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UNTOXIC ANTI-CORROSION PIGMENTS FOR GROUND COAT IN ORGANIC COATINGS

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Abstract. *This work was oriented towards finding adequate replacement for pigments based on lead and chrome with nontoxic corrosion inhibited pigments in basic coating. We will show here the results of the anti-corrosion research which are made on basic coating founded on alkyd and epoxy resins, formulated with more modified orthophosphate and polyphosphate and polyphosphate pigments which would be ecologically accepted.*

1. INTRODUCTION

One of the most important causes for the global crisis of raw material and energy is considered to be corrosion. Anti-corrosion procedure extends durability of raw materials, equipment and constructions. Protection itself ought to fulfill basic expectations: to preserve usability and function ability of the facility, which is protected to prevent from damage in different sectors as well as from possible human victims and material loss and to prevent nature pollution for as long as it is possible [1,2,3]. There are two ways of material protection from corrosion: active and passive protection. Active protection can be realized with adequate choice of constructive materials, by doing away with causes of corrosion and dealing with electrochemical corrosion effect. When talking about passive protection, base is completely protected from external factors by doing coating over. That can be achieved with organic or nonorganic protecting coating.

After drying, organic coating separates base from external factors very effectively. Inhibition of corrosion process of metal surface is achieved by usage of corrosion inhibiting pigments [4,5]. With these pigments it was very obvious that pigments based on lead and chrome dominate. But as lead is very toxic and the fact that waterdilutable salts of chromicacid have bad impact on human health (cause cancer), restricts their

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implementation in basic coating. Our research had the aim to find adequate replacement for pigments based on lead and chrome in basic coating with nontoxic corrosion inhibiting pigments which would be ecologically [6,7,8].

2. EXPERIMENTAL

Basic coating founded an alkyd and epoxy resins were formulated for examining corrosion behavior. The following modified ortophosphate and polyphosphate nontoxic corrosion inhibiting pigments were applied:

Chemical characterization	**Label**
Zinc aluminium orthophosphate hidrate	ZPA
Basic zinc phosphate hydrate processed with organic adding	ZPO
Basic zinc molybate orthophosphate hydrate	ZPM
Basic zinc phosfate hydrate modified with organic/nonorganic adding	ZPZ
Zinc aluminium polyphosphate hydrate	ZAPP
Strontium aluminium polyphosphate hydrate	SAPP
Calcium aluminium polyphosphate silicate hydrate	CAPP
Zinc calcium aluminium strontium polyphosphate silicate hydrate	ZCPP

Their general physical and chemical characteristics are shown in table 1.

First part the research concerned quality fortification of basic coating founded on alkyd and epoxy resins for achieving optimal physical and mechanical characteristics of dry films which would suit application conditions. Clinging to the surface was determined according to JUS H. C8. 050, resistance on impacts according to JUS H. C8. 060 and elasticity to JUS H. C8. 050. Second part of the research included experimental research of the value of corrosion protection kW(%) on test tiles of dry films which were exposed for 200 hours in salty environment according to JUS H. C. A1.554.

Preparation of metal surfaces on test tiles before doing coating over was done according to standard JUS CT7. 301 which is the text of the International standard ISO 8501-1 (1988). The degrees of surface preparing consist of the way the surface is prepared and of the level of purity. The degrees mentioned are defined by the description of the surfaces after cleaning and by the photos of relevant samples. The purpose of physical and mechanical research was to pick up those experimental samples of basic coating founded on alkyd and epoxy resins with modified orthophosphate and polyphosphate pigments, which have the best physical and mechanical characteristics. They were tasted again on corrosion steadiness by establishing their corrosion protection values kW(%).

Based on that by comparing eight tasted orthophosphate and polyphosphate pigments, the experimental samples which were picked up, had values of corrosion protection (kW%) in all conditions. They would be used for replacing toxic lead and chrome pigments in basic coating production, which was final aim of these researches. All the experiments are done on completely net-spread films. That was found out by measuring hardness to constant value.

Table1. General physical and chemical characteristics of applied modified orthophosphate and polyphosphate pigments

TP	MODIFIED POLYPHOSPHATE PIGMENTS				MODIFIED POLYPHOSPHATE PIGMENTS			
PIGMENT	ZPA	ZPO	ZPM	ZPZ	ZAPP	SAPP	CAPP	ZCPP
Chemical composition	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
Zinc	39	55.5	55	56	30			(as ZnO) 37
Aluminium	4.5				(asA l_2O_3) 12	(asA l_2O_3) 12	(asA l_2O_3) 7	(asA l_2O_3) 3
Phosphorus	(as PO_4) 55.5	(as PO_4) 38.5	(as PO_4) 38.5	(as PO_4) 38	(as P_2O_5) 48	(as P_2O_5) 42	(as P_2O_5) 26	(as P_2O_5) 18
Molybdenum			(as MoO_3) 1.7					
Strontium						(as SrO) 31		(as SrO) 5
Calcium							(as CaO) 31	(as CaO) 14
The composition of the organic part			0,3		0,3			
Silicium							(as SiO_2) 28	(as SiO_2) 28
Loss on ignition 600^0C	11%	9%	10%	9.5%	10%	15%	8%	10%
Chromium				Max 0.15				
Chloride	max 0.025	max 0.025	max 0.025	max 0.025	max 0.025	max 0.025	max 0.025	max 0.025
Sulfate	max 0.05	max 0.05	max 0.05	max 0.05	max 0.05	max 0.05	max 0.05	max 0.05
Lead	max 0.001	max 0.001	max 0.01	max 0.01	max 0.01	max 0.01	max 0.001	max 0.001
Cadmium	max 0.001	max 0.01	max 0.001	max 0.001	max 0.001	max 0.001	max 0.001	
Technical characteristics	ZPA	ZPO	ZPM	ZPZ	ZAPP	SAPP	CAPP	ZCPP
PH-value	6	7	6.5	7	6	6	7	7.5
Density	2.8g/ml	3.5g/ml	3.5g/ml	1.1g/ml	2.9g/ml	2.7g/ml	2.8g/ml	3.1g/ml
Oil absorption value	40g/100g	20g/100g	25g/100g	20g/100g	35g/100g	40g/100g	35g/100g	30g/100g
Sieve residue 32 microns	max 0.01	max 0.01	max 0.01	max 0.01	max 0.01	max 0.01	max 0.01	max 0.01
Average particle size	3 microns	3 microns	3 microns	3 microns	2.5 microns	2.5 microns	3.5 microns	3 microns

3. Results and Discussion

By examining the outlook of the experimental samples it was concluded that the films formed of basic coating founded on alkyd and epoxy resins were without failure, i. e. without wrinkling, splitting, crumpling.

The degree of clinging with all experimental samples was zero, which is the result of

certain surface preparation, good formulation of basic coating and adequate degree of net-spreading.

Average thickness of dry for alkyd basic coating was 50-70 microns for epoxy basic coating 20-25 microns, according to usage in alkyd systems and epoxy systems. The corrosion protection values kW(%) of basic coating on experimental samples after 200 hours in salty environment are given in table 2. This table presents the results of experimenting on basic coating founded on alkyd and epoxy coatings. Modified orthophosphate and polyphosphate pigments took part in basic formulation with alkyd resins approximately 6,60% and with epoxy resins 7,50%.

Table 2. The results examination of basic coatings after being exposed in salty environment for 200 hours

Pigment	Number of samples	Basic coatings founded on alkyd resins and 6.6% participation of modified orthophosphate and polyphosphate pigments		Basic coatings founded on epoxy resins and 7.5% participation of modified orthophosphate and polyphosphate pigments	
		Thickness of dry film of basic coating (μm)	Value of anti corrosion protection kW(%)	Thickness of dry film of basic coating (μm)	Value of anti corrosion protection kW(%)
ZPA	1	54	95	25	77.5
	2	58	90	25	77.5
	3	68	85	25	77.5
ZPO	1	37	100	24	70
	2	36	100	22	67.5
	3	38	100	20	65
ZPM	1	65	45	25	82.5
	2	70	95	30	20
	3	75	50	25	10
ZPZ	1	58	95	25	13.75
	2	60	100	22	15
	3	68	80	25	90
ZAPP	1	45	60	25	10
	2	55	60	25	30
	3	55	70	25	20
SAPP	1	75	100	26	70
	2	65	65	22	60
	3	55	60	20	55
ZAPP	1	70	90	20	75
	2	70	85	20	65
	3	70	100	20	90
ZCPP	1	50	70	25	40
	2	50	70	25	35
	3	58	80	25	30

According to the data for corrosion protection values kW(%) which average higher than 65%, the choice is made of more efficient corrosion inhibiting pigments.
They are:

Chemical characterization	**Label**
Zinc aluminium orthophosphate hidrate	ZPA
Basic zinc phosphate hydrate processed with organic adding	ZPO
Strontium aluminium polyphosphate hydrate	SAPP
Calcium aluminium polyphosphate silicate hydrate	CAPP

The research results of corrosion level kW(%) of basic coating with previously mentioned modified orthophosphate and polyphosphate pigments after exposing it in salty environment during 200 hours are given in table 3. The results shown in this table are obtained by examining basic coatings with different participation (%) of chosen more efficient modified orthophosphate and polyphosphate pigments (ZPA, ZPO, SAPP, CAPP).

Table 3. The results of examination of basic coatings with different participation (%) corrosive inhibiting pigments after being exposed in salty environment for 200 hors

Pigment	Basic coatings founded on alkyd resins			Basic coatings founded on epoxy resins		
	Participation of pigment in basic coating (%)	Average thickness of dry coating film (μm)	Average values of corrosion protection kW(%)	Participation of pigment in basic coating (%)	Average thickness of dry coating film (μm)	Average values of corrosion protection kW(%)
ZPA	5	32	80	3	12	50
	6.6	60	90	5	12	55
	7	45	80	7	10	75
	9	45	75	7.5	25	77.5
	11	45	70	10	25	65
ZPO	5	39	60	3	15	35
	6.6	37	100	5	12	45
	7	39	95	7	15	60
	9	35	100	7.5	22	67.5
	11	40	95	10	25	30
SAPP	5	60	70	3	12	50
	6.6	65	75	5	12	45
	7	55	60	7	12	50
	9	50	65	7.5	22	60
	11	35	50	10	22	65
CAPP	5	45	60	3	10	55
	6.6	70	95	5	12	60
	7	50	85	7	12	65
	9	60	95	7.5	20	75
	11	55	90	10	22	70

Some results of examining the value of corrosion protection depending on participation (%) of corrosion inhibiting pigments in basic formulations and the dry films thickness of basic coating, for connecting materials founded on alkyd resins are shown on figure 1 and for connecting materials founded on epoxy resins are shown on figure 2.

High values of corrosion protection kW(%) in basic coating founded an alkyd resins are realized by using corrosion inhibiting pigments with basic zinc orthophosphate hydrate processed with organic adding label ZPO and from the group of modified polyphosphate pigments with calcium aluminium strontium polyphosphate silicate hydrate label CAPP.

In basic coating founded on epoxy resins high values of corrosion protection kW(%) are realized by the use of modified polyphosphate pigments calcium aluminium polyphosphate silicate hydrate label CAPP.

The conclusion is that with this modified polyphosphate pigments which is used as corrosion inhibiting pigment in both systems, high levels of corrosion protection kW(%)

are realized after expressing the experimental samples in salty environment for 200 h.

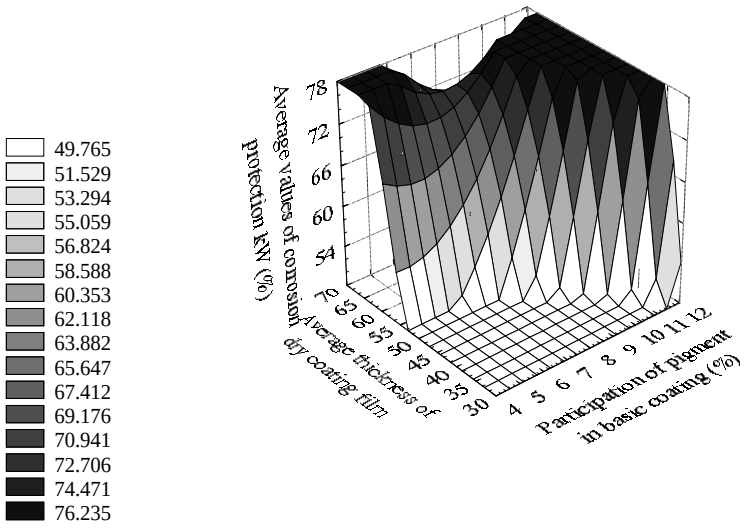

Fig. 1. The value of corrosion protection kW (%) of basic coatings founded on alkyd resins depending of participation (%) of pigment SAPP and thickness of dry films.

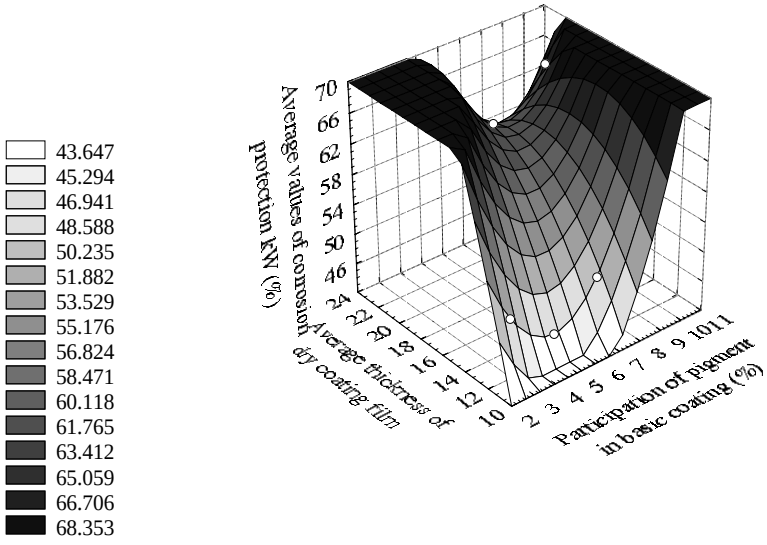

Fig. 2. The value of corrosion protection kW (%) of basic coatings founded on epoxy.

The passive procedure of corrosion protection, which is used separating the base from the external aggressive affluence, in combination with nontoxic corrosion inhibiting

pigments, means even more nowadays considering environment. The separation of the base from the external aggressive influence is realized by using coatings and by forming films by net spreading connecting materials.

For basic coating used in experiments usually are used epoxy resins as connecting materials.

Net spreading of linear epoxy resins is usually done with reaction of extreme epoxy groups with polyfunctional amines alcohol, or with reaction of free hydroxyl groups with polyfuctional acids or anhydride acids.

For achieving the optimal degree of net spreading it is of great importance to insure that the functional groups that react among themselves are equivalent. Those functional groups, which don't react, apart from making smaller the amount of polymer molecules, represent potential sports of degradation of net-spreader polymer. That brings to significant reduce in film's quality especially its solidity towards atmosphere influences, dissolves, stroke resistance, flexibility, etc.

The net spreading of alkyd resins dryable on the air is realized by reaction of double connection from the part of dryable fat acids with oxygen from the air. The net spreading process is done very quickly while peroxide bridges connect large number of molecules.

By the confirmation of good net spreading of connecting materials, which were used, the optimal physical and mechanical characteristics of dry films on experimental samples are realized. Physiological influence concerning environmental problems is nowadays key factor when it comes to choosing corrosion inhibiting pigments.

All the results achieved in this research show that nontoxic pigments founded on modified orthophosphate and polyphosphate which were used, can replace pigments based on lead and chrome concerning efficiency of inhibiting corrosion process. Nontoxic white, almost transparent pigments, enable production of basic coating in various shades. Based on literature and Mayer's theory, formation of complex is the basic for inhibiting corrosion process with tertian zinc phosphate hydrate.

It is common that tertian zinc phosphate hydrate can be combined with chromatic pigments in basic coating. The man purpose for that is efficiency increasing in protection of corrosion process. However the high toxic level of lead and chrome caused implementation of new rules which established highest levels of their concentration, which are not enough for inhibiting of corrosion process in basic coating.

When talking about protection of corrosion process, nontoxic modified zinc phosphate hydrate pigment gains in importance.

Individual substances which perform together with others are not available as physical mixtures but as the mixture of crystals.

In ideal case such pigment ought to active all known mechanisms from anticorrosion process:

a) Making barriers with tile parts

b) Chemical passivization with basic products of hydrolysis

c) Making impermeable layer for protection

d) Electrochemical inhibition.

Based on results of experiments such efficiency in inhibiting of corrosion process is possible to achieve in basic alkyd coatings, with basic zinc orto phosphate hydrate label ZPO that contains highly active organic inhibitor of corrosion.

Inactivates and slowlyness of tertial zinc phosphate hydrate at the beginning of

corrosion aggression is covered by basic products of hydrolysis and electrochemical activity of inhibitor.

High values of corrosion protection kW(%) in basic coating with all experimental samples both founded on alkyd and epoxy resins are realized with use of calcium aliminium polyphosphte silicate hydrate pigment label CAPP. The effect is founded on making basic products of hydrolyses and forming inhibiting complex.

4. CONCLUSION

Toxic pigments based on lead and chrome in basic coating can be replaced with nontoxic modified orthophosphate and polyphosphate pigments. These pigments bearableness with large number of polymers facilitates their implementation.

With usage of these nontoxic pigments the possibility of making these coating is accomplished. They are equal with basic coating founded on lead chrome when we talk about efficiency of initiating.

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NETOKSIČNI ANTIKOROZIONI PIGMENTI ZA OSNOVNE PREMAZE U ORGANSKIM PREVLAKAMA

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Ovaj rad je orijentisan na pronalaženju adekvatne zamene pigmenta na osnovu olova i hroma netoksičnim koroziono inhibirajućim pigmentima u osnovnim premazima. Pokazano je da rezultati antikorozionih istraživanja, urađeni na osnovnim prevlakama alkidnih i epoksi smola i koncipirani modifikovanim ortofosfatima i polifosfatnim pigmentima mogu biti ekološki prihvatljivi.