

Inorganic pigments based on transition-metal oxometallates for protective and decorative aluminophosphate-bonded coatings

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Abstract. Transition-metal oxometallate-based pigments deposited on a dispersed silicate mineral (marshallite, wollastonite) have a bright color and high light- and acid resistance. It is shown that these pigments can be used for protective and decorative aluminophosphate-bonded coatings. Thermal analysis performed on the thermal analyzer SDT Q600 shows that the structure of protective and decorative coatings remains unchanged to temperatures of about 900 °C. Optical studies (Axiovert 200M) demonstrate that colored coatings subjected to heat treatment have a uniform structure without cracks and, therefore, can be used for metal and concrete surfaces. X-ray diffraction (DRON-UM1 diffractometer, CuK_α radiation) confirm that the coating contains AlPO_4 , $\text{Al}(\text{PO}_3)_3$ and $\text{Al}(\text{H}_2\text{PO}_4)_3$ phases, quartz, and pigment. The insignificant amount of $\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ phase is detected.

1. Introduction

Inorganic pigments containing tungstophosphates, tungstosilicates, molybdophosphates and transition-metal molybdosilicates as chromophores, as well as dispersed silicates with different structural groups of silicon-oxygen tetrahedrons, in particular marshallite, talc, kaolinite, wollastonite, as substrates possess high light- and acid resistance and can be used as pigments for aluminophosphate-bonded coatings [1, 2].

Aluminophosphate bond (APB) is a result of the interaction of aluminum hydroxide with orthophosphoric acid and widely used as a binder for wood boards to increase fire resistance and as protective and decorative and anti-corrosion ceramic coatings [3-6]. Depending on the filler used, aluminophosphate compositions acquire different properties. Metal powders and carbon are used to obtain electrically conductive coatings, and a mixture of finely-dispersed corundum and muscovite imparts good electrical insulating properties to hardened compositions [6, 7]. Boron compounds in ceramic compositions absorb neutrons, which is used in nuclear physics, and silicon nitrides well reinforce high-temperature radio-transparent aviation materials [8, 9]. Aluminophosphate bond is also used to obtain fire-resistant colored protective and decorative coatings [10-12]. In this case, the pigments are titanium oxides, colored corundums, as well as other colored pigments that are highly heat-resistant and do not react with phosphoric acid (for example, cadmium sulfides). Along with the mentioned above pigments, inorganic acid-resistant compositions based on oxometallates deposited on a mineral carrier can be used for coloring.

The purpose of this work was to obtain and study the phase composition and heat resistance of protective and decorative aluminophosphate-bonded coatings and inorganic pigments, such as tungstosilicates, tungstophosphates, molybdophosphates, and cobalt and copper molybdosilicates deposited on marshallite and wollastonite.



2. Experimental procedure

Aluminophosphate bond was prepared as follows: a mixture of orthophosphoric acid and aluminum hydroxide in the $\text{H}_3\text{PO}_4 : \text{Al}(\text{OH})_3 = 100 \text{ мл} : 22.5 \text{ g}$ ratio was heated to temperatures of $80 \div 100^\circ\text{C}$ and stirred until complete dissolution of $\text{Al}(\text{OH})_3$. Acid aluminum phosphates have good binding properties.

Oxometallates were synthesized from molybdates, alkali metal tungstates, hydrogen phosphate, sodium silicate (Na_2HPO_4 , Na_2SiO_3), and the transition metal salt in a weak acid medium ($\text{pH} = 5 \div 6$). Wollastonite CaSiO_3 and Marshalite SiO_2 were used as minerals. Cobalt and copper chlorides ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$) were used as transition metal salts.

Inorganic pigments were obtained by the interaction of mineral with oxometallate precipitated and crystallized on the carrier in solution at a temperature of $30\text{--}60^\circ\text{C}$. Synthesis was conducted for 30 minutes, then suspension was filtered, and precipitation was placed in a ceramic container and dried at $120\text{--}180^\circ$.

Colored wollastonite or marshalite were added to aluminophosphate bond in the amount of 10 -15 wt.% with a small amount of boric acid.

Thermal analysis of a ceramic coating consisting of APB and an inorganic pigment based on a heteropoly compound and mineral was performed on a thermal analyzer SDT Q600.

The microstructure of the pigments deposited on the mineral carrier and the protective and decorative coating was determined using scanning electron microscopy (Philips SEM 515) and optical microscopy (Axiovert 200M). The decorative composite obtained was studied using X-ray diffraction (diffractometer DRON-UM1, CuK_α radiation). The reflection spectra of the pigments were recorded with an Evolution-600 spectrophotometer with a reflection attachment.

3. Discussion of results

The conducted studies have shown [2] that most oxometallates formed by acidification of molybdate and tungstate solutions with the addition of other oxoanions, in particular PO_4^{2-} and SiO_4^{2-} , and transition-metal salts have a Keggin structure, for example:

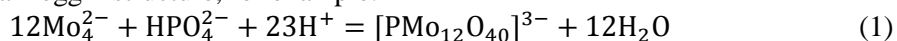
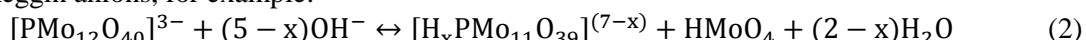


Figure 1 shows the structure of anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$.

Anion hydrolysis reactions $[\text{XMe}_{12}\text{O}_{40}]^n$ take place in weakly acid and neutral solutions and form lacunary Keggin anions, for example:



Tungstophosphates and tungstosilicates are obtained in the same way (at $\text{pH} > 4$):

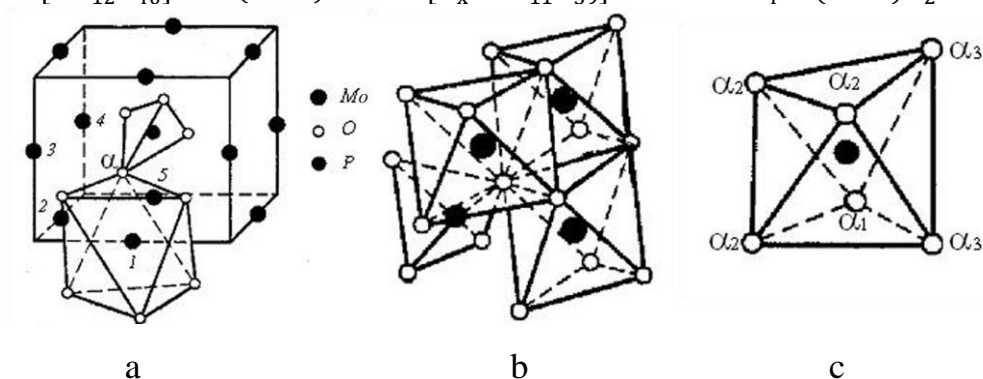
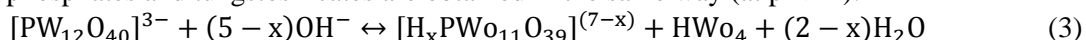


Figure 1. Structure of anion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, where (a) central tetrahedron XO_4 is surrounded by 12 octahedra MO_6 assembled into four groups M_3O_{13} ; (b) triplet M_3O_{13} connected to the central tetrahedron XO_4 by vertices; (c) octahedron MO_6 [13].

It is known that 12-tungstophosphates pass into the lacunar form $PW_{12} \rightarrow PW_{11}$ at $pH = 4.5$. Transition $SiW_{12} \rightarrow SiW_{11}$ is observed in more acid media (at $pH = 1.5$), which is related to a lower charge of PW_{12} . Anion $[PW_{11}O_{39}]^{7-}$ is stable to $pH = 6$ [13].

In all cases the reaction of colored heteropoly compounds takes place directly on the substrate. The active centers of the mineral surface intensify the reaction of pigments. Salt is deposited on the mineral base by two mechanisms: due to displacement of structural OH groups, alkali metals (marshalite, talc, kaolinite, silica gel) and due to the replacement of Ca^{2+} contained in the substrate (wollastonite, diopside) with the cation of the outer coordination sphere (transition metal) [2]. The dispersion of pigments depends on the dispersion of the mineral carrier. Fig. 2 shows the microstructure of marshalite and pigment based on cobalt molybdophosphate (CoPMo) deposited on marshalite. CoPMo crystals have a needle-like structure and are distributed on the surface and between the marshalite grains.

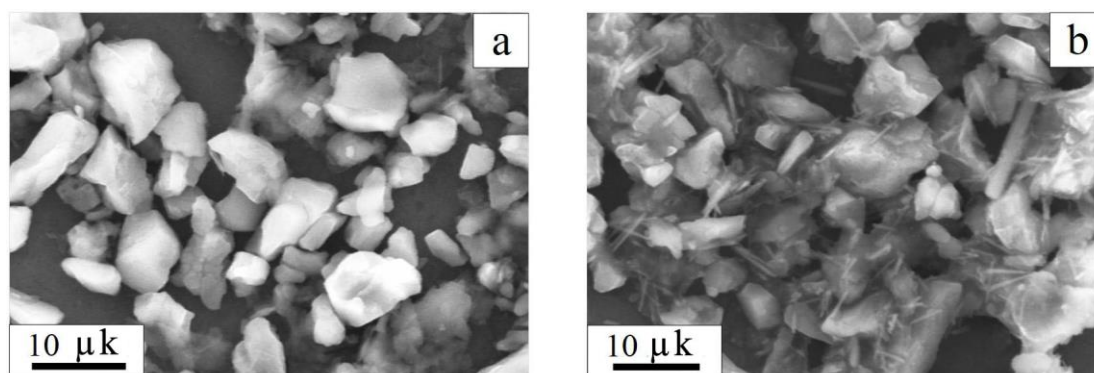


Figure 2. SEM photographs of marshalite (a), CoPMo-based pigment deposited on marshalite (b), Philips SEM 515.

The main attention during the synthesis of pigments should be paid to the acidity of solutions. This is due to the fact that the structure of heteropolysols is very sensitive to pH of the medium. This is especially typical for tungstosilicates ($CoSiW$) and tungstophosphates (CoW) of cobalt. Fig.3 shows the effect of pH of the solution during the pigment synthesis (Marshall + CoPW) on its color.

Molecular non-integrity of octahedral groups WO_6 caused by OH groups in solution and replacing them with the octahedrally coordinated peripheral cation Co^{2+} provides the pigments with pink color.

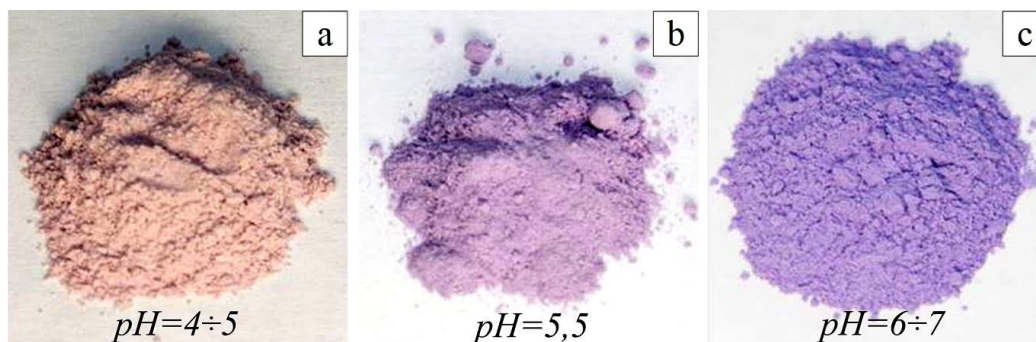


Figure 3. Effect of acidity of the medium on the color of the synthesized pigment (Marshalite + CoPW)

The values of the absorption maxima (λ) in the reflection spectra of these pigments, recorded with an Evolution-600 spectrophotometer (Thermo Electron Corporation, the United States) using the reflection attachment, are shown in Table 1.

Table 1. Color of the pigment versus the length of absorbed light.

λ , nm	530	550	580
Color of pigment	pink	pink-lilac	lilac

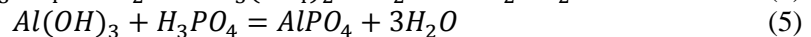
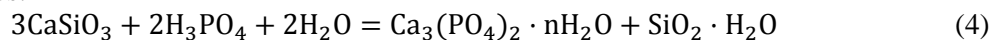
The shift of absorption towards the violet spectrum provides pigment with pink color. The Co^{2+} cation in the octahedral field has three spin transitions d-d. Visible spectrum corresponds to two transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ (arm ~ 400 nm) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (~ 560 nm). Transition ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$ is observed at 1200 nm [14].

Decreasing the acidity of solution, the number of broken groups increases. At the same time, cobalt tungstates are formed in tetrahedral environment where cobalt is blue colored, which provides the pigment with lilac color. The more cobalt tungstate is formed, the darker blue pigment becomes. Anions disintegrate in an alkaline medium, forming lacunary forms and simple tungstates.

Pigments are synthesized in a weakly acid and neutral media, since at low pH, silica gel is formed by dissolving the mineral.

The purest colors are obtained using molybdophosphates of transition-metal salts. Different color pigments can be obtained depending on the transition-element cation and pH of a solution.

APBs become hard already at room temperature, but for full hardening it is necessary to heat the surface at a temperature of 270-300 °C. This heat treatment makes coatings water resistant [1]. The foamed wollastonite paint production technique was used to obtain coatings based on heteropoly compounds deposited on wollastonite (Fig. 4). Painted wollastonite is added to orthophosphoric acid and aluminum hydroxide bond. The reaction of wollastonite CaSiO_3 with aluminophosphate bond is described as follows:



The foamed wollastonite paint obtained is a mixture of hydrated calcium phosphate, aluminum phosphate (hydrophosphate), silica gel and pigment.

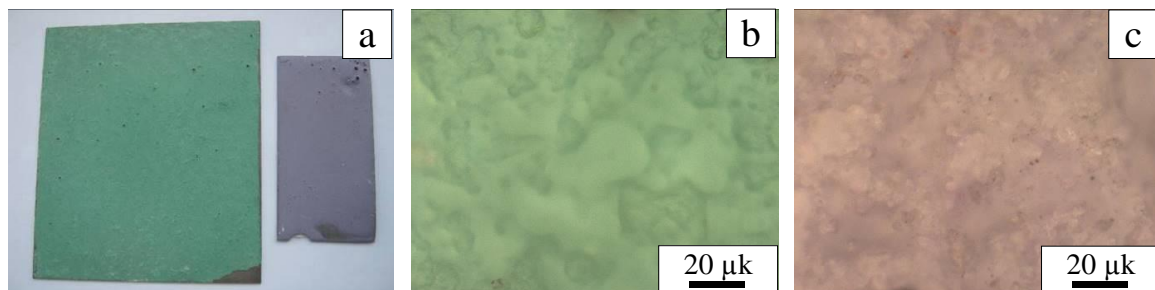


Figure 4. Colored protective and decorative ceramic aluminophosphate-bonded coatings deposited on metal: (a) coatings using pigments based on heteropoly compounds deposited on the mineral (b); (c) microstructures of ceramic coatings deposited on a metal plate: APB + pigment $\text{CuPMo/wollastonite}$ (b), APB + pigment CoPMo/marshelite (c); Axiovert 200M.

The optimal amount of colored wollastonite or marshelite added to aluminophosphate bond is 10–15 wt.% including a small amount of boric acid added to slow the crystallization rate of silicate paint and keep it as suspension for certain time.

The large amount of wollastonite (30 wt.%) leads to the rapid hardening of the composition, which complicates its deposition on the surface. Paint is deposited on the surface and dried. To obtain hard ceramic coating, the colored surface of the product is subjected to heat treatment with a gas burner ($\sim 300^\circ\text{C}$) for $1 \div 2$ minutes.

Optical studies (Axiovert 200M) showed (Fig. 4 b,c) colored coatings subjected to heat treatment have a uniform structure, do not contain cracks and can be used both for metallic and concrete surfaces.

A strong protective and decorative coating was also obtained using pigments based on heteropoly compounds deposited on marshalite. The coating is stable to a temperature of 950°C . Figure 5 shows the thermal analysis of a mixture dried at room temperature and consisting of APB and inorganic pigment based on cobalt molybdophosphate and marshalite. As can be seen, the loss of adsorbed and crystallization water is divided into several stages with maximum at 111.1°C , 168.6°C and minimum at $\sim 225^\circ\text{C}$ and $\sim 260^\circ\text{C}$. In the range of $566.5\text{--}568.8^\circ\text{C}$, a phase transition is observed in marshalite: $\alpha\text{-quartz} \rightarrow \beta\text{-quartz}$ [15]. Over 950°C , the observed mass loss is related to partial breaking of cobalt molybdophosphate.

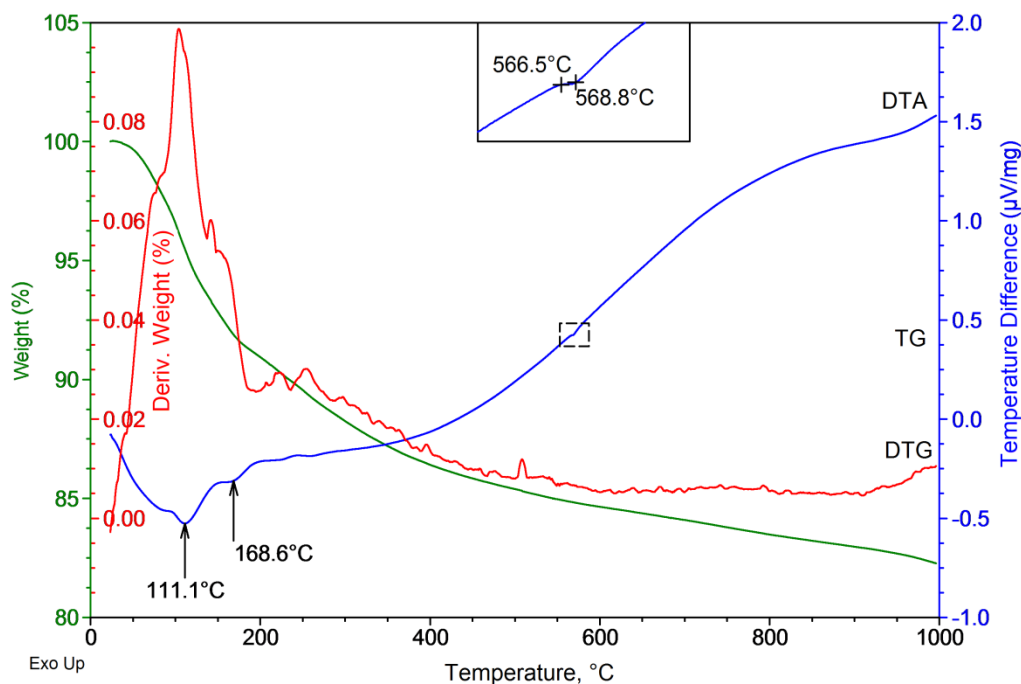


Figure 5. Thermograms of thermal analysis of a mixture consisting of APB and inorganic pigment based on cobalt molybdophosphate and marshalite (maximum weight loss on the DTG curve are directed upwards).

Figure 6 shows an X-ray diffraction pattern of a protective and decorative coating consisting of an APB and inorganic pigment based on cobalt molybdophosphate and marshalite deposited on a metal substrate. Along with marshalite, there are AlPO_4 , $\text{Al}(\text{PO}_3)_3$ and $\text{Al}(\text{H}_2\text{PO}_4)_3$ phases. The phase $\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is detected in the small amount. An amorphous ring is observed in the range of angles of $\sim 2\theta = 15 \div 30^\circ$, which confirms the amorphous component of the coating.

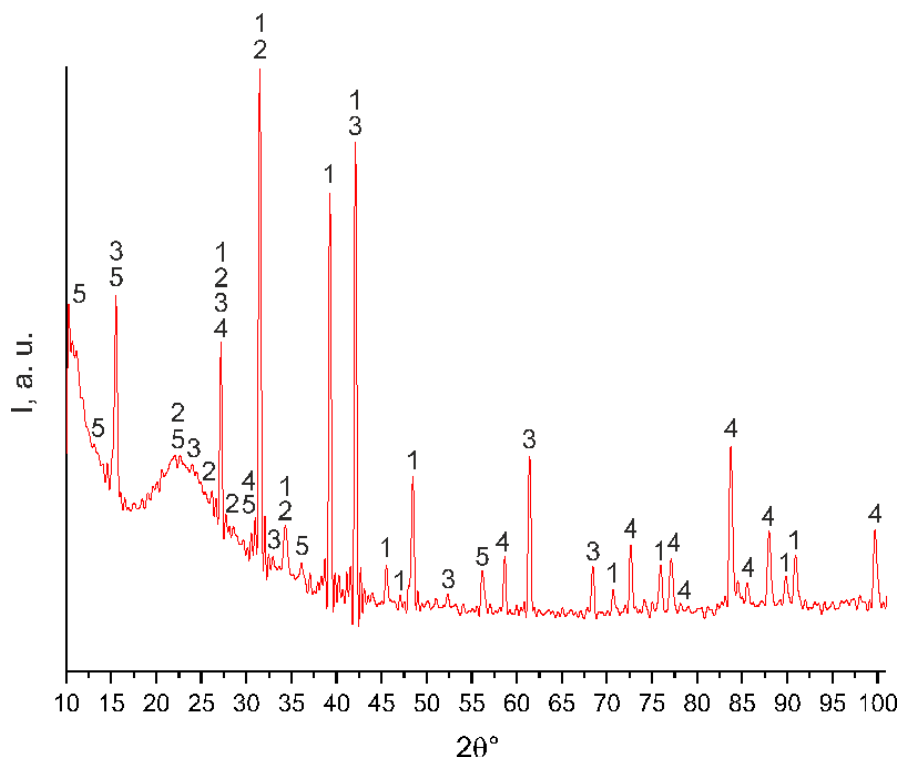


Figure 6. X-ray diffraction pattern of a ceramic coating consisting of APB and inorganic pigment based on cobalt molybdophosphate and marshalite, where 1 is marshalite SiO_2 , 2- $\text{Al}(\text{PO}_3)_3$, 3- $\text{Al}(\text{H}_2\text{PO}_4)_3$, 4- AlPO_4 , 5- $\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

Similar results were obtained using pigments based on tungstophosphates, tungstosilicates, cobalt molybdosilicates and copper.

4. Conclusion

Thus, inorganic pigments based on transition-metal oxometallates deposited on a silicate mineral base are acid- and light resistant and can be used for colored protective and decorative aluminophosphate bonded coatings.

The color of coatings containing inorganic pigments based on tungstosilicates, tungstophosphates, molybdophosphates and cobalt molybdosilicates deposited on marshalite and wollastonite is kept to a temperature of 900 °C, which means that the pigments obtained can be used in the composition of fire-resistant ceramic coatings and in the manufacture of compositions with high heat resistance.

The X-ray diffraction analysis of a protective and decorative coating consisting of APB and inorganic pigment based on cobalt molybdophosphate and marshalite showed that along with marshalite, there were AlPO_4 , $\text{Al}(\text{PO}_3)_3$ и $\text{Al}(\text{H}_2\text{PO}_4)_3$ phases. The phase $\text{Al}_3(\text{OH})_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is detected in the small amount. The amorphous ring was observed in the range of angles of $\sim 2\theta = 15\div 30^\circ$, which confirmed the amorphous component of the coating.

Notifications

APB - Aluminophosphate bond

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