УДК 667

A. L. Shutova, PhD (Engineering), senior lecturer (BSTU);
A. I. Globa, PhD (Chemistry), senior lecturer (BSTU);
N. R. Prokopchuk, Corresponding Member of Belarus NAS , D. Sc. (Chemistry), professor, head of department (BSTU); **E. I. Vinglinskaya**, PhD student (BSTU);
A. L. Glebova, student (BSTU); **E. I. Khovanskaya**, student (BSTU)

APPLICATION FEATURES OF NEW PIGMENTS IN ALKYD ANTICORROSIVE PRIMERS

Article is devoted to valuation the possibility of using new synthesized compounds as anticorrosive pigments in natural drying alkyd primers. Technical and physical properties of new pigments based on transition metal compounds of different nature (oxides, phosphates, car-bides, complex compounds) and phosphorus-containing pigments was investigated; new reci-pes of primers was designed, physical, mechanical and protective properties of coatings was investigated. Dependence of the anticorrosive properties of the synthesized pigments, primers and coatings was established from their chemical nature.

Introduction. The problem of protecting metal surfaces from corrosion during long-term storage and operation is relevant nowadays. Currently, promising direction of research in the coatings industry, reducing costs and improving the quality of protective coatings by applying new types of pigments based on abundant materials is diversification.

Therefore the aim of this study was to evaluate the applicability of newly synthesized compounds at BSTU as anticorrosive pigments in alkyd primers in conjunction with industrial pigments and fillers as well as independently.

Main part Technical and physical properties of the synthesized compounds of different composition (oil absorption, content of water-soluble substances, the pH of the aqueous extract) were studied to solve the problem (Table 1). The appropriate number is assigned to each pigment to simplify the interpretation of the results.

On the basis of the basic recipe [1] the priming compositions were made, in which industrial anticorrosive pigments were replaced with a new synthesized compounds. As a film-forming agent alkyd-styrene oligomer "Chem-Alkyd 40/60" (TU U 24.1-13395997-014: 2006) was used, which is a solution in xylol of Gliphtal alkyd of medium wetness modified by castor oil and styrene. The pigment part of basic primers contained 15% vol. of red iron oxide pigment, 40%. of microtalc, 22.5% vol. of microbarite and 22.5% vol. of zinc oxide or zinc tetraoxychromate. The action of pigments No. 1–7 were examined on a basic compositions in which as an anticorrosive pigment zinc oxide was used, and pigments No. 8-20 were added instead of zinc tetraoxychromate. The number of a new pigment was calculated from the value of its vehicle demand to capture the degree of pigmentation of the paint composition Q = 0,7–0,8. So the deterioration or improvement of protective properties of primer coatings in a new composition in comparison with the base primer will be associated only with the action of the tested pigment.

The pigmented formulations were prepared by dispersing in a laboratory dissolver DISPERMAT®CA with the using of zirconium beads to the degree of grinding no more than 35 microns (GOST 6589) with the rotational speed stirrer 3800-4000 rev/ min. Coatings were obtained by pressure pulverization method on metal and glass substrates.

The formation of coatings was done in natural conditions, fixing the drying time to degree 3 (GOST 19007). 2 days after the application the spreading rate (GOST 8784), the physical and mechanical properties of the coatings (pendulum hardness TML pendulum A (GOST 5233), impact strength (GOST 4765), cross-cut adhesion (GOST 15140), flexibility in bending (GOST 6806) were determined, after 10 days – the static resistance to corrosive media in accordance with GOST 9.403 (Table 2).

Studying of technical and physical properties of the synthesized pigments. Oil-absorption power of the first type indirectly characterizes a specific surface of a pigment (square meter on gram) and its dispersion which in turn together with chemical properties of a surface of a pigment define quantity of components binding, fixed on it, having impact on tightness of packing of entities in covering [2–7]. Therefore this indicator is the keystone for calculation of formulations of primers at research of anticorrosive properties of new pigments.

Oil-absorption power of the recognized pigments mainly is in limits of 20–35 g/100 g that is characteristic for the majority of the pigments applied in paint and varnish industry. Pigment on the basis of carbides of transition metals has the smallest oil-absorption power, this fact will allow to increase the filling of paint and varnish coverings.

Table 1

Technical and physical properties of the investigated pigments

Pigment number	Pigment on the basis	Oil-obsorption power, g/100 g	Content of water soluble substances, %	pH
1	Ironic phosphate	34.9	2.66	9.6
2	Chromous phosphate	24.5	0.35	9.6
3	$CoO \cdot Al_2O_3 \cdot P_2O_5$	19.5	0.63	11.3
4	$NiO \cdot Al_2O_3 \cdot P_2O_5$	23.1	1.76	11.3
5	Fluor apatite	31.0	2.45	12.2
6	Precipitated phosphate	29.3	0.37	12.3
7	Galvanic sludge of "Atlant"	29.5	4.93	11.8
8	Salts of transition metal	30.3	1.20	6.6
9	Oxide of transition metal	27.9	2.69	6.5
10	Carbides of transition metal	8.5	0.00	7.4
11	Zinc phosphate and zink oxide (40 : 60)	12.4	0.75	7.2
12	Ironic phosphate and zink oxide (40 : 60)	21.7	1.12	6.9
13	Nickelous phosphate and zink oxide (40 : 60)	27.2	0.10	7.3
14	Nickelous phosphate and zink oxide (60 : 40)	36.8	0.03	7.5
15	Nickelous phosphate and zink oxide (80 : 20)	33.0	0.75	7.1
16	Nickelous phosphate, chrome and zink oxide (50 : 33 : 17)	33.5	3.25	6.5
17	Cobaltous phosphate and zink oxide (40 : 60)	19.8	1.5	7.6
18	Manganic phosphate and zink oxide (40 : 60)	15.0	0.7	7.5
19	Chromous phosphate and zink oxide (40 : 60)	18.9	0.9	6.7
20	Cupric phosphate and zink oxide (40 : 60)	9.7	3.2	7.1

Table 2

Properties of the developed priming compositions and coverings on their basis

Number of pig-ment	Covering capacity, g/m^2	Physical and mechanical properties			Resistance of a covering at (20 ± 2) °C to static influence, days					
		Impact strength, cm	Hardness by HPL (A), rel. un.	Flexural resilience, mm	Water		0,5% solution HCl		3% solution NaCl	
					Quantity of covering layers					
					1	2	1	2	1	2
1	26.4	100	0.36	1	<1	<1	<1	<1	<1	<1
2	35.8	100	0.37	1	1	1	<1	<1	<1	<1
3	28.2	100	0.38	1	16	16	<1	<1	<1	<1
4	19.7	100	0.33	1	16	16	14	1	<1	1
5	26.2	100	0.37	1	28	8	1	1	1	2
6	69.2	100	0.26	1	1	1	1	1	1	1
7	20.2	100	0.33	1	7	2	2	1	2	1
8	26.5	100	0.34	1	<1	3	<1	<1	<1	3
9	23.4	100	0.34	1	>30	>30	0	0	<1	3
10	30.2	100	0.24	1	2	<1	<1	<1	<1	<1
11	29.8	100	0.30	1	5	21	1	6	1	7
12	35.5	100	0.38	1	2	2	4	4	2	2
13	23.5	100	0.34	1	<1	<1	<1	<1	<1	<1
14	31.7	90	0.35	1	4	15	<1	<1	<1	<1
15	16.3	100	0.36	1	<1	<1	<1	<1	<1	<1
16	36.0	85	0.30	1	<1	<1	<1	<1	<1	<1
17	19.3	100	0.35	1	1	2	1	2	1	3
18	23.5	100	0.39	1	2	3	1	2	2	3
19	22.4	100	0.33	1	1	3	1	2	2	2
20	21.1	100	0.38	1	<1	<1	<1	<1	<1	<1

The low content in a pigment of water-soluble substances is an indispensable condition for preservation of barrier properties of paint and varnish coverings and their protective functions. But for anticorrosive pigments it is allowed to apply the compounds and with higher values of this amount if it positively influences the protective properties of coverings.

The majority of the investigated pigments contain less than 2% of water-soluble substances, but only on this index it is impossible to give an assessment to protective properties of pigments.

Efficiency of protective action of priming coverings is defined by their adhesive and cohesive, diffusive and electrochemical properties on which all components of paintwork material, including pigments and fillers have impact [5].

pH of water extracts of pigments No. 1–7 is shifted into the alkaline direction, therefore, they potentially can show the protective action similar to zinc whitewash based on ability to support alkaline pH on the border of a covering – a carrying base.

Such pigments are called active, and their action depends on the chemical reaction proceeding in the field of contact of a carrying base, a pigment and filming agent or between the pigment and ions getting into a film. Oxidation-reduction reactions lead to formation of protective connections (oxides or hydroxides which may contain pigment cations), saponification of a filming agent or neutralization of acidulous products of decompounding – to increase of the coverings pH [8]. Water extracts of pigments No. 8–20 pH is neutral.

Studying of properties of primers and coverings on their basis. Covering ability of the developed primers depends on structure of pigmentary part, i.e. the covering ability of the used anticorrosive pigment has impact also.

All studied coverings are characterized by high physical and mechanical properties. Adhesion to steel (on a 4-mark scale) and elasticity of coverings at a bend are characterized by the highest values of indicators. Coatings strength at blow is much more than 50 cm. The hardness practically of all coatings is more than 0,3 rel. un. It is very good indicator for alkyd primers of natural air-dry (Table 2). Only coverings of priming compounds with the use of pigments on the basis of a precipitated superphosphate and carbides of transitional metals make the exception, and in the latter case decrease in hardness is connected with low oil-absorption power of the synthesized connection that led to very high extent of filling in a covering (as a result of the offered method of calculation of formulations).

As in each priming composition changed only an anticorrosive pigment, and extent of pigmentation, the quantity and the nature of curing agent were constants, it is possible to draw a conclusion that the qualitative composition of pigmentary part (i.e. the nature of an anticorrosive pigment) has no essential impact on physic and mechanical properties of coverings which in this case are defined by the nature of filming agent and the picked-up complex of drying agent.

High water resistance characterizes coverings on the basis of many studied anticorrosive pigments (No. 3, 4, 5, 7, 9, 11, 14, 18).

Use of connection of $NiO \cdot Al_2O_3 \cdot P_2O_5$ and a pigment on the basis of iron phosphate (or zinc) and zinc oxide (40 : 60) allows to reach also good indicators on acid resistance. Possibly, in the compounds of anticorrosive primers pigments show the inhibiting action based on ability to react with acid stimulating agent of corrosion and to support in a covering alkaline pH, thereby expand area of a passive condition of iron that leads to increase in anticorrosive action of coverings.

Improvement of protective properties of coverings at increase in thickness of a priming coat (characteristic for a sample No. 11 and 14) is caused by increase in length of a way (barrier) in aggressive agents to limit of the section a covering – a carrying base.

For some compositions is noted decrease in protective properties of coverings at increase in thickness that can be connected with undercure of filming agent in volume of a covering, as a result of incomplete course of oxidative polymerization because of bad access of oxygen of air. This deficiency can be adjusted, having changed technology of receiving coverings – drawing the second layer to carry out only after a full cure of the first.

Primer which is include in the compound the pigment on the basis of phosphate and oxide of zinc (40 : 60), allows to receive coverings with most best complex of protective properties in a two-layer covering, i. e. provides at the same time protection against static influence of water, solutions of salt and acid.

Low protective indicators of primers on the basis of pigments No. 1, 2, 6, 10, 13, 15, 16, 20, perhaps, are connected with that phosphates which show protective action and for a while after contact with hostile environment therefore they should be used in a complex with the anticorrosive pigments showing protective action at the initial moment of operation of coverings mainly are their part.

Development of formulations of paintwork material on the basis of investigated pigments. In order to assess the possibility of using new synthetic pigments independently, without industrial ones, it is important to evaluate their direct influence on the properties of the primer compositions based on alkyd styrene oligomer. Therefore, the following phase of research at calculation of formulations the whole base portion of the pigment formulations consisting of iron oxide red, zinc oxide, finntalc M30, microbarite and tetraoxychromate zinc was changed with the analyzed pigment. Calculations of formulations of priming compositions were performed similarly [1] taking into account pH of a water extract of pigments and their oil-absorption power. Results of researches of the following pigments are presented in Table 3:

1* – $CoO \cdot Al_2O_3 \cdot P_2O_5$;

2* – $NiO \cdot Al_2O_3 \cdot P_2O_5$;

3* – pigment based on fluoroapatite;

4* – pigment based on electroplating sludge of «Atlant»;

5* – pigment based on cobalt phosphate and zinc oxide (40 : 60);

6* – pigment based on iron phosphate and zinc oxide (40 : 60).

In accordance with the manufacturing technology primers dispersing was continued until the degree of fineness became not more than 35 microns, but at manufacture of compositions based on pigments No. 1*– 4* it was not possible to reach the same size of particles even with the dispersion. This is probably due to the fact that the primary particle size of these pigments is much greater than 35 microns, and the dispersion process is the destruction only of the agglomerates and to destroy the primary particles is impossible. Also the composition of primers with pigment part number 1*–4* are characterized by very poor covering power, to determine it by instrumental method (when a large number of layers was used) failed. The use of pigments number 5* and 6* made it possible to determine coverage, but it is much worse compared with compositions in which the pigment of red iron oxide pigment was contained (Table 2).

Due to the fact that the developed compositions have poor hiding power, physical and mechanical properties were determined on the coatings, the thickness of which was substantially greater than 20 microns, i. e. several layers were used to achieve opacity or approach to this state.

Since the thickness of the investigated coatings was significant this fact was immediately reflected in the physical and mechanical properties, they are significantly lower than the properties shown in Table 2, particularly impact strength of coatings and hardness.

Decreasing the coating hardness can be explained by the reduced rate of oxidative polymerization in thick coatings, resulting in a reduction in curing. Reduced hardness and probability of presence of the residual solvent in the coating led to decrease of impact strength ((in a place of blow "crushing" coverings was formed).

Indicators of properties of the primer coatings based on pigments only synthesized without adding commercially available pigments and fillers (Table 3) is much lower than those reported in the Table 2. In general, such deterioration of properties caused by a large protective coating thickness values (> 100 micrometers, 20 micrometers when required), which led to their undercure, as mentioned above.

The use of only pigment $CoO \cdot Al_2O_3 \cdot P_2O_5$ and $NiO \cdot Al_2O_3 \cdot P_2O_5$ in primers resulted in a reduction of water resistance over 5 times, but at the same time, acid resistance is improved slightly particularly for coatings based on composition No. 1*. Increasing the acid resistance of these coatings can be explained by the high pH of pigments (11,3) included in the primer compositions, and by increasing their quantity.

Properties of coatings based on iron phosphate and zinc oxide (40 : 60) have not changed compared with the data Table 2. This is certainly due to its good hiding power, thinner coatings and higher degree of cure.

Table 3

Physical and mechanical and protective properties of paint coatings

Number of pigment	Degree of fineness, nm, not more	Drying time to grade 3 at (20 ± 2) ° C, min	Covering capacity, g / m^2	Physical and mechanical properties				Resistance at (20 ± 0,2) °C to static exposure, days					
				Adhesion, point	Impact strength, cm	Hardness, rel. un.	Flexural resilience, mm	Water		0.5% HCl		3% NaCl	
								The amount of coating layers					
								1	2	1	2	1	2
1*	70	20	–	1	60	0.26	1	3	3	2	4‘	1	1
2*	50	30	–	1	60	0.25	1	2	3	1	1	1	1
3*	50	25	–	2	10	0.27	2	2‘	2‘	<1	<1	2	2
4*	40	30	–	1	60	0.22	1	1	1	2	2	1	1
5*	35	25	170.1	1	10	0.25	1	< 1	1	< 1	1	< 1	1
6*	35	20	51.1	1	40	0.29	1	2	2	1	2	2	2

Note: The quotation marks «'» denote the whitening of the coating; a minus sign «–» mark when compositions do not cover the painted surface.

Conclusion. Thus of all the investigated pigments synthesized only pigment based on iron phosphate and zinc oxide (40 : 60) can be used in paintwork materials independently, without additional pigments and industrial fillers, as coating on its basis are characterized by good hiding, high physical and mechanical properties and a good protection. But the economic factor (costs) should be taken into account, as mass fraction of pigments in primers is quite large.

Other pigments, although they allow to achieve good properties of the covering a bearing in combination with other pigments and fillers, independently can not be used because of the sharp deterioration of the coatings properties based on them.

References

1. Оценка защитных свойств покрытий наполненных глифталевых композиций электрохимическими методами / А. Л. Шутова [и др.] // Труды БГТУ. 2011. № 4: Химия, технология орган. в-в и биотехнология. С. 43–49.

2. Брок Т., Гротэклаус М., Мишке П. Европейское руководство по лакокрасочным материалам и покрытиям. 2-е изд. М.: Пэйнт-Медиа, 2007. 548 с.

3. Эссен Б., Оггермюллер Б., Эссен Х. К вопросу о правильном наполнении // Лакокр. материалы и их прим. 2010. № 11. С. 15–20.

4. Rodriguez M. T., Garcia S. J. Influencia de la concentracion de pigmento en volumen en las propiedades de una imprimacion epoxi // Rev. met. 2005. P. 202–203.

5. Ridgway C. J., Gane P. A. Effect of latex and pigment volume concentrations on suspension and consolidated particle packing and coating strength // J. Pulp and Pap. Sci. 2007. Vol. 33, No. 2. P. 71–78.

6. Повышение защитной способности многослойных лакокрасочных покрытий путем регулирования степени наполнения слоев / А. В. Малинин [и др.] // Упр. Качеством в нефтегаз. комплексе. 2008. № 3. С. 52–54.

7. Дринберг А. С., Ицко Э. Ф., Калинская Т. В. Антикоррозионные грунтовки. СПб.: НИПРОИНС ЛКМ и П с ОП, 2006. 168 с.

8. Ермилов П. И., Индейкин Е. А., Толмачев И. А. Пигменты и пигментированные лакокрасочные материалы: учеб. пособие для вузов. Л.: Химия, 1987. 200 с.

Received 24.02.20