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INFLUENCE OF THE CHEMICAL COMPOSITION OF COATED ELECTRODES ON MOISTURE CONTENT OF THE COATING AND DIFFUSIBLE HYDROGEN IN THE WELDED METAL

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Worldwide, there is the question of developing new types of coatings for welding electrodes that lead to a minimum amount of diffusible hydrogen, which is a function of moisture contained in the welding product. The present paper aims to find a new recipe for the basic electrode coating that leads to a low absorption of moisture. Given the diffusible hydrogen is a factor influencing the cold cracking of steels, current research is of particular importance in the development of new types of coated electrodes to be used in the electric arc welding of different metallic materials.

Keywords: electric arc welding, coated electrodes, humidity-resistant electrodes, diffusible hydrogen.

1. Introduction

Welding is a technological process that joins metals by melting the workpieces and adding a filler material to form a pool of melt (the weld puddle) that then cools to become a strong joint [1-5]. Welding is a usual technological procedure for repair and reconditioning, and we have already published some studies previously [6-8]. Electric arc welding is the most common technique used to join most steels, although its industrial use is very expensive due to the costs (80-90%) of involved manual labor [9]; the most widely used is the shielded metal

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arc welding (SMAW) which is also known as ‘stick welding [10]. Recent researches have shown the need for filler material improvement and also the introduction of new recipes for electrode coat without damaging welding behavior and electric arc stability [11]. The core rods are coated with an approximately 100 different materials including oxides, carbonates, silicates, organic substances, fluorides, and iron alloys, according to the intended application [10].

Humidity may be present in the electrode coat/paste in the form of absorbed water, loosely combined water of crystallization due to the chemical substances in the coat, and more firmly bound H_2O molecules (chemically linked water) in chemical substances structure [12-14]. All these forms can break down during welding to produce hydrogen by dissociation and the atomic hydrogen thus formed dissolves in the molten pool. During cooling much of the hydrogen (diffusible hydrogen) escapes from the weld metal and diffuses into the heat-affected zone and the parent metal, tending to collect into the lattice defects and cause cracking. The diffusible hydrogen content is generally expressed in milliliters per 100 grams of deposited metal (DM) [2]. It is naturally a function of moisture contained in the welding product, but there is no a general relation between two parameters [15].

Recently developed low-alloy steel electrodes, designated also as ‘low hydrogen coated electrodes’ [16-19], are used to deposit weld metal with highly reduced levels of diffusible hydrogen in the weld metal as well as in the heat affected zone. Once electrodes of either type are exposed to the atmosphere, they seek to equilibrate their contained moisture level with the moisture contained in the atmosphere. Studies on moisture resistant electrodes are the subject of published papers and patents [20-26]. Other sources can be moisture existing onto the steel surface due to rust, oils and other greases, organic degreasing agents used for cleaning, as well as moisture present in the atmosphere during welding [23]. The welding industry has placed limits on electrode coating moisture to control the hydrogen content of shielded metal arc welds in order to minimize weld cracking in steels due to diffusible hydrogen [27, 28]. Previously, we showed that it is possible to determine the influence of humidification factors on the coat humidity and its resistance to humidification [13].

The low hydrogen electrodes were defined by American Welding Society (AWS) as those having no more than 0.6 wt% coating moisture. As per the new american classification system the upper limit for diffusible hydrogen is 16 mL/ 100 g DM [23] which fits well with the correlation of 0.6 percent coating moisture. However, the upper limit of acceptable weld metal diffusible hydrogen content for high-strength steel welding has been set at 5 mL/100 g of deposited metal; the case of high-performance steels with enhanced mechanical properties requires the diffusible hydrogen level be lowered to 1 mL/100 g of deposited metal [17]. The low-hydrogen basic coated electrodes are commercially either hermetically packed or vacuum packed. The standards limit the time within 6 hours between taking out the welding consumables from drying case and its final usage [29, 30].

Much research work has been directed in recent years toward developing moisture-resistant electrodes, designated as “R” electrodes. Their moisture resistant coatings absorb moisture very slowly when they are exposed to the humidified air for extended periods. The AWS test for R electrodes consists in an exposure to an atmospheric environment of 27°C and 80% relative humidity (RH) for a period of not less than 9 hours; the moisture content of the exposed covering should not exceed 0.40%, maximum specified moisture content for the electrode.

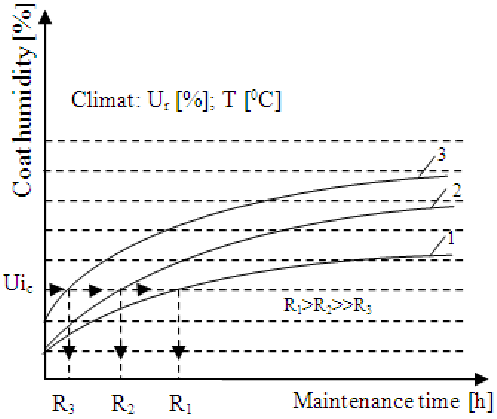

Fig. 1. Humidity variation of electrode coating over time in a humid climate [2]

Regarding to the resistance to humidity of electrode coating, if some electrodes are maintained for a certain period of time (8 hours – time for a working shift), in a climate characterized by 80% relative humidity and 27^{o}C temperature, we will observe very big differences from the point of view of humidity content (U_i). Fig. 1 shows the humidity of coating U_i depending on time when kept in a humid climate. Curves 1 and 2 are for two low-humidity absorption electrodes and curve 3 for normal coated electrodes (with normal humidity absorption), The U_{ic} parameter is the conventional coating humidity to determine humidity resistance.

By considering a certain conventional humidity of the coating (corresponding to diffusible hydrogen about 5 mL/ 100 g DM), it is observed that the electrodes 1 and 2 have a much higher humidity resistance than the electrode 3 under the same humidification conditions. This has a practical consequence that when R_1, R_2 and R_3 are exceeded, an increase in diffusible hydrogen from the welded material can occur, which increases the risk of cold cracking in the presence of hydrogen. It also requires re-drying (re-baked) the electrodes before use after a much lower exposure time, meaning additional costs.

Several researches for making low-moisture absorption electrodes were performed. Of course, the simple method of drying the electrodes in vacuum oven or passing an electric current through the rod is a procedure which leads to an exaggerated labor and energy consumption. Covering coated electrodes with a thin layer (0.012-0.076 mm), but compact metal or with a foil of 0.05 mm of polyethylene, polyvinyl chloride, etc. leads also to extra labor consumption, and in the case of coating with a metal layer it can lead to a considerable worsening of the weld ability.

A large number of compositions have been developed for use as fluxes in arc welding both for use generally as welding fluxes and for use as a coating on a metallic core. Binders are used in electrode coatings to maintain the desired shape of the electrode coating around the metallic core during normal handling. The phenomenon responsible for the production of moisture resistance in the treated electrodes is related to the formation of a film on the electrode coating's surface. This film fills the surface pores of the untreated electrode, thereby preventing moisture from being absorbed. In a similar manner, this film prevents moisture from being desorbed.

A research direction to make low-moisture absorption electrodes is the addition of hydrophobic substrate to the electrode coating, which in a reduced amount (about 3 wt%) in the pressed mixture reduces 7-10 times the amount of water absorbed by the coating in wet environments. It is sufficient for the surface of the hygroscopic granules to have a monomolecular layer of such substances to substantially change the hygroscopicity of the coating. In the concave meniscus, the vapor pressure is insignificant, while in the convex is raised. Decreasing the vapor pressure above the concave meniscus leads to the condensation of the water vapor from the atmosphere and the water penetrates deep into the existing capillaries as well as in the water-bearing granules. Hydrophobic substances protect both the granules themselves and the capillary channels from the water. As hydrophilizers were proposed combinations of vinyl- or methyl methacrylate, 16-20% borax blend and 56-60% B_2O_3, as well as silico-organic polymers. It has been found by experimental testing that this method leads to a lower absorption of humidity but produces two major drawbacks: (i) worsens weld ability, a very important thing because the steels that use the basic electrodes have a more difficult weld ability; (ii) results in a very high content (> 10-15 mL/ 100 g DM) of diffusible hydrogen in the deposited metal due to the organic substances contained in the coating.

Another method to obtain low-moisture absorption of the coating can be elimination of hygroscopic components and using as coatings some alkaline chemical compounds (potassium or sodium carbonate, potassium, sodium and/or calcium oxides) and drying them at temperatures of 520-620°C. Most recipes use binders of alkali metal silicates [31-42]. It has been discovered that if porous surface of the electrodes are treated with a dilute aqueous dispersion consisting of colloidal soluble silicates of lithium and potassium the resistance of the coatings to moisture absorption is remarkably increased and can, in fact, approach totality. When DC electrical power is used in welding, the sodium silicate binder is used, because is not quite as hygroscopic as potassium silicate and it can dry to lower moisture content than the potassium silicate. On the other hand, potassium silicate is normally selected when the electrode is used with an AC power source. In general, the binders of sodium silicate or potassium silicate have been particularly useful because they do not decompose under conditions of use. In addition, their specific properties make each attractive for the manufacture of welding electrodes.

A research direction is the design of low-hydrogen-coated basic electrodes, particularly adapted to the welding of statically and/or dynamically wound steel. Attention was paid to improvement in the manufacturing technique of coated electrodes, in particular as regards the appropriate dosing of raw materials, compliance with the conditions and techniques for drying, calcining, storing and packaging. If the packaging materials are not effective, after the packaging has been unloaded at the welding site the electrodes may become unusable because they have absorbed too much humidity in the ambient air. Also, the development and refinement of re-drying furnaces and thermostats for use in workshops and the welding site may also lead to a low absorption of humidity.

In order to obtain an acceptable level of hydrogen in the deposited metal, two main ways can be used successfully at present, namely: (i) designing the coating to maintain a controlled humidity content when exposed to the environment; (ii) designing the coating to produce low hydrogen transfer in metal deposited by welding. If we consider two different coated electrodes of equal humidity content but producing hydrogen content in the deposited metal, the hydrogen amount transferred by the electrodes is different. This phenomenon, caused by the chemical nature of the coating components, can be used to favor low hydrogen content in the deposited metal, even if the coating can retain a relatively large amount of humidity. The present paper aims to find a new recipe for the basic electrode coating that leads to a low absorption of moisture, thus to a small amount of diffusible hydrogen in the deposited metal by welding.

2. Experimental Part

Our own experimental researches, the results of which will be presented, were based on the following considerations:

(a) The part of the electrode that acts as a source of hydrogen in the deposited metal is almost the entire coating. The dry powder in the coating is composed of a large number of components many of them contain a negligible amount of humidity. Thus, the binder (used by dissolving in water) is the main source of hydrogen in the deposited metal.

(b) Regarding hydrated alkaline silicates used on the electrode coating, the hydrated potassium silicate is more stable than hydrated sodium silicate, the first retaining more chemically bound water than the second one after a calcination at about 400°C. This difference is also reflected in the increased tendency to favor the absorption of humidity by potassium silicate coatings, compared to those based on sodium silicate.

(c) When sodium and potassium silicates are mixed, the hydrated ion aggregates are formed by a polymerization reaction resulting in a tighter ion packing compared to pure silicates, which reduces the tendency to form bound hydrogen. When a mixture of silicates has low humidity absorption properties, the electrode can better withstand an aggressive climate over a long period, absorbing only a limited amount of humidity and thus being able to produce controlled hydrogen content in the deposited metal. This opens the possibility of laying the basis for designing electrodes with low moisture absorption properties.

It can be supposed (at this stage of research) that there is an optimal proportion of sodium and potassium silicates that offer the lowest absorption of moisture and this particular composition requires an optimal calcination temperature. In order to prove this last aspect, six Saf-Fro superbasic type electrodes commercially available have been prepared with both silicates in the coating but varying their proportion (Table 1). There were used two identical Superbaz electrodes for each coating composition, as rods with 3.25 mm diameter. First, sodium and potassium silicate colloidal solutions were prepared from reagents (Sigma Aldrich) mixed with distilled water. Then, the covered electrodes were calcined in quiet air before humidification.

Initial humidification conditions were 32°C test temperature and 70% relative air humidity and the experiments were made using a VTRK-500 climate chamber produced by Heraeus Vötsch (Germany). Other used equipment consisted in an analytical balance for weighing the electrodes after a certain humidification time, an oven for drying the electrodes before being placed in the humidification chamber and a device for determining the initial humidity of electrodes coatings by thermogravimetric method.

3. Results and discussion

The results of the determinations are shown in Table 1, with the specification that the values correspond to the determined humidity as an average of the two electrodes used for each type of coated electrode. The electrodes were calcined before humidification at temperatures of 350 and 400°C and exposed to a climate of 32°C and 70% relative humidity for 0-8 hours.

Drawing the curves of coating humidity variation with chemical composition expressed as the proportion of sodium and potassium silicates (Fig. 2) and of coating humidity vs. the exposure time (Fig. 3), it can easily be observed that the electrodes with the lowest moisture absorption are those covered with 60% sodium silicate and 40% potassium silicate. The optimal calcination temperature was approximately 400^{o}C.

Table 1

Coating humidity of electrodes after different exposure times

Calcination temperature (^{o}C)	**Chemical composition of the binder**	**Initial humidity of the coat, U_{io} (%)**	**Coating humidify (%) after certain exposure time**			
			0.5 h	**1 h**	**3 h**	**8 h**
350	100% potassium silicate	0.19	0.84	2.10	2.94	3.90
	20% sodium silicate 80% potassium silicate	0.22	0.69	1.60	2.51	3.08
	40% sodium silicate 60% potassium silicate	0.19	0.60	0.95	1.66	2.43
	60% sodium silicate 40% potassium silicate	0.21	0.47	0.84	1.05	1.19
	80% sodium silicate 20% potassium silicate	0.24	0.55	0.88	1.18	1.24
	100% sodium silicate	0.21	0.66	1.38	2.50	2.70
400	100% potassium silicate	0.21	0.58	1.84	2.85	4.40
	20% sodium silicate 80% potassium silicate	0.15	0.58	1.50	2.60	2.84
	40% sodium silicate 60% potassium silicate	0.19	0.53	0.90	1.60	2.40
	60% sodium silicate 40% potassium silicate	0.21	0.50	0.78	0.95	1.11
	80% sodium silicate 20% potassium silicate	0.19	0.51	0.80	1.10	1.22
	100% sodium silicate	0.18	0.60	1.20	2.28	2.60

Fig. 3 also shows that the change of the calcination temperature from 350 to 400^{o}C does not lead to an appreciable difference in humidity absorption. If the conventional coating moisture is considered to be 0.8%, the humidity resistance of a conventional R1 electrode is about 30 minutes, and for low moisture absorption electrode R2 is about 105 minutes under the same humidification conditions. As a result, the moisture resistance of the new electrode coatings is about 3.5 times higher.

Significant progress has been made in preventing the absorption of moisture by the base electrode coating. From metallurgical point of view, the lowest moisture absorption means that hydrogen has limited possibilities to penetrate the deposited metal by welding and cause the defects.

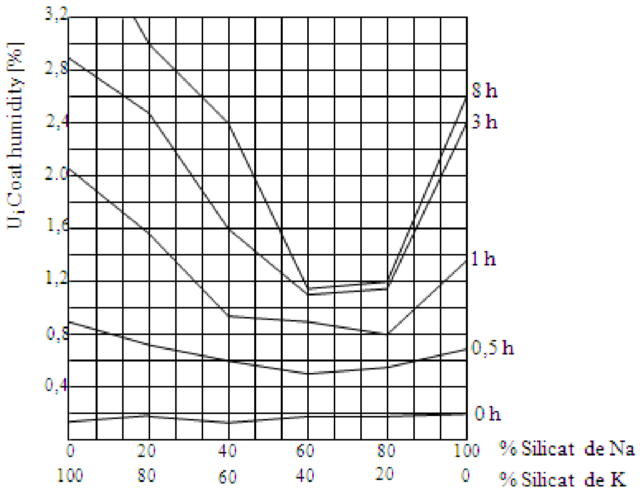

Fig. 2. Coating humidity variation with chemical composition of binder at 350°C constant temperature

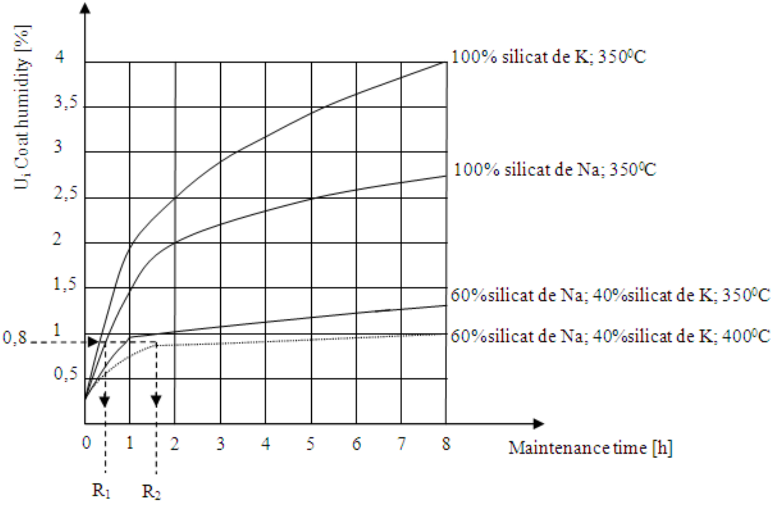

Fig. 3. Coating humidity variation with exposure time for different types of electrode coatings and temperatures

Among the advantages of new types of low-moisture-absorbing electrodes we can mention a very important advantage of not destroying the electrode welding properties. The low-moisture-absorbing electrode does not alter other features such as mechanical properties or electrode classification. When re-calcining is required, the calcination times are reduced by about 50%, which means lower energy consumption and easier handling. Increasing safety in operation reduces the risk of a significant amount of hydrogen in welded seams. Another practical consequence is that in many cases the users of basic electrodes have greater possibilities to simplify manipulation of electrodes in workshops and as well at the welding site. As a conclusion, this work succeeded in establishing the optimal composition of the silicate coating on the welding electrode (60% sodium silicate and 40% potassium silicate) as well as the optimal calcination temperature (400°C) for achieving the lowest moisture absorption.

REFERENCES

[1]. *D.L. Olson, T.A. Siewert, S. Liu, G.R. Edward* (Eds.), Welding, Brazing, and Soldering—ASM Handbook, Vol. 6, 9th edition, Materials Park, Ohio, 1993.

[2]. *G.Iacobescu, Gh.Solomon, I.Voiculescu*, Special Welding Processes and Technologies, Bren Publ. House, Bucharest, 1999.

[3]. *R. Mohler* (Ed.), Practical Welding Technology, Industrial Press Inc., New York, 2005.

[4]. *R. Blondeau* (Ed.), Metallurgy and Mechanics of Welding: Processes and Industrial Applications, J. Wiley & Sons, Hoboken, NJ, 2008.

[5]. *C.Rontescu, G. Iacobescu*, Welding by Melting, Vol. 1, Bren Publ. House, Bucharest, 2016.

[6] *D.T. Cicic, G. Solomon, G. Iacobescu, C. Rontescu*, Method of establishing the optimum technique for reconditioning by welding, taking into account the consumption of filler metals and electrical power, UPB. Sci. Bull. Series D, **vol. 73** (1), 2011, pp. 85-98.

[7]. *D.T. Cicic, C. Rontescu, A.M. Bogatu, C.G. Amza, O.R. Chivu*, The influence of the deposit parameters on the medium chemical composition of the welded joint, Rev. Chim. (Bucharest), **vol. 68** (10), 2017, pp. 2261-2264.

[8]. *D.T. Cicic, C. Rontescu, A.M. Bogatu, O.R. Chivu, I.G. Ghionea*, Research on the effect of applying the sacrifice layer technique on the chemical composition of the welded deposits, Rev. Chim. (Bucharest), **vol. 68** (11), 2017, pp. 2529-2532.

[9]. *G. Amza, C. Rontescu, D.T. Cicic, Z. Apostolescu, D. Pică*, Research on environmental pollution when using Shielded Metal Arc Welding (SMAW), UPB Sci. Bull., Series D, **vol. 72** (3), 2010, pp.73-88.

[10]. ***, SMAW electrode coverings. Varieties and functions, Kobelco Welding Today, **vol. 9** (4), 2006, pp. 3-7.

[11]. *D.T. Cicic, C. Rontescu, C.G. Amza, O.R. Chivu*, The combined effect of chemical elements on the properties of a layer deposited by welding, Rev. Chim. (Bucharest), **vol. 66** (9), 2015, pp. 1299-1301.

[12]. *V. Miclosi, G. Iacobescu, I. Tonoiu (Voiculescu)*, The kinetics of moisture absorption on some electrodes of Romanian electrodes (Cinetica absorbţiei de umiditate la unele învelişuri de electrozi româneşti), Sudura, **1993 (**2), 1993, pp. 17-19.

[13]. *G. Iacobescu, I. Voiculescu*, A mathematical model for humidity the electrodes coats, UPB Sci. Bull., Series D, **vol. 68** (4), 2006, pp. 51-58.

[14]. *G. Iacobescu, I. Voiculescu, G. Solomon*, A theoretical model for estimating the effects of the humidity in some electrode pastes of the diffusible hydrogen in the weld deposit, UPB Sci. Bull., Series D, **vol. 69** (2), 2007, pp. 69-76.

[15]. *J.H. Kiefer*, Effects of moisture contamination and welding parameters on diffusible hydrogen, Welding Journal, Welding Research Supplement, May 1996, pp. 155s-161s.

[16]. *D.D. Harwig, D.P. Longenecker, J.H. Cruz*, Effects of welding parameters and electrode atmospheric exposure on the diffusible hydrogen content of gas shielded flux cored arc welds, Welding Journal, Welding Research Supplement, September 1999, pp. 314s-321s.

[17]. *M. Matsushita, S. Liu*, Hydrogen control in steel weld metal by means of fluoride additions in welding flux, Welding Journal, Welding Research Supplement, October 2000, pp. 295s-303s.

[18]. *M.P. Dhanuka*, Life line of welding low hydrogen electrodes, Bulletin of Process Plant and Machinery Association of India (PPMAI), June/July 2009, pp. 4-8.

[19] *C. Turani Vaz, A. Queiroz Bracarense, I. Felizardo, E.C. Pereira Pessoa*, Impermeable low hydrogen covered electrodes: Weld metal, slag, and fumes evaluation, Journal of Materials Research and Technology, **vol. 1** (2), 2012, pp. 64-70.

[20]. *B. Chew*, Moisture loss and regain by some basic flux covered electrodes, Welding Journal, Welding Research Supplement, May 1976, pp. 127s-134s.

[21]. *D. McKeown*, Hydrogen and its control in weld metal, Metal Construction, **vol. 17** (10), 1985, pp. 655-661.

[22]. *T. Geraghty*, Preventing weld defects through proper consumables care. How to minimize moisture pickup in SMAW electrodes, Practical Welding Today, March/April 2014.

[23]. *M.P. Dhanuka*, Lifeline of welding: low hydrogen electrodes – Moisture-resistant E7018 H4R and E7018-1 H4R, WelfabTech Times, Oct-Nov. 2017.

[24]. *D.C. Hill, E.M. Flanigen*, Method for producing moisture resistant electrodes, US Patent 4045593A / 30 Aug. 1977.

[25]. *G. Falberg*, Corrosion resistant, weldable coating compositions, EP 0898598B1 / 4 February, 2004.

[26]. *A.D. Bernardina Jr.*, Method to produce an electrode with a low level of hydrogen and low absorption of moisture, US Patent 20120198685A1 / 9 Aug. 2012.

[27]. *T.A. Siewert*, Moisture in welding filler materials, Welding Journal, **vol. 64** (2), 1985, pp. 32-41.

[28]. *T.A. Siewert*, Testing of welding electrodes for diffusible hydrogen and coating moisture, in: Hydrogen Embrittlement: Prevention and Control, ASTM STP 962, L. Raymond (Ed.), ASTM, Philadelphia, Pa, 1988, pp. 238-246.

[29]. *American Welding Society*, Standard welding terms and definitions (ANSI/AWS A3.0-94), Miami, Fl., 1994.

[30]. *American Welding Society*, Standard methods for determination of diffusible hydrogen content of martensitic, bainitic, and ferritic steel weld metal produced by arc welding (AWS A4.3), Miami, Fl., 2006.

[31]. *J.M. Campbell*, Method of applying sodium silicate binder, US Patent 2481390A / 6 September 1949.

[32]. *R. Schneider*, Silicate coatings compositions, US Patent 3721574A / 20 Mars 1973.

[33]. *H. Makishima, M. Hoshino, T. Shinohara, H. Nii, M. Hosoda, T. Hayashi*, Anti-corrosive coating compositions, US Patent 4011088 / 3 August 1977.

[34]. *J.B. Schutt*, Alkali-metal silicate binders and methods of manufacture, U.S. Patent 4162169 / 24 July 1979.

[35]. *NASA*, Alkali-metal silicate binders and methods of manufacture, US Patent 4162169A / 24 July 1979.

[36]. *K.H. Brown, K.M. Wolma*, Method of producing silicate binders and coatings, US Patent 4290811 A / 22 September 1981.

[37]. *J.B. Schutt*, Silicate binders and coatings, US Patent 4479824A / 30 October 1984.

[38]. *Unilever Patent Holdings B.V.*, Silicate binders, US Patent 5151121A / 29 September 1992

[39]. *H.W. Burr*, Silica-based binder, US Patent 5607503 A / 4 Mars 1997.

[40]. ***, Corrosion resistant, weldable coating compositions, CN Patent 1218493A /2 June 1999; CN Patent 1151209C / 26 May 2004.

[41]. *R.R. Savin*, Silicate coating compositions, US Patent 6638628 B2 / 28 October 2003.

[42]. *C.B. Dallam, N. Karogal*, Colloidal silica binder system, US Patent 7147725 B2 / 12, December 2006.