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Yaroslav Vakhula, Victor Vasijchuk, Anna Romaniv and Oleg Semchuk

PECULIARITIES OF FORMATION OF SOL-GEL COATINGS BASED ON WATER GLASS

Lviv Polytechnic National University
12 Bandera str., 79013 Lviv, Ukraine
sylikat@polynet.lviv.ua

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Abstract. The work deals with the development of compositions of protective, insulating and decorative glass coatings, as well as coating formation using sol-gel technology. Conditions for the preparing of homogeneous colloidal solutions necessary for the formation of coatings and coating properties have been determined. The peculiarities of glass coating formation based on water glass have been developed.

Key words: sol-gel technology, glass coating, colloidal solution, water glass.

1. Introduction

Modern science of materials faces the problem of search and development of new materials with the complex of high operational performances. Implementation of modern requirement is possible at application of different surface coatings. Glassy and glass-ceramic coatings are of special interest among bulk of coating materials.

Glassy materials are widely used in different branches of industry. They increase durability and quality of various products made from metal, plastic mass, glass and ceramics. Moreover, they impart the necessary technical properties to the surface of metals. Depending on service conditions, as well as nature, form and sizes of products on which glassy coatings are applied, compositions of glass and methods of coating formation may be chosen.

Majority of glass coatings is obtained in a silicate, borate and silicophosphate systems. However, most number of coatings of polyfunctional purpose are developed in the silicate system which is successfully used in many spheres. Silicate glass is characterized by high durability, corrosion resistance and thermomechanical properties. The choice of formation method depends not only on properties and form of undercoat or necessary parameters of coating but also on its chemical composition.

One of perspective methods of glass coating formation is a sedimentaion method out of film-forming solutions [1, 2]. This method is based on the use of true solutions which contain water-soluble salts of ingredients. The main requirement to solution is absence of coagulation and ability of sediment formation.

Glass coatings obtained from sol and colloidal solutions have substantial advantages comparing with those obtained via traditional trailing technology. Glass coatings form compact gas-proof film over surface of undercoat. Moreover, they have a row of important advantages over traditional coatings: lower molding temperature, less thickness and greater flexibility. The difference between coefficient of linear expansion of coating and undercoat during their application is less perceptible.

As it was mentioned above, silicate coatings form a large group. Among the perspective methods of their forming sol-gel method is of special interest. It's caused not only by high quality of coatings, but also by the considerable energy-saving. It should be noted that colloidal silicate solutions have special gelanizationing susceptibility, which allows to obtain gels and accordingly glass coatings in short time.

In practice most researchers use the products of complete or partial hydrolysis and polycondensation of tetraetoxysilane $Si(OC_2H_5)_4$ and other alcosilanes for the obtaining of colloidal silicate solutions [3, 4]. Silicium oxide should be introduced into solution composition using aqueous solution of alkaline silicates, so called water glass [5].

2. Results and Discussion

The detailed analysis of influence of individual oxides on glass properties allowed to develope the system of prognostication of choice of chemical composition of colloidal solutions depending on silicium-containing component for the formation of glassy and glass-ceramic coatings for glass, ceramics and metals.

Forecast scheme for the choice of chemical composition of industrial coatings based on water glass is shown in Fig. 1.

Thus, the alkaline silicate systems (soluble glass) have wide range of compositions, which are characterized by different alkalinity and nature of cations. Apparently, those solutions of lithium, sodium and potassium silicates are of special interest for the obtaining of coating.

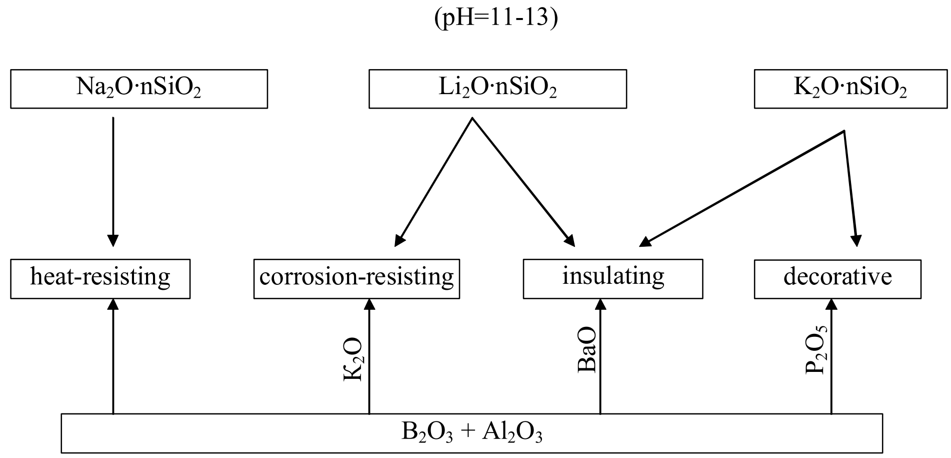

Fig. 1. Forecast scheme of chemical composition choice of glass coating based on water glass

The essence of coating formation technology consists in spraying of colloidal solution over hot surface of undercoat followed by heat treatment. For the obtaining of glass-ceramic coatings undercoat surface was additionally treated at the temperature of crystallization. In the case of obtaining of decorative glass coating, the suspension of gel powder was applied to undercoat surface followed by heating.

2.1. SiO_2-(Na_2O+K_2O)-R_2O_3 system (on the basis of Na – water glass system)

Introduction of the limited amount of R_2O_3 oxides (e.g. B_2O_3, Al_2O_3) into composition of glass considerably increases corrosion resistance and mechanical durability. The presence of B_2O_3 decreases viscosity and improves forming property of glass bath.

Composition of protective coating based on water glass was chosen by taking into account the previous results of researches and specific of preparation of colloid solutions stable to gelanization. Composition of protective coating based on water glass is represented in Table 1.

Table 1

Number of glass	Content of oxides, mol. %					Coefficient of linear expansion $\alpha{\cdot}10^7$, degree^{-1} (according calculations)
	SiO_2	Na_2O	K_2O	B_2O_3	Al_2O_3	
1	72.2	26.0	1.1	-	0.6	136
2	71.3	23.1	4.2	-	1.3	135
3	66.4	30.0	1.1	-	2.5	150
4	69.3	22.2	4.2	3.7	0.6	130
5	71.6	23.2	1.1	3.5	0.6	116
6	70.1	25.8	1.1	1.8	1.2	135
7	71.7	20.5	3.0	3.6	1.2	117
8	67.5	24.9	1.1	5.3	1.2	126
9	66.9	24.8	1.7	5.4	1.2	128
10	72.5	21.1	3.0	1.8	1.6	119
11	63.3	29.5	1.1	3.6	2.5	143

Composition and coefficient of linear expansion of glass coatings

Sodium water glass (M = 3.5), sodium aluminate, boric acid and to potassium hydroxide were used for introduction of the indicated oxides to composition of glass coating and obtaining of solutions stable to gelanization. 1-4 % of K_2O in glass bath decreases its viscosity, extends the interval of coating forming, and increases corrosion resistance of glass.

2.2. SiO_2-(Li_2O+K_2O)-BaO-R_2O_3 system (on the basis of Li, K – water glass system)

Taking into account the influence of oxides on glass properties and technological features of the offered method, Li_2O-K_2O-BaO-B_2O_3-Al_2O_3-SiO_2 system was chosen for the obtaining of glass-ceramics insulating coatings. The peculiarity of such system is the availability of two alkaline oxides, what increases electro-resistance and decreases softening temperature. Moreover, BaO provides the coatings with dielectric properties, as well as improves crystallization ability of glass.

Composition of glass chosen for the synthesis of glass-ceramic coatings is presented in Table 2.

One can see from Table 2 that in compositions 12-14 there is an increase of BaO content owing to B_2O_3. Li_2O/K_2O ratio is constant and equal to 1. Such ratio is necessary for the obtaining of glass with high dielectric properties. At constant basic of the components, the increase of SiO_2 in compositions of glass 15-17 increases electrical resistance. The conducted calculations confirm the forecasts.

Lithium and potassium water glasses, as well as lithium hydroxide, boric acid, barium and aluminium nitrates were used for the preparation of solutions.

Table 2

Composition of glass

Number of glass	Content of oxides, mol. %						Calculated values	
	SiO_2	Li_2O	K_2O	B_2O_3	BaO	Al_2O_3	Coefficient of linear expansion $\alpha \cdot 10^7$, degree^{-1} (according calculations)	Dielectric permeability, ε f = $4.5 \cdot 10^8$ Hz; T = 293 K
12	58	7	7	18	5	5	80	6.3
13	58	7	7	13	10	5	90	7.2
14	58	7	7	8	15	5	99	8.1
15	60	6	6	8	15	5	93	7.9
16	61	7	7	5	15	5	101	8.1
17	65	7	7	6	10	5	102	7.3
18	65	8	5	7	10	5	86	7.1

2.3. K_2O-Al_2O_3-B_2O_3-SiO_2-P_2O_5 system (on the basis of K – water glass system)

Decorative glass coatings are widely used in finishing of wares from glass, ceramics and metal. Low forming temperature, high chemical stability and high-quality colouring are the main requirements to meet.

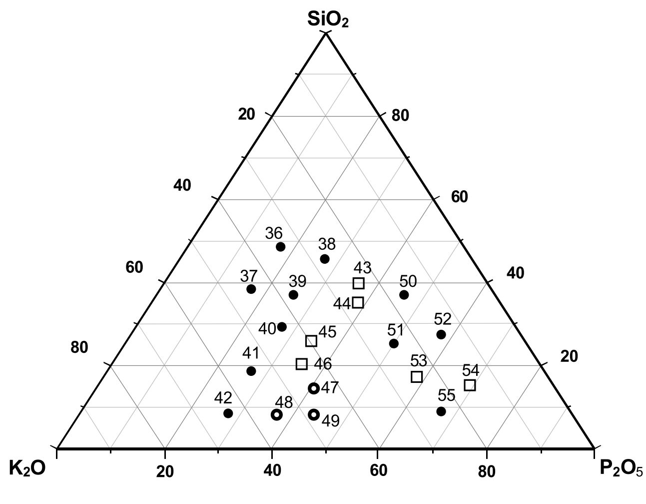

Fig. 2. Composition of the synthesized K_2O-SiO_2-P_2O_5 glass

Taking into account above-mentioned requirements, we established the optimum composition of glass: P_2O_5 is within the range of 39-45 mol %, SiO_2 – 8-15 mol %, K_2O – 40-52 mol % (Fig. 2). However, the synthesized glass is characterized by low chemical stability and collapses in the air. Modification of glass composition may increase its chemical stability.

Since the majority of phosphatic glasses have low chemical stability and collapse under the action of air moisture the synthesis of K_2O-SiO_2-P_2O_5 system is foreseen by adding of Al_2O_3 and B_2O_3, both separately, and jointly.

Compositions of glass with the variable amount of P_2O_5 (48.0-54.0 mol %) is presented in Fig. 3. The Al_2O_3 content is 2.0-8.0 mol %, accordingly. The net of compositions allows to cover all possible variants with the purpose to receive chemically stable glass with the low temperature of his synthesis.

Potassium water glass, potassium aluminate, ammonium, boric acid and to potassium hydroxide were used for the preparation of solutions.

It is known that the basis of majority of glass coatings is alkali-boron-aluminium glass, from which one can obtain glass coatings with the assigned properties by certain combinations between some components. The main problem is obtaining homogeneous multicomponent glass-forming solutions based on water glass containing Al^{3+}, B^{3+}, P^{5+} ions. For their obtaining in the area of high pH sodium (M = 3-4), potassium (M = 3.5) and lithium (M = 4-6) water glass, as well as aluminium and barium nitrates, boric acid and ammonium hydrophosphate were used. The special difficulty of obtaining of homogeneous colloidal solutions based on water glass consists in the fact that adding of even negligible quantity of salts of elements of II and III groups to silicates solutions causes heterogeneity in such systems. The formation of insoluble silicates of most metals is the main reason.

SiO_2 = 10 mol. %
K_2O= 30 mol. %

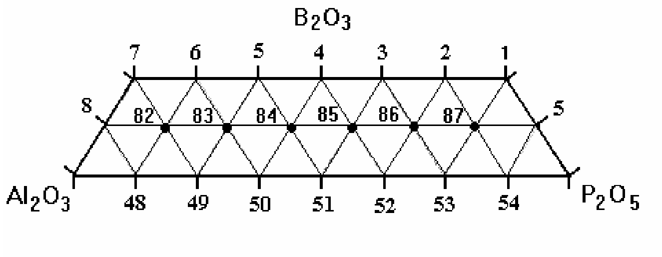

Fig. 3. Composition of the synthesized K_2O-Al_2O_3-B_2O_3-SiO_2-P_2O_5 glass

We established that stability of colloidal solutions increases considerably, when Al^{+3+} ion is in anionic form as aluminate. The increase of aluminate content without sediment formation is limited to boundary amount. The increase of sodium water glass module from 3 to 4 decreases aluminate boundary amount almost in 2.5 times.

It should be noted that solutions based on potassium water glass with similar module are more stable. The increase of stability is connected with higher ability to dissociation of K^+ ions.

Addition of even negligible quantity of aluminate (V =0.5-1.0 ml) to 10 ml of water glass forms the spongy admixtures on the boundary of liquids mixing. This phenomenon was absent while introducing aluminate by separate drops. Hence, for preparation of colloidal solution the aluminate was added to water glass by small portions under intensive stirring. Homogeneity of solution was saved only to the certain boundary amount of aluminate, which, in the turn, depends on a kind of alkaline cation and module of water glass. At equal modules (M = 3) in solution of potassium and sodium water glass gelanization begins after addition of 3 ml and 2 ml of aluminate, correspondingly. The effect of alkaline silicate module is more considerable. At increase of module to 4 gel is formed when adding 1 ml of aluminate (*vide* Table 3).

Table 3

Boundary amounts of Al_2O_3 in solutions based on water glass

Composition of liquid glass	$Na_2O{\cdot}3SiO_2$	$Na_2O{\cdot}3.5SiO_2$	$Na_2O{\cdot}4SiO_2$	$K_2O{\cdot}2SiO_2$	$K_2O{\cdot}2.5SiO_2$	$K_2O{\cdot}3SiO_2$
Boundary amount of Al_2O_3 (%)	8.0	6.3	3.2	14.1	12.3	10.6

We determined aluminate boundary amounts and re-calculated Al_2O_3 amounts, which may be added to the solution of water glass without gelanization.

If there are not difficulties in obtaining of sodium and potassium water glass of wide module intervals, the synthesis of lithium water glass with the module M>2 has some peculiarities. Literary information on this question is limited. Lithium water glass (LWG) with M>2 is heterophase system which consists of solution of lithium silicate and suspended particles of polymerized SiO_2 with OH-groups on a surface. The increase of LWG module from 2 to 10 increases content of suspended particles. For LWG synthesis the optimal temperature of LiOH solution is 323-348 K. The rise in temperature results in LWG hydrolysis and increases number of suspended particles. Weak LiOH solutions (c = 0.1-0.5 N) lead to intensive interaction between components and decrease size of particles. Strong LiOH solutions (c = 1.5 N) increase number of suspended particles up to formation of high-viscous LWG solution. Thus, an amount and size of suspended particles depend upon the module of water glass, temperature, synthesis time and LiOH concentration.

Taking into account the fact that concentration of colloidal solutions is one of effective factors during their stabilization, we diluted synthesized lithium-potassium water glass with water till the concentration became 6.5 mass %.

The general scheme of components confluence is given below:

$$K_2O{\cdot}3.5SiO_2 + Li_2OЧ4SiO_2 + LiOH + Al(NO_3)_3 + +H_3BO_3 + Ba(NO_3)_2$$

The gelanization depends on chemical composition of solutions and it becomescomplicated at availability of two or more glass-formers.

We established that in solutions of potassium-silicium-phosphate system there is deviation from the established regularities of gel-forming process in the different interval of pH. In particular, in the area of pH<6 solutions do not increase their stability, but it takes place in silicates solutions. The introduction of phosphatic component into gel structure was confirmed by a chemical analysis. Maximal amount of P_2O_5 is introduced actually at pH = 4, that considerably adjusts the existent gel-forming theory of silicates aqueous solutions and allows to understand essence of such rejection. Introduction of phosphatic component into gel structure is explained with high charge of phosphate-ions and their inclination to be adsorbed on the surface of porous gel.

The decrease of concentration of colloidal solution decreases the number of SiO_2 collisions. Moreover, the increase of number of hydroxyl ions results in depolymerization of phosphatic and silicium-containing chains, which in general increases the gelanization time.

The effect of temperature on gelanization time is complicated. The minimum value of time is observed at 333 K. It is possible to assert that decrease of viscosity at mentioned temperature interval decreases the number of colloidal particles sharply and decelerate the aggregation process.

For the preparation of solutions of $K_2O–Al_2O_3–B_2O_3–SiO_2–P_2O_5$ system potassium water glass (M=3.5; c=14.47 mass %), KOH (9M), $(NH_4)_2HPO_4$ (1.5M), H_3BO_3 (0.7M) solutions were used. The general concentration of colloidal solution was 17.7 mass % and pH was 9.1.

The solutions of this system have high ability to gelanization, which is especially sensible to the value of concentration of hydrogen ions. We established experimentally that a sharp change in the behavior of solutions is observed in the area of pH = 10. That is why it is important in every case to establish the characteristic features of solutions preparation. At the obtaining of solution with pH < 10 order of components confluence is the following:

$(NH_4)_2HPO_4 + H_3BO_3 + KOH + K_2O·3.5\ SiO_2 + +K_n[Al(OH)_m]$

At the obtaining of colloidal solution of investigated system with pH > 10 according to mentioned scheme, insoluble sediment is precipitated after the adjustment of $(NH_4)_2HPO_4 + H_3BO_3$ mixture with ammoniac water. In this connection there is a necessity to change order of component confluence:

$K_n[Al(OH)_m] + KOH + K_2O·3.5SiO_2 + (H_3BO_3 + +(NH_4)_2HPO_4)$

Table 4

Physical and chemical properties of protective glass coating

Properties	Glass coating	
	Composition 7	Industrial analogue
Chemical stability, loss of mass, mg/dm^2	0,14	-
Microhardness, MPa	5370	-
Thermal stability, K	723	-
Heat-resistance, g/m^2·hour	0.058	0.25
Working temperature, K	773	700-750
Time of protective action, hrs	4-6	3
Coefficient of linear expansion ($\alpha·10^7$), degree^{-1}	110	110
Adhesion, points	5	-
Thickness of coating, mcm	20-50	100-150

Table 5

Physical and chemical properties of glass-ceramic insulating coating

Properties	Units	Glassy		Glass-ceramic
		Coating 14	Industrial analogue	
Chemical stability (a loss of mass in 4% vinegar acid)	mg/cm^2·hour	0.20-0.15	0.40-0.35	0.30-0.20
Dilatometric initial softening temperature	K	923	833	923
Thermal stability	K	703	823	873
Adhesion	points	3	-	4
Microhardness	MPa	4480	-	6220
Thickness	mcm	60-80	-	60-80
Heat-resistance (increase in mass) at 1023 K at 1173 K	g/hour·cm^2	 0.0034 0.0550	 - -	 0.0008 0.0036
Dielectric permeability, at 293 K, 1 kHz		8.5	9.0-10.0	8.0
Specific volume electric resistance at 293 K	Ohm·m	7.31010	1011	3.41012
Specific surface electric resistance at 293 K	Ohm	3.51012	-	1.11013
Tangent of angle of dielectric loss at 293 K, 1 kHz		7610-4	11010-4	4510-4
Coefficient of linear expansion ($\alpha·10^7$)	degree^{-1}	120	91	107

Table 6

Physical and chemical properties of decorative glass coating

Properties	Units	Values
Initial softening temperature	K	753-793
Temperature of drop formation	K	793-833
Complete flow temperature	K	833-893
Coefficient of linear expansion ($\alpha \cdot 10^7$)	degree^{-1}	143
Microhardness	MPa	4460
Chemical stability ("spot" method)		without changes

3. Conclusions

1. For the obtaining of functional coatings in the R_2O-SiO_2 (R – Li,Na,K) system the complex of chemical compositions is developed by large-scale modification of the system with MgO, CaO, BaO, B_2O_3, Al_2O_3, P_2O_5 oxides with the purpose of achieving such necessary technological characteristics of coating as coefficient of linear expansion, chemical and thermal stability, forming viscosity and crystallization ability. We developed glass coatings with the following functional properties: Li_2O and Na_2O have protective temperaturestable properties, Li_2O + K_2O – insulating properties and K_2O – fusible decorative ones.

2. Compositions of stable to gelanization solutions on the basis of R_2OЧ$nSiO_2$ water glass were developed. Peculiarity and difficulty of preparation is related to formation of sparingly soluble salts of silicium acid. We established that stability of colloidal solutions increases considerably, when Al^{3+} ion is in anionic form as aluminate. The increase of aluminate amount without sediment formation is possible only to the certain boundary amount. The increase of sodium water glass module from 3 to 4 decreases aluminate boundary amount almost in 2.5 times. Solutions based on potassium water glass with similar module are more stable, what is related to the greater ability of K^+ ions to dissociation. There is chemical interaction between components during the solution preparation. As a result, system of pH is changed, which leads to gelatinization or sedimentation.

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ОСОБЛИВОСТІ ФОРМУВАННЯ ЗОЛЬ-ГЕЛЬ ПОКРИТЬ НА ОСНОВІ РІДКОГО СКЛА

Анотація. *В роботі розглянуто одержання композицій для захисного, ізоляційного і декоративного покриття, а також формування покрить з використанням золь-гель технології. Визначені основні умови, необхідні для приготування гомогенних колоїдних розчинів для формування покрить, а також їх основні характеристики. Приведені особливосcті формування золь-гель покрить на основі рідкого скла.*

Ключові слова*: золь-гель технологія, склопокриття, колоїдний розчин, рідке скло*