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EFFECT OF HYDROXYLAMINE ON PHOSPHATING IRON IN SULPHATE SOLUTION

Abstract. We have researched on hydroxylamine influence on corrosion characteristics of phosphate coatings obtained on iron samples in sulfate solutions containing Mazhef salt. It was found that in the presence of hydroxylamine protective anticorrosive properties of phosphate coatings on iron samples are sharply amplified. The optimum parameters of the phosphating process: concentration of hydroxylamine, temperature, exposing time of sample solution used for phosphating. It is found that when the Mazhef salt concentration - 70 g/l, temperature of 50-550C, phosphatizing time 50-55 minutes and hydroxylamine concentration of 0.05 - 0.06 g/l, the phosphate coatings with high corrosion resistance are formed. Electron microscopy method determined the elemental composition of the phosphate coatings on metal surfaces of the samples. It has been shown that increasing the concentration of hydroxylamine in the phosphate solution leads to an increase in the percentage of phosphorus, oxygen and a manganese in phosphate coating. It is concluded that in contrast to the heterogeneous processes of formation of phosphate compounds of iron, manganese phosphate is formed as a result of supply of the solution volume. The source of manganese ions may be Mazhef salt. This process is enhanced with increasing concentration of hydroxylamine. The presence of phosphate compounds of iron and manganese on the surface of the investigated iron samples provides amplification of anticorrosion properties of phosphate coatings.

Key words: iron phosphate coatings, hydroxylamine, protective properties and optimal conditions.

The formation of phosphate coatings should be considered as a result of the simultaneous occurrence of electrochemical, chemical, crystal-chemical and physical processes in heterogeneous environment [1-7]. The most informative and comprehensive understanding of the mechanism of formation of the phosphate layer is described in the works of Ya.M. Kolotyrykin [8-16], which presents theoretical views on the course of the two electrochemical reactions - metal oxidation and reduction of oxidized component by aggressive environment. It is a reasonable conclusion that the metal surface is equipotential, and places of localization of paired cathode and anode processes flow are continuously changing in time according to the laws of statistical distribution.

Based on the fact that the phosphating process usually begins with a rapid electrochemical dissolution of metal, which is accompanied by evolution of hydrogen and the following deceleration of reaction due to blockage of the treated surface by the evolved hydrogen gas, there is need for a method of accelerating the formation of a phosphate film. The most effective in this regard were the intensification methods using accelerators [17-19]. Introduction of accelerators to the phosphating solution leads to the depolarization of the cathodic process. In this regard, of particular interest are compounds which are able to recover in the potential - 0,2 ÷ -0,4V realized in the process of phosphating. The presence of such substances capable of cathodically recover, besides the restoration of hydrogen ions and molecular oxygen, leads to increase the rate of anodic conjugation process and thus to accelerate the phosphating process itself. It should be noted that the presence of accelerators promotes the crystal-chemical reactions with formation on the treated metal surface of denser phosphate layer having a smaller crystal size and higher corrosion characteristics.

For obtaining phosphate coatings most widely usage in practice were received phosphating solutions based on the Mazhef salt. However, these solutions do not currently meet the highest modern standards that apply to the phosphating coatings. To enhance the protective properties of the phosphate coating to

the phosphating solution there are introduced salts of several metals (Ni, Zn, Cr, Co, Ti, etc.), the use of which is not always economically justified and impractical.

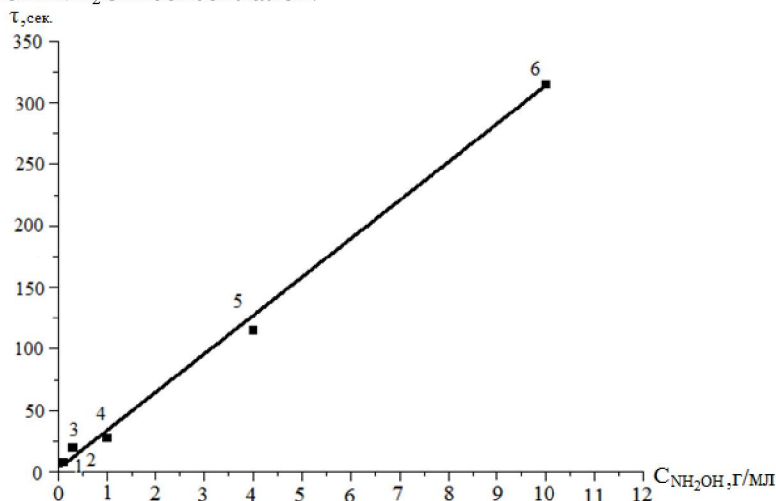
In connection with the above mentioned it is interesting to use hydroxylamine as the accelerator of the phosphating process, which affects the process of iron phosphating from solutions containing Mazhef salt.

Experimental procedure

Phosphating was carried out on iron samples from solutions containing 70 g/l Mazhef salt with addition of NH_2OH hydroxylamine, the concentration of which was varied from 0.001 to 0.1 g/l. The protective properties of formed phosphate coatings were evaluated by the G.V. Akimov method [20] by measuring the time from the moment of application of the control solution drop until changing its color from blue to yellow. Electronic images of phosphated coatings on iron samples and elemental composition in % were determined using the instrument LaB6 JSM-6610LV of "JOEL" company (Japan).

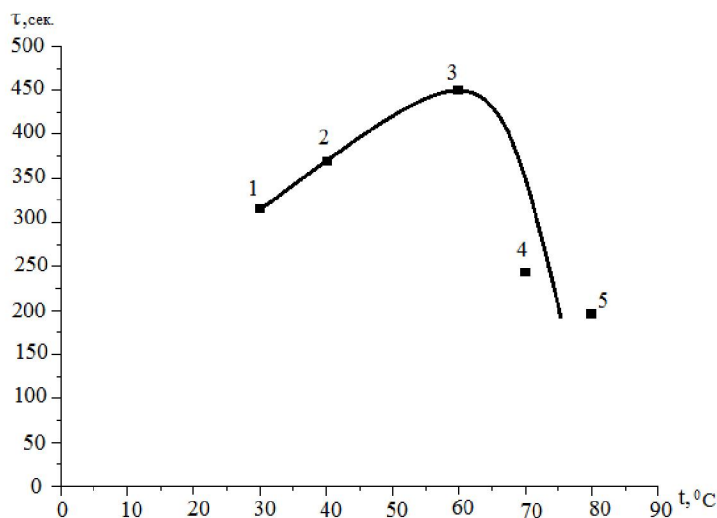
There was conducted a study of the concentration of hydroxylamine to modify the protective ability of obtained phosphate coating. Hydroxylamine concentration was varied from 0.01 to 0.1 g/l.

Figure 1 shows dependence of the change of color drops from blue to yellow after application of a phosphate coating from NH_2OH concentration.



Phosphating solution: Mazhef salt - 70 g/l + 0.1 g/l NH_2OH ; temperature - 300C; phosphating time - 60 minutes.

Figure 1 - Time changing of color of the dropping sample from the concentration of hydroxylamine



Phosphating solution: Mazhef salt - 70 g/l + 0.1 g/l NH_2OH ; phosphating time - 60 minutes.

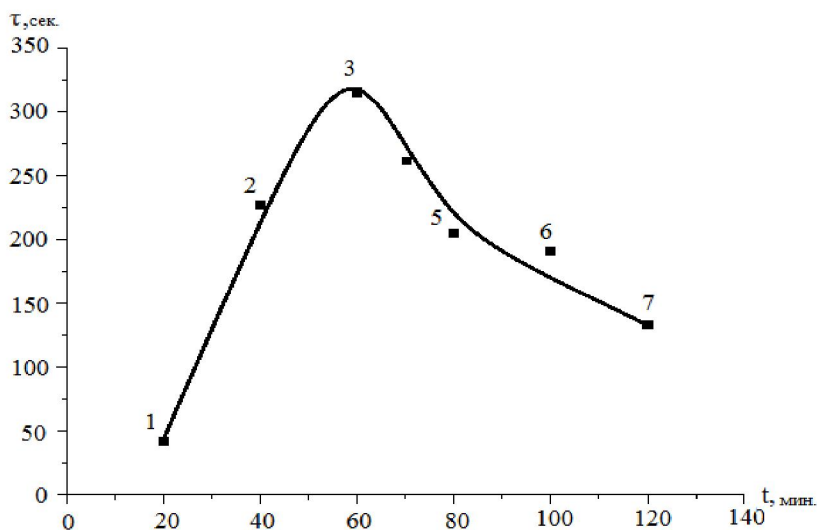
Figure 1 - Time changing of color of the dropping sample from temperature of phosphating solution

From Figure 1, it follows that with increasing concentration of NH_2OH time change of color drops (τ) is from 7 to 315 s. In other words, with the increase in concentration of NH_2OH in Mazhef solution (70 g/l) protection properties of phosphate coatings are enhanced at the condition of constant solution temperature of 30C and duration of incubation of the iron sample in the studied solutions - 60 s.

Figure 2 shows the dependence of color change of the dropping sample by the temperature of the solution in which the iron sample phosphate was conducted.

According to Figure 2 with temperature increasing from 30 to 60°C of proposed solution for phosphating time of color change of the dropping sample was increased from 315 to 450 s. However, with further increase of phosphating solution temperature, time of color change of the dropping sample is appreciably reduced, at 80°C this value becomes even less than at 30C.

An important characteristics of the phosphating process is the exposure (incubation) time of the test iron sample in used phosphating solution (70 g/l Mazhef + 0.1 g/l NH_2OH) at a constant temperature of 30C. Figure 3 shows the dependence of color change of the dropping sample from time, during which the iron sample was heated in the test solution.



Phosphating solution: Mazhef salt - 70 g/l + 0.1 g/l NH_2OH ; temperature – 30°C;

Figure 3 - Time change of the color of the dropping samples on the time-keeping of the iron sample in phosphating solution

According to Figure 3 with increasing duration of phosphatizing from 20 to 60 minutes at constant temperature of 30C time changing of drop color increases from 40 up to 315 s. However, further increasing incubation duration of iron sample in the test solution for phosphatizing reduces time change of drop color (τ) from 315 to 133 s. Based on the data it follows that NH_2OH availability in solution for phosphatizing results in enhancing protective properties of phosphate coatings. The optimal conditions of phosphating of iron samples in solutions for phosphating containing NH_2OH phosphating accelerator were determined. It was found that the greatest protective ability is for phosphate coatings obtained by Mazhef salt concentration - 70 g/l, temperature - 50-55C, phosphatizing time - 50-55 minutes, hydroxylamine concentration of 0.05 - 0.06 g/l.

With the hepl of electron microscopy it was evaluated the content of iron, phosphorus, oxygen, and manganese on iron sample coated with phosphate film from solution 70 g/l Mazhef with varying concentrations of NH_2OH at constant temperature of 30C and incubation time of 60 min. Figure 4 (a, b, c, d) shows changes depending of % content of iron, phosphorus, oxygen, and manganese on the iron sample after applying a phosphate coating from the test solution at different NH_2OH concentration.

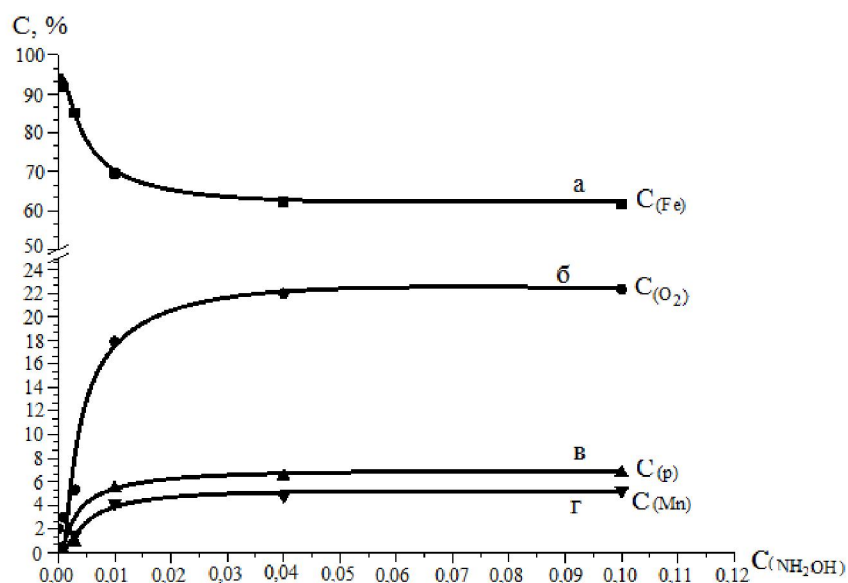


Figure 4 - Change in percentage of iron (a), phosphorus (b), oxygen (c), manganese (g) from the concentration of hydroxylamine in the test solution on the iron sample

According to Figure 4a it is shown that with an increase of NH_2OH in the used solution percentage content of iron decreases, while under similar conditions the phosphorus content (Figure 4b), oxygen (Figure 4c) and manganese (Figure 4d) increases.

The obtained dependences allow us to conclude that with increasing NH_2OH concentration in the test solution on the iron sample surface it is amplified formation of the phosphate film. Oxygen to phosphorus ratio is closed to 4:1, which can be connected to formation of phosphates, which may be associated with ions of iron and manganese. The fact that the percentage of manganese increases in the phosphate film, indicates that the presence of hydroxylamine in the test solution promotes formation on the sample surface of manganese phosphate, which enhances the protective properties of the obtained phosphate coating. Obviously, the presence of fine-grained dense coating of obtained phosphate film leads to blocking of the iron sample surface and reducing the percentage of iron content.

Thus, on the basis of the experimental data it was determined that

- at Mazhef salt concentration - 70 g/l, temperature - 50-55°C, phosphatizing time - 50-55 minutes, hydroxylamine concentration of 0.05 - 0.06 g/l there are formed phosphate coatings with high corrosion resistance;

- the presence of phosphate compounds of iron and manganese in the iron sample surface provides amplification of anticorrosive properties of phosphate coatings;

- It is concluded, that, in contrast to the heterogeneous processes of formation of iron phosphate compounds, manganese phosphate on the surface of the iron sample are formed by feeding them from the solution volume. The source of manganese ions may be Mazhef salt. This process is enhanced with increasing concentration of hydroxylamine.

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СУЛЬФАТ ЕРІТІНДІЛЕРІНДЕГІ ФОСФАТТАЛҒАН ТЕМІРГЕ ГИДРОКСИЛАМИННІҢ ӘСЕРІ

Аннотация. Құрамында Мажеф тұзы бар сульфат ерітіндісіндегі темір үлгілерінен алынған фосфаттық жабындылардың антикоррозиялық қасиеттеріне гидроксиламиннің әсері зерттелді. Гидроксиламиннің қатысуымен темір үлгілерінде фосфатты жабындылардың коррозияға қарсы қорғау қасиеттерінің күрт

күшеюі анықталды. Фосфаттау процесінің оңтайлы параметрлері анықталды: гидроксиламиның концентрациясы, температура, пайдаланылған үлгілердің фосфаттау ерітінде экспонаттау уақыты. Мажеф тұзының концентрациясы 70 г/л, температурасы 50-55 °С, фосфаттау уақытты 50-55 минут және гидроксиламиның концентрациясы 0,05-0,06 г/л кезінде антикоррозиялық төзімділігі жоғары фосфаттық жабындылар түзіледі. Электрондық микроскопия әдісімен темір үлгілерінде фосфатты жабындылардың элементтік құрамы анықталды. Фосфаттау ерітіндісінде гидроксиламиның концентрациясының жоғарлаумен фосфаттық жабынды құрамында фосфардың, оттегінің және марганецтің пайыздық қатынасы артады. Марганец ионының қоры ретінде Мажеф тұзын алуға болады. Гидроксиламиның концентрациясын көтеру арқылы процесі күшейтуге болады. Темір және марганецтің фосфаттық қосылыстардың темір үлгілердің беті нде болуы фосфаттық жабындылардың антикоррозиялық қасиеттерінің күшеюін қамтамасыз етеді.

Кілт сөздер: темір, фосфатты жабындылар, гидроксилламин, қорғау қасиеттері, оптималдық жағдайлар.

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ВЛИЯНИЕ ГИДРОКСИЛАМИНА НА ФОСФАТИРОВАНИЕ ЖЕЛЕЗА В СУЛЬФАТНЫХ РАСТВОРАХ

Аннотация. Исследование влияния гидроксиламина на антикоррозионные характеристики фосфатных покрытий полученных на железных образцах в сульфатных растворах содержащих соль Мажеф. Установлено, что в присутствии гидроксиламина защитные антикоррозионные свойства фосфатных покрытий на железных образцах резко усиливаются. Определены оптимальные параметры процесса фосфатирования: концентрация гидроксиламина, температура, время экспонирования используемого образцов растворе для фосфатирования. Установлено, что при концентрации соли Мажеф 70 г/л, температуре 50-55°С, времени фосфатирования 50-55 минут и концентрации гидроксиламина 0,05 – 0,06 г/л образуются фосфатные покрытия с высокой антикоррозионной стойкостью. Методом электронной микроскопии определен элементный состав фосфатных покрытий на поверхности железных образцов. Показано, что увеличением концентрации гидроксиламина в фосфатном растворе приводит к увеличению процентного содержания фосфора, кислорода и марганца в фосфатном покрытии. Сделан вывод, что в отличие от гетерогенных процессов формирования фосфатных соединений железа, фосфаты марганца образуются в результате их подвода из объема раствора. Источником ионов марганца может быть соль Мажеф. Этот процесс усиливается с ростом концентрации гидроксиламина. Наличие фосфатных соединений железа и марганца на поверхности исследуемых железных образцов обеспечивает усиление антикоррозионных свойств фосфатных покрытий.

Ключевые слов: железо, фосфатные покрытия, гидроксилламин, защитные свойства, оптимальные условия