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INFLUENCE OF THE COMPOSITION OF ELECTRODE COATING BINDER ON TOXICITY OF WELDING FUMES

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Results of sanitary-hygienic evaluation of coated electrodes for welding high-alloyed chromium-nickel steels were used to study the influence of the composition of electrode coating binder on the toxicity of fumes, which form at application of these electrodes. Express-method of determination of cytotoxicity, levels of evolution and chemical composition of welding fumes, as well as their calculated hygienic indices in accordance with international standard DSTU ISO 15011-4:2008 were applied for this purpose. It is shown that in order to develop new grades of welding electrodes with improved hygienic characteristics, it is reasonable to have not only the data of primary sanitary-hygienic evaluation, but also the results of biological studies of the toxicity of welding fumes. It is found that application in electrode coating of a binder based on pure lithium or lithium-sodium-potassium liquid glass instead of potassium-sodium one, enables reducing the level of welding fume evolution into the air, its content of highly toxic hexavalent chromium, and lowering its general toxicity due to that. 14 Ref., 3 Tables, 4 Figures.

Keywords: *coated electrodes, welding fumes, hexavalent chromium, cytotoxicity index*

Electric arc welding is characterized by evolution of fumes harmful for the human body into the working zone air, the toxic action of which is determined by the chemical composition of welding electrodes [1]. Therefore, development of new grades of welding consumables must be accompanied by their primary sanitary-hygienic evaluation, in keeping with the international standards DSTU ISO 15011-1:2008 [2] and DSTU ISO 15011-4:2008 [3]. These standards allow obtaining the necessary information on the chemical composition of welding fumes (WF) and performing tentative calculation of the risk of their harmful effect on the body of the welder. In order to create new grades of welding electrodes with improved hygienic characteristics, it is worthwhile to have not only the data of primary sanitary-hygienic evaluation, but also the results of biological studies of WF toxicity. Such investigations, particularly using experimental animals, are realized during a rather long time and require considerable expenses.

In order to assess the toxic action of poorly soluble industrial aerosols, including welding fumes, the most important is such key property as cytotoxicity that determines the risk of development of occupational illness — pneumoconiosis [4]. Cytotoxicity, as a property of dust particles (aerosol) is the determinant factor for assessment of the extent of its action on the human body and mathematical prediction of comparative risk of pneumoconiosis development. Cytotoxicity determines the kinetics of dust accumulation and retention in human lungs and lymph nodes, as well as the intensity of harmful effect on the tissues of these organs. This characteristic is assessed in different short-term tests, that is related to the prevailing ideas of the key role of dust particles damaging the macrophages in pathogenesis of silicosis and other kinds of pneumoconiosis. Also used are tests, based on recording the phenomena of macrophage activation or on some kind of combination of these phenomena. However, interpretation of test results and their application for prediction of the effect of fumes on the human body are often performed without allowing for the role of the processes of activation and damaging of the macrophage, either in mechanisms which are at the basis of the test, or in the pathogenesis of pneumoconiosis [5].

Application of the so-called alternative toxicological models (cell cultures, express-tests, etc.) provides data on the toxicity and hazardousness of chemical compounds and materials using less costly ways and approaches in shorter terms and more humanely from the viewpoint of bioethics, compared to the traditional methods of experimental studies on laboratory animals in vivo. In its turn, the data, obtained in vitro experiments can be used for screening the welding consumables as a «vector» for conducting in-depth experimental studies in vivo. In particular, express-assessment of WF toxicity, using short-term suspension

Table 1. WF evolution indices and chemical composition

Kind of liquid glass (coating binder)	Evolution intensity V_f, g/min	Specific evolution G_f, g/kg	Weight fraction, % in WF					
			Cr^{6+}	Cr^{3+}	Mn	Ni	F_p	$F_{??}$
K–Na (0 %)	0.51	11.58	1.96	2.62	4.81	1.47	11.68	1.30
Li–Na–K (0.7 %)	0.45	10.10	1.77	2.67	5.27	1.38	10.24	1.69
Li–Na–K (1.8 %)	0.35	7.28	1.44	2.82	5.69	1.29	10.35	1.88
Li–Na (2.7 %)	0.26	5.52	0.89	3.04	5.73	1.62	11.65	1.34
Li (3.2 %)	0.20	4.52	Not found	3.91	5.20	1.39	5.76	1.56

Note. Li_2O mass fraction in liquid glass is shown in brackets.

culture of bull sperm as a test object markedly lowers the labour consumption and cost of testing. The method allows assessment of the cumulative effect from the impact of the totality of toxicants present in WF on the culture by the biological effect of its extract on the test object during time not longer than 3 hours [5].

Applicability of the above procedure of express-assessment for comparative hygienic evaluation of welding electrodes was confirmed in reference [6]. Here, it was verified that the toxicity of WF, forming during welding of high-alloyed steels, is much higher than that in welding carbon and low-alloyed steels, and it is predominantly determined by the content of carcinogenic hexavalent chromium (Cr^{6+}) and nickel in electrode coating [7]. At the same time, as shown in work [8], WF toxicity essentially depends on the ratio of lithium, sodium and potassium (Li–Na–K) in the composition of electrode coating binder (liquid glass), that is exactly what determines presence of carcinogenic hexavalent chromium (Cr^{6+}) in WF composition.

The objective of this work was determination of the influence of chemical composition of Li–Na–K binder of electrode coating for welding high-alloyed chromium-nickel steels on cytotoxicity of WF forming at their application.

WF sampling for determination of their sanitary-hygienic characteristics was performed in keeping with the standard [2] by the method of complete trapping of fumes that form during welding, using a special stand with FPP filter, mounted in the path of WF movement from the welding zone enclosure. The following characteristics of WF formation were determined: evolution intensity, V_f, g/min; specific evolution G_f (mass of WF forming at melting of a kilogram of welding electrodes), g/kg; WF chemical composition, wt.%).

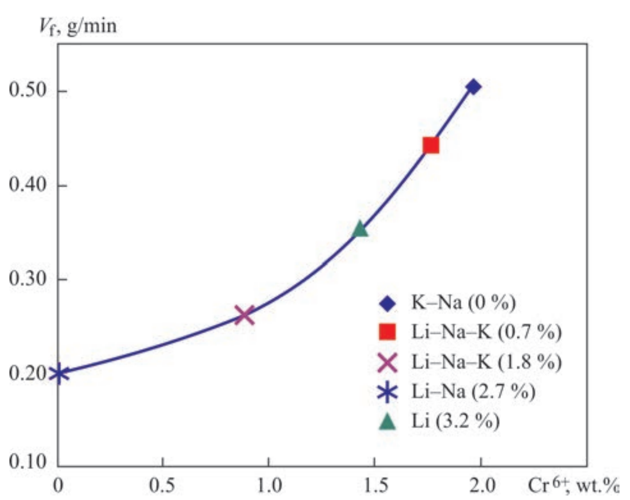

Figure 1. Dependence of WF evolution intensity V_f on the content of hexavalent chromium Cr^{6+} in it (Li_2O mass fraction in liquid glass is shown in brackets)

Toxicity assessment was performed on the basis of experimentally determined cytotoxicity index I_t by the procedure [5] of express-assessment of WF toxicity in vitro in serial analyzer AT-05 and (for comparison) by the calculated hygienic indices — limit value and class of WF in keeping with DSTU ISO 15011-4:2008 [3]. The above-given values of WF evolution intensity, V_f, mg/s and their chemical composition were used for this purpose, in keeping with the procedures of [2, 9].

Test grades of welding electrodes of E-08Kh20N9G2B type with different composition of liquid glass-binder in the coating were used for taking WF samples (Table 1). Surfacing was performed on a plate from 12Kh18N10T steel at direct current (150 A) of reverse polarity using VDU-504 rectifier. Minimum three experiments were performed for each variant. Obtained investigation results (Table 1) show that application of Li–Na–K liquid glass instead of K–Na as binder in the electrode coating allows (depending on its Li content) lowering the values of WF evolution approximately 1.2–1.5 times and reducing its content of highly toxic hexavalent chromium (Cr^{6+}) up to 1.4 times, whereas application of Li–Na binder allows lowering WF evolution 2 times and reducing its Cr^{6+} content 2.2 times (Figure 1). Application of Li-liquid glass in the coating allows lowering WF evolution 2.5 times and preventing Cr^{6+} formation in it (Figure 2).

Absence of Cr^{6+} in WF composition in this case is attributable to chemical properties of rare-earth elements. It is known that during melting and WF formation, presence of K and Na in the electrode coating usually leads to formation of their chromates and bichromates, as a result of interaction of these substances with chromium:

$$Cr + K_2O, Na_2O \rightarrow K_2CrO_4, Na_2CrO_4,$$
$$Cr + K_2O. Na_2O \rightarrow K_2Cr_2O_7, Na_2Cr_2O_7.$$

Table 2. Classification of welding consumables, depending on evolution level and calculated WF limit value [3]

WF limit value $LV_{WF(A)}$, mg/m^3	WF evolution intensity V_f, mg/s	< 3	3–8	8–15	15–25	> 25
	Welding consumable class	A	B	C	D	E
> 4.5	5	5a	5b	5c	5d	5e
3.5–4.5	4	4a	4b	4c	4d	4e
2.5–3.5	3	3a	3b	3c	3d	3e
1.5–2.5	2	2a	2b	2c	2d	2e
0.5–1.5	1	1a	1b	1c	1d	1e
< 0.5	0	0a	0b	0c	0d	0e

These are exactly the chemical compounds, that are extremely hazardous (carcinogenic) substances, which is this case determine the value of WF toxicity. Now application of Li_2O in the electrode coating, owing to the peculiarities of its chemical properties, does not lead to formation of similar chromates [8, 10–12]. Formation of other extremely hazardous compounds of hexavalent chromium CrO_3 was not confirmed, either, except for moderately toxic trivalent Cr_2O_3 [13]. The next stage of this work was determination of the effect of liquid glass composition on the value of WF toxicity [14]. For this purpose the following calculated toxicity indices [3] were determined and analyzed: WF limit value $LV_{WF(A)}$ and hygienic class of electrodes, which, in its turn, is determined by this limit value and intensity of WF evolution (Table 2), as well as experimentally determined cytotoxicity index.

Investigation results (Table 3) showed that WF limit value $LV_{WF(A)}$ decreases with increase of hexavalent chromium content in the electrode coating: it is minimum (0.31 mg/m^3) in the case of welding with electrodes with K–Na binder, increases with increase of lithium content in it and has maximum value (0.97 mg/m^3) at application of liquid glass based on pure lithium in the coating. Minimum value of $LV_{WF(A)}$ is indicative of WF maximum relative toxicity (for comparison WF are of the same mass) and, accordingly, maximum value points to smaller toxicity, characteristic for WF, generated in welding by electrodes containing lithium in their coating. Determined value $LV_{WF(A)}$ leads to the conclusion that toxicity of

Table 3. WF hygienic characteristics

Kind of liquid glass (coating binder)	WF evolution intensity V_f, mg/s	WF limit value $LV_{WF(A)}$, mg/m^3	Electrode class	Cytotoxicity I_t, %
K–Na (0 %)	8.3	0.31	0C	22.3
Li–Na–K (0.7 %)	7.5	0.33	0B	12.5
Li–Na–K (1.8 %)	5.8	0.37	0B	18.8
Li–Na (2.7 %)	4.3	0.44	0B	29.0
Li (3.2 %)	3.3	0.97	1B	66.2
Note. Li_2O mass fraction in liquid glass is shown in brackets.				

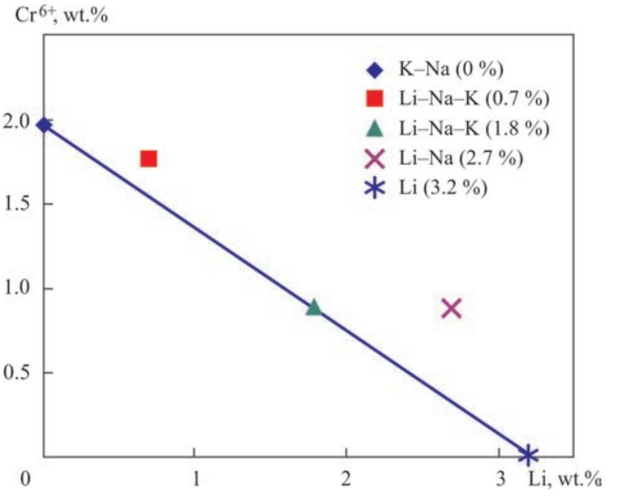

Figure 2. Dependence of hexavalent chromium Cr^{6+} on lithium content in liquid glass

WF generated in welding by electrodes with lithium-containing binder, is approximately three times smaller than that of WF, generated at application of Na–K liquid glass, that is attributable to absence of hexavalent chromium in WF (Figure 3).

As regards hygienic class of electrodes as a general (practically absolute) characteristic of toxicity, it has zero «0» value for all electrodes, except for electrodes with lithium binder in the coating, which belongs to class 1 and is indicative of lower WF toxicity. Thus, electrodes with Na–K and Li–Na–K binder belong to the worst hygienic class, as hexavalent chromium is present in the composition of WF, which form in welding with them, while electrodes with lithium binder belong to less hazardous class «1».

At the same time, taking into account the index of WF evolution intensity, we determine more precisely to which generalizing class of electrodes they belong. So, electrodes with Na–K binder of the coating belong to the worst hygienic class — «0C» with maximum intensity of WF evolution (V_f = 8.3 mg/s), and

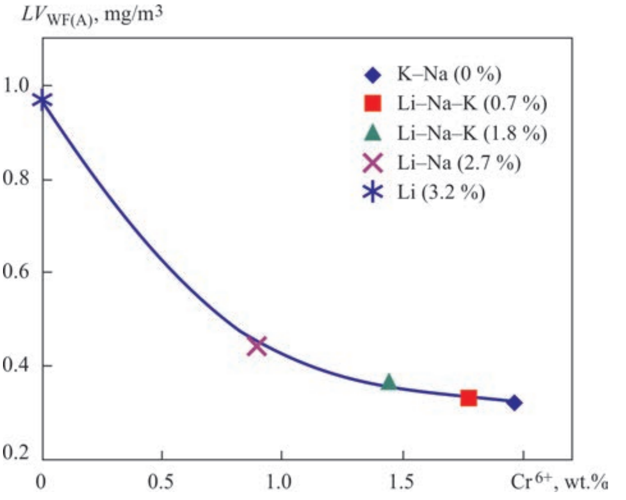

Figure 3. Dependence of WF limit value on the content of hexavalent chromium Cr^{6+} (Li_2O mass fraction in liquid glass is shown in brackets)

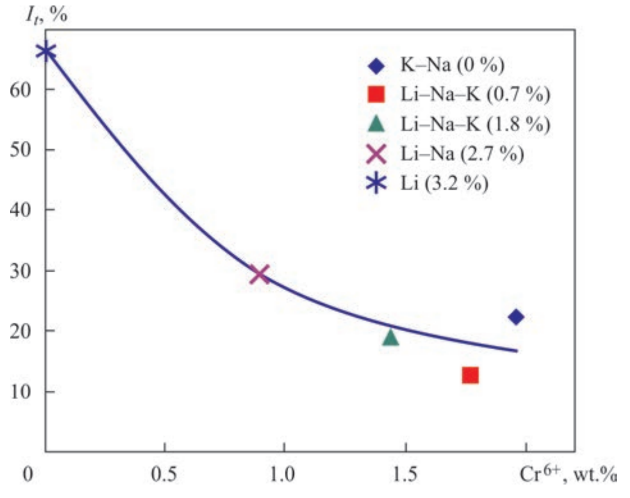

Figure 4. Dependence of cytotoxicity index I_t on the content of hexavalent chromium Cr^{6+} in WF (Li_2O mass fraction in liquid glass is shown in brackets)

electrodes with lithium binder are in the best class in this case (V_f = 3.3 mg/s). Here, it should be noted that practically all the electrodes for welding high-alloyed chromium-nickel steels belong to class «0», limit value $LV_{WF(A)}$ of which should not exceed the most stringent threshold of 0.5 mg/m^3 (see Table 2), according to standard DSTU ISO 15011-4:2008 [3]. Thus, for welding high-alloyed chromium-nickel steels it is desirable to use electrodes with binder based on pure lithium liquid glass. This allows going beyond the limits of the most toxic hygienic class «0», i.e. improving the hygienic characteristics of the electrodes.

And, finally, the index of WF cytotoxicity allowed determination of numerical values of their toxicity I_t (see Table 3). So, at application of lithium binder in electrode coating it has the maximum value (I_t = = 62.1 %), that is indicative of minimum WF toxicity (as at values I_t = 70–120 % the test material is considered non-toxic). In welding by electrodes with other binders, it changes from 12.5 up to 29.0 %, depending on binder composition, that is indicative of the tendency of increase of WF toxicity at lowering of lithium content in liquid glass composition. Certainly, this, in its turn, is accounted for by hexavalent chromium content in WF: with increase of its concentration in WF composition, the cytotoxicity index decreases, i.e. WF toxicity rises (Figure 4).

It should be noted that application of this screening method [5] in practice at sanitary-hygienic evaluation of welding electrodes does not allow making an unambiguous conclusion on WF toxicity dependence on Li, Na, K and hexavalent chromium content in the coating, as WF toxicity is also affected by other components of electrode coating, such as nickel, manganese, dissolved fluorides, etc.

Conclusions

Application of known international standardized methods of sanitary-hygienic evaluation of welding consumables together with the method of determination of cytotoxicity index of welding fumes showed that use of a binder based on pure lithium or lithium-sodium-potassium liquid glass, instead of potassium-sodium one, in the coating of electrodes for welding high-alloyed chromium-nickel steels, allows reducing the level of welding fume evolution into the air, its content of highly toxic hexavalent chromium, and, due to that lowering its general toxicity.

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