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DEVELOPMENT OF SnO_2/Sb-BASED CERAMIC PIGMENTS

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Abstract

The color efficiency of ceramic glaze blue pigments obtained by the Pechini method was presented in this work. The fired pigments and enameled samples were characterized by thermogravimetry (TG) and differential thermal analysis (DTA), XRD, UV-VIS-NIR spectroscopy and CIE-L*a*b* color-measurements. The pigments obtained by the Pechini method present a better solubility in the molten glazes than the pigments obtained by the mechanical mixture of the precursor oxides.

Keywords: pigments, $SnO_2 \cdot 9\%Sb_2O_3$, thermal analysis

Introduction

Inorganic natural and synthetic pigments that are produced and marketed as fine powders are an integral part of many decorative and protective coatings and are used for the coloration of plastics, fibers, papers, rubbers, glasses, cements, glazes, ceramic bodies and porcelain enamels [1–3]. In addition, these materials are colorants for printing inks, cosmetics, and markers. In all these applications, the pigments are dispersed (i.e. they do not dissolve) in the media, forming a heterogeneous mixture.

The $SnO_2 \cdot Sb$ system is one of the most requested as conductive pigment, for application in facilities that manipulate flammable gases and explosive substances, circumstances that request special conditions of safety. This work aimed at investigating ceramic pigments of the $SnO_2 \cdot Sb$ system obtained from the polymeric precursor method.

Experimental

The polymeric precursor solution was prepared by the Pechini method, which has been used to synthesize polycationic powders [4, 5]. The process is based on the metallic citrate polymerization using ethylene glycol. A hydroxycarboxylic acid, such as

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citric acid, is used to chelate cations in an aqueous solution. The addition of a glycol such as ethylene glycol leads to the formation of an organic ester. The polymerization, promoted by heating the mixture, results in a homogeneous resin in which metal ions are uniformly distributed throughout the organic matrix. The tin citrate was separately prepared from $SnCl_2 \cdot 2H_2O$ and the dopant source used was Sb_2O_3. Nitric acid was used to improve the solubility.

The heat-treatment range used was between 250 and 1200°C, consisting in heating the powders up to the appropriate temperature in order to obtain a monophasic structure for the pigments.

A mixture of glaze and the sieved pigments (mass volume ratio of the pigment: glaze equals to 12 g of pigments: 100 mL of liquid glaze) was homogenized in a ball mill during 10 min. The slip was poured on the ceramic biscuits obtaining a uniform glaze layer, which was then fired following a fast heat-treatment (up to 500°C with a heating rate of 10°C min^{-1}, from 500 to 1180°C heated at 15°C min^{-1}, a plateau of 1180°C for 1 h and a cooling back to room temperature at 10°C min^{-1}).

The thermal effect of oxidation of the samples, as well as the formation of the crystalline phases was studied by differential thermal analysis (DTA) and thermogravimetry (TG) (Netzsch, STA 402), under a synthetic air atmosphere with flow rate of 20 mL min^{-1} and heating rate of 10ºC min^{-1}. The reference material for DTA was Al_2O_3.

The determination the crystalline phases and the cell volume was carried out using SiO_2 as an external standard. For this, X-ray diffraction (XRD) patterns were used, which were obtained with a Siemens D-5000 diffractometer with CuK_α radiation (λ=1.5406 Å and θ=19 to 110°), at room temperature.

UV-Vis-NIR spectroscopy (diffuse reflectance) of the fired pigments was performed with a Varian 5G spectrophotometer. In addition, the L^*, a^* and b^* color parameters and diffuse reflectance of enameled samples were measured through the Gretac Macbeth Color-eye spectrophotometer 2180/2180UV, in the 300 to 800 nm range, using the D65 illumination. The CIE-$L^*a^*b^*$ colorimetric method, recommended by the CIE (Commission Internationale de l'Eclairage) [6] was followed. In this method, L^* is the lightness axis [black (0)→white (100)], b^* is the blue (-)→yellow (+) axis, and a^* is the green (-)→red (+) axis, and ΔE is the hue variation.

Results and discussion

The techniques of thermal analyses were used to verify the thermal decomposition of the resins. Although the method is basically qualitative, the alterations in the mass can be correctly measured. On the other hand, the assessment of the temperatures at which these alterations take place is qualitative, depending on the instrumental parameters and of the characteristics of the samples.

In Figs 1a–d are presented the thermal analyses (TG/DTA and DTG) and results of the undoped SnO_2 and SnO_2 doped with 9 mol% of Sb_2O_3 resins.

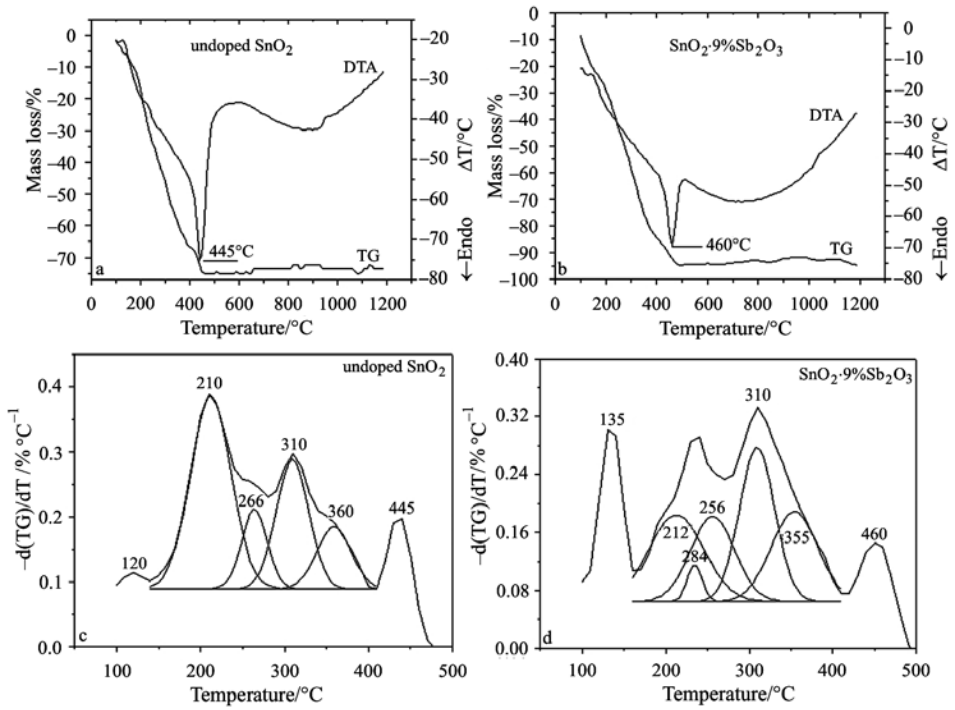

Fig. 1 DTA and TG curves of the resins: a – undoped SnO_2 and b – SnO_2·9%Sb_2O_3 and DTG curves of the resins: c – undoped SnO_2 and d – SnO_2·9%Sb_2O_3

It was observed that a series of exothermal reactions takes place during the oxidative thermal decomposition, due to the several events of thermal decomposition of the organic material. Some of these events are described, as follows:

- Between 100 and 200°C the mass loss can be associated to the elimination of H_2O, ethylene glycol and breakage of the organic chains (event 1);
- Between 200 and 350°C the breakage of the polymeric chain and elimination of CO_2, H_2O and species containing anhydride corresponding to reactions of decomposition of the salt and total elimination of the ethylene glycol (event 2) should happen;
- Between 350 and 500°C the exit of CO_2, H_2O and species containing the anhydride function and total thermal degradation of the polymer formed (event 3) should happen [7]. The phase formation temperature of the undoped SnO_2 was 445°C. For the SnO_2·9%Sb_2O_3 it was 460°C and the overall mass losses were 74 and 75%, respectively.

It is observed in Fig. 2 that in the studied SnO_2·9%Sb_2O_3, at 500°C a single homogeneous phase, cassiterite, was already formed. This result, obtained by XRD, confirms thus the information obtained by thermal analysis, that the thermal decom-

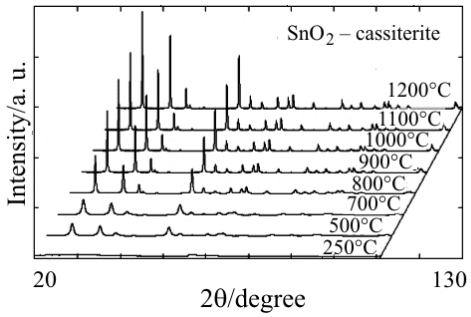

Fig. 2 XRD pattern of the powders, heat-treatment ranged from 250 and 1200°C

position of the polymer is complete at that temperature, with the consequent formation of the tin oxide.

In Tables 1a and b the chromatic coordinates of the undoped SnO_2 and SnO_2·9%Sb_2O_3 pigments obtained by the Pechini method are displayed, as a function of the heat-treatment temperature. In these pigments, the SnO_2-based matrix presents a white color, and this oxide is an opacifier within a vitreous system. Gray colors are formed by doping (9 mol% Sb_2O_3) and by calcining at temperatures of 800 and 900°C.

Table 1a Chromatic coordinates of the undoped SnO_2 pigments obtained by the Pechini method as a function of the heat-treatment temperature

Temperature/°C	L^*	a*	b*	ΔE
800	75.45	6.06	15.20	77.20
900	77.83	6.85	15.68	79.69
1000	79.74	4.74	10.96	80.63
1100	76.65	6.47	15.58	78.49
1200	76.64	4.41	12.15	77.72

Table 1b Chromatic coordinates of the SnO_2·9%Sb_2O_3 pigments obtained by the Pechini method as a function of the heat treatment temperature

Temperature/°C	L^*	a*	b*	ΔE
800	36.59	–1.99	–1.31	36.67
900	29.29	–2.95	–5.08	29.87
1000	21.38	–7.33	–17.70	28.71
1100	27.74	–7.14	–14.68	32.18
1200	33.67	–5.99	–11.91	36.21

Figure 3 presents the data of diffuse reflectivity evolution as a function of the heat treatment temperature in an air environment. It is quite evident that the system

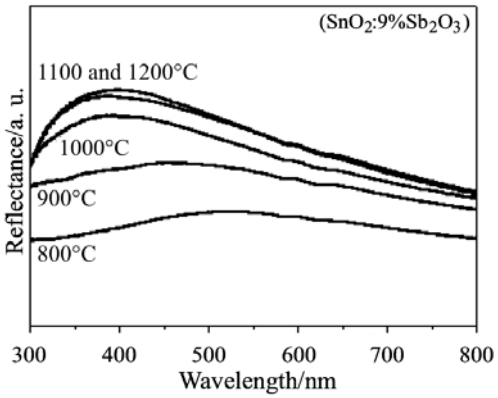

Fig. 3 Diffuse reflectivity data of the SnO_2·9%Sb_2O_3 system, as a function of the heat-treatment temperature in an air environment

undergoes a remarkable modification, in the whole spectrum range, up to 900°C. Above this temperature, only in the UV region a more important modification occurs, and at a lower extension in the IR region, remaining the system practically stable in the visible region, between 400 and 700 nm. For temperatures higher than 1000°C the bands are overlapped, which indicates that the color of the pigment has already been defined, a bluish hue, confirmed by the characteristic bands in the region from 390 to 450 nm. An increase in the reflectance can also be noticed along with the increase in the temperature.

Conclusions

Pigments with intense and uniform colors were produced from the SnO_2·9%Sb_2O_3 system. The Pechini method employed led to achieve a high degree of homogeneity at molecular level, as well as finer powders presenting thus higher surface areas. Monophasic powders were obtained at temperatures as low as 500°C and a completely defined color was observed at 1000°C. The Pechini method was shown to be superior to the conventional oxide mixture method in terms of color intensity, homogeneity and heat-treatment temperatures.

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