DOI: http://dx.doi.org/10.15407/tpwj2019.01.04

DEPENDENCE OF HYGROSCOPICITY OF COATINGS OF LOW-HYDROGEN ELECTRODES ON COMPOSITION AND STRUCTURE OF LIQUID GLASS

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Presented were the results of investigation of hygroscopicity of coatings of low-hydrogen electrodes depending on composition of liquid Li-, Na- and K-glasses as well as their binary mixtures, which were interpreted from point of view of evolution of a silicon-oxygen structure in the process of glass formation under effect of changing type and relationship of cations of alkali metals. Carried diagnostics of structure-functional self-organization of the silicon-oxygen anions in composition of the liquid glasses was performed based on data of a nuclear magnetic resonance. The spectra of nuclear magnetic resonance ^{29}Si were used. Generalized data were considered taking into account dominance of polycondensation mechanism. Correlation between the indices of coating hygroscopicity and relationship of bridge Q^4, Q^3, Q^2 and nonbridge Q^1 connectivities in structure of the silicon-oxygen anions were determined. 19 Ref., 2 Tables, 12 Figures.

Keywords: *arc welding, welding electrodes, coating hygroscopicity, production technology, liquid glass, structure of liquid metal, spectroscopy of nuclear magnetic resonance*

Atmosphere always contains some amount of water vapor, i.e. has a relative humidity. When reaching saturation the water vapor is condensed in form of dew, mist, hoarfrost, snowflakes or rain-drops depending on ambient environment.

In course of regular heat treatment of the electrodes in a temperature range of 150–400 °C the humidity (moisture content) of electrode coating is led to a level lower than equilibrium moisture content of the environment, i.e. coating is hygroscopic and characterized with the capacity to absorb moisture as many other dehydrated capillary-porous and colloidal materials.

Moisture which has penetrated the coating initiates with time chemical transformations of its constituents. After reaching specific concentration typical for that or another composition of the coating the absorbed moisture promotes significant deterioration of welding-technological characteristics of electrodes connected with change of appearance, formation of defects, decrease of coating strength and, as a result, formation of weld porosity and near-weld cracks (Table 1).

Welding engineering spends enormous resources [1, 2] on detection, removal, restoration of defective areas of the welds and verification of quality performance of repair operations.

For keeping electrode condition on humidity at the level of regulatory requirements the specific types of their packaging are used, and for condition restoration and further storage of the electrodes until application a fleet of drying-baking units is used. Performance of reanimation activities, list and sequence of performance of which is presented on Figure 1, also requires engagement of enormous resources.

In order to overcome the problems there is a need in development of technological methods which allow dramatically improve moisture resistance of the coating. One of the tasks is to keep such condition of coating of electrodes taken out of package, at which during at least eight-hours working shift content of

Table 1. Types and place of appearance of inadequacies caused by hygroscopic humidity of coating

Object of control	Type and nature of appearing inadequacies
Appearance of electrodes	Spots on coating surface
	Bulbs in the coating
	Core corrosion
Electrode coating	Reduction of strength
Welding — technological properties of electrodes	Deterioration of arcing stability
	Excessive spattering of molten metal
	Unsatisfactory weld formation
	Bad separability of weld crust
Weld	Porosity
	Hydrogen embrittlement
	Cold cracks

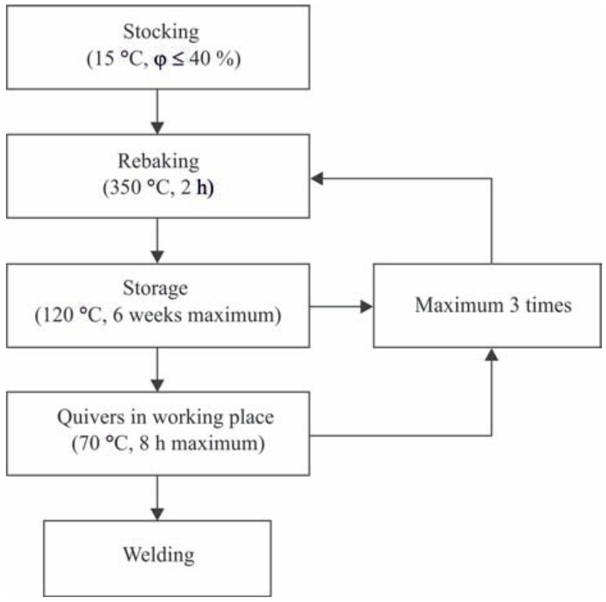

Figure 1. Scheme of regulation of preparation to welding and application of electrodes with low-hydrogen coating

hydrogen in the deposited metal remains within the regulatory limits. At the same time, without compromising welding-technological, metallurgical and sanitary-hygienic characteristics of the electrodes.

Such electrode manufacturers as ESAB [3, 4], Smith weld [5], Oerlikon [6], Metrode Product [7], Quasy Arc [8, 9], Thyssen Draht, Kobelco, Lincoln Electric, etc. as well as series of domestic SRO, including E.O. Paton Electric Welding Institute [10, 11] have dealt with this problem.

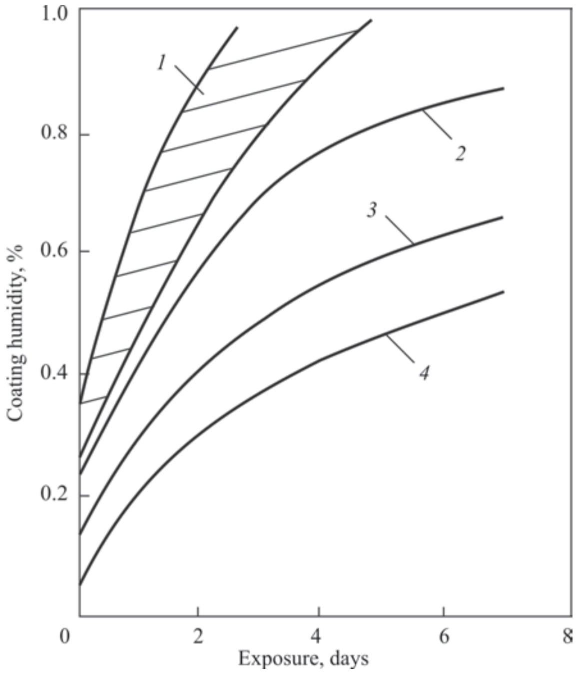

Figure 2. Hygrosorption resistance of electrode coatings depending on method of regulation of polymer condition of silicon-oxygen anions in liquid glass (φ = 75 %, T = 25 °C; designations *1–4* see in the text) [7]

As a result a range of technological procedures were developed for rising a hygrosorbtion resistance of the electrode coatings. The most important of them are based on a regulation of level of polymerization of alkali silicates in the binary liquid glass. They can be divided on 3 groups by efficiency (Figure 2).

Number 1 designates common electrodes, number 2 is the electrodes produced based on binary NaK liquid glasses with relationship of alkali ion-modifiers providing the minimum hygrosorption capacity of alkali hydrosilicate binder. Number 3 marks the electrodes with coating based on NaK glass, module of which was reached by means of regulation of molar ratio $SIO_2/(Na_2O + K_2O)$, including by addition in liquid glass of ammonia silicate. Number 4 marks the electrodes with the low hygroscopicity of the coating, reached due to additional modification of structural network of high-module silicate with cation-glass former.

The electrodes with high hygrosorbtion resistance of the coating are marked with R, MR, EMR, HMR or LMA symbols. The electrodes marked with that symbols satisfy the requirements to hygrosorption resistance of the coating mentioned above and allow getting significant economic result due to decrease of heating temperature, reduction of weld repair expenses, rebaking and maintenance of baked electrodes [1, 5, 11].

Reasons of hygroscopicity of electrode coatings are ambiguous. There are six types of adsorption isotherms, using each of which or their specific combination it is possible to characterize individual properties of any natural adsorbent, including the indices of absorption kinetics and limits of their saturation with moisture (equilibrium moisture content). Among them are mono- or biparametric isotherms of Henry ($x = kP$), Langmuir ($x = kP/(1 + kP)$), Freundlich ($x = kP^{1/n}$), BET, Zsigmondy and hysteresis shape given on Figure 3.

The hygrosorption characteristics of the electrode coatings do not match on shape with any of given isotherms. It is explained by the fact that the electrode coatings have several types of sorption centers. Among them are:

- grains of mineral gas-slag-forming materials, ferroalloys-deoxidizers and iron powder;
- dry residue of liquid glass in form of alkali hydrosilicates, contained in the space between them;
- particles of mineral plasticizers in form of kaolin, bentonite, mica, talc, carbonates of Na and K as well as alginates, CMC and other organic hydrocolloids;
- ash residues of thermo-oxidative degradation of organic hydrocolloids.

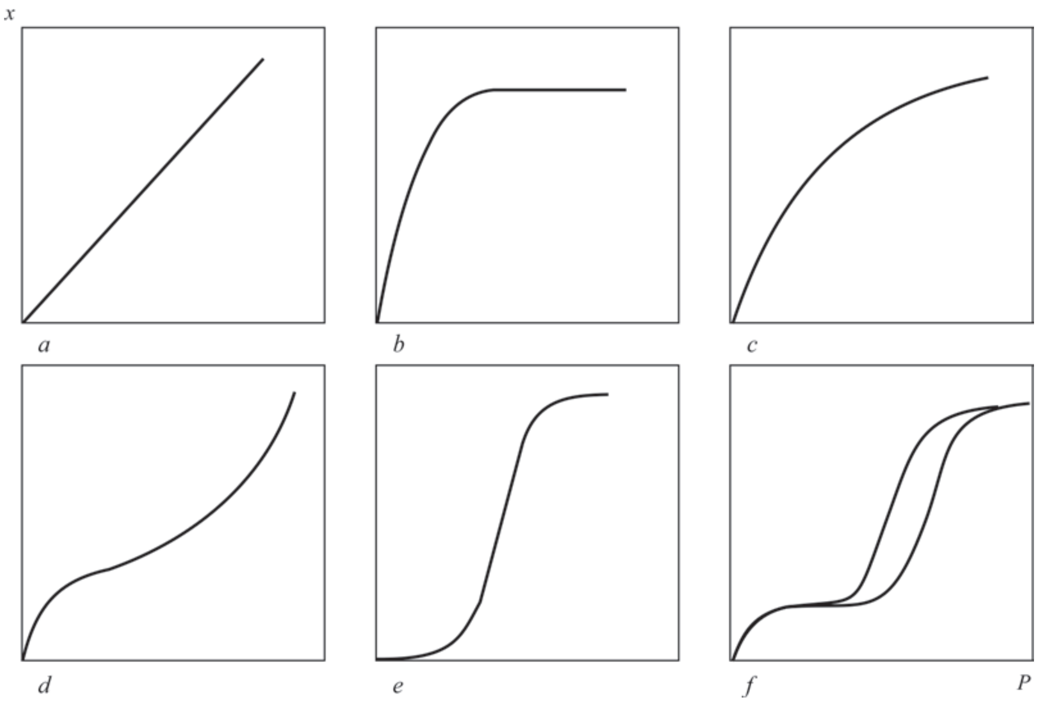

Figure 3. Typical variants of absorption isothermal curves [12]: *a* — Henry; *b* — Langmuir; *c* — Freundlich; *d* — BET; *e* — Zsigmondy; *f* — hysteresis shape

The moisture, absorbed from atmosphere, in course of time changes its physicochemical state in the coating, gradually transforming from capillary into chemically connected form.

Since moisture absorption isotherms of the electrode coatings can not be linearized, that allows determining the parameters necessary for matching the different coatings on hygroscopicity, they are compared by general view of hygrosorption curves obtained under standard conditions.

Procedure. The procedures based on this for determination of hygroscopicity of electrode coatings are divided on 3 groups by designation, namely:

- for investigation of nature and characteristics of hygrosorption process;
- for classification (certification) tests of the electrodes on capability of their coatings to resist absorption of atmospheric moisture;
- for technological control of electrode products.

In any case equipment includes a climatic chamber, designed to maintain of set (or standard, if we are talking about classification tests) climatic conditions, in which the electrodes are exposed during tests. It consists of humidistat and thermostat.

Humidistat is the box made of glass, plastic or another inert material, which contains:

- support with tested electrodes laid on it without connection with each other;
- thermometer;
- open tank with saturated salt solution, providing guaranteed atmosphere humidity with set value of partial pressure of moisture (relative humidity φ). Change of φ in course of testing is not allowed since measurement would provoke air circulation in the humidistat, which, respectively, would result in violation of results reproducibility.

Thermostat is made in a form of safely heat-insulated and tightly closed chamber, in which a temperature regulator by signal from the probe automatically, with ±1 °C accuracy keeps the set temperature and built-in fan uniformly distribute it over chamber workspace.

The International Institute of Welding (IIW) and International Organization for Standardization (ISO) developed the standards regulating the conditions, order of performance of classification tests and certification of low-hydrogen electrodes for resistance of coatings to atmospheric pressure absorption.

In the first of them a classification feature is coating limit humidity, reaching which the electrode shall be heat-treated for reconstruction of its condition. In the second, such a feature is an allowable content of hydrogen in the deposited metal, which as a result of humidity adsorption by coating in the climatic conditions regulated by standard ($\varphi = 80$ %, $T = 27$ °C, $t = 24$ h) shall not be exceeded in any case. For keeping such conditions saturated solution of ammonia sulfate $(NH_4)_2SO_4$ is used.

IIW standard simultaneously regulates the conditions for preparation of the electrodes to tests, preservation of achieved hygrosorption humidity of the coating during testing, that is provided by use of transportable leak proof ampoules for the electrodes as well as order of treatment of electrodes during the

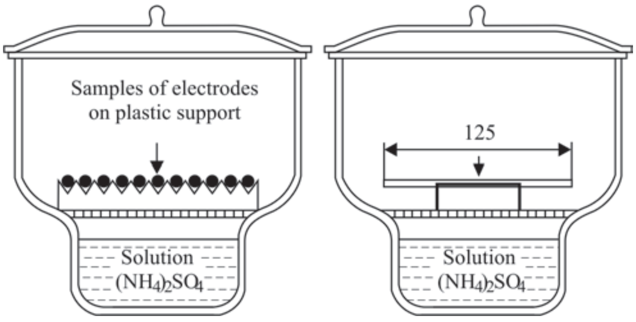

Figure 4. Humidistat for determination of hygrosorption capacity of electrode coating

procedure of measurement of hydrogen content in the deposited metal, corresponding to the provisions of ISO 3650 [13].

E.O. Paton Electric Welding Institute applies the procedure for evaluation of hygrosorption capacity of the electrode coatings to the maximum approached to these requirements. Kinetics of moisture sorption by coating immediately after electrode heat treatment is evaluated. Short-term (8 h) and long-term (14 days) exposure of the electrodes in atmosphere with φ = = 80 % and $T = 27 \pm 1$ °C is used.

The essence of the procedure lies in the following:

- several electrodes are taken from the controlled batch and three samples of 125 mm length are cut out of them;
- cut out samples of the electrodes are baked at the modes prescribed in specification;
- after cooling on air to 20–30 °C samples of the electrodes are weighed on the analytical balances and at once transferred to the humidistat, being a standard glass exiccator (Figure 4), in which set climatic conditions are kept;
- humidistat with samples of the electrodes is placed in the work chamber of thermostat TVZ-25 (TU 64-1-619–76, heater power 300 W), in which 27 ± 1 °C temperature is kept.
- kinetics of moisture absorption by coating is controlled with weighing of each electrode on the analytical balances every 1, 2, 3, 5 and 8 h, and them after 1, 2, 3, 5, 8, 10, 12 and 14 days. During weighing the exiccator is removed from the thermostat. The electrodes are removed from it one by one and weighed. Duration of weighing of one electrode does not exceed 10 s;
- the calculations are made on formulae

$$x = \frac{(P_x - P_0)}{(P_0 - P_c)}100, \qquad (1)$$

where x is the amount of absorbed by coating moisture in form of mass increment of adsorbent in course of humidification, %; P_0, P_x are the mass of electrode before and after hygrosorption humidification, g; P_c is the mass of electrode core, g.

Set relative humidity in the humidistat, if necessary, was changed using another salt diluted in a humidistat bath. The same is referred to the duration of process observation.

As it was mentioned above, when investigating hygroscopicity of electrode coatings it is assumed that increment of adsorbed substance mass is caused only by moisture absorbed from atmosphere. For electrode coatings such an assumption is not always true due to the fact that alkali hydrosilicate absorbs not only moisture, but also CO_2 in the case of long-term exposure. For this reason in the expert cases a check of the composition of adsorbed material, for example, by means of performance of special analyses using gas analyzer combined with DTA is carried out.

Role of combined liquid glasses in hygrosorption process inhibition. In electrode coatings made using binary (relatively ions-modifiers) liquid glasses, in variation of relationship of alkali constituents in the liquid glass, there was detected changes of hygrosorption characteristics [4, 10], which do not subject to additivity rule.

Figure 5 compares dynamics of change of coating hygroscopicity of UONI 13/55 electrodes made on binary NaK liquid glasses depending on Na- and K-ingredients in the mixture. Modules of initial monoalkali glasses $M_{Na} = M_K = 2.9$, toughness 500 MPa·s. It can be seen that coatings on liquid glass with molar fraction of potassium constituent very close to 30–40 %, are characterized with minimum hygrosorption capacity. Coatings with larger fraction of potassium com-

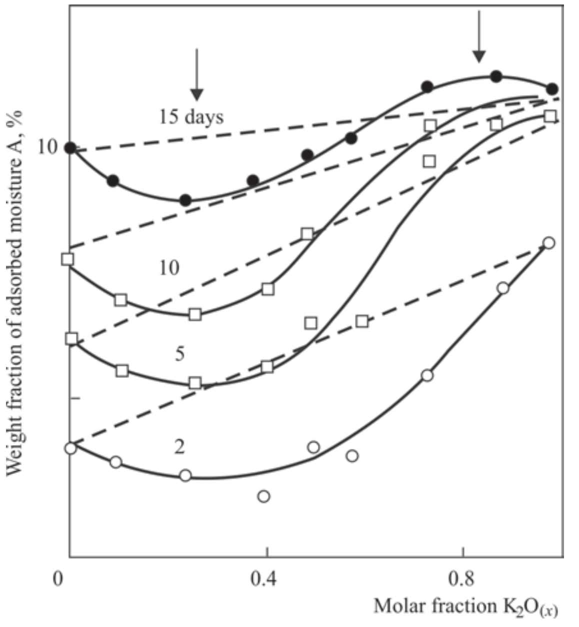

Figure 5. Effect of relationship of alkali oxides in NaK-liquid glass on hygroscopicity of electrode coating (φ = 95 %; T = = 25 °C). The numbers show the exposure time of electrodes in humidistat [7]

ponent than in the minimum point accumulate moisture more intensive than made based on glasses with smaller fraction of indicated component. Ascending (potassium) branches of the curves at short exposures is sharper than descending (sodium). Together with minimum, at 70–80 % of potassium constituent, the curve demonstrates the maximum of hygroscopicity (marked, as a minimum, by arrow). Rise of exposure aligns the slopes of ascending branches and a level of deviation of the extreme point from additive value reduces. Extremeness is studied for change of liquid glass toughness (maximum appears), and for water retaining capacity of dry residues of binary glasses and electrode coatings on their basis (the minimum appears as in hygroscopicity). This picture is changed under effect of type and module of solutions of alkali silicates, taken for preparation of binary liquid glasses [7, 10, 14, 15].

Figure 6 showed the nature of change of hygroscopicity of electrode coatings depending on relationship of initial sodium (Na$_s$) and potassium (K$_s$) constituents as well as module of made of them NaK liquid glasses, designed for electrode manufacture. In order to preserve similar Na$_s$/K$_s$ relationship in the compared binary mixtures of glasses the authors [7] increased their module by addition of 5 % of ammonium silicate Quaram into the prepared mixture.

Accepted designations:

- 1 and 1′ are the electrodes directly after baking;
- 2, 3, 4 and 2′, 3′, 4′ are the electrodes exposed in humid medium during 24, 48 and 168 h, respectively;
- solid lines show the variants of the samples manufactured based on mixtures of glasses with lower, and dashed with larger values of module.

Humidity of the coating was determined after baking at 1000 °C (using IIW method).

Data given on Figure 6 verify that amount of moisture absorbed by electrode coating from corresponding atmosphere, has different effect on relationship of alkali constituents and their module depending on exposure duration. The minimum humidification is observed not at one fixed relationships of Na$_s$/K$_s$ as it was determined in works [4, 10, 16]. According to Figure 6 a position of minimum of reached moisture contents in rise of the electrode exposure in humid condition can be displaced to the side of bigger or smaller from initial values.

Rise of module of liquid glass promotes decrease of moisture absorption in the minimum and point of minimum really displaces to the side of larger portion of potassium constituent in the mixture of liquid glasses. Asymmetry of the moisture absorption curves appears simultaneously, in the right i.e. potassium branch has more slope than sodium, particular in the case of long-term exposures.

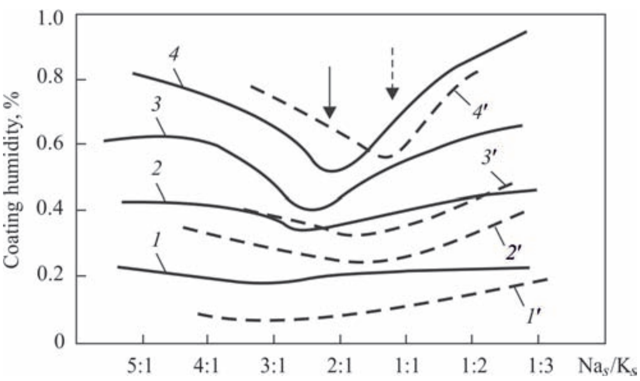

Figure 6. Dependence of amount of moisture absorbed by coating from relationship Na$_s$ and K$_s$ constituents, as well as module of binary liquid glasses (φ = 75 %; T = 25 °C, see description in the text) [7]

The pattern becomes more complex when binary mixtures are made of monoalkali solutions of silicates with larger difference of cation size than in K and Na. Figure 7 compares hygrosorption curves received during investigation of pilot variants of UONI 13/55 electrodes, marked with T-99 index. Coatings are manufactured using Li, Na and K liquid glasses with M = 3.2 and their binary mixtures. Electrode diameter is 4 mm.

It can be seen that during short-term exposure the coatings on liquid Li-, Na- and K-glasses absorbed 0.1, 0.3 and 2.0 % of moisture. Amount of absorbed moisture with rise of electrode holding to 14 days increases almost 3 times in Li- and K-variants, and in Na-variant in 5 times. At short-term exposure amount of moisture absorbed by coating monotonically grows with increase of fraction of second component in the liquid glass mixture. At long-term exposure the curve of coating moisture absorption of NaK-series contains the minimum and maximum, which are only displaced left and more expressed than in series of the electrodes manufactured based on liquid NaK glasses with 2.9 module (see Figure 5).

It is necessary to pay attention that effect on coating hygrosorption properties of the component added to lithium glass is significantly neglected by lithium constituent. In short-term exposure it only refers to potassium, and at long-term exposure to sodium constituent as well. The same pattern is observed in the case of effect of NaK-liquid glasses on coating hygroscopicity. At short-term exposures the sodium constituent suppresses hygroscopicity of potassium constituent and at long-term holding they almost equalize on the level of effect on coating sorption capacity as if modularity of the potassium component significantly rise due to some reason.

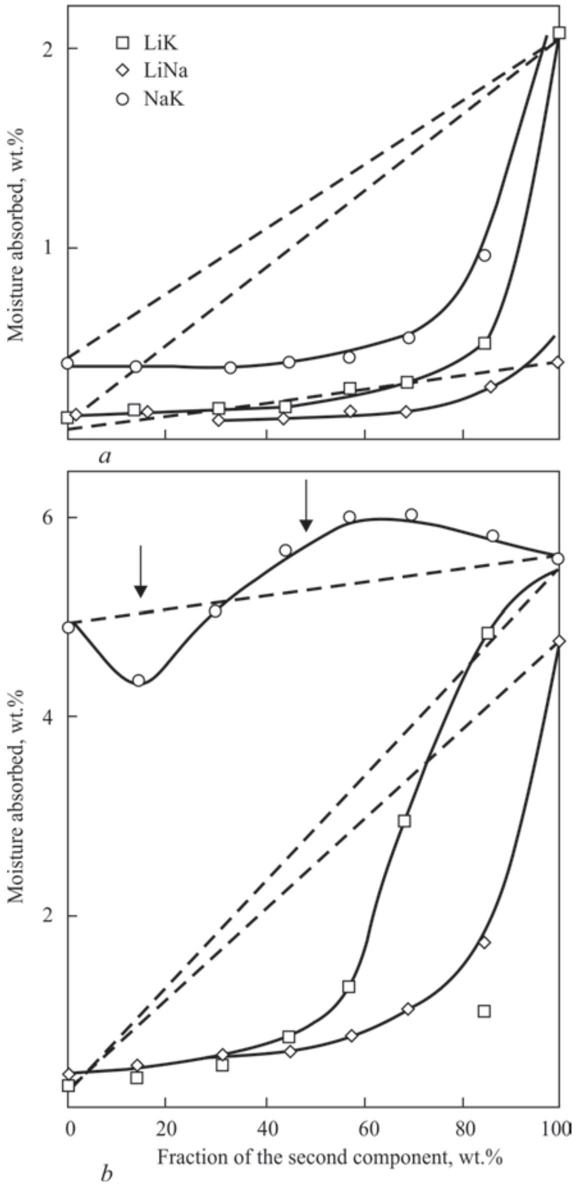

Figure 7. Effect of content of binary high module liquid LiNa-, LiK- and NaK-glasses on hygroscopicity of coating of pilot electrodes T-99: *a* — 8 h; *b* — 14 days

Based on mentioned above it can be concluded that change of hygroscopicity of electrode coatings in use of the combined liquid glasses has a complex nature. It can not be explained only by effect of increase of portion of more «hygroscopic» cations in the composition with less hygroscopic, if it is a priory supposed that change of integral hygroscopicity of cation constituent follows the linear law. A role of structure of anion constituent, apparently, shall also be taken into account since a structure of silicon-oxygen anions (SOA), which is changed under the effect of relationship of cation-modifiers, is essential in a synergism of toughness of the binary liquid glasses and in nonlinear change of water-retaining capacity of the binary mixtures of hydrosilicates at their thermal dehydration.

In this connection the paper studies the hygroscopicity of low-hydrogen electrode coatings ANV-35 in conjunction with SOA structure of liquid LiNa-, LiK- and NaK-glasses, which were prepared from monoalkali liquid Li-, Na- and K-glasses with the values of modules 2.8, 3.0 and 3.6, respectively. Composition of the initial glasses is given in Table 2 [17]. Toughness of the initial glasses made 350 MPa·s. Dose of glasses in the paste is 25, 26 and 23 %.

Monoalkali liquid Li-, Na- and K-glasses were used for preparation of pastes of pilot electrodes with the same consistency that in work [17].

In contrast to them binary glasses in advance were brought to the level of toughness of initial monoalkali glasses by means of dissolution with small additions of water in order to neglect the synergy effect. In LiK liquid glasses, containing from 16.3 to 50.0 wt.% of potassium constituent, in initial state the synergy burst reached 20800 MPa·s. Therefore, the level of their dissolution was significantly larger than in the rest samples of indicated series.

Produced electrodes were dried for 24 h on air, after what were hold for 1 h at 200 °C and then baked at 400 °C.

The values of chemical shift (δ, ppm) of ^{29}Si signals for samples of monoalkali and combined liquid glasses were determined at room temperature using NMR-spectrometer of AVANSE 400 model. A source of information on SOA structure of liquid glasses was a relative integral intensity of signals of corresponding structural groups Q_m in the primary ^{29}Si NMR analytical spectra. Procedure of work is outlined in [17]. The average value of connectivity Q_{av} was calculated using $\sum x_i Q_i$ expression, where Q_i is the index of chemical shift, characterizing connectivity *n*, and x_i is the partial value of this type of connectivities. The hygroscopicity of electrode coatings was investigated under conditions $\varphi = 84$ %, $T = 25$ °C. Figure 8 shows the results of evaluation of hygroscopicity.

As in the series of experiments T-99 the minimum hygroscopicity was revealed in a coating made based on lithium liquid glass. As it follows from Table 2 in structure of their SOA there is the highest fraction of bridge connectivities Q^4. During 4 hours the composition absorbed 0.1% of moisture, and 0.6 % of Na- and K-glass. However, after 14 days the sorption reached the values of 0.3, 0.5 and 5.5 % of H_2O, respectively, i.e. 3–10 times more. As can be seen, the hygrosorption capacity of the coating samples of these series is significantly higher in comparison with coatings T-99, made based on liquid glasses with M = 3.2.

It also follows from Figure 8 that hygroscopicity of the coatings with appearance of the second compo-

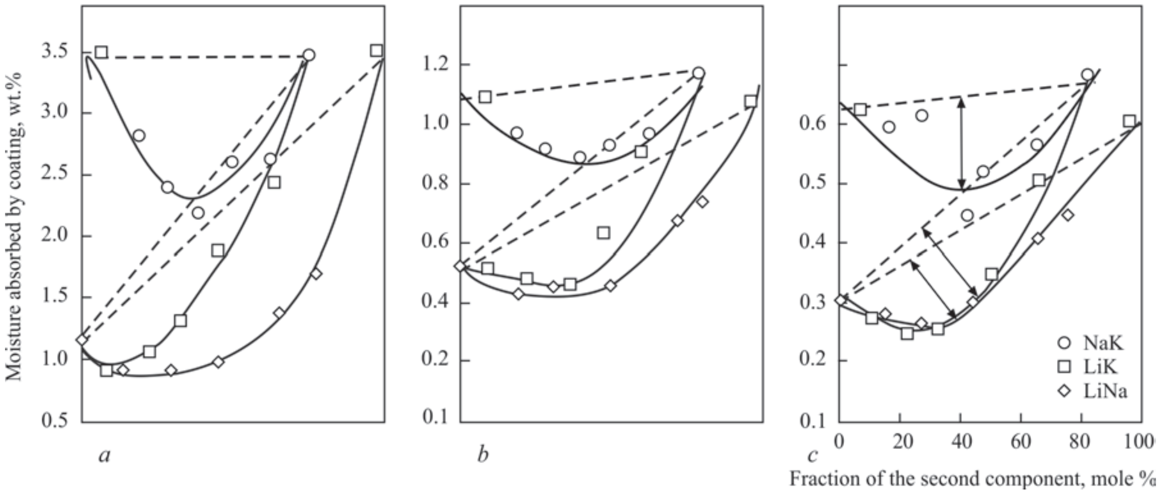

Figure 8. Dependence of amount of moisture absorbed by coating on content of liquid glass and duration of observation: *a* — 14 days; *b* — 24 h; *c* — 8 h

nent in the binary glasses is firstly below the expected one according to additivity rule. Then, after reaching the minimum, it monotonously grows, moreover for LiK-series it is significantly more intensive than for LiNa and NaK-series. Duration of electrode exposure in the humid medium has small effect on evolution of absorption capacity of the considered coatings.

Figure 9 shows the change of the weighted average value of connectivity index in SOA structure of the combined liquid glasses depending on concentration in them of the second component. Dependence of amount of moisture, absorbed by coatings, on index $Q_{av}\sum x_i Q_i$, is given on Figure 10.

Comparing meaningful aspects of indicated Figures, it is possible to assume that different hygrosorption capacity of the electrode coatings, made at combination of relationship of components of liquid glasses, is actually determined by tendency to hydration of ion-modifiers as well as, to significant extent, by structure of liquid glasses SOA dominating in specific conditions, which is formed under determining effect of corresponding cations.

At that the weighted average value of connectivities is changed. As a result, as it follows from data given on Figure 10, hygroscopicity of the coatings is, in particular, determined by Q_{av} index. At that, as it follows from Figure 11, Q_{av} rises due to increase of $Q^4/Q^2 + Q^3$ relationship.

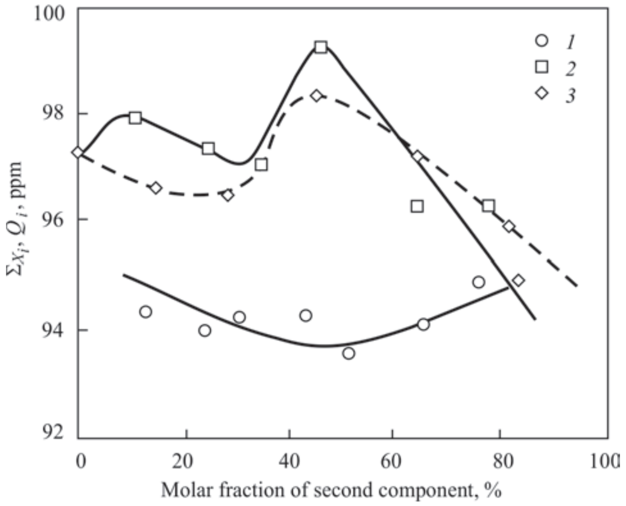

Figure 9. Change of Q_{av} depending on concentration of the second component in NaK (*1*), LiK (*2*) and LiNa (*3*) liquid glass

The results being out of general pattern are referred to three liquid LiK-glasses in composition of which molar ratios $K_2O/Li_2O \geq 1$.

Complete encapsulation of hygroscopic K-cations by high-module silicon-oxygen shall becomes impossible at that.

Effect of cation-glass former on hygroscopicity of electrode coatings. In liquid glasses, the results of investigation of which are outlined in the previous chapters, silicon is the single so-called cation-glass former determining variety of spatial constructions in the content of forming SiO_4^{-4}. Fine regulators of

Table 2. Composition, density and toughness of Li, Na and K liquid glasses

Type of glass	Module	Weight fraction, %				Glass properties		
		SiO_2	Li_2O	Na_2O	K_2O	ρ, $kg\cdot m^{-3}$	η, mPa·s	Q^4, ppm
Li	2.77	25.52	4.60	–	–	1313	325	26.5
Na	3.09	28.54	–	8.40	1.70	1433	325	16.0
K	3.67	26.37	–	1.66	8.93	1422	360	13.5

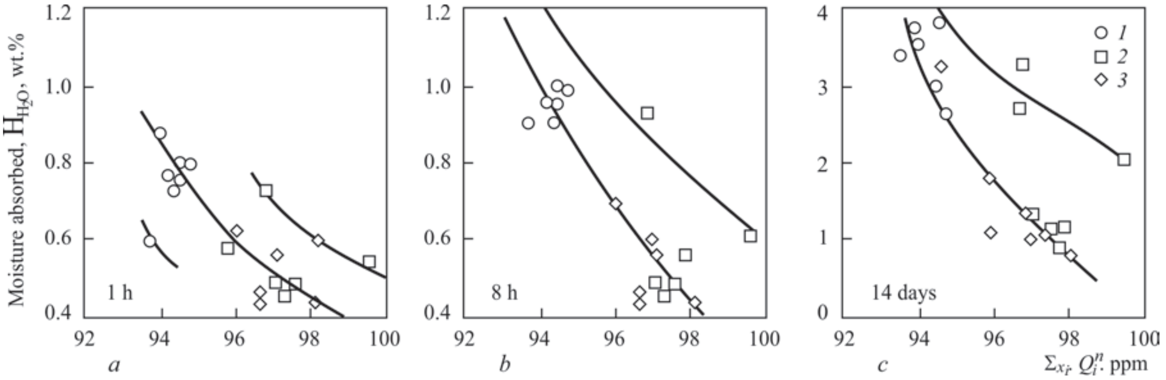

Figure 10. Dependence of amount of moisture, absorbed by coating from humid atmosphere, from Q_m of binary liquid glasses: *a* — 1 h; *b* — 8 h; *c* — 14 days (see designations on Figure 9)

structure of the forming SOA, and, as a consequence, physicochemical properties of liquid glasses, used in production of electrodes, are alkali cation-modifiers (Li$^+$, Na$^+$, K$^+$, NH_3^+ and rarely — Rb$^+$ and Cs$^+$). Even such, it would seem, limited list of the modifiers significantly expands the possibilities of rise of production efficiency, reaching set technical characteristics and indices of welding electrode quality.

Really, hygroscopicity of the coating can be significantly reduces with addition of ammonia hydrosilicate into a paste composition or liquid glass, promoting increase of its module and decrease of pH value [7]. The level of coating hygroscopicity reached at that can be provided by increase of electrode baking temperature from 400 to 450 °C, but it will require larger energy consumption than at introduction of modifying ammonium additive.

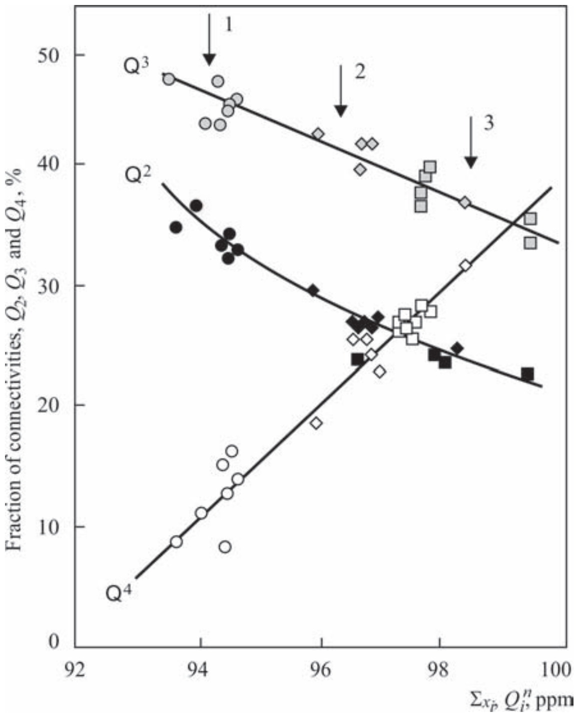

Figure 11. Change of relationship of connectivities in SOA structure of NaK (arrow 1), LiNa (arrow 2) and LiK (arrow 3) of liquid glasses depending on weighted average value of chemical shift

In the silicate technologies regulation of SOA structure of the silicate melts is carried out using modifiers in form of cation-glass formers (based on Al^{3+}, P^{5+}, etc.)[18]. Their effect of SOA structure can be performed by different mechanisms depending on force of corresponding cation being present in anionic part of modifying additive. Entering the silicate it tries to form its closest surrounding in new environment from nonbridge (Q^1, Q^2) and bridge (Q^3, Q^4) fragments.

At that the anion groupings with different level of polymerization are formed. Those of them, which were formed by stronger acids will be less polymerized in comparison with the anion groupings formed at participation of weaker acids. In any case, the re-

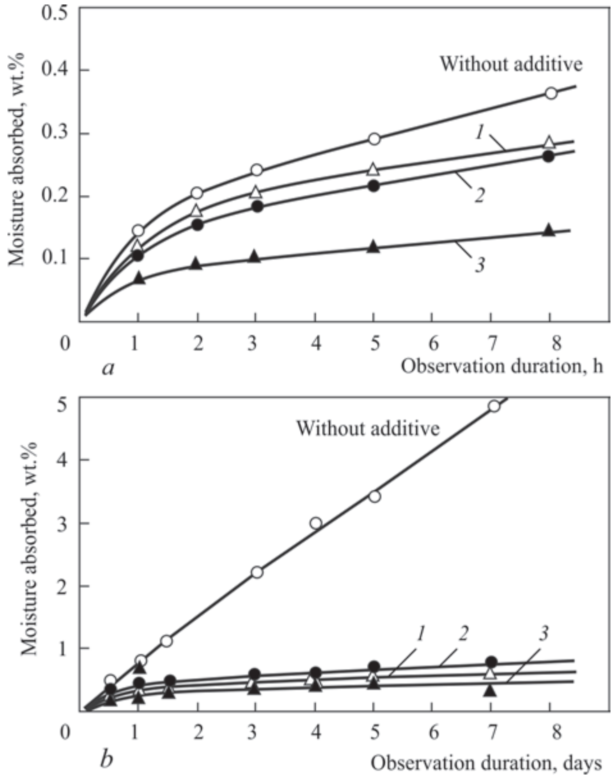

Figure 12. Comparison of kinetics of moisture sorption by common and modified electrode coating with 0.5 (*1*), 1.0 (*2*) and 1.5 % (3) of modifying additive based on cation-glass former. Exposure 1 (*a*) and 14 (*b*) days

sult is reached significantly larger than using cation modifier.

Figure 12 shows the results of testing of one of such additives in the coating of pilot electrodes UONI 13/55. It can be seen that hygroscopicity of electrode coating under its effect is reduced 5–10 times.

Let's note the following in the conclusion. SOA structure of a liquid glass intergranular film in the electrode coating in course of its heat treatment is formed on polycondensation mechanism.

Dehydration of alkali hydrosilicates is as deep as long molecules of water, precipitated in course of polycondensation reaction, are kept in a reaction zone and participate in the next acts of polycondensation transformation as original catalyst [19].

It can be assumed that different size SOA modifications, which appear in the modified liquid glasses, form dense, i.e. less permeable for precipitating water vapors packages than the packages from similar on size SOA — formations typical for non-modified liquid glasses.

Respectively, deeper dehydration in the dense packages provides reliable blocking of coarse, more susceptible to hydration cation-modifiers that rises hygrosorption resistance of electrode coatings, made based on the combined liquid glasses including using technical additives containing modifiers of different functional link.

Conclusions

1. Studied was a hygroscopicity of the low-hydrogen electrode coatings made based on liquid Li-, Na-, and K-glasses as well as composed of them binary LiNa-, LiK- and NaK-variants with different relationship of contained ion-modifiers. The lowest hygroscopicity has the coatings made based on liquid Li-glasses. It is explained by domination of fragments with Q^4 connectivities in the SOA structure of lithium liquid glasses.

2. Increase of coating hygroscopicity with rise of concentration in the binary mixture of glasses of the second differing by larger density of Z/r cation charge is not proportional to its concentration. Unfavorable from point of view of hygroscopicity effect of Na- and K-component is blocked in the binary compositions of lithium constituent, i.e. short-term exposure suppresses effect of dominating potassium and at long-term also sodium component. Sodium constituent in the content of binary liquid NaK-glasses at small exposures blocks increase of coating hygroscopicity, caused by potassium component and at long-term holding Na and K constituents effect the sorption capability of coating almost with similar level.

3. There is a tight connection between hygroscopicity of electrode coatings, on the one hand, and concentration of different forms of connectivities in SOA of the binary liquid glasses on the other hand. The higher the weighted average value of connectivities $Q_{\text{av}} \sum x_i Q_i^n$ the lower is hygroscopicity of the coating. It is true for mono- as well as binary liquid glasses. Indeed, in the first and the second case the hygroscopicity of coatings reduces with rise of module of liquid glass that is explained by increase of contribution of the higher connectivity forms into total SOA structure.

4. In the binary liquid glasses, in contrast to their monoalkali analogues, there are no static distribution of ion-modifiers. Cations with the lower values of Z/r, for example K^+, fill place in the surrounding of highly-polymerized fragments of SOA (Q^3 and Q^4), and cations with the larger Z/r (Na^+ or Li^+) in the environment of less polymerized SOA, i.e. with larger amount of bridge connectivities (Q^2 and Q^1). As long as the cation more susceptible to hydration is «blocked» by high module, i.e. less hygroscopic and less moisture permeable SOA forms, it, as surrounding SOA, has low susceptibility to moisture absorption and hydration. As a result, there is no single-valued connection between physical composition of the binary liquid glasses and average weighted value of the connectivities in SOA structure. More than two number of combinations Q_i^n correspond to the same Q_{av}, and, respectively, characteristics of liquid glasses and made of them filled compositions.

5. In short-term holdings the effect of potassium ion blocking by «high module» SOA is felt at weight fraction of Li_2O in the mixture with K_2O, in our experiments equal approximately 30 %, and sodium ions at even smaller dose. Q^2 and Q^3 connectivities prevail in the SOA structure of liquid NaK-glasses. Therefore, effect of encapsulation is revealed in smaller degree, and decrease of hygroscopicity in the minimum is expressed more obvious than in taken for comparison coatings on lithium-containing liquid glasses.

6. In liquid glasses with two cation-glass formers the cations also compete for place in SOA structure as cation-modifiers. Caused by such competition increase of inhomogeneity of distribution of nonbridge atoms of oxygen promote delay of the process of coating moisture absorption from atmosphere.

1. Smith, R. (1987) Improved consumables can change shopfloor practice. *Met. Construct*., 19(**5**), 282–283.
2. Barbin, L.M. (1977) The new moisture resistance electrodes. *Weld. J*., 56(**7**), 15–19.
3. (1983) LMA-a new quality concept for low hydrogen electrodes with low moisture absorption. *Svetsaren (A Welding Review)*, **2**, 3–5.

4. Almqist, G., Budgifvars, S., Lindström, L. et al. (1983) Some principles for low moisture absorption properties of basic MMA electrodes. In: *Proc. of 2nd Int. Conf. on Offshore Welding Structure* (London, 16–18 Sept. 1982). Abington, 1–6.
5. *Van* Nassau, L. Recent welding consumable improvements providing major handling advantages for offshore fabricators. *Smitweld International Report*, 00774.
6. Becker, H. von (1964) Über die Feuchtigkeitsaufnahme, die Auswirkung und die Zweckmässige Rücktrocknung bei Schweisselektroden. *Oerlikon Schweissmitteilungen*, 22(**52**), 12–19.
7. Marshal, F.W., Farrar, J.C.M. (1983) Progress in moisture/hydrogen control of lime-fluorspar and lime-titania electrodes. In: *Proc. of 1st Int. Conf. on Developments and Innovations for Improved Welding Production* (13–15 Sept. 1983, Abington). London, 28, 1–10.
8. Kaljee, J. (1978) Hydrogen in weld metal; causes and remedies. *Welding Reporter*, 14(2), 5–10.
9. Kaljee, J. (1986) Moisture resistant electrode coating. *FWP J.*, 26(1), 29, 30, 32–34, 38–40.
10. Marchenko, A.E., Skorina, N.V. (1989) Combined alkali silicates in manufacture of low-hydrogen electrodes. Metallurgical and technological problems of basic covered electrodes. In: *Proc. of 2nd Int. School for Countries-Members of CMEA* (Sofia, 1989). Kiev, Naukova Dumka, 123–130.
11. (2004) New electrodes for welding of carbon and low-alloy steels, demand and supply (in cooperation with I.R. Yavdoshchin et al.). In: *Proc. of 3rd Int. Conf. of CIS Countries on Welding Consumables. Development. Technologies. Manufacture. Quality* (Dnepropetrovsk, 1—4 June 2004). Dnepropetrovsk, 64–67.
12. Hirai, Y., Minakawa, S., Tsuboi, J. (1980) *Prediction of diffusible hydrogen content in deposited metal with basic type covered electrodes*. IIW Doc. II-929–80.
13. *ISO 14372:2000 (E)*: Welding consumables — Determination of moisture resistance of manual metal arc welding electrodes by measurement of diffusible hydrogen.
14. Marchenko, A.E., Skorina, N.V. (1981) Synergism of toughness of combined liquid glasses and properties of electrode compounds. *CMEA: Inform. Materialy*, 20(**2**), 109–115 [in Russian].
15. Marchenko, A.E., Skorina, N.V. (1987) Water-retaining ability of alkali silicates and its effect on dehydration of electrode coatings. *Ibid.*, 31(**1**), 43–60 [in Russian].
16. Schleyer, W.L. (1970) Welding electrodes and the properties of soluble silicates. *Weld. J.*, 49(**12**), 918–924.
17. Marchenko, A.E., Skorina, N.V., Kiselev, M.O., Trachevsky, V.V. (2017) Nuclear magnetic spectroscopy study of the structure of liquid glasses for welding electrodes. *The Paton Welding J.*, **1**, 41-45.
18. Anfilogov, V.N., Bykov, V.N., Osipov, F.F. (2005) *Silicate melts*. Moscow, Nauka [in Russian].
19. *Dent* Glasser, L.S., Lee, C.K. (1971) Drying of sodium silicate solution. *J. of Appl. Chemical Biotechnology*, 21(**5**), 127–133.

Received 30.10.2018