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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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PROTECTIVE ZINC COATINGS FROM ACID ELECTROLYTE OF ZINC-PLATING

Abstract. The aim of the work is to select the a combination of surfactants to be introduced into the galvanizing electrolyte in order to obtain uniform, thick, non-porous zinc coatings, with a high probability of protecting the product surface from corrosion in corrosive environments - wet, underground, hot.

The object of research is the process of electrodeposition of zinc from simple sulfate galvanizing electrolytes with a combination of surfactants: succinic acid with urotropin, citric acid with thiourea, at a current density of 1-3 A/dm^2, at a constant fixed pH value at room temperature. For an objective evaluation and comparison of the quality of zinc coatings obtained from electrolyte with combined surfactants, studies of electrolytic zinc production from an electrolyte containing no surfactants were performed. For both cases, an energy-dispersive electron microscopic expertise of zinc coatings was performed and presented in the form of photographs and tabular data. The elemental composition of zinc coatings obtained from electrolyte without surfactant and with combined surfactants is determined and presented. The chemical expertise of the zinc coating was carried out to determine its thickness and porosity. The effective effect of the selected surfactant combination on the quality of the zinc coating is shown. The conclusions are drawn and recommendations are given on the results of the conducted research.

Keywords: sulfate electrolytes, zinc coatings, surfactants (surfactants).

The metallic constructions can be protected from atmospheric, marine, underground, gas and other types of corrosion with the help of various protective coatings: metalic, paint and varnish, etc.

The hot methods for applying metallic protective coatings (methods of immersion in molten metal), diffusion methods, methods of metallization (spraying by compressed air of metal or alloy on the metallic surface), paint coatings, chemical coatings exploitative in different corrosive environments can't effectively to resist the aggressive corrosive environment. Effectively to protect the metallic products from corrosion only by way of electrolytic method applying possibly to their surface of the metallic coatings. The valuable property of the electrolytic method is the opportunity to regulate of the coating thickness, down to fractions of the micron, which allows at coating efficiency of coating to save electrolyte. Electrolytic zinc, copper, chrome, nickel, cadmium galvanic coatings attached to the protected metallic product not only decorative finish (coating color and gloss), but also impart the necessary properties to the coating, such as hardness, porosity, uniformity over the entire surface of the protected product [4, 5].

To receive high-quality cathodic zinc coatings obtained from acidic sulfate electrolyte containing succinic acid as the surfactant in combination with urotropine, reagents of the grade " chemically pure" were used: zinc sulfate, sodium sulfate, aluminum sulfate, surfactants, anodes from electrolytically pure zinc, steel cathodes brand ST-3.

We carried out researches of electrolyte without surfactant to compare the quality of zinc coatings. In the table 1 shows the results of the quality of the zinc coatings obtained from the acid sulfate electrolyte

Table 1 – Zinc coatings obtained from electrolyte without surfactant

I_k, A/dm^2	CO, %	Appearance of zinc coating	Thickness, mkm	Porosity	Scanning electron microscope data JSM-6490LV	
					% impurities in the coating	% Zn in the coating
0,5	76,6	Gray, coarse-grained	24,8	Porous	C, O, Al, Fe - 10,15	89,85
1	76,1	Gray, coarse-grained	23,5	Porous	C, O, Al, Fe - 13	87,0
2	56,2	Dark gray, coarse-grained	21,6	Porous	C, O, Al, Fe - 18	82
3	56,2	Dark-gray, along the edges with cadmium	22,3	Porous	C, O, Al, Fe - 16,93	83,07

without surfactant. External parameters and data's on zinc coating obtained with the scanning electron microscope (% of zinc in the coating) are described, and the calculated values of the zinc current yield are shown.

Protective zinc coatings obtained from electrolyte without surfactants, coarse-grained, porous, with a low current yield (56-75%). At that, than the current density increased, than the coatings darken, peel off along the edges of the coating, and dark molds are formed.

The elemental composition of the zinc coatings described with the JSM - 6490LV of electron microscope from a single coverage area for a current density of 0.5 A/dm^2 is shown in figure 1.

Element	Weightily, %
C	4.76
O	2.00
Al	0.14
Si	0.07
S	0.09
Fe	0.43
Zn	92.51

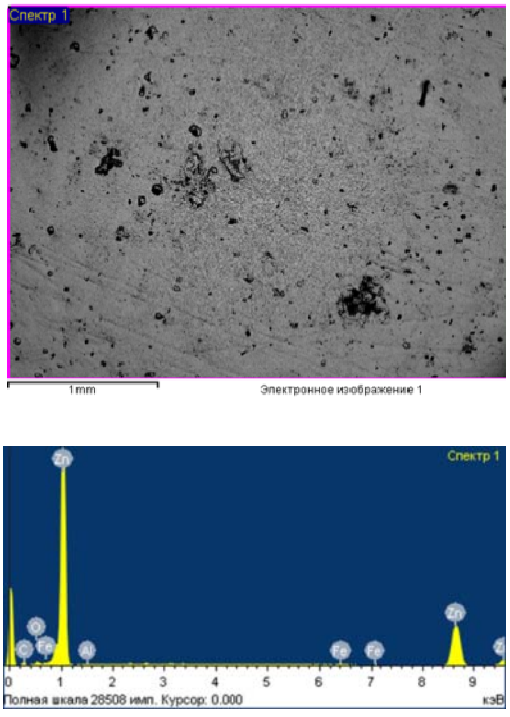
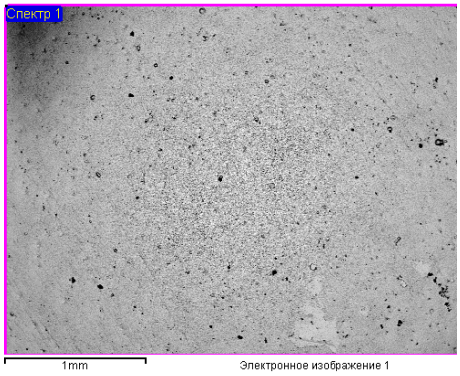


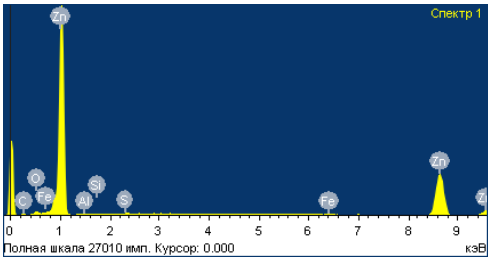
Figure 1 – Zinc coating and its elemental composition in electrolyte without surfactant

An analysis of the elemental composition of the zinc coating shows the content of zinc in the coating. From the electronic photograph, the presence of pores and fuses along the edges of the zinc coating is evident.

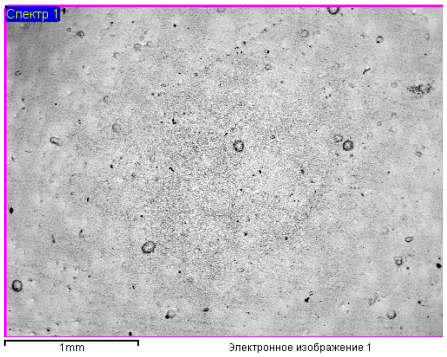
In figure 2 is given the elemental-weight composition of the zinc coatings and the electronic image of the surface of the coating obtained from the electrolyte with surfactant (succinic acid with urotropine) at a current density of 1 and 2 A/dm^2. The content of zinc in the coating is higher, as compared to coatings obtained from electrolyte without surfactant. The zinc coating is light, non-porous, with no fumes. However, the composition of the elements differs from the coating of zinc, obtained without surfactants in the electrolyte. Sera and silicon appear, probably present in the surfactant.

Element	Weightily, %
C	7.62
O	1.53
Al	0.21
Fe	0.79
Zn	89.85





Element	Weightily, %
C	3.50
O	1.11
Al	0.18
Si	0.08
S	0.07
Fe	0.15
Zn	94.91



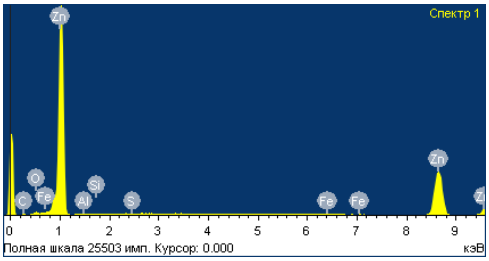


Figure 2 – Zinc coating and its elemental composition
from electrolyte with surfactant at a current density of 1 and 2 A/dm^2

In the table 2 are given the quality indices of zinc coatings obtained from an electrolyte with the surfactants. At the current density of 1 A/dm^2, the coatings are light gray, much lighter when compared to coatings obtained from an electrolyte without surfactant. Non-porous, which have the high current output of 98.6%. At the current density of 2 A/dm^2, the zinc coatings are lighter, non-porous, with a zinc current output of 98.2%. The presence of sulfur impurities: 0.07-0.09% by weight, does not negatively affect the quality of zinc coatings. It is possible that the sulfur impurity has a positive effect in that it promotes more active adsorption of the surfactant on the surface of the article to be protected, crushing and improving the coating structures. It should be noted the high yield of zinc current in the whole investigated current density range (from 90 to 98%).

Table 2 – Quality of zinc coatings from electrolyte with the addition of succinic acid with urotropine

	CO, %	Appearance of zinc coating	Thickness, mkm	Porosity	Scanning electron microscope data JSM-6490LV	
					% impurities in the coating	% Zn in the coating
0,5	92,0	Light Gray	21,68	Non-porous	C, O, Al, S, Fe General : 10,37	88,63
1	98,6	Light Gray	22,36	Non-porous	C, O, Al, S, Fe General 7,49	92,51
2	98,2	Light coloured	23,24	Non-porous	C, O, Al, S, Fe General 5,09	94,91
3	90,7	Light Gray	21,2	Non-porous	C, O, Al, S, Fe General 8,7	91,3

Also was researched the combination of surfactants: citric acid with thiourea in the galvanizing electrolyte. The quality of zinc coatings is given in table 3.

Table 3 – The quality of coatings of zinc and BT in the electrolyte with the addition of citric acid and thiourea

I_k, A/dm^2	CO, %	Appearance of zinc coating	Thickness, mkm	Porosity	Scanning electron microscope data JSM-6490LV	
					% impurities in the coating	% Zn in the coating
0,5	71,6	Dark grey, without fumes	16,04	Porous	C, O, Al, S, K, Fe - 30,06	69,94
1	73,0	Gray, with spots	15,88	Porous	C, O, Al, S, K, Fe - 34,06	65,94
2	68,2	Gray, with spots	15,72	Weakly porous	C, O, Al, S, Fe, K - 30,24	69,76
3	69,3	Dark grey, along the edges of the coke	16,64	Porous	C, O, Al, S, Fe, K - 40,24	59,76

The elemental composition of the zinc coating shows 6.52% by weight of sulfur. Sulfide sulfur in contens in thiourea is probably to have a detrimental effect on the quality of the zinc coating. Coatings at all current densities are dark, porous.

Element	Weightily, %
C	5.53
O	27.29
Al	0.27
S	6.52
K	0.55
Fe	0.07
Zn	69.76

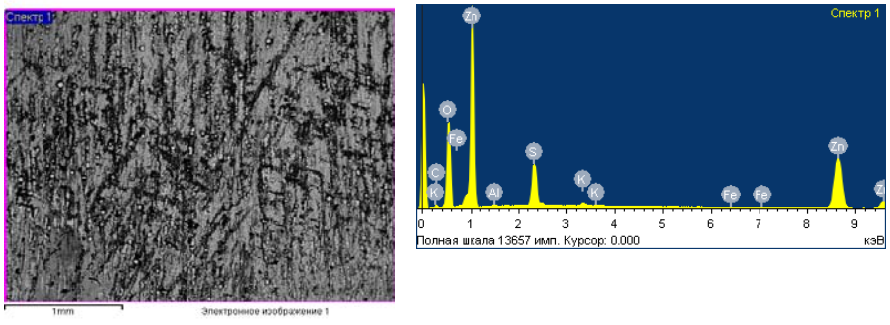


Figure 3 – Zinc coating and its elemental composition from electrolyte with surfactant at a current density of 2 A/dm^2

In all the investigated range of current densities, the current efficiency is low, within 70%. Appearance also does not meet the requirements; zinc coatings are dark, with cracks, with spots. The thickness of the zinc coating is also lower, compared to another combination of surfactants in the electrolyte, all the coatings obtained are porous, which is clearly visible in figure 3.

Conclusions.

1. The conditions of electrodeposition of zinc coatings from electrolyte with combined surfactants are researched.

2. Quality indicators of zinc coatings obtained in the current density range of 0.5-3 A/dm^2 without surfactants and with additives are given.

3. The effective combinations of surfactants in the electrolyte (succinic acid and urotropine) to obtain high-quality zinc coatings are shown.

4. An energy-dispersive electron-microscopic analysis of the composition and appearance of zinc coatings obtained from pure electrolyte and in electrolyte with surfactant has been performed.

5. The optimum mode for obtaining a high-quality zinc coating is shown.

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ҚЫШҚЫЛДЫ МЫРЫШТАУ ЭЛЕКТРОЛИТІНЕН ЖАСАЛҒАН МЫРЫШТЫ ҚОРҒАНЫС ЖАБЫНДЫЛАРЫ

Аннотация. Жұмыстың мақсаты: ылғалды, жер асты, жанғыш – агрессивті орталардағы бұйымның бетін коррозиядан қорғаудың жоғары ықтималдылығымен, қалыңдығы бойынша біртекті, тығыз, кеуек емес мырыш жабындыларын алу мақсатында, мырыштау электролитіне ендіруге арналған беттік белсенді заттардың (ары қарай ББЗ) комбинациясын таңдап алу.

Зерттеу объектісі – қарапайым сульфатты электролиттерді ББЗ комбинациясымен мырыштау кезінде: 1–3 А/дм^2 ток тығыздығындағы, бөлме температурасындғы pH-тың тұрақты белгіленген мәнінде: уротропинді янтарь қышқылымен, тиомочевиналы лимон қышқылымен мырышты электротұндыру процесі болып табылады. Комбинацияланған ББЗ-мен электролиттен алынған мырыш жабындыларының сапасын салыстыру және объективті бағалау үшін, ББЗ-ы болмайтын электролиттен мырышты электролитті алу үшін зерттеулер жүргізілген. Екі жағдайда да мырыш жабындыларының энергодисперсиялық электрондық микроскопиялық сараптамасы жүргізілген және нәтижелері сурет, кесте түрінде келтірілген. Комбинацияланған ББЗ - мен және ББЗ-сыз электролиттен алынған мырыш жабындыларының элементтік құрамы анықталған және келтірілген. Мырыш жабындысының қалыңдығы мен кеуектілігін анықтау үшін оның химиялық сараптамасы жүргізілген. Таңдалып алынған ББЗ комбинациясының мырыш жабындсының сапасына тиімді әсері көрсетілген. Жүргізілген зерттеу нәтижесі бойынша ұсыныстар берілген және қорытынды жасалған.

Түйін сөздер: сульфатты электролиттер, мырыш жабындылары, беттік-белсенді заттар (ББЗ).

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ЗАЩИТНЫЕ ЦИНКОВЫЕ ПОКРЫТИЯ ИЗ КИСЛОГО ЭЛЕКТРОЛИТА ЦИНКОВАНИЯ

Аннотация. Цель работы заключается в подборе комбинации ПАВ для введения в электролит цинкования, с целью получения равномерных по толщине, плотных, беспористых цинковых покрытий, с высокой вероятностью защиты поверхности изделия от коррозии в агрессивных средах – влажных, подземных, горячих.

Объектом исследований является процесс электроосаждения цинка из простых сульфатных электролитов цинкования с комбинацией ПАВ: янтарная кислотас уротропином, лимонная кислота с тиомочевиной, при плотности тока 1–3 А/дм^2, при постоянно фиксируемом значении pH при комнатной температуре. Для объективной оценки и сравнения качества цинковых покрытий, полученных из электролита с комбинированными ПАВ, проведены исследования электролитического получения цинка из электролита, не содержащего ПАВ. Для обоих случаев проведена энергодисперсионная электронномикроскопическая экспертиза цинковых покрытий и представлена в виде фотографий и табличных данных. Определен и представлен элементный состав цинковых покрытий, полученных из электролита без ПАВ и с комбинированными ПАВ. Проведена химическая экспертиза цинкового покрытия для определения его толщины и пористости. Показано эффективное влияние подобранной комбинации ПАВ на качество цинкового покрытия. Сделаны выводы и даны рекомендации по результатам проведенных исследований.

Ключевые слова: сульфатные электролиты, цинковые покрытия, поверхностно-активные вещества (ПАВ).

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