperatura camerei se introduce o anumită cantitate de reagent, apoi are loc tratamentul termic, în timpul căruia suprafața sticlei se dezalcalinizează. În cercetări au fost folosite diferite tipuri de produse cave din sticlă: ambalaj (butelii, flacoane, borcane etc.) din sticlă incoloră, verde-închis şi brună, vase de laborator şi de menaj, fiole din sticlă medicinală, difuzoare din sticlă incoloră transparentă şi opacă placată. Suprafața sticlei a fost dezalcalinizată cu oxid de sulf, fluorură şi clorură de hidrogen, difluordiclormetan, difluorclormetan şi amestecurile lor. Reagenții se introduc în produsele din sticlă, fie în stare gazoasă, fie apoasă sau solidă. Tratarea termochimică a produselor cave recoapte din sticlă cu reagenți gazoşi, sporeşte stabilitatea la apă şi acizi a sticlei cu 1-2 ordine, rezistența mecanică – cu 30 %, stabilitatea termică şi microduritatea - cu 10 %.

***Keywords:** hollow glassware, surface layer, gas reagent, dealkalization, water resistance*

1. Introduction

Thermochemical treatment by acid gases, which takes place during the process of glassware production, is a simple method to improve the physical and chemical properties of glass [1-3]. For this purpose the glass surface is blown with reagents during the glassware founding stage or immediately thereafter, more rarely during annealing. In certain cases, for various reasons (disruption of the production technology, bad storage and operation, etc.), the chemical stability of glass does not meet its standards [4], because of this entire batches of products are discarded.

The aim of the undertaken experiments was to investigate the effect of thermochemical treatment by gaseous reagents on physical and chemical properties of annealed hollow commercial glassware.

2. Experimental

Experiments were held in laboratory and industrial conditions. The subjects of investigation were various types of annealed hollow glassware (i.e., after their manufacturing) as well as of those stored and used: bottles, flasks and jars of colorless glass, bottles of green and brown glasses, laboratory and assorted glassware, ampoules made from medical glass, illuminating glassware made from transparent colorless and milk glasses etc. The chemical compositions of industrial glasses are given in Table 1.

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Table 1

Chemical compositions of industrial glasses
Compoziţiile chimice ale sticlelor industriale

Glassware *Produse din sticlă*	Weight content of oxides *Oxizi, partea de masă, %*								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Other
Laboratory *Laborator*	80.19	2.32	0.08	0.60	-	3.62	-	-	13.35 B_2O_3
Colorless container *Ambalaj incolor*	71.81	2.55	0.07	6.53	4.63	13.94	-	0.34	-
Bottles of green *Butelii verzi*	68.24	4.92	1.48	6.20	3.95	14.57	0.43	0.29	-
Colorless ampoules *Fiole incolore*	72.81	4.52	0.05	6.05	0.82	8.15	1.64	-	6.11 B_2O_3
Colorless scatterers *Difuzoare incolore*	73.02	1.92	0.04	6.85	-	16.58	1.17	0.29	-
Milk scatterers *Difuzoare lăptoase*	66.96	7.02	0.04	3.74	-	13.71	4.11	0.27	4.23 F^-

Sulfur oxide, nitrogen oxide, carbon oxide, hydrogen fluoride and chloride, difluorodichloromethane, difluorochloromethane and mixture of these gases were used as gas reagents.

Thermochemical treatment in laboratory conditions was carried out in the following way: a fixed quantity of reagent is introduced into glassware at room temperature, followed by heat treatment, during which the glass surface is leached out. Regimes of treatment of glassware by reagents are the following: temperature – between 300 and 600 ^{0}C, duration – between 30 and 60 min, volume fraction of gas (gas volume vs. container capacity) between 0.1 and 100 %.

Thermochemical treatment in industrial conditions was carried out in the following conditions. A part of these experiments have been carried out at Glass-manufacturing plant (Chisinau, Republic of Moldova), where a number of jars and bottles are made using sectional glass-forming machines (IS-8-2, IS-6-2, AL-106-2) and rotor glass forming machines (BB-7, BB-12). Experiments were also carried out at Glass-manufacturing plants in the Ukraine and Russia. The main conditions of treatment of glassware by gaseous media are: glass temperature – between 500 and 800 °C; duration of reagent feed - 1 s; volume fraction of gas (gas volume vs. container capacity) between 0.1 and 100 %. Containers were treated in different places: conveyor for transportation of glassware towards annealing and lehr.

The reagents were fed into the glassware mainly in gaseous state and in the form of solutions and solid substances.

The following annealed hollow glassware properties were determined: chemical durability, mechanical strength, microhardness and thermostability.

Besides, the intensity of glass dealkalization by acid gases was estimated using the extraction rate of alkaline cations [3]:

$$\nu_{Me^+} = C_{Me^+} \cdot V \cdot S^{-1} \cdot \tau^{-1},$$

where ν_{Me^+} - dealkalization rate of Me^+ from glass by acid gases, μmol Me^+/dm^2 of glass surface;

C_{Me^+}- Me^+ concentration in solution after the washing of the bloom by distilled water, μmol Me^+/l;

V - solution volume, l;

S - sample surface, dm^2;

τ - treatment duration, min.

The majority of industrial glasses contain both Na^+ and K^+. So, separate rates ν_{Na^+} and ν_{K^+} as well as sum rate ν_{Me^+} were calculated [3].

The conditions for the thermochemical treatment with reagents were chosen on the basis of the chemical composition of the glass, type and configuration of the glassware. In no case was the maximum treatment temperature higher than the highest annealing temperature. The quantity of the reagent for one article was roughly calculated using the results of industrial experiments on the thermochemical treatment of newly molded glassware (in hot state) [3].

The research procedure was the following.

Glassware had been treated by active gases and then they were tested. There had not been taken any special precautionary measures with the treated glassware. The salient feature of the conducted experiments is the fact that to determine glass maintenance properties jars and bottles were selected from one and the same party.

It is well-known that thermochemical treatment by gases is the most effective for the improvement of chemical durability of glass [3]. As for bottles, there is a State Standard to determine water resistance. The average value of water resistance, measured for 5 bottles using the dealkalization of internal surface, was considered as the index of water resistance. The analysis of error didn't exceed 0.003 mg Na_2O.

Water resistance in laboratory conditions was determined in the following way: samples were washed by water after thermochemical treatment and boiled for 10 hours in distilled water and then losses of Na_2O were determined. Acid resistance was characterized by losses of glass mass at boiling it in 1 N H_2SO_4 for 10 hours.

The value of microhardness was measured by microhardnessmeter PMT-3M. The procedure of microhardness measuring was the following. Each sample was pricked by a diamond pyramid about 20 times. In order to obtain reproducible results the duration of loading on the pyramid was 10 s and duration of exposition to glass surface – 5 s for every measurement. The indentation length was measured twice. The load on the indenter of the diamond pyramid Vickers made 0.5 N. The relative error of determination of microhardness did not exceed ± 4 %.

Mechanical properties of glassware were characterized by resistance to internal hydrostatic pressure, resistance to the compression in the direction perpendicular to the body walls and microhardness. Mechanical strength of jars and bottles were characterized by value of internal hydrostatic pressure resistance. The pressure had risen until the glassware was broken. Absolute error of measuring of pressure didn't exceed ± 0.01 MPa. Not less than 10 glassware items were used for each treatment regime. Additionally, the jars were tested on the resistance of the compression in the directions both along and perpendicular to the body walls. Loading speed was 20 mm/min using the press UMM-5. The jars were located between support plates of press, the joint line being aligned always at the same position. The absolute error of measuring was ± 10 N.

Table 2

Water resistance of juice annealed bottles treated by gases
Rezistența la apă a buteliilor recoapte pentru sucuri, tratate cu reagenți gazoşi

Gas reagent *Reagent gazos*	Gas flow rate per bottle, ml *Consumul de gaz pentru o butelie,* ml	Volume part of gas, % *Partea de volum,* %	Water resistance, mg Na_2O *Stabilitatea la apă,* mg Na_2O	Type of dealkalizition bloom *Caracterul depunerii de dezalcalinizare*
-	-	-	0.120	no bloom / *lipsesc*
SO_2	0.1	0.02	0.116	no bloom
	0.2	0.04	0.112	no bloom
	0.5	0.1	0.085	trace/ *urme*
	1.0	0.2	0.070	trace
	2.0	0.4	0.053	trace
	5.0	1.0	0.040	intensive/ *intensiv*
	10.0	2.0	0.012	intensive
	50.0	10.0	0.000	intensive
	100.0	20.0	0.000	intensive
	500.0	100.0	0.000	intensive
NO_2	0.5	0.1	0.115	no bloom
	25.0	5.0	0.061	trace
CO_2	0.5	0.1	0.120	no bloom
	5.0	1.0	0.117	no bloom
	25.0	5.0	0.120	no bloom
	500.0	100.0	0.116	no bloom
HCl	0.5	0.1	0.051	trace
	5.0	1.0	0.006	intensive
	25.0	5.0	0.000	burnt/*strat ars*
HF	0.5	0.1	0.000	trace
	5.0	1.0	0.016	intensive
	25.0	5.0	0.020	burnt
CF_2Cl_2	0.1	0.02	0.122	no bloom
	0.25	0.05	0.119	no bloom
	0.5	0.1	0.105	no bloom
	1.0	0.2	0.065	no bloom
	2.0	0.4	0.021	trace
	5.0	1.0	0.003	trace
	10.0	2.0	0.000	intensive
	100.0	20.0	0.000	burnt
	500.0	100.0	0.000	burnt
CHF_2Cl	0.05	0.01	0.120	no bloom
	0.25	0.05	0.117	no bloom
	0.5	0.1	0.113	no bloom
	2.5	0.5	0.025	trace
	5.0	1.0	0.006	trace
CHF_2Cl + SO_2 (1:1)	0.25	0.25	0.072	trace
	0.5	0.5	0.054	trace
	5.0	5.0	0.000	intensive

The number of jars used for testing in one experiment was not less than 20. To obtain comparable results the jars were taken up from the same form of glass-forming machine.

Thermostability of glassware was determined by the following means. The glassware was heated in reservoir with hot water and then was carried into a bath with cold water. The temperature drop was increased till the destruction of the glassware. The temperature deviation in reservoir was not higher than ± 0.5 ^{0}C. Twelve glassware items from each lot were tested in the experiments.

Thermochemical treatment of glassware by active gases have been carried at six Glass-manufacturing plants. In most cases dealkalization bloom appeared on the internal surface of glassware after the thermochemical treatment.

As an example, let us examine the conditions of thermochemical treatment of 0.5 liter bottles, manufactured at the Chisinau Glass-manufacturing plant.

The chemical composition of colorless glass bottles and jars used to produce different assortment is as follows (%, here - weight content): 71.68 SiO_2 2.62 Al_2O_3, 0.07 Fe_2O_3, 6.67 CaO, 4.06 MgO, 14.63 Na_2O, 0.25 SO_3. Water resistance of newly molded bottles of 0.5 liter capacity (for juices and cognac) without treatment consists of 0.089 to 0.096 mg Na_2O, meanwhile, in accordance with State Standard, its allowable value should not exceed 0.108 mg Na_2O.

During storage in warehouse for six months the water resistance of the bottles fell to 0.110 - 0.130 mg of Na_2O. Consequently, after storage all of the glass articles may be rejected.

The effect of the consumption of gas reagent, fed into the annealed bottle cavity, on water resistance is shown in Table 2.

On the one hand, the data given in Table 2 witness the fact that the gases have different ability to influence the glass. Usually the result of reaction between glass and gases is the formation of dealkalization bloom [2]. The more intensive this bloom. the more considerable effect of chemical durability improvement [3]. One can see from Table 2 that under the same treatment conditions nitrogen dioxide has a less effect on the glass among all gas reagents.

On the other hand, while treating glass by gases, it was found to increase water resistance (up to 1-2 times). The maximal effect is achieved using the mixture of difluorodichloromethane and sulfur dioxide (1:1 volume ratio). If volume part of fluorine-. chlorine-containing reagents is more than 1 % the reaction proceeds very energetically - the "burning" of bloom is observed. The bloom formed was not washed by water completely so the results of water resistance measured were not adequate. ones. The use of carbon dioxide for treatment of bottles didn't change the water resistance of glass. the volume part of gas varied from 0.1 till 100 %.

It is very important that a considerable rise of water resistance was achieved when volume part of fluorine-containing gases was about 0.05-1.0 %. In that case the formation of bloom was not visually observed, so replacement of OH^- and O^{2-} by F^- seems to happen on the glass surface [3]. To describe the following data it is more convenient to name this kind of treatment "modification of glass surface".

The efficacy of the developed technique was also confirmed by the use of such gaseous reagents as hydrogen fluoride and chloride. Depending on the shape of the articles and their wall thickness, the safe heating rate is 10-50 ^{0}C/min. The maximum heating temperature, at which the gases react with the glass surface, depends essentially on the alkali oxide content of the glass and ranges from 450 to 600 ^{0}C. Holding the maximum temperature of the thermal treatment is not obligatory because the time for preheating and cooling of the articles is quite enough for dealkalization of the glass surface by the gases.

It is interesting to note that qualitative determination of the corrosion of the glass using methylene blue [5] also showed that the bottles from the storehouse are unsuitable for foodstuff, but no corrosion was noted after treatment with the reagent and annealing. This made it possible to produce an experimental batch of 10 thousand bottles with "restored" chemical stability, which passed successful tests at a distillery.

After the thermochemical treatment of glassware by active gases it was found to increase acid resistance by one-two levels of magnitude.

The technique, which developed the reaction of the inner surface of glassware with the gases, is accompanied by an increase in their mechanical strength, hardness and thermal stability. Thus, the resistance of 0.8 liter champagne bottles, made from dark-green glass, to internal hydrostatic pressure increases by 10-20 %. After treatment of jars and bottles with sulfur dioxide and difluorodichloromethane their thermostability rises by 5-I0 ^{0}C (by 10 %).

The reaction of gases with the glass surface increases the compactness of the surface layer, as evidenced by the increase in the Vickers microhardness (with a load of 0.2 N on a diamond-pointed pyramid) by 10 %.

Some Recommendations on the Treatment of Glassware with Reagents. In terms of sanitary reasons, it is undesirable to introduce sulfur dioxide hydrogen chloride and fluoride into glass articles because of the toxicity of these gases. For this, it is convenient to use gases of the freon type (difluorodichloromethane. difluorochloromethane. etc.) which are safe under normal circumstances and decompose upon heating above 400 ^{0}C forming hydrogen fluoride and chloride. Moreover, for dealkalization of glass by sulfur dioxide it is simpler to introduce into the article sulfur powder or tablets than gas. Experience showed that sulfur burns completely upon heating and the improvement in the chemical stability, in this case is the same as in the treatment of glassware with sulfur dioxide. Because of this, it is better to use solutions of acids of salts of fluorine and chlorine than to introduce gaseous halogen compounds into the glassware.

It was proved experimentally that gases partially volatilize from the articles during heating and that the smaller the size of their narrowest part (for example, diameter of the neck of flasks, bottles, etc.), the greater the chemical stability of the glass and correspondingly, the lower the reagent consumption for the treatment.

An intimate relation between the rate of dealkalization of glass surface by gases and the physical and chemical properties of the articles was established earlier [3]. In the cases, where no standard methods are available to determine the chemical stability and strength of glassware (for instance, for high-quality vessels), the improvement in the physicochemical properties due to the action of the gases can be assessed from the data on the determination of the rate of extraction of alkali cations from the glass. Formation of a prominent encrustation of the reaction products on the glass surface is clear evidence of improvement in the service characteristics of the glassware.

The technique developed for the "restoration" of the chemical stability of glass is applicable both to individual articles (for instance, museum exhibits) and to large batches of industrial glassware. The merit of this technique lies in the possibility of simultaneous thermochemical treatment of different types of glassware differing in chemical composition.

3. Conclusions

Thermochemical treatment by gas reagents results in 1-2 times increase of water resistance of annealed commercial glassware (i.e. after their manufacturing). The use of mixture of fluorine-containing and acid gases is of maximal interest. The main factors influencing on the effect are temperature, nature of reagent and its rate of gas flow.

The dealkalization by gases and modification of surface structure leads to 30 % increase in glassware strength, thermostability and microhardness increased by 10 %.

The technique developed for the "restoration" of the chemical stability of glass, is applicable both to individual articles (for instance, museum exhibits) and to large batches of industrial glassware.

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