

ANTI-KOROZNÍ VLASTNOSTI KŘEMIČITOWOLFRAMOVÉ A FOSFOWOLFRAMOVÉ HETEROPOLYKYSELINY V NÁTĚROVÝCH FILMECH

ANTICORROSIVE PROPERTIES OF SILICOTUNGSTIC ACID AND PHOSPHOTUNGSTIC HETEROPOLYACID IN THE PAINT FILMS

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Souhrn

C ilem pr ce byla prvotn  charakterizace heteropolykyselin a jejich chov n  a vlastnost  v n t rov ch hmot ch, a to p i rozd ln  objemov  koncentraci pigmentu a plniva. Jako pojivo byla pouřita epoxyesterov  pryskyřice rozpouřt dlov ho typu. P ipraven  n t rov  hmoty byly aplikov ny na ocelov  i sklen n  panely, kde byly testov ny pomoc  zkouřek mechanick  a korozn  odolnosti. Organick  povlaky byly vystaveny p soben  korozn  atmosf ry NaCl, kde tato zkouřka byla podlořena elektrochemick m m řen m. Mezi vyhodnocovan  parametry patřila mechanick  i antikorozn  u innost n t rov ho filmu. A z roveň, ur en  vhodn ho aplika n ho prostřed  pro nov  p ipraven  n t rov  hmoty.

Summary

The aim of this work was to provide an initial characterisation of heteropolyacids and examine their behaviour and properties as pigments in paints using different concentrations of the pigment and filler. Solvent-based epoxy-ester resin served as the binder. The paints were applied to steel and glass panels for mechanical and corrosion resistance testing. The organic coatings were exposed to a corrosive atmosphere with NaCl. This test was completed with electrochemical measurement. The parameters examined included the paint film's mechanical and anticorrosion efficiency. The environments in which the new coatings are most efficient were also sought.

Key words: Heteropolyacids, epoxy-ester resin, organic coatings

Introduction

Metal corrosion is a topic that has been known from the times mankind started using iron (and steel) not only for day-to-day uses [1]. Global (39 countries) raw steel production was 1.548 billion tonnes in 2013 and even more, 1.598 billion tonnes, in 2015; iron production was then 1.155 billion tonnes. The most recent data for 2016 (as of 22 August) are 930 billion tonnes of steel and 670 billion tonnes of iron (data from the World Steel Association [2]). Iron and steel can be used efficiently and economically only if their surface is protected against the ambient corrosive effects [3]. Organic coatings represent an option to protect the metal surfaces against corrosion. Such coatings consist (as a minimum) of a binder, a filler, and a pigment which co-determines the properties of the system [4].

In the present work we used heteropolyacids (HPAs) as the anticorrosion pigments. Heteropolyacids are compounds that were used only once in paints [5]. Generally speaking, a heteropolyacid is a polyacid that is obtained by condensation of an inorganic acid involving two (or more) different metals [6], hydrogen, oxygen, a metal or non-metal. Acids of this type are known for their potential repeatable use as acid catalysts in chemical reactions [7]. HPAs are complex protic acids with universal structures and physico-mechanical properties [5, 8]. They are economically

attractive and environmentally friendly [9] crystalline substances that are very well soluble in polar solvents, exhibit a very high acidity [8, 10] and possess tunable redox properties, whereby they are interesting both as acids and as redox catalysts [12-14]. Hydrated HPAs such as phosphotungstic heteropolyacid (PTA) and silicotungstic heteropolyacid (STA) have been known for over a century but it was not until 1979 that the HPA hydrates were found to exhibit exceedingly high proton conductivity [15]. Proton conductivity is a manifestation of hydrogen bonds of various strengths due to the water molecules of the x-hydrate [16]. The behaviour of molybdophosphoric type HPAs in paints was described by Xu, who applied this HPA to a steel substrate, exposed it to a corrosive environment and analysed the protective film's composition. The components included mainly complex compounds such as $\text{Fe}_n[\text{PMo}_x\text{O}_y]$ and $\text{M}_n[\text{PFeMo}_x\text{O}_y]$ where $\text{M} = \text{K}, \text{Na}$ [17].

Experimental part

Preparation of the heteropolyacids

Polyaniline base was prepared by the oxidation of 0.2M aniline hydrochloride with 0.25M ammonium peroxydisulfate in aqueous medium followed by the deprotonation of the solids with 1M ammonium hydroxide and drying. Polyaniline base (30 g) was reprotonated by suspension in the solutions of phosphotungstic or tungstosilic acid (30 g of heteropolyacid dissolved in 300 ml of water) for 24 h. The resulting polyaniline salts then were collected by filtration, rinsed with ethanol, and left to dry in air.

Pigment characteristics, paint preparation and application

Some properties of the HPA pigments were determined pycnometrically (AccuPyc II 1340 Pycnometer, USA) as per ISO 787-10. The critical pigment volume concentration (CPVC) was calculated based on linseed oil consumption (ISO 787-5) per 100 g of the pigment by using the mortar-and-pestle method (CSN 67 0531). A concentration series was then set up based on the known CPVC value. The pigment particle shape and morphology (Fig. 1a: STA; Fig 1b: PTA) were examined on an electron microscope (JEOL – JSM 5600 LV, Japan). The paint systems were dispersed in a ball mill (Ballotini, 3.4 mm diameter) and filtered. The homogenised binder/pigment systems contained the pigment at volume concentrations $\text{PVC} = 0.5, 1, 3$ and 5 wt%. CaCO_3 was used as the filler to keep the Q coefficient constant at $Q = 10$. Two coatings, viz. the non-pigmented epoxy-ester resin and the coating with the filler only, served as the reference systems in this study.

The paints were applied to clean and degreased glass panels and steel panels (Q-LAB Corporation, UK) by using a box ruler. The dry film thickness was $80 \pm 5 \mu\text{m}$.

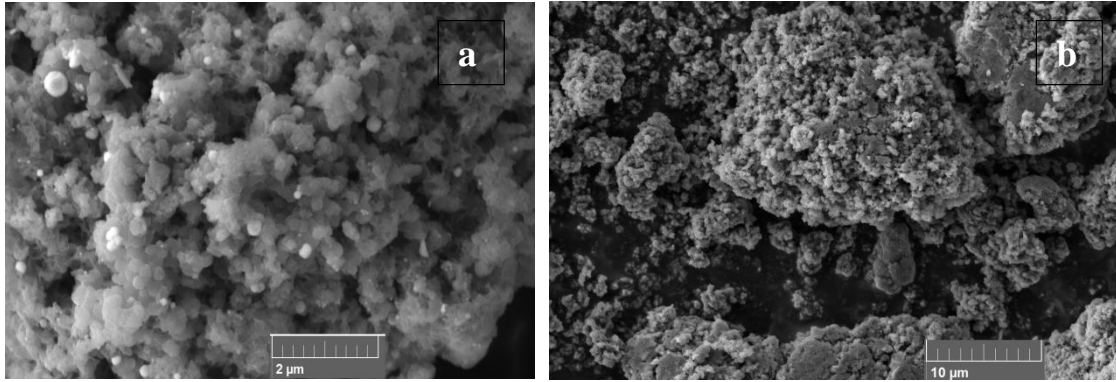


Figure 1: SEM photographs of the pigments: a - STA (2 μ m scale); b - PTA (10 μ m scale)

The specific electric conductivity (χ) and pH of a 10% pigment suspension in redistilled water were measured during 21 days as per ISO 789-9 and ISO 787-14. The suspension was filtered and a steel panel was submerged in the suspension and allowed to stay there for another 15 days. The data provided the corrosion loss of the material ($X_M/\%$). The hot-water-soluble and cold-water-soluble contents were also determined (ISO 787-8 and 787-3).

Physico-mechanical tests

The physico-mechanical tests were performed on steel panels 76 mm x 75 mm x 0.8 mm size (Q-LAB Corporation, UK).

Film resistance to impacts was evaluated by the falling weight method as per ISO 6272. The 1000 g weight was allowed to fall freely on the painted steel panel's averse and reverse sides, and the largest height at which the paint film still remained intact was recorded.

The cupping test, during which a steel ball 20 mm in diameter was indented into the painted panel, was carried out as per ISO 1520. The lowest depth at which the paint film was damaged was recorded.

Film adhesion to a steel substrate was evaluated by the cross-cut method described in ISO 2409. A cutting tool with the blades 2 mm apart was used to cut a square lattice having a defined area through the paint film down to the substrate. Adhesion was evaluated on the 0 to 5 scale where 0 denotes the highest film resistance.

The bending test using a cylindrical steel mandrel was performed by following ISO 1519. The largest mandrel diameter at which the paint film cohesion failed was recorded.

The arithmetic mean of the data obtained was calculated as the paint films' physico-mechanical efficiency parameter.

Corrosion tests

The coated steel panels 152 mm x 102 mm x 0.8 mm size (Q-LAB Corporation) were subjected to an accelerated corrosion test. A vertical cut 7 cm long was made through the paint film to the substrate metal of all the samples tested. The corrosion effects in the cut area were then evaluated.

The samples were exposed to a salt fog atmosphere with 100% relative humidity for 1500 hours and 2184 hours. The test chamber was run in 12-hour cycles, a cycle comprising 6 hours of exposure to the

salt fog solution (pH 6.5 – 7.2) at 35 °C ± 2 °C; 2 hours of exposure at 23 °C ± 2 °C; and 4 hours in condensed moisture at 42 °C ± 2 °C.

The following corrosion effects were evaluated as per ISO 4628-2 to 4628-5 after removing the panels from the chamber: blister formation on the entire paint film surface (ASTM D 714-78), degree of corrosion in the test cut (ASTM D 1654-92) and degree of steel substrate surface corrosion after removing the paint film (ASTM D 610-85). The paint's anticorrosion efficiency in the test environment was expressed through the arithmetic mean of the scores.

Results and discussion

It should be noted that the non-pigmented epoxy-ester resin (nEP) itself exhibits excellent physico-mechanical properties and provides an outstanding mechanical resistance (= 100%) in all the tests. Figs. 2a-d demonstrate that a weight falling from 100 cm left the specimens previously exposed to (NH₄)₂SO₄ for 672 hours intact.

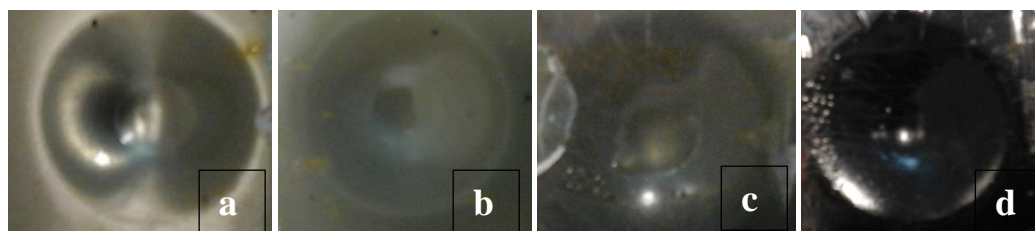


Fig. 2: Impact test of the paint films: a) nEP; b) reference CaCO₃; c) STA (1 wt%); d) PTA (3wt%)

However, nEP on its own is unable to protect the substrate metal against corrosion, and so the HPAs were added to improve the paint's corrosion resistance. The various heteropolyacids differ mainly in the extent of linseed oil absorption. For instance, PTA can absorb up to 30 g/100 g pigment more oil (Table 1). This difference is mirrored in the CVPC, where PTA does not allow the system to be filled to the same level as STA.

Table1. Characterisation of the pigments and fillers

CPVa ¹⁾ wt%	Density	Oil absorp.	CPVCb ¹⁾ wt%	Solubility in waterc ¹⁾		XM _{pig.} ^{d)} %	XM _{filme} ¹⁾ %
	at 23°C g/cm ³	(linseed oil) g/100g		at 23 °C %	at 100 °C %		
STA (Silicotungstic heteropolyacid)							
0.5							0.1
1	1.593	73.1	44.4	0.744	0.96	20.95	0.18
3							0.18
5							1.64
PTA (Phosphotungstic heteropolyacid)							
0.5							0.18
1	1.513	104.0	37.2	0.429	0.429	36.07	0.91
3							0.18
5							1.46
CaCO₃ - Omyacarb							
Q = 10	2.725	46.9	67.9	0.611	0.611	38.25	0.36

- a) Critical pigment volume concentration calculated by linseed oil consumption
- b) Determination of water soluble matter for pigments (CSN EN ISO 787-3 and 787-8)
- c) Corrosion losses of steel panels submerged in aqueous extracts of the powdered pigments, in 35 days
- d) Corrosion losses of steel panels submerged in aqueous extracts of the free paint films, in 35 days

The aim of the study was to characterise the pigments and ascertain if they are well suited for use as agents for anticorrosion protection of steel. They are substances of acid nature (Table 2) – pH on day 21 was 4.78 – 5.4. When a homogenised mixture of the HPA and CaCO_3 was added to the coating system, the pH of the aqueous extract of the free paint film increased to nearly approach the neutral region, depending on the pigment volume concentration. The system with the highest PVC = 5 wt% was an exception, where the filler proportion was not that appreciably high and the initial pigment nature predominated. Furthermore, the steel panel weight losses in the two types of aqueous extracts were determined in 36 days of submersion. The lowest weight loss, mere 0.01%, was observed in the aqueous extract of the film with STA at CPV = 0.5 wt%. This concentration also provided the highest corrosion protection in the salt fog atmosphere, and the electrochemically measured corrosion rate was in the order of $10\text{E-}12$. The optimum PTA pigment concentration was PVC = 3 wt%, at which the corrosion loss was lowest, viz. 0.18%, and the anticorrosion protection efficiency highest, viz. 89%. This system proved to be the most efficient also in the long run, on exposing the samples to the same environment for as long as 2184 hours. The efficiency of the remaining systems decreased as much as to 62%. While the system with an HPA retains its protective properties if exposed to the corrosive environment for 1500 hours or less, its long-term protective properties are not adequately good. A comparison of the paint films is shown in Fig 3 (3a, 3b: in 1500 hours; 3c, 3d: in 2184 hours).

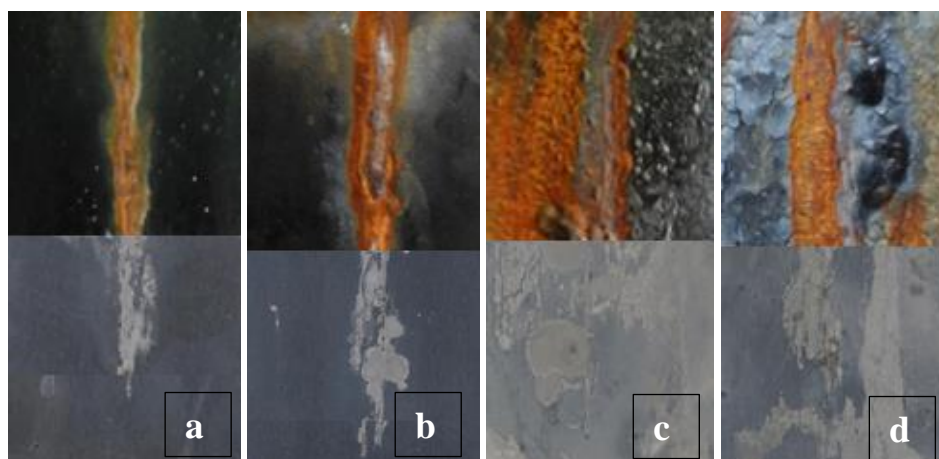


Fig.3. Panels exposed to the salt solution atmosphere, photographs before and after removing the paint films. a) STA 5 wt%; b) PTA 3 wt% after 1500 h of exposure; c) STA 5wt%; PTA 3wt%) after 2184 h of exposure. Table 2 also lists the proton conductivity data of the HPAs, decreasing with increasing pigment volume concentrations for the free pain films. The conductivity increased appreciably during

the experiment in the case of the powdered pigments. Paint film blistering decreased with decreasing conductivity, the paint film adhesion, however, increased, whereby the paint film was losing adhesion to the substrate metal. The foregoing applies to the STA system. As to the PTA system, PVC = 3 wt% appears to provide the best results: no blistering took place, substrate metal corrosion was lowest, 0.03%, and no adhesion loss was observed.

The novel paint systems are suitable for C5-I type environments (ISO 12944-2 and ISO 7253) at a medium to long lifetime. This is industrial atmosphere or indoor atmosphere with elevated humidity.

Table 2. Corrosion characteristics of the paint systems with HPAs

CPV	OFME ^{e)}	Anticor. efficiency		Corr.rate ^{f)}	pH _{pig.}	pH _{film.}	χ _{pig.}	χ _{film.}
	after 30d	NaCl _{1500h}	NaCl _{2184h}		at 7/21day		at 7/21day	
wt%	%	%	%	mm.year ⁻¹	± 0.01 %		± 0.5 % μS.cm ⁻¹	
STA (Silicotungstic heteropolyacid)								
0.5	100	83	62	69.0 E-12		6.57/6.68		537/621
1	100	77	63	69.0E-12	4.44/4.78	6.58/6.73	475/1219	433/498
3	100	76	66	12.0E-11		6.46/6.37		405/376
5	100	78	66	12.0E-11		4.99/4.10		84/111
PTA (Phosphotungstic heteropolyacid)								
0.5	100	67	62	36.0E-11		6.54/6.75		675/774
1	100	49	62	75.0E-11	4.73/5.4	6.48/6.97	1022/1380	765/841
3	100	89	72	16.0E-11		5.91/6.20		312/295
5	100	62	68	88.0E-11		4.87/4.97		104/114
CaCO₃ - Omyacarb								
Q = 10	100	79	69	59.0E-12	7.5/7.71	6.47/6.90	174/295	962/1021
Non-pigmented epoxy ester resin								
-	100	42	48	58.0E-12	-	3.81/3.75	-	91/139

^{e)} Paint films' overall physico-mechanical efficiency (average of the scores; %)

^{f)} Corrosion rate measured by the electrochemical method (VSP-300, France)

Conclusions

New heteropolyacid-based coating materials were prepared. Two heteropolyacids, viz. silicotungstic heteropolyacid and phosphotungstic heteropolyacid, were tested and compared with reference paint systems containing either the binder (epoxy-ester resin) alone or the binder and CaCO₃ serving as the filler. The performance of the paint systems was inferred from the comparison. The two HPAs-differ in the optimum pigment volume concentration, which is PVC = 0.5 wt% for STA and PVC = 3 wt.% for PTA. The mechanism of their protective function is not fully understood yet; some authors suggest that it consists in the formation of complex compounds of the phosphate, silicate and tungstate types. Studies to precisely identify the protective function and composition of the corrosion products are under way or planned.

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