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Research paper

Composite pigments based on surface coated kaolin and metakaolin

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ABSTRACT

Synthesis: The method of homogeneous hydrolysis of Fe, Co, Cr, Ni, Mn, Ti, Al, and Zn salts with urea in aqueous solutions in the presence of substrates (kaolin, metakaolin and mullite) was used for the preparation of composite pigments. In these composites individual kaolinite platelets were covered by a thin layer of hydroxide or oxy-hydroxides of selected metals, which were transformed into a metal oxide layer strongly bond to the aluminosilicate surface by heat treatment. An analogous method, homogeneous hydrolysis of thioacetamide in the presence of Cd and Zn salts was used for pigments based on sulphides.
Characterization: The mineralogical composition of the pigments was identified by X-ray powder diffraction (XRD), the particle morphology was studied by transmission electron microscopy (TEM) and the color was characterized in CIEL*a*b colours coordinates.
Results: The kaolin and metakaolin coated with layer of metal oxides are interesting new composite materials, obtained by a very simple preparation process at a low cost.

1. Introduction

Kaolinite ($Al_4(OH)_8Si_4O_{10}$) is a clay mineral which is a major component of the industrial clay kaolin. It consists of a regular stack of $(Si_2O_5)^{2-}$ tetrahedral sheets linked through oxygen atoms to parallel octahedral sheets of alumina octahedra $[Al^2(OH)_4]^{2+}$. Endothermic dehydroxylation of kaolinite begins at 500–600 °C yields structurally disordered metakaolinite $Al_2Si_2O_7$ (Mitra and Bhattach, 1970). Next heating to 925–950 °C converts metakaolinite to a defected aluminium–silicon spinel, $Si_3Al_4O_{12}$ (Vesely et al., 2010). Upon further calcination to ~1050 °C, the spinel phase transforms to mullite, $3Al_2O_3 \cdot 2SiO_2$ and highly crystalline cristobalite, SiO_2 (MacKenzie et al., 1996). Metakaolin is considered a suitable precursor for geopolymer production (Rovnaník, 2010) due to its reactivity and predictable properties both during preparation and densification (Duxson et al., 2006). Mullite has long been used as a refractory material with excellent high temperature strength, thermal shock resistance, thermal stability, electrical resistivity, insolubility in most acids and resistance to oxidation and attack at high temperatures. Recently, high performance and low cost anticorrosive hybrid pigments based on kaolin and ferrite were synthesized (Ahmed and Selim, 2010a, 2010b). This synthesis involved deposition of a surface layer of an expensive but efficient anticorrosive pigment, ferrite, on a bulk of cheap extender pigment, kaolin. New types of pigments were prepared in this research by coating an Egyptian kaolin core by simple and mixed zinc-, magnesium-, and zinc–magnesium phosphates instead of using bulk phosphates (Ahmed and Selim, 2010a, 2010b). These new pigments combine the advantageous properties of both their cores and covers. Ahmed et al. (2011) highlighted the role of a new prepared core–shell pigment, kaolin coated by cobalt oxide and magnesium oxide. These two pigments and the varying ratio of cobalt oxide to magnesium oxide in the shell were incorporated in different styrene–butadiene rubber vulcanizates, and their rheological, physical, mechanical and dielectric properties were studied.

Nanosized anatase TiO_2-coated kaolin composites were prepared by the chemical deposition method starting from calcined kaolin and $TiCl_4$, which yielded TiO_2 (anatase) nanoparticles on the kaolin surfaces after calcination at 200, 400 and 900 °C (Lu et al., 2009). Kibanova et al. (2009) studied the synthesis and photocatalytic activity of small-sized TiO_2 supported on hectorite ($Na_{0.4}Mg_{2.7}Li_{0.3}Si_4O_{10}(OH)_2$) and kaolinite. Deposition of TiO_2 on the clay mineral surface was conducted by using a sol–gel method with titanium iso-propoxide as a precursor. Anatase particles were formed by hydrothermal treatment at 180 °C. TiO_2 coated kaolinite nanocomposite particles were synthesized by using a sol–gel technique and electro-rheological fluids prepared by dispersing the particles in silicone oil (Wang and Zhao, 2003). Titanium dioxide compound pigments were prepared by hydrolysis of tetrabutyl titanate on the surface of kaolin substrates (Yan et al., 2010). Atomic layer deposition was used to produce a titanium dioxide (TiO_2) layer onto both silica- and kaolin surfaces. The reactive vapours of $TiCl_4$ and H_2O were used in a cyclic reaction sequence to grow the titania layer on silica and kaolin (Ninness et al., 2003). Calcined kaolin/TiO_2 composite material was prepared by

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TiO_2 coating on the surfaces of calcined kaolin particles by the mechano-chemical method. The TiO_2 coats evenly the surfaces of calcined kaolin particles by Si – O – Ti and Al – O – Ti bonds on their interfaces (Wang et al., 2010).

Composites of kaolin with ferric oxide (Fe_2O_3) may be used as barrier pigments in paint industry (Bludska et al., 2009). Corrosion protection under severe conditions is achievable by coatings containing natural pigment specularite (a platy form of hematite, α-Fe_2O_3), known as "micaceous iron oxide". Specularite platelets in coatings are organized in parallel layers with the protected surface, the coating solidifies mechanically and α-Fe_2O_3 (absorbing most UV and Vis light <500 nm) efficiently prevents UV photodegradation (Kalenda et al., 2004). The disadvantage of specularite is its very high price and unacceptably high density causing fast pigment settling in paint formulations. Both these obstacles would be solved by α-Fe_2O_3-coated aluminosilicates. The coloured pigments based on kaolin and metakaolin can also be used in the manufacture of colour refractory materials, as an ingredient in the manufacture of porcelain, sanitary ware, ceramic tiles, coloured pottery, and refractory materials and as a pigment for paints. The coated kaolin-based materials would additionally afford lowering environmental load of heavy metals, which are components of most common contemporary inorganic pigments.

In this contribution, we report on a specific method of their preparation, based on homogeneous hydrolysis, which allows preparation of surface coated lamellar kaolin and metakaolin particles (Cerny et al., 2009). The aim of our work was to decrease the amount of heavy metals in the resulting pigment and decrease its specific gravity by using light alumosilicate cores, which affords relatively large platy particles suitable for protection efficiency of the resulting composite. The surface of kaolin or metakaolin was coated by a thin layer of poorly crystalline or amorphous oxides and oxy-hydroxides by wet impregnation, followed by heating at temperature up 800 °C. The surface layers were converted, for example, to well crystalline oxides with structures of corundum (Cr_2O_3, α-Fe_2O_3), spinel ($CoAl_2O_4$) or perovskite ($NiTiO_3$). These listed phases are well established pigments. Their properties can be tuned and improved by including in the composites.

2. Experimental

2.1. Synthesis of samples

All chemicals used, copper(II) sulphate $CuSO_4 \cdot 5H_2O$, nickel(II) sulphate $NiSO_4 \cdot 6H_2O$, cobalt(II) sulphate $CoSO_4 \cdot 7H_2O$, iron(II) sulphate $FeSO_4 \cdot 7H_2O$, zinc(II) sulphate $ZnSO_4 \cdot H_2O$, chromium(III) sulphate $Cr_2(SO_4)_3 \cdot xH_2O$, aluminium(III) sulphate $Al_2(SO_4)_3 \cdot 16H_2O$, zinc selenite $ZnSeO_3$, cadmium(II) sulphate $CdSO_4 \cdot 8H_2O$, $ZnSO_4 \cdot 7H_2O$ and cadmium chloride $CdCl_2 \cdot 2.5H_2O$ were of analytical grade and were supplied by Fluka. Manganese(III) acetate $(CH_3COO)_3Mn \cdot 2H_2O$, iron(III) sulphate $Fe_2(SO_4)_3 \cdot xH_2O$,titanium-oxo sulphate $TiOSO_4$, urea $(NH_2)_2CO$ and thioacetamide CH_3CSNH_2 (TAA) were of analytical grade and were supplied by Sigma-Aldrich Ltd. The kaolin, metakaolin and mullite were purchased from their Czech industrial producer České lupkové závody, a.s. (ČLUZ). The kaolin raw materials come from the Czech deposits in the Eger Graben in the western part of the Czech Republic, which have been used for many decades for the production of ceramics. To prepare the composite pigments, kaolin and metakaolin 5, 40 and 60 μm were used.

The transition metal oxy-hydroxides and sulphides were prepared by hydrolysis of sulphate aqueous solutions using urea and thioacetamide, respectively, as the precipitating agents. In suspension with substrates the metal salts (Tables 1–5) were dissolved in 500 mL hot water acidified by 98% H_2SO_4 to pH ~ 2–3. The pellucid liquid was diluted into 4 L of distilled water and mixed with 50–300 g of urea. The mixture was heated at 95–100 °C under stirring and for 6 h until pH 7.2–7.5 and ammonia started to be released from the solution.

For homogeneous hydrolysis with thioacetamide in suspension with substrates, the metal salts were dissolved in 500 mL water acidified by 98% H_2SO_4 to pH = 2 and the reaction solution was heated at 80 °C under stirring for 4 h. The precipitates were decanted in distilled water, filtered off and the solid was dried at ambient temperature. The dry composite was annealed at 95–800 °C for 2 h. (see Tables 1–5 for actual temperature).

2.2. Characterization methods

X-ray diffraction (XRD) patterns were collected with a PANalytical X'Pert PRO diffractometer equipped with conventional X-ray tube (Cu-Kα radiation, 40 kV, 30 mA) and a linear position sensitive detector PIXcel with an anti-scatter shield. A programmable divergence slit set to a fixed value of 0.5 deg., soller slits of 0.02 rad and mask of 15 mm were used in the primary beam. A programmable anti-scatter slit of 0.5 deg., a soller slit of 0.02 rad and a Ni beta-filter were used in the diffracted beam. Qualitative analysis was performed with the DiffracPlus Eva software package (Bruker AXS, Germany) using the JCPDS PDF-2 database (2001). The database contains also solid solutions, such as Fe-bearing sillimanite, Fe_2O_3–Cr_2O_3, and binary and ternary spinels, which allow the estimation of their tentative formulas from the diffraction line positions. For quantitative analysis of XRD patterns we used Diffrac-Plus Topas (Bruker AXS, Germany, version 4.1) with structural models based on ICSD database (2008). This program permits the estimation of the weight fractions of crystalline phases and mean coherence length by Rietveld refinement. The refinement includes only the crystalline portions of the samples; amorphous components, such as metakaolinite, are omitted as they only contribute to a baseline.

Scanning electron microscopy (SEM) was performed using a Philips XL30 CP microscope equipped with energy dispersive X-ray microanalysis (EDAX). The morphology of sample powders was observed by transmission electron microscopy (TEM) using a 120 kV TEM

Table 1
Characteristics of kaolin pigments based on simple oxides on metakaolin substrate.

Sample	Desired pigment C.I.	Metal ions	Synthesis conditions (Weights of raw materials)				Products				
			Kaolin (g)	Metal sulphates (g)	Urea (g)	Temperature of annealing (°C)	Colour	XRD crystalline components	L*	a*	b*
Sox 1	Green 19	$Co^{II} + Zn^{II}$	100	28 + 18	100	800	Light green	Co_2O_3*ZnO	60.73	−1.5	6.44
Sox 2	Green 17	Cr^{III}	50	50	100	800	Green	Cr_2O_3	58.27	−5.61	6.07
Sox 3	Red 101	Fe^{III}	50	50	100	800	Red	α-Fe_2O_3	56.44	15.19	9.24
Sox 4	Red 230	$Al^{III} + Fe^{III}$	100	32 + 40	200	800	Orange	α-$(Al,Fe)_2O_3$	62.45	19.27	18.52
Sox 5	-	$Al^{III} + Cr^{III}$	100	32 + 40	200	800	Light green	$(Al,Cr)_2O_3$	59.85	−5.61	−6.83
Sox 6	Brown 6	$Fe^{II} + Fe^{III}$	50	28 + 40	200	95	Brown	Fe_3O_4	69.72	4.27	12.51
Sox 7	White 24	Al^{III}	50	50	100	800	White	Al_2O_3	87.93	1.35	4.00
Sox 8	Yellow 42	Fe^{III}	50	25	50	95	Yellow	α-FeO(OH)	75.07	7.97	20.17
Sox 9	White 6	Ti^{IV}	50	100	200	800	White	TiO_2	96.31	0.25	5.61

L*, a*, b* are designation optical coordinates in the CIELAB colour space.

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