Thermochimica Acta, 214 (1993) 19–26
Elsevier Science Publishers B.V., Amsterdam

Thermoanalytical Studies on TiO_2-Mica Pigments

Markku Leskelä[a], Pekka Eskelinen[b] and Mikko Ritala[a]

Department of Chemistry, University of Turku, SF-20500 Turku, Finland

[a]Present address: Department of Chemistry, University of Helsinki, SF-00100 Helsinki, Finland

[b]Kemira TiO_2, SF-28840 Pori, Finland

Abstract

Small mica (muscovite and phologopite) flakes coated by thin TiO_2 films (40-150 nm) were studied by TG, DTG and DTA methods. The films were prepared by precipitation from two different titanium chemicals, viz. $TiCl_4$ and $TiOSO_4$. During heating both the precipitated TiO_2 hydrate films and the micas dehydrated. By thermoanalytical measurements the amount of TiO_2 on the mica and the water content of the precipitate could be determined. The TG curves could also be used for identification of the titanium source chemical, precipitation process and the mica substrate used.

1. INTRODUCTION

TiO_2-mica pigments, so called pearlescent pigments, consists of small mica plateles (thickness < 1μm, diameter 5-50 μm), coated by thin TiO_2 films (40-150 nm). The color of the pigments can be controlled by the thickness of the films [1]. The pigments are non-toxic and therefore used in cosmetic products. They also are chemically and thermally stable and usable in paints and plastics.

The pearlescent pigments are prepared precipitating water-containing TiO_2 from acidic Ti(IV) solutions. In preparation of the pigments calcination is an essential step to transform the amorphous precipitate to crystalline TiO_2 film. In unsupported

---

This paper was presented at the 13th Nordic Symposium on Thermal Analysis and Calorimetry, Stockholm, Sweden, 9–11 June 1992.

TiO_2 powders the temperatures for crystallization and anatase-rutile phase transition depend on the preparation method of the TiO_2 precipitate, the presence of impurities or additives and the atmosphere present during calcination [2]. The type of mica and the calcination temperature affect the crystal structure of the TiO_2 films [3]. During calcination the cations of mica may diffuse through the TiO_2 film and the surface composition of the pigment is a mixture of Al, Na, Si and Ti oxides [4]. Some cations originating from the mica substrate, for example aluminium, affect the crystal structure of TiO_2 stabilizing the anatase modification [5]. For applications rutile form is desired.

In the present work thermoanalytical measurements were carried out in order to characterize the $TiO_2 \cdot nH_2O$ precipitates and to get information on the processes occuring during the calcination. Thermal behaviour of pure, unsupported titanium hydroxides and hydrated oxides has earlier been studied by DTA [6], TG [7,8] and ETA [9] methods. The kinetics of the dehydration process has been investigated as well [10].

2. EXPERIMENTAL

In the present work two micas, muscovite and phlogopite were used. The phlogopite was from the Siilinjärvi ore in Finland and muscovite from India.

The TiO_2 films were prepared using three different methods. In the first method aqueous $TiCl_4$ solution was introduced to an agitated water suspension of mica ($T = 70\ ^\circ C$). pH was first adjusted to 2.2 by HCl and kept constant by NaOH during the deposition. The second method was similar to the previous one but instead of chloride $TiOSO_4$ solution was used. In the third method the desired Ti amount was added in one portion as $TiOSO_4$ solution, heated to the boiling point and refluxed for 3 hours. The TiO_2 amounts in the pigments varied between 20 and 40 % and it could be controlled by the amount of Ti solution added. A more detailed description of the synthesis has been reported elsewhere [3].

Thermoanalytical measurements were carried out in a dynamic air atmosphere using a Setaram TAG24 instrument recording simultaneously the TG, DTG and DTA curves up to 1250 °C. The sample sizes were typically 30 mg and heating rate 10 °C/min. Alumina was used as reference material in DTA.

3. RESULTS AND DISCUSSION

The micas loose weight at high temperatures due to the release of water originating from the OH groups. Different thermal behaviour has been reported in the literature for micas even of the same class. This is probably because micas as natural materials differ slightly chemically and structurally although they belong to the same class. These differences can be seen in the temperatures where the dehyration takes place [11]. In the present work the muscovite substrate lost 4.3 % of its weight between 710 and 870 °C and phlogopite (3.5 %) between 1060 and 1140 °C (Fig. 1). The materials were very stable up to the temperature where the dehydration begun. Some micas may slowly loose weight before the beginning of the faster dehydration.

The unsupported titanium oxide hydrate precipitate prepared from $TiCl_4$ begun to loose weight already above 50 °C. The fast weight decrease was over at 400 °C and the weight loss (25 %) indicates that the oxide precipitate contains 1.48 water molecules (Fig. 2). It seems that the precipitate is a mixture $TiO_2 \cdot H_2O$ (or $TiO(OH)_2$) and $TiO_2 \cdot 2H_2O$ (or $Ti(OH)_4$). The weight did not remain constant above 400 °C but slow decrease can be observed up to 1250 °C. This indicates the presence of some OH groups in the precipitate. The results obtained are in a good agreement with earlier TG studies on the dehydration of TiO_2 hydrates [7,8]. The resulting oxide may be amorphous even at 400 °C.

The powders precipitated from $TiOSO_4$ by the constant pH process dehydrate similarly as those prepared from tetrachloride but their water content is smaller (12 %). The TG curve of pow-

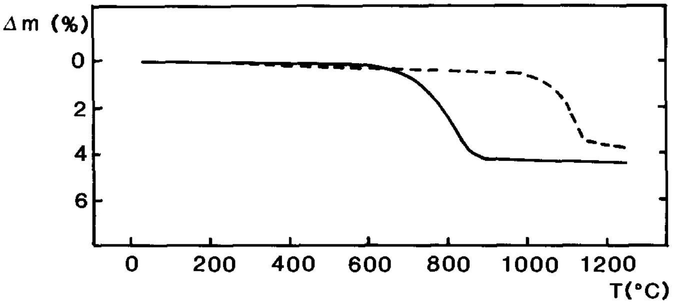

Figure 1. TG curves for the muscovite (solid line) and phlogopite (broken line) micas used as substrates.

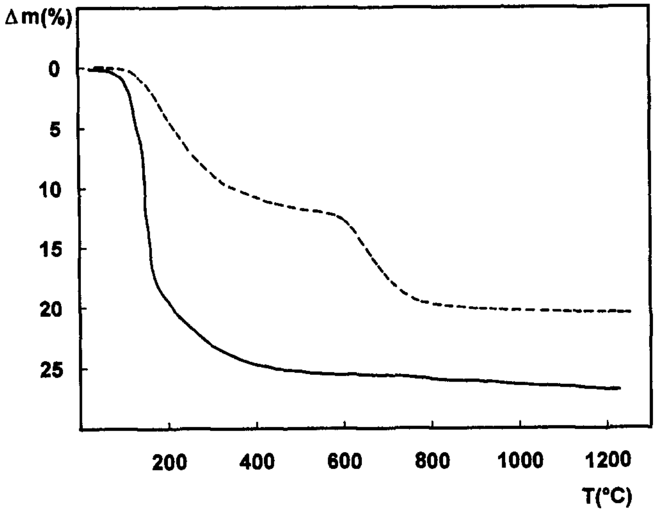

Figure 2. TG curves for unsupported $TiO_2 \cdot nH_2O$ precipitates prepared from $TiCl_4$ (solid line) and $TiOSO_4$ (broken line).

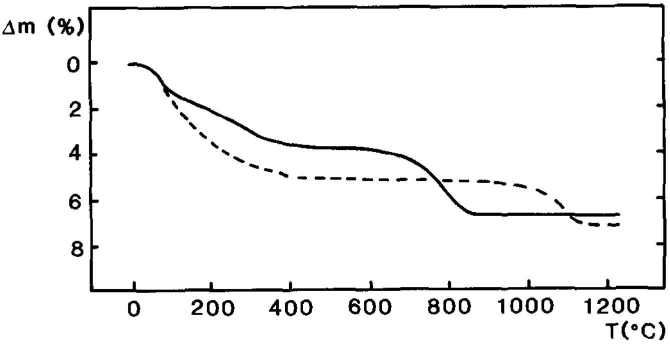

Figure 3. TG curves for samples prepared from $TiCl_4$ on muscovite (28 % TiO_2) (solid line) and on phlogopite (32 % TiO_2) (broken line).

der made from sulfate solution (Fig. 2) shows, however, a second decomposition step (9 %) at 550–750 °C. This indicates that a small amount of sulfate is coprecipitated during the process. Calculations from the weight changes give to the $TiO_2:H_2O:SO_3$ ratio values of 1:0.61:0.11.

The TG curves of the pigment samples prepared from $TiCl_4$ on mica contained two steps, the first between 50 and 400 ° corresponding to the dehydration of TiO_2 precipitate and the second the dehydration of the substrate mica (Fig. 3). Calculating from weigth loss between 50 and 400 °C (13.9 - 15.8 % from the amount of film precipitate) and by comparing to the amount of Ti-solution added in the deposition and found by AAS-measurements in the final pigments the formula of the precipitate can be confirmed as $TiO_2 \cdot nH_2O$ where n = 0.76–0.86. This means that in the presence of mica the TiO_2 precipitate contains only half of the water content of unsupported powder. The reproducibility in the precipitate composition was good. When the formula of the precipitate is known the TG measurements can be applied in the determination of TiO_2 amount in the pearlescent pigments. The temperature ranges and weight losses observed in the second steps above 700 °C correspond well to those recorded for pure muscovite and phlogopite micas. On mica substrates after drying

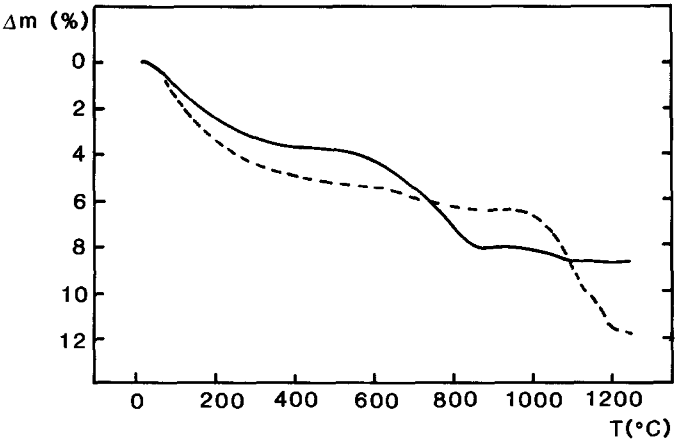

Figure 4. TG curves for samples prepared from $TiOSO_4$ by the constant pH process on muscovite (31 % TiO_2) (solid line) and on phlogopite (20 % TiO_2) (dotted line).

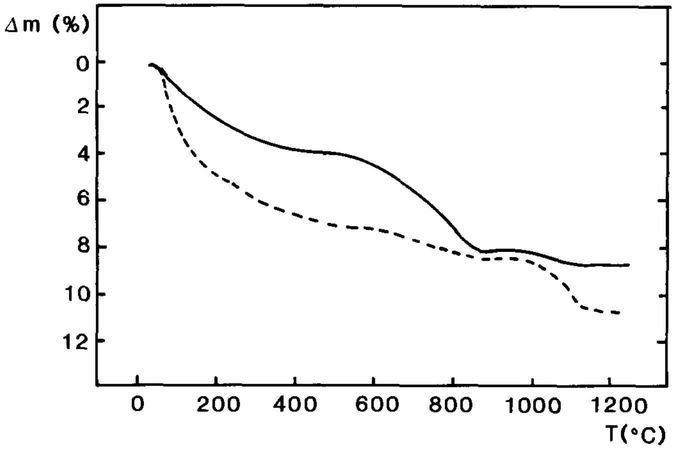

Figure 5. TG curves for samples prepared from $TiOSO_4$ by the boiling process on muscovite (25 % TiO_2) (solid line) and on phlogopite (20 % TiO_2) (broken line).

at 100 °C peaks of anatase modification appear in the XRD pattern.

The precipitates processed by the constant pH and boiling method from $TiOSO_4$ showed similar dehydration behaviour. In sulfate samples a difference exists in substrates used. The TG curves of the mica supported samples prepared by the sulfate processes showed typically three stages locating at 50-400, 625-850 and 995-1055 °C (Figs. 4,5). On muscovite the weight change in the first step in similar (14-15 % from the amount of the precipitate) to that found in samples prepared from $TiCl_4$. The second step at 625 - 850 °C indicates the decomposition of sulfate. In unsupported powders this decomposition occurs at slightly lower temperature (Fig. 2) [12]. The weight change observed corresponds to the TiO_2:SO_3 ratio of 1:0.15.

On phlogopite the samples precipitated from $TiOSO_4$ showed larger total weight loss (11-12 %) than those on muscovite (9 %). In addition, the TG behaviour of samples from constant pH and boiling process had some differencies. The samples from boiling process lost 7 % of its weigth between 50 and 500 °C which corresponds 35 % of the weigth of TiO_2 precipitate. This indicates that the water content of the precipitate is higher ($n = 2.5$ in $TiO_2 \cdot nH_2O$) than in samples prepared by the other processes. The weight change at 600-900 °C gives to the $TiO_2:SO_3$ ratio a value of 1:0.12. According to the TG curves the precipitates from constant pH process contain 1.6 water molecules. The curve has, besides a small sulfate decomposition step, an exceptional large weight decrease above 1000 °C. This may indicate that sulfate is released only at high temperatures or slight damaging of the mica during the sulfate process.

The DTA curves below 800 °C showed endothermic peaks for the dehydration of $TiO_2 \cdot nH_2O$ and the release of sulfur oxides. Above 800 °C the baseline begun to raise and the detection of the high temperature peaks was difficult.

The decomposition of the the micas at high temperatures destroy their plate-like structure. This is fatal for the pearlescent pigments since their optical properties rely on the flat substrate. In fabrication of TiO_2-mica pigments the optimum annealing temperature depends on the mica and precipitation process used and must be carefully studied for each material combination.

4. CONCLUSIONS

Thermoanalytical measurements are rarely used in studies of thin films. In this work these methods could be used because the samples consisted of mica powder coated by a TiO_2 precipitate and thus could be handled as usual powders. The TA measurements yielded useful data and the following four properties of the pigment precursors could be characterized: (i) the amount of TiO_2 precipitate on the mica, (ii) the water content of the precipitate, (iii) the titanium source chemical and precipitation process used and (iv) the mica substrate used.

5. REFERENCES

1 L.M. Greenstein, Pigment Handbook, Vol. 1 P.E. Lewis (ed.), John Wiley & Sons, New York 1988.
2 A. Dassler, A. Feltz, J. Jung, W. Ludwig and E. Kaisersberger, J. Therm. Anal., 33 (1988) 803 and references therein.
3 P. Eskelinen, J. Solid State Chem. In press.
4 P. Eskelinen, M. Ritala and M. Leskelä, J. Solid State Chem. In press.
5 P. Eskelinen, J. Solid State Chem. Submitted.
6 G.V. Jere and C.C. Patel, J. Sci. Ind. Res., 20B (1961) 292.
7 C. Heitner-Wirguin and A. Albu-Yaron, J. Inorg. Nucl. Chem., 28 (1966) 2379.
8 D. Vivien, J. Livage and C. Mazieres, J. Chim. Phys. Physicochem. Biol., 67 (1970) 199.

9 V. Balek, Therm. Anal. Proc. Int. Conf. 4th, Vol. 2, I. Buzas (ed.), Heyden, London 1975, p. 551.
10 A. Przepiera, M. Jablonski and M. Wisniewski, J. Therm. Anal., 36 (1990) 2135.
11 E. Aitta, M. Leskelä, J. Moilanen and K. Jyrkäs, J. Chem. Tech. Biotechnol., 37 (1987) 73.
12 F. Imoto and S. Kaneko, Kogyo Kagaku Zasshi, 74 (1971) 591.