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NEW FRIENDLY ENVIRONMENTAL ETCHING TECHNOLOGIES FOR SOME STEELS AND COPPER ALLOYS

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Abstract: *New compositions containing some organic inhibitors were tested in the carbon steels and copper alloys etching processes. The analysis of the etching efficiency and harmful products emission proves that significant reduction in the specific discharge of the waste waters and emission of nitrogen oxides can be achieved at the appropriate etching quality.*
This reduction is caused mainly by adsorption of the organic inhibitors on the metal surface by decreasing its excessive dissolution. On the other hand, the effective aggregation and dispersion of the corrosion products promotes faster transportation of the rust and dross particles away from the treated metal surface reducing the total processing time.

Keywords: *environmental safety; corrosion; etching; carbon steels, copper alloys*

1. Introduction

The galvanic industry is the second highest pollution source after the surface transport branch and it causes continuous and long-lasting contamination of the entire environment (air, water and soil). Therefore, the extensive efforts should be directed to prevent this dangerous contamination bringing many aggressive components of the galvanic (including metals etching) composition into the enevironment [1-7].
Among the others, the metal etching technologies produce significant amounts of the air and water pollution agents and extended activity is directed onto investigation of possible mitigation steps, which should provide same etching quality and efficiency at lower emission of pollutants.
Sulfuric, hydrochloric and nitric acids are used as the main components for the low-alloy carbon steel etching compositions [2-3]. Significant amounts of iron can dissolve in sulfuric acid during this process while dissolution of iron in the hydrochloric acid compositions is less influential. On the other hand, a rate of the metal rust and scale dissolution in the latter compositions is higher than in the former, therefore, the hydrochloric compositions are more suitable for the low-allow carbon steel etching [2, 3, 8]. An optimal content of sulfuric acid in the regular etching compositions is 20-22 %; hydrochloric acid – 18-20 %. Additional organic substances are usually added to the both types of the compositions to counteract excessive metal dissolution, decrease emission of the gaseous pollutions agents and minimize amount of the wastewater formed.
Thiocarbamide- hydrosulfite-, sulfite-, thiosulfate- and thiocyanate compounds are used regularly in the nitric acid based etching compositions in order to protect the metal surface from its dissolution. However, these compounds are quite toxic and

can provide effective surface protection within quite a narrow pH range only [2, 3, 8-11].

It is obvious, that such inhibitors should be substituted with different, less toxic substances with the wider working pH range.

The phosphoric acid etching compositions are also used in industry. Trace amounts of the unwashed acid can provide additional corrosion protection since iron phosphates are insoluble and form quite dense surface protection film. On the other hand, this acid is weaker and effective etching requires the solution to be heated up to 85 ^{0}C, causing rise in the processing cost. Due to this shortcoming, the phosphoric compositions have quite limited usage and are recommended mostly for the fine etching of the surfaces to be dyed.

A number of the mixed acids compositions are also used in the modern industry for etching [2, 3].

Two types of compositions are used for the chemical polishing of copper and its alloys. The first type consists of various mixtures of nitric (5-20 vol. %), phosphoric (30-80) and acetic (10-50) acids and the second type is based on hydrogen peroxide. The higher is concentration of nitric acid, the worse is the surface glitter while efficiency of the polishing decreases with rise of the phosphoric acid content. Excessive concentration of the acids may result in the unwanted etching process running along with the polishing. Most polishing compositions are effective only for the temperatures under 323-373 K and for the copper contents below 30-36 g/l [2, 3 12-14]. This process is unsafe environmentally and causes emission of harmful nitrogen oxides [2, 3].

Various nitrogen- and sulfur-containing substances can be used in the polishing technology as inhibitors. For instance, urotropine is widely used in various composite inhibitors together with catapine, tribenzenamine or thiocarbamide. The former substance exhibits own inhibition activity and promotes higher activity of the other components. However, such compositions are used at the temperatures above 298 K, which increases the production cost. As reported in [15-19], some nitrogen-containing heterocycles (derivatives of quinoline, pyridine, acrydine, indole and others) can provide an effective inhibition for the acidic polishing mixtures. However, development of specific polishing compositions is still required in various industrial branches.

This paper deals with investigation of some new effective, nontoxic, environment-friendly, inexpensive compositions for the acidic etching of the carbon steels, copper and its alloys, which produce reduced amounts of the harmful products.

As stated above, the carbon steel etching compositions are usually based on the mixture of hydrochloric and nitric acids.

As the latter agent is the strong oxidizer, the proposed inhibition compositions should remain active and stable in such aggressive solution.

Two or more different inhibition agents are usually mixed in various compositions [2, 3. 14-19] in order to cover all technological range of temperatures, pH and other parameters of the solutions.

The protective activity of the compositions and the range of their usability can be changed by selection of various concentrations of the components.

On the other hand, changes in these concentrations would also influence the technological characteristics of the etching process and emission of the harmful compounds.

Therefore, such an investigation should be aimed onto finding of the environmental friendly compositions ensuring high technological efficiency

2. Experimental

Two groups of parameters have been measured in order to evaluate influence of the admixtures on the process of the metal surface etching.

A: Environmental parameters: specific emission of nitrogen oxides; concentration of metal ions in the wastewater; specific amount of the wastewaters formed;

B: Technological parameters: etching quality; mass loss and rate of the metal dissolution.

All experiments were carried out at 293±2 K during 5 minutes (for the steel samples) or 30 seconds (copper and copper alloys samples) using the etching compositions with two different inhibitors. The first inhibitor was taken from the group I: benzenesulfonic acid; sulfosalicylic acid; sulfanilic acid while the second agent was taken from the group II: thiosemicarbazide; acetylcarbamide; pyrimidone; carbamide; N-n-etoxyphenylcarbamide.

The most optimal concentrations of the inhibitor I and inhibitor II for the carbon steels St10 and St3 were sought for the following acidic etching composition (1) (g/l):

Hydrochloric acid (ρ = 1.19 g/ml)	200;
Nitric acid (ρ = 1.34 g/ml)	120;
Inhibitor I	up to 10
Inhibitor II	up to 2.0.

As seen from the electrochemical data (see Table 1, 2), the majority of the group II inhibitors show good efficiency for etching the St10 steel samples in the composition (1) with sulfosalicylic acid (10 g/l). The group I inhibitors exhibit the mixed type of activity and can decelerate both cathodic (hydrogen release) and anodic (metal dissolution) processes (see Table 1). A technologically sufficient metal protection can be ensured at 293 K by adding of 2 g/l of acetylcarbamide or 0.2 g/l of thiosemicarbazide together with 10 g/l of sulfosalicylic acid to the composition (1) (Table 2). For example, the corrosion retardation coefficient γ = 4,8 and 15.0 and the metal surface protection degree was 79.2 % and 93.3 % for acetylcarbamide and thiosemicarbazide simultaneously.

Since effective corrosion protection requires $\gamma \geq 8$ or the metal protection degree over 87 %, thisosemicarbazide can be classified as very effective inhibitor while efficiency of acetylcarbamide is lower but still sufficient.

Both substances contain atoms of nitrogen and oxygen (or sulfur) with the opposite effective charges, which facilitates possible adsorption on both anodic and cathodic areas on the metal surface and formation of the dense adsorption layer. Sulfosalicylic acid provides additional retardation of the metal dissolution because it contains the functional groups SO_3H^- i OH^-, which exhibit some inhibition effect on the anodic areas.

All these properties ensure good inhibition effect and prove the assumption of higher efficiency of the two-component inhibitors protecting the metal surface during its etching [2, 3].

Table 1

Some electrochemical parameters of the St10 steel etching processes with or without inhibitors of the group I

Inhibitor	i,A/dm^2	φ_s, V	Z, %	γ	C_a, %	W_c, g/mm^2·year
Source composition (no inhibitor used)	0.024	0.391	-	-	40	1.68
Benzenesulfonic acid	0.017	0.370	29.17	1.4	33	1.16
Sulfosalicylic acid	0.016	0.382	33.3	1.5	37.5	1.12
Sulfanilic acid	0.014	0.382	41.7	1.7	44	0.96

3. Results and discussion

The inhibition efficiency has been estimated (see Tables 2, 3) using the following parameters: *i* – current density (A/dm^2); φ_s – potentials of the metal sample surface (V); W_c – index of the metal corrosion dissolution (g/mm^2 hour); Z – inhibition activity coefficient (%); γ – corrosion retardation coefficient; C_a – anodic control degree (%).

Current density (*i*) and potentials of the metal sample surface (φ_s) were determined through direct instrumental measurements.

Index of the metal corrosion dissolution (W_c) was calculated by the formula:

$$W_c = \Delta m /(S \times t),$$

where Δm – change in the steel or copper sample mass, g; t – duration of the process, h; S – surface area of the metal sample, m^2 (we used samples with S = 0.1 m^2); W_c – rate of the metal surface dissolution, g/m^2·h.

The value (Z) – metal surface protection degree characterizes depth of the corrosion retardation and can be calculated by the formula:

$$Z = \frac{\rho_0 - \rho}{\rho_0} \cdot 100\%,$$

where ρ and ρ_0 – corrosion rates with and without inhibitor simultaneously.

The dimensionless corrosion retardation coefficient γ shows the ratio of the corrosion rate retardation by the given inhibitor and can be calculated as:

$$\gamma = \frac{\rho_0}{\rho},$$

where ρ and ρ_0 are similar to the formula above. Anodic control degree (C_a) was calculated by the formula:

$$C_a = 100 \frac{\Delta E_a}{\Delta E^0} \%,$$

where ΔE_a – is a shift of the working anodic potential from its initial value under the given electric current; ΔE^0 – the initial potentials difference between the cathodic and anodic areas.

Table 2

Some electrochemical parameters of the St10 steel etching process in the solution consisting sulfosalicylic acid and some inhibitors of the group II

Inhibitor	*i*,A/dm^2	φ_s, V	Z, %	γ	C_a, %	W_c, g/mm^2·year
1 g/l acetylcarbamide	0.014	0.362	41.7	1.7	50	0.96
2 g/l acetylcarbamide	0.005	0.380	79.2	4.8	50	0.36
1 g/l carbamide	0.01	0.396	58.3	2.4	50	0.68
2 g/l carbamide	0.006	0.397	75.0	4.0	50	0.4
1 g/l N-n-etoxyphenylcarbamide	0.018	0.376	25.0	1.3	50	1.24
2 g/l N-n-etoxyphenylcarbamide	0.02	0.375	0.17	1.2	50	1.4
1 g/l pyrimidone	0.01	0.382	58.3	2.4	67	0.68
2 g/l pyrimidone	0.009	0.391	62.5	2.7	60	0.64
0.1 g/l thiosemicarbazide	0.002	0.397	91.7	12.0	50	0.12
0.1 g/l thiosemicarbazide	0.0016	0.398	93.3	15.0	60	0.12

Table 3 represents some parameters of St10 and St 3 etching in the acidic composition (1) with some inhibitors of the group I. As seen from Table 3, efficiencies of benzenesulfonic acid and sulfosalicylic acid are similar and higher than efficiency of sulfanilic acid. Therefore, the two former agents can ensure more efficient etching with better environmental parameters.

Since sulfosalicylic acid is cheaper and used widely in the industry, it was selected for our further investigations as the most effective inhibitor of the group I.

Table 3

Some parameters of St10 and St 3 etching in the composition (1) with some inhibitors of the group I (*)

Inhibitor	C. g/l	(Δm.mg)/(d. μm)	W_c. g/m^2·h	V_{NOx}. mg/l	V_s. l/m^2
Composition (1). no inhibitors	-	98/1.4	117.6	112.3	38
Benzenesulfonic acid	10.0	28/0.40	33.6	52.9	14
Sulfosalicylic acid	10.0	29/0.41	34.8	41.7	15
Sulfanilic acid	10.0	51/0.73	61.2	71.3	24

(*) C – inhibitor concentration in the etching composition; Δm – changes in the sample mass after etching; d – thickness of the dissolved metal layer; W_c *– rate of the metal dissolution;* V_{NOx} *– specific emission of* NO_x*;* V_s *– specific volume of the wastewater formed.*

An influence of the group II agents together with sulfosalicylic acid has been investigated at the next stage (see results in Table 4).

Table 4

Some parameters of St10 and St3 steels etching in the composition (1) with sulfosalicylic acid and the group II agents (*)

Inhibitor	**C. g/l**	**(Δm.mg)/(d. μm)**	**W_c. g/m^2·h**	**V_{NOx}. mg/l**	**V_s. l/m^2**
Carbamide	2.0	20/0.29	24.0	24.3	10.0
Acetylcarbamide	2.0	7/0.10	8.4	4.5	3.5
Pyrimidone	2.0	10/0.14	12.0	5.6	5.0
N-n-etoxyphenylcarbamide	1.5	42/0.60	50.4	34.4	21.0
Thiosemicarbazide	0.2	3/0.04	3.6	3.75	3.0

(*) All notations are similar to those in Table 3.

The compositions with acetylcarbamide (2.0 g/l) and thiosemicarbazide (0.2 g/l) together with sulfosalicylic acid prove the best inhibition efficiency since their inhibition and dispersing properties ensure better environmental and technological parameters of surface treatment of the carbon steels, copper and its alloys (see Table 4 and 5). Specific emission of the nitrogen oxides reduces tenfold (from 0.0082 to 0.00048 mg/m^3 for the carbon steel etching and down to 0.088 mg/m^3 for the copper alloys).

Amount of the wastewaters formed reduces 3-4 times, the rate of the metal dissolution decreases by one order of magnitude and quality of the surface after the treatment becomes significantly higher comparing to the results achieved by the traditional technologies. Therefore, the following two compositions can be recommended for the carbon steels etching:

Table 5

The compositions recommended for the carbon steels etching

Composition №1 (g/l):	***Composition №2 (g/l):***	***Composition №3 (g/l):***
Hydrochloric acid (ρ=1.19 g/ml) – 200; Nitric acid (ρ=1.34 g/ml) – 120; Sulfosalicylic acid – 10; Acetylcarbamide – 2.0; Distilled water – up to 1 *l*	Hydrochloric acid (ρ =1.19 g/l) – 200; Nitric acid (ρ =1.34 г/см^3) – 120; Sulfosalicylic acid – 10; Thiosemicarbazide – 0.2; Distilled water – up to 1 *l*	Phosphoric acid (ρ = 1.834 g/ml) – 275; Acetic acid (ρ = 1.049 g/ml) – 125; Nitric acid (ρ = 1.340 g/ml – 100; Thiosemicarbazide – 0.15; Distilled water - up to 1 l.

A series of the thioamides derivatives was checked for their inhibition efficiency in the copper and copper alloys etching and polishing (see Table 6) and phenylthiosemicarbazide and thiosemicarbazide (0.15 g/ml) have shown the best inhibition and brightening performance. These substances also facilitate the significant reduction in nitrogen oxides emission and in amount of the wastewaters formed.

Table 6

Some parameters of the copper alloys polishing with and without inhibition agents (*)

Inhibition agent	C. g/l	Δm. mg / d. μm	W_c. g/sm^2·hour	V_{NOx}. mg/l	V_s l/m^2	Δ. %
Polishing mixture. no inhibitor	-	430/6.14	860.0	181.0	18.2	+2
Thiocarbamide	0.15	250/3.57	500.0	76.1	4.0	+15
Thioacetamide	0.15	190/2.71	380.0	65.0	3.0	+4
Rubeanic acid	0.15	170/2.43	204.0	59.0	12.5	-7
Thiosemicarbazide	0.15	130/1.86	260.0	7.6	0.65	+17
Phenylthiosemicarbazide	0.15	115/1.64	230.0	7.5	0.6	+12

(*) All notations are similar to those in Table 3. Δ means changes in the surface glitter. %.

Therefore, the following composition can be recommended for polishing of copper and its alloys (column 3 in Table 5) .

A character and nature of the inhibition activity of various agents can be understood from analysis of changes in the associative interaction between the group I and group II compounds. This interaction causes some changes in the spectral parameters of the solution described in details below.

At the next stage, an influence of the corrosion inhibitors (sulfosalicylic acid. thiosemicarbazide, carbamide, acetylcarbamide and pyrimidone) on environmental safety and performance of the metal etching compositions has been investigated. Special attention has also been given to the predicted associative interaction between the group I agent (sulfosalicylic acid) and the group II agents (thiosemicarbazide, carbamide, acetylcarbamide and pyrimidone).

Results of this investigation are represented in the Tables 7 and 8. It can be seen that pyrimidone and thiosemicarbazide do not form any associates with sulfosalicylic acid since the characteristic light absorbance maximum of sulfosalicylic acid does not shift after mixing with both agents (see Tables 6 and 7). Therefore, these inhibitors adsorb on the metal surface independently.

In contrary, formation of the associates between sulfosalicylic acid and carbamide has been determined and position of the light absorbance peak shifts for about 80 nm – from 250 to 330 nm (See Fig. 1).

Sulfosalicylic acid and acetylcarbamide also form associates causing the acetylcarbamide maximum absorbance peak in the mixture to shift for 55 nm in comparison to the pure acetylcarbamide solution (see Fig. 2).

Table 7

Position of the light absorbance peak and its intensity for sulfosalicylic acid, pyrimidone and their mixture

Compound	λ_{max}	Lgε
Sulfosalicylic acid	337.5	4.83
Pyrimidone and sulfosalicylic acid	337.5	4.90

Table 8

Position of the light absorbance peak and its intensity for sulfosalicylic acid. thiosemicarbazide and their mixture

Compound	λ_{max}	Lgε
Sulfosalicylic acid	337.5	4.83
Sulfosalicylic acid and thiosemicarbazide	338.0	4.79

The above mentioned associates are comparatively instable since the shifted absorbance peaks were found returned to the previous positions in 2-3 hours. For instance. the pure acetylcarbamide spectral data showed the peak in the position 1. admixture of sulfosalicylic acid caused its shifting to the position 2 and then the peak was recorded in the position 1 again in 2-3 hours (see Fig. 1).

Since C/A dependence (C – adsorbate concentration; A – adsorption value) on adsorbate concentration is linear (see Fig. 3). the process of adsorption can be represented by the monomolecular Langmuir mechanism.

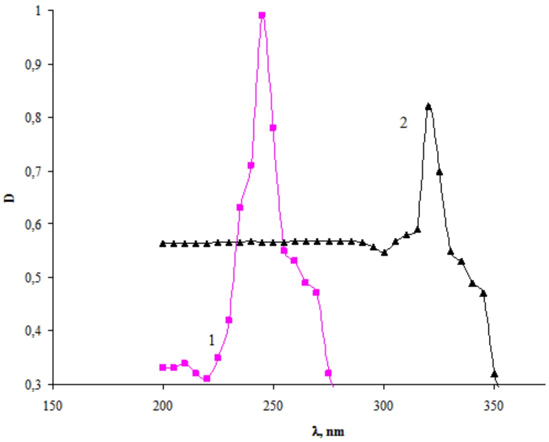

Fig.1. Dependence of the optical density (D) on wavelength (λ) for aqueous solutions of carbamide. and its mixture with salicylic acid; 1 – carbamide; 2 – mixture of sulfosalicylic acid and caramide (concentration of both compounds is 1•10-5 m/l).

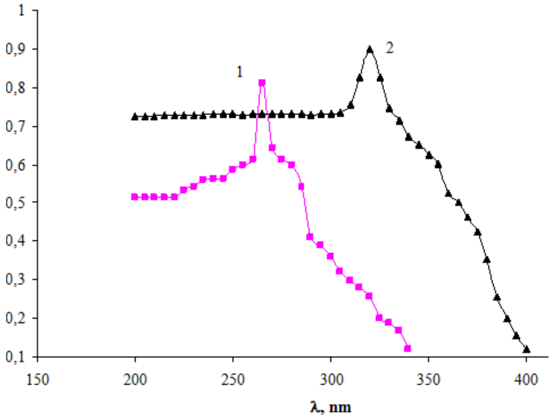

Fig. 2. Dependence of the optical density (D) on wavelength (λ) for aqueous solutions of acetylcarbamide. and its mixture with sulfosalicylic acid; 1 – acetylcarbamide; 2 – mixture of sulfosalicylic acid and acetylcaramide (concentration of both compounds is 1•10-5 m/l).

As seen from Fig. 4. sulfosalicylic acid adsorption on the iron oxides powder is higher than on iron and steel. Similar comparison for acetylcarbamide proves its better adsorption on iron, then on steel and iron oxides (see Fig. 5).

As seen from the Fig. 4 and 5, according to the descending adsorption activity in relation to sulfosalicilic acid (a) and acetylcarbamide (b), the adsorbents can be arranged in the following sequences:

(a): FeO > Fe_2O_3 > Fe > St10
(b): Fe > St10 > FeO > Fe_2O_3.

It was found that the descending adsorption activity sequence related to carbamide. pyrimidone and thiosemicarbamide is similar to the row (a).

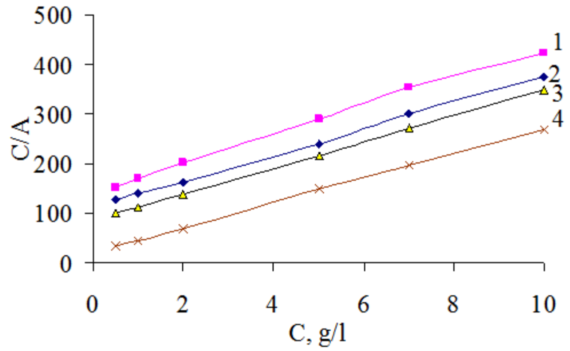

Fig. 3. Near-to-linear dependencies of C/A on the adsorbate (sulfosalicilic acid) concentration proves the Langmiur mechanism of its adsorption on the following samples: steel St10 (1); iron powder (2); Fe_2O_3 powder (3) and FeO powder (4).

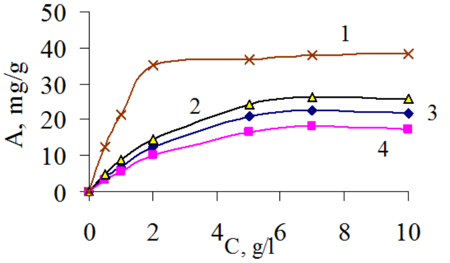

Fig. 4. Adosrption isotherms of sulfosalcylic acid on: 1 – FeO. 2 – Fe2O3. 3 – Fe. 4 – steel St10.

Effective aggregation and dispersion of the corrosion products are essential to ensure higher environmental safety of the etching composition. Fast aggregation and dispersion of the rust and dross particles promote faster transportation of these products away from the metal surface, increase in the etching surface area and in general, higher rate of the process. Therefore, total etching time decreases causing reduced emission of the hazardous etching gases. In this context, an influence of sulfosalicylic acid, thiosemicarbazide and their mixtures on the aggregation stability of the aqueous suspensions containing iron oxides and some corrosion products has been investigated.

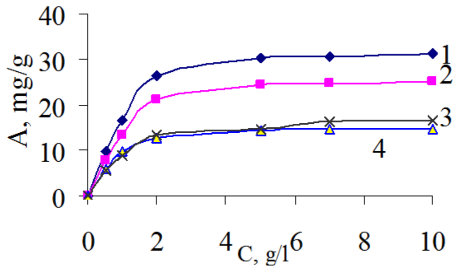

Fig. 5. Adosrption isotherms of acetylcarbamide on: 1 – Fe. 2 – steel St10. 3 – FeO. 4 – Fe_2O_3.

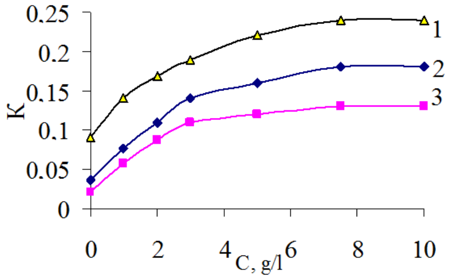

Fig. 6. Dependence of the sedimentation stability coefficient (K) on the concentration of sulfosalicylic acid for: 1 – St10 steel corrosion products; 2 – particles of Fe2O3; 3 – particles of FeO.

The data of Fig. 6 prove that increase in the inhibitor concentration results in higher sedimentation stability.

An optimal etching mode can be achieved at some ratio between two inhibitors (sulfosalicylic acid and acetylcarbamide or sulfosalicylic acid and thiosemicarbazide) when the inhibitors provide sufficient metal surface protection and high dispersion of the corrosion products.

4. Conclusion

An effective and environment friendly composition is proposed for the etching solutions to be used for steel and copper alloys. These compositions ensure significant reduction in the harmful gases emission and decrease amount of the technological waste water formation. Specific emission of nitrogen dioxide can be nine times less and formation of the spent solution – four time less comparing to the standard etching compositions. Besides. no special surface cleaning reagents are required in the proposed compositions because of the enhanced surface activity of the components used.

A mechanism of the components adsorption on the metal surface is the main factor determining the overall performance of the proposed compositions.

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