Phosphatizing of Metals With Easily Detachable Polymer Coatings

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The phosphate treatment of ferrous metals with easily peeled off polyamide (PFE2/10) coatings was investigated. The coatings contain various phosphatizing agents including ammonium dihydrophosphate, ammonium molybdate, sodium hexamethaphosphate, and anti-adhesives (oleic acid, N-cethylpyridinchloride) as well as such corrosion inhibitors as sodium nitrites and hydroxylamine. The film adhesive strength as a function of concentration, its nature and drying duration was established. The efficiency of phosphatizing agents was assessed using electrochemical and X-ray structural investigation methods and optical surface analysis. The protective features of the phosphate films received their theoretical foundation, which was confirmed by the experiments. Peeling force of the polymer film was determined and the optimal phosphatization composition was proposed.

Keywords: polyamide coating, adhesive strength, phosphatizing, anticorrosive protection.

INTRODUCTION

There are numerous ways of protection of steel from corrosion (metallic and non-metallic, organic coatings are used for this purpose) [1, 2]. However, this problem remains without its final solution. Therefore, we have chosen most widely used carbon steel 3 (further – steel) as the object of our investigations. It is well known that surface phosphatization increases resistance to corrosion [3, 4] and strengthens paint adhesion [5]. At present phosphatization can be carried out by immersion of the product into phoshatization solution or by usual painting procedures. During it the continuos not soluble crystal or amorphous film forms on the surface having series of technically useful properties including anti-frictional, insulating electrically, anticorrosive, enhancing paint adhesion and life of service ones. These film properties depend on a lot of factors among them on phosphatizing solution composition, kind of metal being coated, surface preparation quality, type of its processing and on solution temperatures. Iron, manganum, zinc, and ammonium dihydrophosphates are most frequently used for phosphatizing as well as sodium polyphosphates, FOSFAKOR liquid and others [6, 7]. Sometimes before phosphatizing the metal surface is processed with process activator, or process intensifiers are used. The quality and properties of the film formed depend not only on the factors cited but also on various special additives. The holding much promising but little known phosphatizing method is phosphatizing with the coatings, which can be easily peeled off when phosphatizing materials are constituents of the coatings. As most phosphatizing salts are soluble in water, for coating formation such polymers must be chosen which are compatible with water. This phosphatizing method is simpler and cleaner ecologically one, especially for phosphatizing surfaces of large steel products. These coatings are applied by means of flushing, spraying and painting.

Once created, the phosphatizing coating may be left for long time and peeled off only just before painting of a product.

When steel surfaces are covered with polymers, chemical and morphologic substrate structure features have great influence on system interaction and interface zone formation [8, 9]. Substrates often bear on their surface thin layers of protection oils, dirt and corrosion products. If impurities will not be solved in adhesive, they will act as a weak boundary layer on the substrate surface and will limit longevity of the adhesive connection. Longevity can be increased by surface processing [10, 11].

The aim of this work is to investigate phosphatizing of ferrous metals with chemical compounds introduced into detachable polymer coatings and to regulate strength of bond between the coating and the metal surface using anti-adhesives.

METHODS OF INVESTIGATION

To carry out this work we have chosen the polymer (methylolpolyamide) being able to form detachable coatings, anti-adhesive substances (oleic acid, sodium oleate, N-cethylpyridin chloride) and metal phosphate treatment agents (sodium hexamethaphosphate, ammonium dihydrophosphate, ammonia molibdate) as well as inhibitors (sodium nitrite and urotropine). Experimental results were obtained using electrochemical, X-ray structural and optical microscopy methods.

Coating adhesion strength was measured using the adhesiometer. Force necessary to peel off a coating strip 1 cm wide from the metal surface was established during measurement. Coating thickness was 80 to 100 micrometers.

The automatic image processing system including the microscope Olympus, digital camera Sony DXC – 151 AP and the code NIH IMAGE 1.61 was used for the sample surface structure investigations.

Small construction steel pieces were used for investigation of surface structure changes. For X-ray method the steel surfaces were flushed with epoxy resin, then ground, polished using special equipment and etched while for optical analysis etching was excluded.

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Solution used for etching consisted of 40 ml HCl (1.19 g/cm³), 5 g of CuCl₂, 30 ml of distilled water, 25 ml of ethanol.

Akimov's or drop method was used to establish resistance to corrosion of the phosphate film. The solution consisted of: $CuSO_4 \cdot 5H_2O$ – 80 g/l, HCl (1:1) – 13 ml, NaCl – 33 g/l. Resistance to corrosion of the phosphatized and reference steel samples was evaluated according to the standard GOST 9.042-75 "Polymer coatings with inhibitors (Accelerated corrosion examination methods)".

For corrosion process investigations taking into account link between potential and corrosion current steel samples were cut from steel. The samples had forms of rods with dimensions $2.7 \times 1.2 \times 60$ mm. Sample surface area part immersed in the electrolyte was 2 cm².

The corrosion process can be evaluated according to its corrosion current density i in electrolyte solutions as function of the steel potential φ. The potential is raised (or reduced) gradually from its constant value at the rate of 1 mV/s. For this purpose the potentiostat PI-50-1.1 with the programmer PR-8 was used. If the steel potential is given in reference to silver chloride electrode, then the steel potential in reference to hydrogen electrode is

$$\varphi_s = \varphi_s' + 0.288 \ (V), \tag{1}$$

here φ_s' is the steel potential with respect to the silver chloride electrode (found experimentally).

During experiments the potential of the samples was measured in reference to the silver chloride electrode.

EXPERIMENTAL RESULTS

For improvement of corrosion resistance envisaged or planed sometimes it may be more useful to change chemical composition of its surface layers only. The way to do this is formation of phosphate coatings on the steel surface. The steel samples were phosphatized using polymer solution and concentrations of phosphatizing agents and anti-adhesives were varied widely from experiment to experiment. The content of investigated coatings is shown in Table 1.

The investigations of the coating adhesion and corrosion resistance have shown that the optimal compositions of coatings for steel surface phosphatizing were compositions No.4 and No.9. They were included into the further experiments. The coatings with compositions No.1, No.6 and No.7 exhibited good adhesion strength to steel, however, the coating film was not uniform enough. The bond strength of coating compositions No.2, No.3 and No.8 was too great (the polymer coating after phosphatizing must be easily peeled off if needed).

We used solution proposed by Akimov to determine corrosion resistance of the phosphate films. One drop is placed on the phosphate film surface and the time interval is registered during which color of the solution changes. Color change is caused by the chemical reaction

$$CuSO_4 + Me \rightarrow MeSO_4 + Cu$$
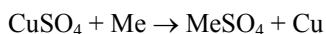
The longer is the time interval of color change the better is corrosion resistance. When for phosphatizing the polymer coatings (compositions No.4 or No.9) are used, the films obtained have color change time from 2 to 5 min

and it corresponds to middle corrosion resistance. Color change time of the phosphate film obtained by phosphatizing coatings with compositions No.1 – No.3, No.6 – No.8 varies from 30 seconds to 2 minutes.

The polymer coatings used for steel phosphatizing and for its temporary protection from corrosion must have limited adhesion (50 – 100 N/m, to be peeled off as a continuos strip). Strength of the bond between the polymer coating and steel surface can be regulated using chemical compounds. One of such compounds investigated in this work is oleic acid. Investigation revealed, that if 4 % of oleic acid is added into polymer coating, the bond between the coating and steel surface shrinks 4 times if compared with reference (Fig. 1, curve 1). The cause of this phenomenon is explained by formation of new hydrogen links between polymer NH groups and the hydrophilic oleic acid part, when part of hydrogen links break down. Analogous results were obtained also for sodium oleate (Fig. 1, curve 2).
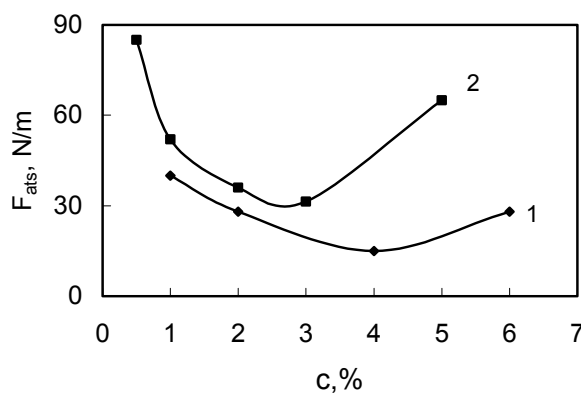
Fig. 1. Film adhesion strength as a function of anti-adhesive concentration. Curves: 1 – oleic acid, 2 – sodium oleate

It was found that adhesion strength of coatings depends on concentration of adhesive and on coating drying time with its optimal value of 8 to 10 days.

For improvement of corrosion resistance sometimes it may be sufficient to change chemical composition of its surface layers only by creating phosphate film layer resistant to atmospheric corrosion. Under influence of corrosive media optical microscopy is informative enough enabling to reveal corrosion points of origin, their nature and their spread.

Phosphatizing efficiency was assessed taking into account surface structure changes of phosphatized, using polymer coatings, steel samples. Polished and ground steel samples were phosphatized with polymer coatings of compositions No.4 and No.9 (see Table 1).

As it may be seen in pictures phosphatizing with polymer coating having composition No.4 forms homogenous and continuous phosphate film (Fig. 2, b), while phosphatizing with polymer coating of composition No.9 forms non-uniform and discontinuous phosphate film. In addition we can see black spots of corrosion (Fig. 2, d). The protective features of the phosphate films were assessed after the phosphatized sample was held at humidity of 96 ± 2 %. Already after 18 days on the phosphatized sample surface zones affected by corrosion appear (Fig. 2, c). It indicates that protective feature of the film is of short duration. The sample phosphatized using composition No.9 was held for

Table 1. Phosphatizing polymer coatings

Coating No.	PFE 2/10 solution, ml	Concentration, g/l			Dissolved amounts of additives (g) in 10 ml of solution (NH$_4$H$_2$PO$_4$+NH$_4$MoPO$_4$) or Na$_6$P$_6$O$_{18}$ indicated in columns 6 – 11					
		NH$_4$H$_2$PO$_4$	NH$_4$MoPO$_4$	Na$_6$P$_6$O$_{18}$	Hidro-xilamine	N-cethyl-pyridine chloride	Oleic acid	NaNO$_2$	Urotropine	Ca(OH)$_2$ saturated solution
1	2	3	4	5	6	7	8	9	10	11
1	100	15	0.15	–	0.24	–	0.4	0.02	–	2.0
2	– " –	15	0.15	–	0.60	0.08	–	1.2	–	–
3	– " –	30	0..30	–	0.24	0.16	–	0.6	0.6	-
4	– " –	30	0. 30	–	0.60	0.32	–	1.2	–	–
5	– " –	–	–	50	0.125	–	–	0.5	–	–
6	– " –	–	–	50	0.125	–	0.4	–	–	–
7	– " –	–	–	100	0.125	–	–	0.5	–	–
8	– " –	–	0.025	100	–	–	–	0.25	–	–
9	– " –	–	–	300	0.24	0.16	–	1.2	–	–

Note. Preparation of the phosphatizing polymer coating: the amounts of materials, shown in columns 6 to 11 (g) are dissolved and added to methylolpolyamides solution in 10 ml of solution which consists of (g/l) for example (NH$_4$H$_2$PO$_4$ – 30 + NH$_4$MoO$_4$ – 0.30) or Na$_6$P$_6$O$_{18}$ – 100.
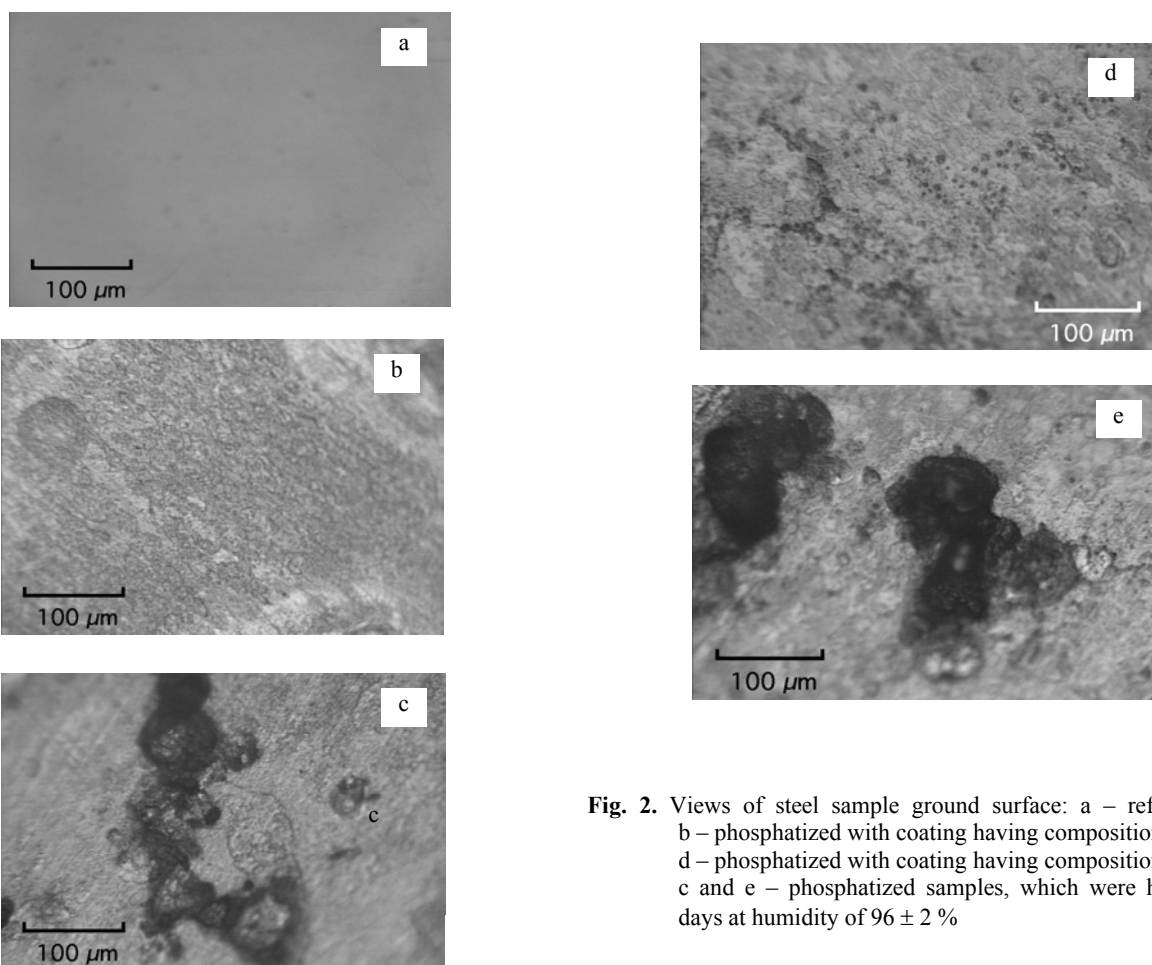

Fig. 2. Views of steel sample ground surface: a – reference, b – phosphatized with coating having composition No.4, d – phosphatized with coating having composition No.9, c and e – phosphatized samples, which were held 18 days at humidity of 96 ± 2 %

18 days in the same conditions and on its surfaces developed large areas of corrosion (Fig. 2, e).

The experiments carried out suggested the coating with composition No.4 to be suitable for short-term protection of steel surfaces from corrosion.

During investigations of corrosion processes it is necessary to know the governing process of electrochemical reaction: cathodic or anodic. Slower one is governing and must be accelerated if effective potential enhancement method is to be found. The anodic reaction is accelerated, when electrode potential is moved from stationary to more positive side.

Potentials of the reference steel surface and one with the phosphate film differ slightly (≈ 0.1 V) (Fig. 3). This difference is noticeable in the initial moment only, yet it is sufficient to form a galvanic cell. If the phosphate film covers the sample surface non-uniformly (potential of steel without film is slightly more negative), corrosion will take place.
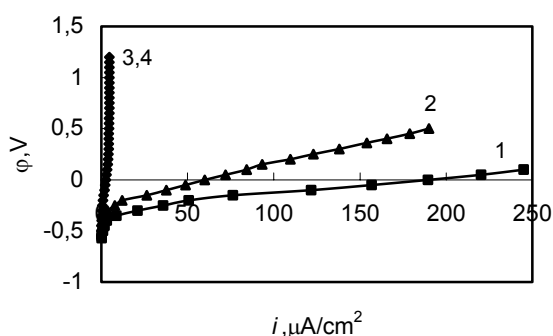

Fig. 3. Steel anodic polarization curves: 1 – reference; 2 – the sample phosphatized with coating of composition No.9 for 24 hours at 68 °C temperature (polymer coating peeled off); 3 and 4 – the samples covered with the polymer coating of composition No.9. This experiment was carried out in 0.5 N NaCl solution (curves 1 to 3) and in 0.1 M Na$_2$SO$_4$ solution (curve 4)

In the investigation of corrosion process of reference and phosphatized with polymer coating samples the curves of their anodic polarisation in solutions of 0.5 N NaCl and 0.1 M Na$_2$SO$_4$ were obtained. All anodic polarisation curves of this sample are similar with corrosion current density equal to 0.1 mA/cm².

The corrosion rate may be found from Faraday's law:

$$K = i\frac{A}{Fn} \, , \qquad (2)$$

here K is the corrosion rate, n is the valence of metal entering solution, A is the atomic mass, $F = 96500$ C/gekv (Faraday's number), i is the current density. The (2) equation may be rewritten in form:

$$K = i \cdot 10^4 \cdot 10^5 \cdot 0.86 \cdot 10^5 \cdot 56/3 = i \cdot 1.60 \cdot 10^5 \; [\text{g/m}^2\text{day}] \, . \qquad (3)$$

A and n values are ones of iron, as iron creates main amount of corrosion products.

Quantitatively evaluated investigation results are presented in the Table 2 below. In case of the surface being phosphatized with polymer coating of compositions No.4 and No.9 (see Table 1) and polymer coating is not peeled off, corrosion rate of the samples in the solutions of 0.5 N NaCl and 0.1 M Na$_2$SO$_4$ slows down 3.3 times. The phosphate film retards corrosion rate noticeably less (≈ 1.2 times). This confirms conclusively that the phosphate film without anti-corrosion coating is not reliable.

It may be seen from the anodic polarisation curves presented in Fig. 3 and Fig. 4 that reference samples dissolve in electrolyte solutions anodicly (without passive zone). Very similar curves were obtained for samples covered with the phosphate film (when polymer coating is detached, curves 2 and 3).

During investigation of the samples with phosphatizing polymer coating a wide enough passive zone was observed. The polymer coating slows down anodic metal dissolution.
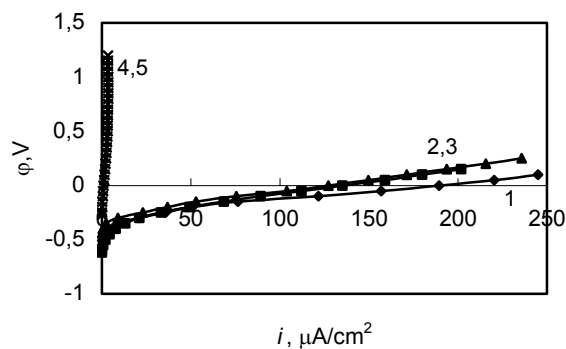

Fig. 4. Steel anodic polarisation curves: 1 – reference; 2 – the sample phosphatized with coating of composition No.4 for one hour at 68 °C temperature; 3 – for 10 hours at the temperature of 20 °C (experiments were carried out with polymer coating peeled off); 4 and 5 – the samples covered with the polymer coating of composition No.4. This experiment was carried out in 0.5 N NaCl solution (curves 1 to 4) and in 0.1 M Na$_2$SO$_4$ solution (curve 5)

The surface of the sample becomes passive. This is confirmed also by the shift of the electrode potential towards more positive values from -0.5 V to -0.3 V.

The experiments carried out substantiate the conclusion that metal corrosion resistance is increased only when the phosphate film is covered by paint or the polymer coating. The laboratory investigations of the phosphatizing polymer coatings have shown that they can be successfully applied for steel protection from corrosion.

The phosphatizing polymer coating is applied on the properly prepared (mechanic cleaning and clearing surface of oil) metal surface. These coatings can be used for protection from corrosion, temporary protection from surface pollution or small mechanical damages. If the easily detachable polymer coating is intended for using for temporary protection of products from surface pollution, during preparation of coating solution addition of phosphatizing compounds is not necessary.

Table 2. Influence of phosphatizing on stell corrosion rate

No.	Phosphatizing polymer coating	Corrosion rate K (g/m²day) in solutions		K_0/K_f	
		0.5 N NaCl	0.1 M Na$_2$SO$_4$	0.5 N NaCl	0.1 M Na$_2$SO$_4$
1	Reference steel	21.92	8.5	–	–
2	Phosphatized, composition No. 4 polymer coating (exp. after coating was peeled off)	6.64	12.1	1.4	0.7
3	Phosphatized, composition No.9 polymer coating (after coating was peeled off)	6.58	13.8	135	0.61
4	Phosphatized, composition No.4 polymer coating (exp. with coating)	6.64	6.72	3.3	1.3
5	Phosphatized, composition No.9 polymer coating (with coating)	6.58	7.04	3.3	1.2

Note. The polymer coatings of composition No.4 and of composition No.9 are presented in Table 1.

CONCLUSIONS

1. Phosphatizing the steel surface with detachable polymer coating creates the phosphate film, which increases its corrosion resistance.
2. It was established that the optimal adhesion strength of detachable coatings is 50 to 100 N/m.
3. The structure investigations revealed that steel surface, phosphatized using the polymer coating with ammonium dihydrophosphate, becomes coated with the continuous phosphate film and its corrosion rate decreases 3.3 times.

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