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PROTECTIVE COATINGS BASED ON ALKALI SILICATE

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The protective coatings based on the silicate based binders prepared and filled with standard pigments and fillers were hardened by the following methods: physical procedure, zinc powder with isometric spherical particles, zinc powder with lamellar particles, blocked polyisocyanate in an organic solvent, blocked polyisocyanate in water dispersion, with condensed aluminum phosphate, hydrated aluminum phosphate, and alkoxysilyl isocyanurate. With coatings, the physical-mechanical property tests of the coats on steel or glass panels, as the case may be (adhesion by the grid method, bending strengths, cupping stability, shock resistance, and coating hardness) and corrosion resistance in a condensation chamber and salt chamber with cycles tests were performed. The results obtained were evaluated from the silicate binder type point of view, as well as the used hardening system type point of view. The overall best results were obtained with a lithium-sodium water glass, the coats of which exhibit good physicomechanical and anticorrosion properties. From the composition point of view, the coating materials filled with zinc powder exhibit very good results. Zinc with lamellar particle shape exhibits a higher anticorrosion efficiency.

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Introduction

The soluble synthetic silicates, in the liquid form called also sodium water glass, potassium water glass, lithium water glass (and/or their combinations) are quite frequently used as binders for various systems (coating compositions, cements, forms, cores and coatings in foundries, welding electrodes, building materials, refractories, insulation materials). They give to them not only ecological harmlessness, but also, e.g., acid resistivity (cements), high steam permeability (facade coating compositions), incombustibility (fire resistant coating compositions), anticorrosive protection (zinc rich paints).

The basic starting material for the products based on synthetic silicates and silicon dioxide is silica sand, which is the initial material for technologies of dry and wet processes. Various procedures can be used for processing the crystalline silicon dioxide to synthetic amorphous silicon dioxide with precisely defined properties for specific applications. The most usual product and/or the semiproduct for further processing comprise alkaline silicates in solid and liquid forms. Sodium silicate belongs to basic inorganic chemicals, and its production in Europe presents more than 500 000 t y^{-1}. Potassium silicate is used as a binder for coating compositions, refractories, cements and for the production of welding electrodes; its consumption in Europe is at a level of about 21 000 t y^{-1}. The lithium water glasses belong among chemical specialities and their usage is limited to the region of coating compositions (coating compositions, destined for heavy anticorrosion protection, rich in zinc powder filler), to the technologies of restoring the historical buildings (stabilizing means for synthetic and natural stones), and for the production of welding electrodes (application as a binder).

Theory

Properties of Silicate Binders

Water glasses - solutions of alkali silicates can be ordered among colloidal systems, wherein the particles are smaller than average light wavelength but larger than the average molecule size. The water glass particle size fluctuates between 1 to 500 nm and can be verified by the Tyndall effect observation or by a microscopic method. On evaluating the colloidal properties of water glass it is necessary to follow two states: water glass as a dispersion system (sol) and water glass as a transient system (gel) [1]. The sols are characterized as the systems containing particles, among which a large number of limited surfaces can be found. The sols can be divided to phase dispersion systems and molecular colloids [2]. The water glass belongs to phase dispersion systems. The particles represent an independent phase separated by the dispersion medium. Large surface of interface is characterized by a high surface energy and thus a great thermodynamic instability. The system can be destabilized by a small impact and transformed through a transient gel form to the solid compound.

On evaluating the colloidal properties of water glass we follow three basic characteristics: solvation, size and charge. Generally the particles obtain an electric charge by the ionic adsorption or electrolytic disscotiation. There takes place the formation of electric double layer. This layer is of diffusion character, on the movement of particles only the internal part of the double layer adheres on it. The particle appears on outside as electrically conductive particle. The micelle is a sol particle composed of a core and solvate layer. Water glass may be ordered among the isostable sols, the solvate layer thereof is formed as of ions as well as of the solvent molecules. The solvate layer of colloid water glass particles has two components: the inside strongly bound layer, which exhibits the Brownian motion with a particle, and the outside diffusion layer. Thus in water glass water occurs in three forms. On the one side it is a free water in an intermicallar space, further water bound at the outside lyosphere diffusion layer, and water bound strongly at the inside lyosphere layer. In the case of the commercial sodium water glass sorts the hydration varies on the following level (Fig. 1): inside bound water (W_1) ~ 8 %, outside bound water (W_2) ~ 36 % and free water (W_v) ~ 12 %.

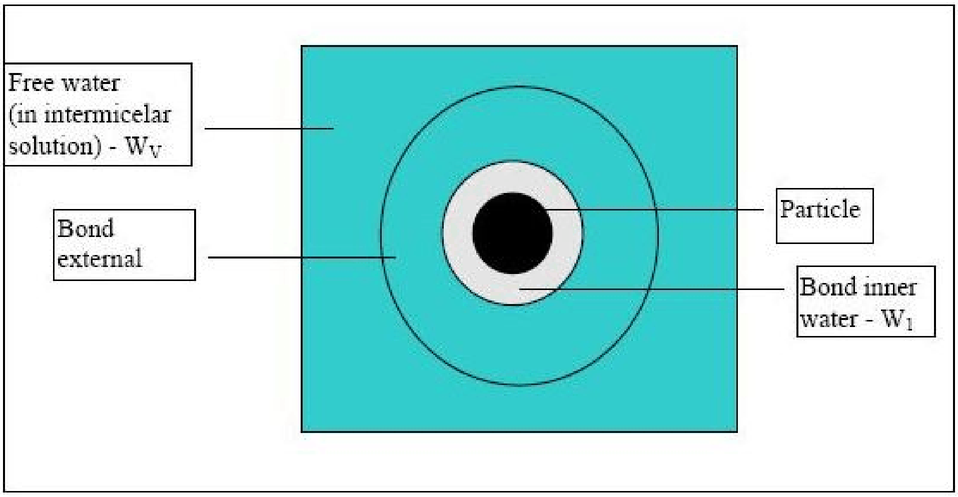


Fig. 1 Schematic structure of solutin of water glass

Hardening of Silicate Binders

The solutions of glass alkali silicates can be used as binders in coating compositions pigmented with zinc powder. In these systems, the capability of zinc to form the cathodic protection on the contact with steel surface is used. As far as the conductive contact between individual zinc particles and steel surface is achieved, the electric Zn-Fe cell in which the steel is a cathode and, therefore, does not suffer corrosion, is formed. As long as the cell is functioning, an increase of the water pH value takes place, on diffusing through the coating film and acting on the zinc particles and also on the steel surface. Therefore, it is necessary to select the binders stable in alkaline medium. With this in mind polystyrene, chlorinated rubber, epoxy resins and vinyl copolymers were used for this purpose in the past. The silicon polymers are really suitable binders, both in the form of colloidal aqueous solutions of alkali silicates, and in the form of alkoxy silicates, soluble in organic solvents. Coating compositions pigmented with zinc powder protect the steel surfaces primarily by an electrochemical mechanism.The porous coatings of this type enable the water diffusion through the coat and thus the formation of electrolyte, which has inhibition properties (pH effect), but primarily the galvanic cell is formed. As a result of the electrochemical reaction the reaction products are formed, which seal the pores in film, and this film is gradually converted to the barrier protection mode.

In the process of hardening water-borne zinc silicate coatings the whole complex of physicochemical processes as the water evaporation on the drying of coat, the diffusion of carbon dioxide throuth the coating, the chemical reaction with carbon dioxide, the transport of eventually formed gaseous reaction products — hydrogen out of the coating, etc., find application. At first the coating dries, which runs comparatively fast — to max. several hours in dependence on the temperature and relative humidity. The further subsequent processes are slower and take, in dependence on temperature, several days to weeks. Out of the proper chemical processes, the following reactions make themselves useful: the reaction with atmospheric carbon dioxide, the reaction of water glass with zinc metal, and, under limitation to the adhesion interlayer, also the reactions between steel surface iron and water glass.

The hardening of water glass with inorganic salts runs by a similar mechanism as the hardening with organic esters. During the salt hydrolysis similarly as during the ester hydrolysis an inorganic acid, which hardens water glass, is freed. Therefore, the salts of weak bases and strong acids are used primarily. The velocity of hardening is controlled by the dosed amount of hardening agent on the one side, and by the type of used salt on the other, as the determining reaction of the whole process is the velocity of inorganic salt hydrolysis. In the building industry, fluorides and fluorosilicates were used frequently [3]. With respect to toxicity of fluorosilicate it is more suitable to use a mixture of aluminum phosphates, which are used for the hardening in the building industry (dry mortars, refractory cements and adhesives) [4]. Combinations of polyphosphates showing a low polymerization degree (3-6 structural units) and a high polymerization degree (more than 40 structural units) are used. The rate of hardening is controlled by a mutual ratio of both polyphosphate types. The phosphates showing a short chain are hardened at a higher rate than the phosphates showing a long chain [5]. The phosphates are prepared by a thermal reaction of aluminum hydroxide with ammonium phosphate in solid phase at temperatures about 400 °C [6].

The colloidal solutions of alkali silicates belong among principal inorganic chemicals with a broad spectrum of usage. One of the significant applications of water glasses is the application as a binder for foundry sand mixtures. The mixtures are hardened either by carbon dioxide or by liquid organic hardening agents mostly on the basis of esters [7]. In practice the acetic acid esters and two- to five-member polyhydroxyalcohols, namely glycerol acetates, are used most frequently. Hydrolysis of glycerol triacetate leads across diacetate, monoacetate, and ends at the formation of acetic acid and glycerol. Gradually formed acetic acid reacts with water glass under the formation of sodium acetate, which disturbs the compactness of the formed silicon dioxide gel. Glycerol monoacetate is hydrolyzed most rapidly, the glycerol triacetate most slowly. By the mutual ratio of individual esters the rate of water glass hardening is controlled (elimination of the climatic summer-winter effects).

For the applications in building industries (solidification of road beds), it is described hardening with esters of olefinic alcohols with carboxylic acids having a carbon atom number in the chain by 18 C (vinyl and methylvinyl esters of acetic, propionic, lauric, stearic and lactic acids) under adding further organic compounds of the halogenated hydrocarbons, ketones, aldehydes and acrylic acid ester [8] types.

For the building mortars a hardening system is described, which is based on acting mixtures of aluminum or ferric salts with organic hydroxyacids [9] (citric acid, lactic acid, glyceric acid, tartaric acid), the mole ratio of hydroxyacid/SiO_2 fluctuating between 0.05 and 0.3. The cements bound with sodium or potassium water glasses are hardened with organic compounds bearing free amino or amido groups, which react with water and water glass, e.g., formamide and cyanamide [10] or their compounds with bivalent metals (lead, calcium, barium) [11].

Usage of Alkali Silicates

The binding properties of alkali silicates are widely used in various applications and with various combinations of binders, fillers, and pigments. For the production of coating compositions, mortars and plasters, the water glass is combined with burnt or hydrated limes and silicate powders. Into facade coating materials bound with acrylic dispersions the water glass additions up to 2 wt. % acting here as a conservation agent or a combination of both binder types (acrylate + silicate) are used. As a binder for the facade coating compositions, primarily a potassium water glass of a suitable modulus or a potassium water glass adapted with colloidal silicon dioxide solution is used. Potassium water glass presents also a basis for coating compositions on glass. Zinc silicate coatings or coats based on inorganic silicate binder together with organic coatings pigmented with zinc belong into the group of the so-called zinc coatings with a high content of zinc metal of 80-95 wt. % in the nonvolatile coating fraction (Fig. 2). Dry layers of nominal thicknesses of 60-90 :m are used for long-duration anticorrosion protection of steel structures, especially in atmospheres of the corrosion aggressivity degree C3, C4, and C5 (ČSN ISO 9223).

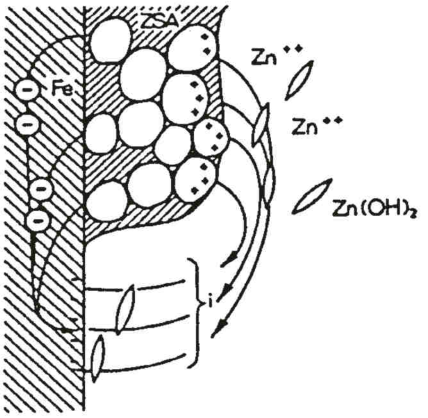


Fig. 2 Cathodic protection of metal substrate with zinc rich coatings

Experimental

Production of Binders

Polysilicate binders based on the potassium and sodium water glasses were prepared from industrially produced semiproducts, in which the silicate modulus was adapted with colloidal silicon dioxide solution. Lithium and lithium-sodium water glasses were prepared by the sol-gel method from the colloidal silicon dioxide and corresponding hydroxides. The binder compositions are given in Tables I-III.

Preparation and Formuluation of Coating Compositions

The coating compositions (Table III) were prepared on the Dissolver Dispermat equipment by dispersing all the components in attritor. The coating composition dispersing was performed at 3000 rpm for 30 minutes. To the attritor at first all the liquid system components were introduced. For reaching a better dispersing effect,

Table I Basic composition of the prepared silicate binders*

Silicate binder type	Sodium water glass	Potassium water glass	Lithium water glass	Sodium-lithium water glass
Dry matter content, wt. %	31.39	24.48	20.84	21.39
SiO_2 content, wt. %	25.59	18.39	19.28	18.37
Na_2O content, wt. %	5.80	-	-	1.19
K_2O content, wt. %	-	6.09	-	-
Li_2O content, wt. %	-	-	1.56	1.83
Mole ratio	4.55	4.74	6.16	3.82
Weight ratio	4.41	3.02	12.36	6.08
Density, g cm^{-3}	1.286	1.208	1.166	1.203

* Silicate binder: sodium water glass (NaWG), potassium water glass (PWG), lithium water glass (LiWG) and sodium-lithium water glass (NaLiWG)

Table II Silicate binders - water distribution

Water glass type	Water distribution, wt. %			
	W	W_1	W_2	W_v
Sodium water glass	69.03	5.42	49.82	13.8
Potassium water glass	75.14	3.33	41.54	30.27
Lithium water glass	79.08	2.04	44.3	32.7
Sodium-lithium water glass	76.96	2.45	65.84	8.67

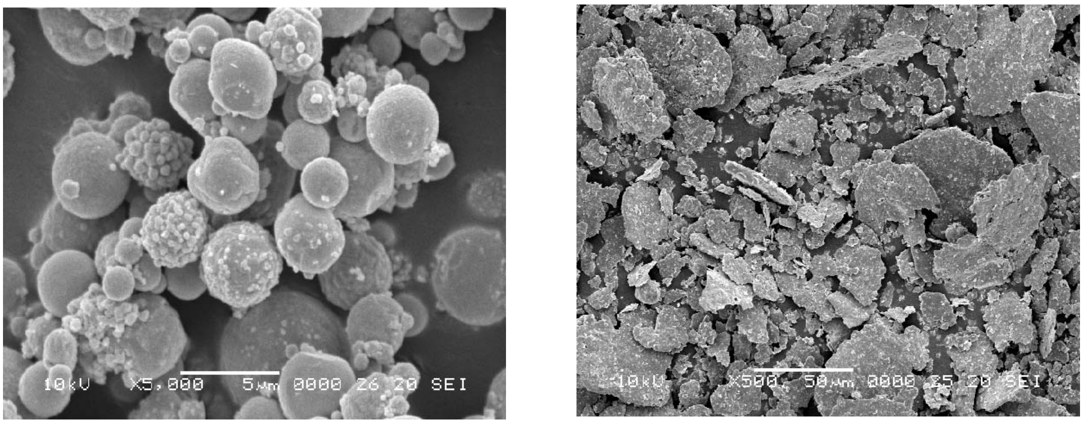
the dispersing bodies (ballotine having 3 mm in diam.), the volume of which amounted to about 1/3 of the coating composition volume, was used. The mixture was homogenized, and afterwards all the powdery components were added. On finishing the dispersion the glass balls were separated on a screen and the coating composition was applied to steel testing panels and glass plates for the corrosion and mechanical tests. Figure 3 brings morphology of zinc particles (SEM).

Table III Composition of coatings

Starting material/ coating	Coating 1	Coating 2	Coating 3	Coating 4	Coating 5	Coating 6	Coating 7	Coating 8
Silicate binder*	53.57	29.19	39.84	53.93	53.93	48.62	47.79	51.79
Sokrat 2431	8.93	13.47	13.6	8.93	8.93	8.62	8.85	8.93
Plastorit Micro	5.89	-	4.39	6.07	6.07	6.9	7.08	7.14
Bentone SD-2	3.21	2.74	3.74	2.86	2.86	3.1	3.18	3.21
Fepren TP 200	16.6	-	5.53	8.0	8.0	15.51	15.9	16.07
Potassium dichromate	-	0.01	0.01	-	-	-	-	-
Distilled water	10.71	9.68	9.76	10.71	10.71	13.79	10.62	10.71
Hydropalat A	0.9	0.8	0.8	0.9	0.9	0.9	0.9	0.9
Dehydran 1293	0.18	0.16	0.16	0.18	0.18	0.18	0.18	0.18
Zinc Dust VM-4P16	-	44.2	-	-	-	-	-	-
BLITZ Zinkpulver Z 2031	-	-	21.95	-	-	-	-	-
Alphos	-	-	-	8.21	-	-	-	-
Targon HS	-	-	-	-	8.21	-	-	-
Desmodur BL 4265	-	-	-	-	-	2.41	-	-
Bayhydur® BL 5140	-	-	-	-	-	-	5.13	-
Silquest® Y 11597 Silane	-	-	-	-	-	-	-	1.07
PVC (%)	38.5	51.14	44.9	36.8	37.1	39.24	39.47	39
Q (%)	*90*	*95*	*95*	*90*	*90*	*90*	*90*	*90*

Used Processing Methods

The following quantities belong to basic characteristics of water glasses: silicate modulus, water content, dry matter content, specific density, viscosity, and admixture contents. For evaluating the water glass properties, especially the stan-



Zinc Dust VM-4P16 BLITZ Zinkpulver Z 2031

Fig. 3 Morphology of zinc particles (SEM)

dard volumetric analysis was used. For determining the individual oligomers in water glass, the NMR method was used. The pigments were characterized by means of electron microscopy, X-ray spectral analysis, laser granulometry, BET, and helium pycnometry methods. The physicomechanical properties of coating films were ascertained by means of measuring the film hardness, shock resistance, cupping stability in Erichsen instrument, bending strength and adhesion by the grid method. The anticorrosion coating film properties were ascertained in a condensation chamber with a condensing humidity and SO_2 content. The test was performed according to the ČSN ISO 69 88. In the testing chamber space, a temperature of about 38 °C and a relative humidity of 100 % were kept during the test. Sulfur dioxide in the testing chamber was prepared by the reaction of sodium sulfite with sulfuric acid. The sample exposure was selected as a continuous for 120, 240, 480, and 720 hours. Further a corrosion cyclic test of the coatings was performed. The cyclic test resents a combination of condensation and salt chambers in dependence on the selected program. The samples fitted with a cut and placed in stands were exhibited to spraying a 5 % NaCl solution, the humidity of water condensation and a subsequent drying of the sample. Individual cycles were connected to each other. The temperatures and duration times of the cycle were selected for individual cycle component separately (Salting: 10 hours at a temperature of 35 °C; condensation: 1 hour at a temperature of 55 °C; drying out: 1 hour at a temperature of 23 °C). The coating films were exhibited to the individual cycle actions for 240 and 720 hours.

Results

Evaluation of Binders

Table IV brings a comparison of the alkali metal ion hydrations for water glasses for lacquer purposes with water glasses for foundry purposes (Silbond) and standard commercial glasses of *m* = 2.4 and 3.2. At long-duration following the foundry water glasses, the hydration was obtained in an adsorption layer in a range of 1.1 to 1.9 mol H_2O per 1 mol Na, and in a diffusion layer in a range of 9 to 45 mol H_2O per 1 mol Na. The lacquer binders exhibit a hydration of alkali ions in an adsorption layer the same as standard silicate binders, but in a diffusion layer the hydration is much higher, which is caused by a low dry matter content, i.e., by a high water content in the water glass of interest. Table V brings results of Si^{29} - NMR of silicate binders.

Table IV Hydration of sodium silicate binder ions

Type of binder	Hydration of alkali ions, mol H_2O/mol Me	
	adsorption layer	diffusion layer
Sodium water glass	1.60	-
Potassium water glass	1.76	94
Lithium water glass	1.70	65
Sodium-lithium water glass	1.37	60
Silbond CO 6.5, standard	1.90	9.7
Silbond ST L/01	1.80	11.1
Water glass 48-50	2.20	10.5
Water glass 36-38	1.60	45

Table V Results of Si^{29} - NMR of silicate binders

Binder type/wt. % of polymers	Q^0	Q^1	$Q^2+Q^3_{(cy-3)}$	Q^3	Q^4
Sodium water glass	0.7	4.4	21.3	53.8	19.8
Potassium water glass	1.1	4.6	24.6	54.1	15.6
Lithium water glass	1.4	4.8	22.0	53.4	18.5
Sodium-lithium water glass	0.8	4.5	25.2	53.8	15.8

Q^0 – monomer, Q^1 – dimer, Q^2 – trimer, Q^3 – octamer, Q^4 – colloidal phase; Sodium water glass diluted to 24 wt. % dry matter

Evaluation of Coating Compositions

Physicomechanical Properties

The best results of all the systems are exhibited by lithium-sodium water glass; especially after burning out at 150 °C for a time of 2 hours the results obtained in all the formulations are very well balanced (Table VI). Additional burning out of the coating exhibits an advantageous effect on the mechanical coating properties, which undergo about 10 % improving and are more balanced than in the case of nonburnt-out coatings. The results allow to order the tested binders from the best one to the worst one: lithium-sodium water glass, potassium water glass, sodium water glass, lithium water glass. Especially the results obtained with lithium water glass as a binder are really nonbalanced and the types of coating compositions hardened with aluminum phosphates could not be prepared at all in applicable form (no mixture lifetime), which is caused by a high reactivity of lithium water glass.

From the point of view of composition of coating material (hardener type), it is possible on the basis of the mechanical test results to order the individual hardening systems from the best one to the worst one: the system hardened by the reaction with solvent isocyanate type (coating 6), system hardened by the reaction with isometric particle zinc (coating 2), system hardened by the reaction with alkoxsilyl isocyanurate (coating 8), system without active components (coating 1), system hardened by the reaction with lamellar particles zinc (coating 3), system hardened by the reaction with aqueous isocyanate dispersion (coating 7), system hardened by the reaction with condensed aluminum phosphate (coating 5), and system hardened by the reaction with hydrated aluminum phosphate (coating 4). Figures 4 and 5 show the morphology of zinc pigmented coatings at various PVC (isometric and lamellar particles).

Table VI Average values of coating hardness for individual binder types

Binder type in coating	Average hardness prior to burning out, %	Average hardness after burning out, %
Lithium-sodium water glass	38.4	40.5
Sodium water glass	36.4	39.1
Potassium water glass	39.9	38.7
Lithium water glass	45.6	44.6

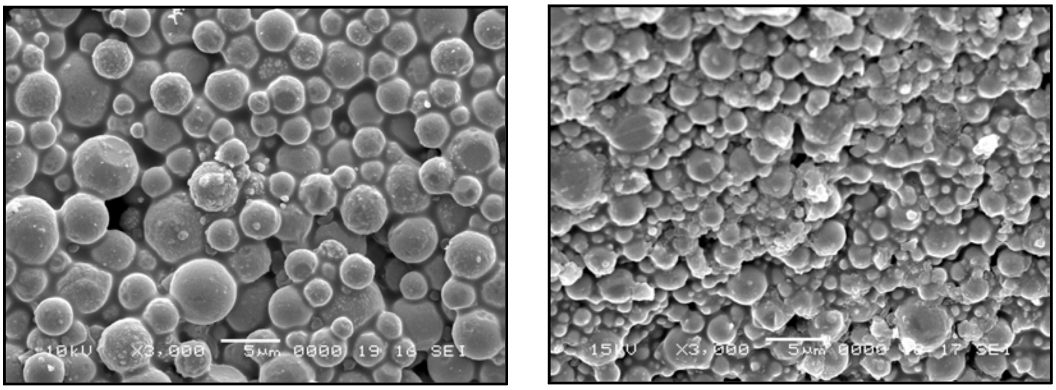


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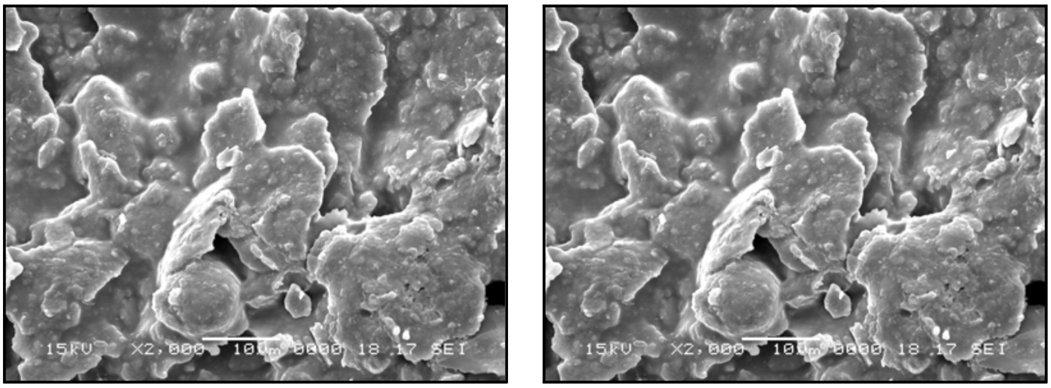
Fig. 4 Morphology of zinc pigmented coatings at various PVC (isometric particles). a – Spherical particles: $PVC_{70\%}$ > CPVC (3000×); b – spherical particles: $PVC_{60\%}$ > CPVC (3000×)



a b

Fig. 5 Morphology of zinc pigmented coatings at various PVC (lamellar particles). a – Lamellar zinc: $PVC_{50\%}$ > CPVC (2000×); b – lamellar zinc: $PVC_{50\%}$ > CPVC (3000×)

Test in Condensation Chamber

The tested samples of steel panels with deposited coating films were exposed to condensation chamber conditions for 120, 240, 480, and 720 hours. With samples the corrosion of substrate was evaluated after 120, 240, 480, and 720-hour exposure. The corrosion in cut was evaluated only after 720-hour exposure. No formation of osmotic blisters was observed with the samples. The order of individual silicate binder is as follows: lithium-sodium water glas, lithium water glass, sodium water glass and potassium water glass. The results obtained with the sodium and lithium water glasses are at an almost same level (Table VII). With the lithium water glass it was not possible to prepare coating compositions hardened by aluminim phosphates owing to too rapid reaction with the hardener. The worst results were obtained with potassium water glass.

In Table VIII the overall anticorrosion efficiency in the condensation chamber after 720-hour exposure is given. The results are affected by a considerable substrate corrosion after this exposure. The lowest anticorrosion efficiency and thus the highest corrosion was observed in the system, which contained besides the silicate binder only inert pigments, fillers and additives. The results of system without active components are after 720-hour exposure identical for all binder types, but the course of corrosion phenomena is suppressed in the highest degree in lithium-sodim water glass. The best results of anticorrosion protection were observed in the systems filled with zinc particles, the systems filled with lamellar zinc particles exhibiting better results than the systems filled with isometrical zinc particles (Fig. 6).

Table VII Effect of the binder type on substrate corrosion with individual coatings

Order[A]	Coating 1	Coating 2	Coating 3	Coating 4	Coating 5	Coating 6	Coating 7	Coating 8
1.	NaLiWG	NaLiWG	NaLiWG	NaWG	NaWG	NaLiWG	NaWG	NaWG
2.	PWG	LiWG	LiWG	NaLiWG	NaLiWG	NaWG	LiWG	PWG
3.	LiWG	PWG	PWG	PWG	PWG	LiWG	NaLiWG	LiWG
4.	NaWG	NaWG	NaWG	-	-	PWG	PWG	NaLiWG

[A] 1 – the lowest substrate corrosion, 4 – the highest substrate corrosion

Table VIII Overall anticorrosion efficiency (%) in the condensation chamber after 720 hours

Coating	Lithium water glass	Sodium water glass	Potassium water glass	Lithium-sodium water glass
Coating 1	56.25	56.25	56.25	56.25
Coating 2	62.5	56.25	62.5	70.0
Coating 3	67.5	67.5	62.5	72.5
Coating 4	-	72.5	62.5	62.5
Coating 5	-	77.5	62.5	70.0
Coating 6	65.0	75.0	56.25	72.5
Coating 7	67.5	72.5	56.25	57.5
Coating 8	61.25	56.25	56.25	56.25

In the systems hardened with aluminum phosphates, the inhibition action of aluminum phosphate manifests itself as anticorrosive pigment, yet better results being obtained with condensed aluminum phosphate, probably owing to lower solubility compared to hydrated aluminum phosphate. The blocked polyisocyanates give better results with isocyanate dissolved in an organic solvent than with isocyanate in water dispersion. Out of actively hardened systems, the worst results from the anticorrosion protection point of view are offered by the system hardened with alkoxysilyl isocyanurate, which does not contain any active pigment and the content of hardening agent is the lowest one.

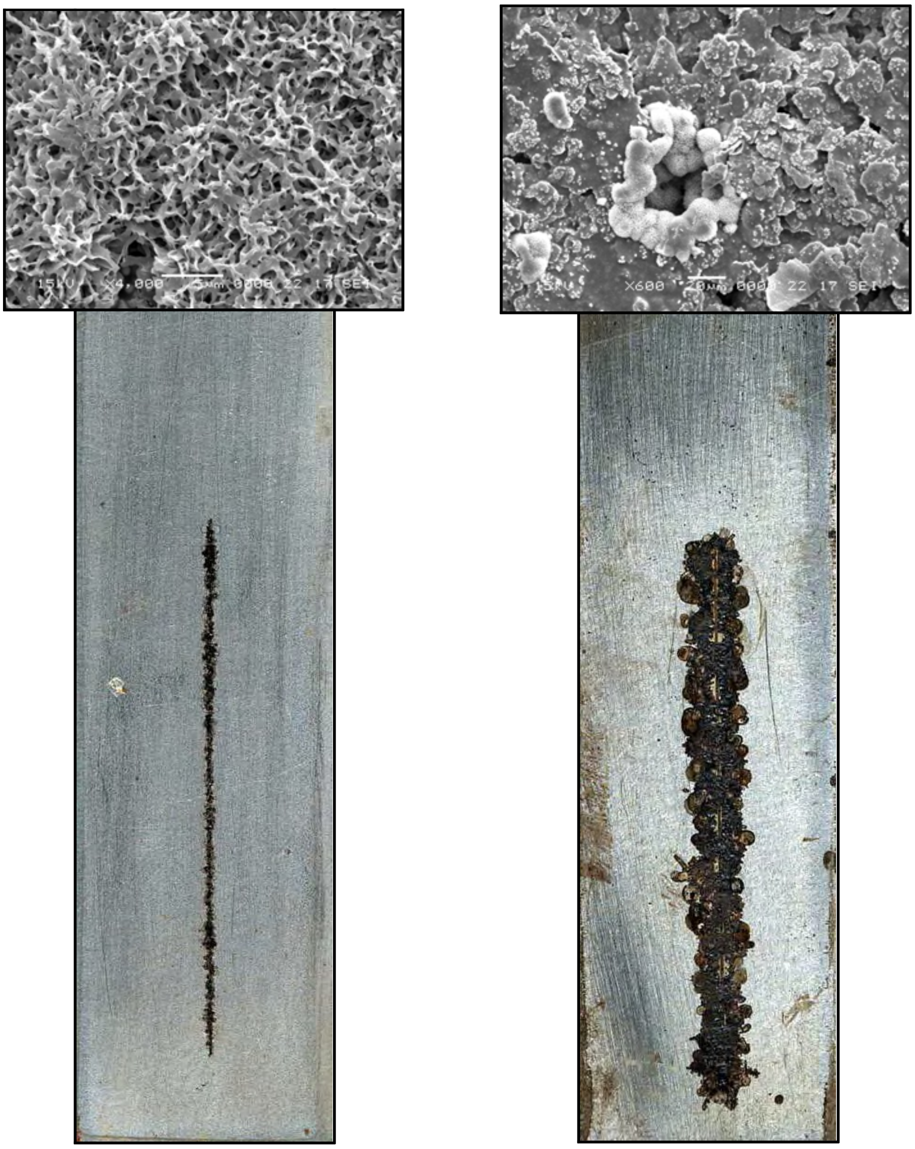
The overall worst results are observed in the system, which does not contain any active anticorrosion component, either a component which could cross-link silicate binder, and the coating film protects the metal surface only by the barrier mechanism. The order of anticorrosion efficiency of individual systems in the condensation chamber is as follows: the system hardened with zinc powder with lamellar particle shape, system hardened with zinc powder with spherical particle shape, system hardened with condensed aluminum phosphate, system hardened with hydrated aluminum phosphate, system hardened with isocyanate in an organic solvent, system hardened with an aqueous isocyanate dispersion, system hardened by the reaction with alkoxysilyl isocyanurate, and system without any hardener and active components.

Table IX Overall anticorrosion efficiency (%) in a salt chamber with cycles

Coating	Lithium water glass	Sodium water glass	Potassium water glass	Lithium-sodium water glass
Coating 1	66.25	73.75	82.5	66.25
Coating 2	72.5	70.0	66.25	70.0
Coating 3	70.0	75.0	72.5	77.5
Coating 4	not evaluated	66.25	66.25	66.25
Coating 5	not evaluated	66.25	66.25	66.25
Coating 6	66.25	66.25	66.25	66.25
Coating 7	66.25	66.25	66.25	66.25
Coating 8	66.25	66.25	72.5	66.25

Test in Salt Chamber with Cycles

The tested samples of steel panels with deposited coating films were exposed to a salt chamber medium with cycles of 240 hours. In samples after 240 exposure hours, the corrosion of substrate and the corrosion in cut were evaluated. In no samples the formation of osmotic blisters was observed. The overall anticorrosion efficiency is given in the following Table IX. The corrosions of samples was considerable after 240 exposure hours, so that it is not possible to follow the effect of silicate binder type on the efficiency of coating film. The substrate corrosion fluctuated at 100 % except for the systems filled with zinc, failure at the cut exhibited 2-3 mm. The anticorrosion efficiency was shown in the coating compositions filled with zinc, which only showed a higher anticorrosion efficiency and in which the substrate corrosion was about one third compared to other samples, and failure in the cut fluctuated at 1-2 mm. Again better results were given by the system filled with zinc powder with lamellar particles than a system filed with zinc powder consisting of spherical particle shapes.



a b

Fig. 6 Photos of experimental steel panels fitted with a cut after the 500 h exposure to a condensation chamber medium and after the coating removal. A – spherical Zn particles; b – lamellar Zn particles

Conclusion

For the coating compositions based on alkali silicates the sodium, potassium, lithium, and lithium-sodium water glasses of a high SiO_2/M_2O mole ratio and suitable physicochemical properties for the preparation of coating compositions were prepared or produced. The silicate coats based on the prepared binders and filled with standard pigments and fillers were hardened by the following methods: a physical mode, a zinc powder with isometrical spherical particles, a zinc powder with lamellar particles, a blocked polyisocyanate in an organic solvent, a blocked polyisocyanate in the water dispersion, a condensed aluminum phosphate, a hydrated aluminum phosphate, and alkoxysilyl isocyanurate.

In coating compositions the tests of physicomechanical properties of the coats on steel and/or glass panels, especially the adhesion by the grid method, the bending strength, the cupping stability, the shock resistance and the hardness value of coating, and tests of corrosion stability in a condensation chamber and a salt chamber with cycles were performed.

The results achieved were evaluated as from the effect of silicate binder type point of view, so as the type of used hardening system type point of view. According to the physicomechanical properties of coats, it is possible to order the tested binders from the best one to the worst one: lithium-sodium water glass, potassium water glass, sodium water glass and lithium water glass. According to the point of view of the composition of coating material and the type of hardener, it is possible on the basis of the mechanical testing results to order individual hardening systems from the best one to the worst one: the system hardened by the reaction with solvent isocyanate type, system hardened by the reaction with isometric-particle zinc, system hardened by the reaction with alkoxysilyl isocyanurate, system without hardener and active components, system hardened by the reaction with lamellar particle zinc, system hardened by the reaction with aqueous isocyanate dispersion, system hardened by the reaction with condensed aluminum phosphate, and system hardened by the reaction with hydrated aluminum phosphate.

The order of silicate binders according to the anticorrosion efficiency in a condensation chamber is as follows: lithium-sodium water glass, lithium water glass, sodium water glass and potassium water glass. The order of anticorrosion efficiency of individual systems in a condensation chamber is as follows: the system hardened with zinc powder with lamellar particle shapes, system hardened with zinc powder with spherical particle shapes, system hardened with condensed aluminum phosphate, system hardened with hydrated aluminum phosphate, system hardened with isocyanate in an organic solvent, system hardened with aqueous isocyanate dispersion, system hardened by the reaction with alkoxysilyl isocyanurate, system without any hardener and active components.

The overall best results were achieved with lithium-sodium water glass, the coats of which exhibited good physicomechanical and also anticorrosion properties. From the point of view of the composition of coating material, very good results are exhibited by the coating materials filled with zinc. Zinc with lamellar particle shapes exhibits a higher anticorrosion efficiency.

References

[1] Burian A., Křístek J.: Foundry Industry (in Czech), **25**, 125 (1977).

[2] Pouchlý J., Vavrouch I.: *Physical Chemistry of Colloidal Systems*, SNTL Prague, 1960.

[3] Hoechst Ag. GB902935. 1962-08-09. *Self-hardening water glass cement composition*.

[4] Hoechst Ag. US 344525777. Inventors: Medic N. *et al*. 1969-05-20. *Hardener for water glass cements.*

[5] Hoechst Ag. US 4138261. Inventors: Adrian R. *et al*. 1979-02-06. *Hardeners for use in water glass cement compositions and process for making them*.

[6] Pennwalt Corp. US 4395387. 1983-07-26. inventors: Goltz K., West W. *Method for manufacturing water glass cement hardeners.*

[7] Hoechst Ag. GB 737554. 1955-09-28. *Self-hardening water glass compositions yielding acid-resistant masses and process for making such compositions.*

[8] Hustinx E. US 3016358. 1962-02-09. *Modified water glass for casting and its preparing process.*

[9] Taki Chem Co, Ltd. JP 11116956. 1999-04-27. Inventor: Matsuda J. *Hardening of water glass for grout.*

[10] Hoechst Ag. GB 891488. *Self-hardening water glass cement compositions* 1962-03-14.

[11] Hoechst Ag. GB865860. 1961-04-19. *Self-hardening alkali- and acid-resistant water glass cements capable of swelling.*