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New Titanium Precursors for Manufacture of Colored Pigments

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ABSTRACT

Buff pigments obtained by introducing colored impurities (Cr^{3+}) in the TiO_2 rutile lattice are usually prepared by solid state synthesis route. The final optical aspect of the material depends mainly on the possibility to observe the formation during the thermal process of a homogeneous solid solution. By looking accurately at the processes occurring during the thermal treatment, it has been demonstrated that the homogeneity of the solid solution depends on the rutilization kinetic of the titanium precursor. The higher the rutilization temperature the better the pigment quality. These technical data have been used to develop a new generation of titanium precursors suitable for high quality pigment manufacturing. © 1998 Elsevier Science Ltd

Keywords: titanium precursor, pigment, rutilization.

INTRODUCTION

Rutile TiO_2 doped with trivalent chromium is a well established inorganic color compound used in the pigment industry [1]. When Cr^{3+} atoms are introduced in the rutile structure we can observe the formation of two absorption bands in the visible responsible for the buff color. Since the final optical aspect of the pigment is essentially related to the intensity and shape of these bands, some relationships can be expressed between the nature of the solid solution $(Ti_{1-2x}Cr_xSb_x)O_2$ and the optical response of the pigment [2] (antimony atoms are introduced in the crystal to prevent the formation of vacancies by a charge compensation process).

Three parameters are of major importance:

— The amount of chromium introduced in the lattice, which governs the color tone;

— The phase purity, as unreacted Cr_2O_3 reduces the pigment color strength; and
— The dispersion of the dopant in the crystal matrix. For reliability purpose, the dopant has to be homogeneously dispersed.

Since these pigments are currently prepared by solid state reaction, the control of these three parameters depends upon the reactivity of the precursor salts and has to be done through a careful monitoring of the firing process performed at high temperature.

Investigation of the thermal behaviour of various titanium dioxide samples has been performed to describe the existing relationships between the nature of the precursor and the optical quality of the pigment. We have used these results for the development of a special grade suitable for the formation of the most homogeneous solid solution with chromium by solid state synthesis.

SAMPLE PREPARATION

The samples are prepared by solid state synthesis. The titanium salt is mixed with Sb_2O_5 (Aldrich Chemical Company) and Cr_2O_3 (Prolabo). Before making a pressed pellet (1 T cm^{-2} during 30 s) the powder is manually crushed in a mortar. The pellet is fired in a gold crucible for 10 h at 900°C under pure oxygen atmosphere. After firing, the pellet is ground to a powder, and heated in a silica crucible for 12 h at 950°C under air.

The optical behaviour of the powder has been characterized in the 380–780 nm range with a spectrophotometer (Pacific Scientific) equipped with an integrating sphere.

RESULTS

Color vs Cr content

To identify the formation of a solid solution, Vegard's law is commonly used, describing when applicable the evolution of the cell volume as a function of the amount of dopants introduced in the crystal. In our case this approach is not valid since the ionic radii of the various species involved in the colored phase are very close (Ti^{4+} = 0.605 Å, Cr^{3+} = 0.615 Å, Sb^{5+} = 0.610 Å) [3], and parameter variation cannot be detected through normal X-ray diffraction analysis.

In order to verify the solid solution formation during the chemical process used to prepare the samples, we have studied the existing relationships between the powder reflectivity at 700 nm and the dopant amount. The Kubelka-Munk approach has been used to calculate (K/S) for various x values in the

$(Ti_{1-2x}Cr_xSb_x)O_2$ system, as illustrated in Fig. 1. Since the particle size is x independant, we assume that the scattering coefficient S does not vary with x, and then the $K/S(\lambda)$ factor must be a linear function of the amount of absorbing species x introduced in the crystal [4]:

$$K/S(\lambda) = \varepsilon(\lambda)\xi$$

where $\varepsilon(\lambda)$ is the molar absorption coefficient.

In these conditions the linearity observed in the studied range $0.005 < x < 0.12$ between K/S and x confirms that chromium and antimony cations are involved in a TiO_2 based solid solution that can be expressed as $(Ti_{1-2x}Cr_xSb_x)O_2$.

One can thus conclude that the proposed procedure to prepare the samples is suitable to observe the formation of a solid solution between the oxides.

Color evaluation as a function of the quality of the titanium dioxide involved as a precursor

Colored powders have been prepared with two different titanium dioxides, A: anatase + traces of rutile, B: pure anatase. The reflectance spectra are plotted on Fig. 2 for $x = 0.06$ and the color coordinates expressed in the CIELab system are reported in Table 1.

From these data it is clearly established that the final quality of the pigment strongly depends on the nature of the titanium dioxide used as the raw material: a drop of 10% in the reflectance of the pigment for sample A at 625 nm is the reason for a strong decrease in the L, a and b values, making the pigment unacceptable for industrial use.

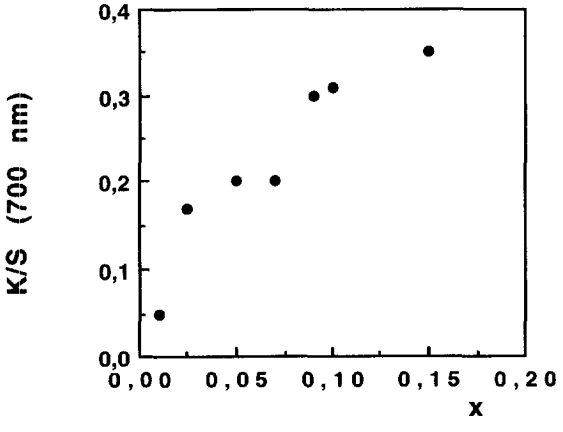

Fig. 1. K/S vs atomic chromium content x in TiO_2 rutile structure.

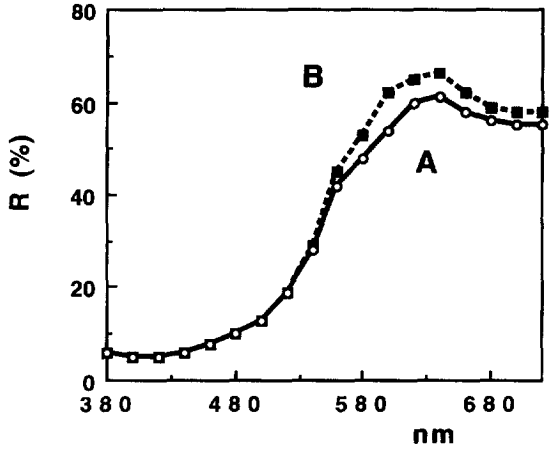

Fig. 2. Reflectance spectra measured between 380 and 720 nm on powder samples.

TABLE 1
Color Coordinates Measured On Powder Samples

Sample	*L*	*a*	*b*
A	66.0	18.2	55.3
B	68.5	21.7	59.8

Thermal behavior of the precursors

In order to explain the differences expressed above, and since the optical quality of the pigment depends mainly upon the possibility during the thermal process to create an homogeneous solid solution, we investigated the behaviour of the titanium dioxide during a thermal treatment. A DTG analysis was performed to investigate the decomposition of the titanium dioxide between 0 and 1000°C. No significant difference between the two samples was observed.

Finally, the crystal structure evolution during heating was determined by X-ray diffraction. The rutile content evolution with temperature is plotted in Fig. 3:

- For temperatures below 650°C, both samples crystallize in the anatase form.
- At intermediate values $650 < T < 1100$°C the rutile/anatase ratio depends on the nature of the raw material. For sample A the rutile structure appears at 700°C and at 900°C the powder has been totally transformed into rutile structure. In the case of sample B, traces of rutile are detected only at 1000°C. The transformation is not complete

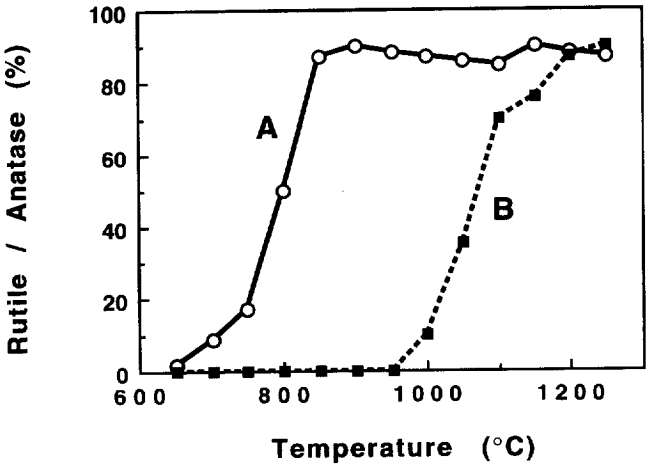

Fig. 3. Rutile formation kinetic. The rutile–anatase ratio has been determined by X-ray measurements performed on powder samples.

before 1150°C. These observations clearly demonstrate that the rutile formation kinetic differs between the two studied samples.

DISCUSSION

In order to control the homogeneity of the dopants dispersed into the matrix during the solid state process, the thermal treatment needs to be adjusted to ensure a complete diffusion of the dopants, which results in optimum optical properties. The right choice for the thermal treatment depends on the thermal diffusivity of the elements into the matrix phase.

In the case of sample B: Cr and Sb diffuse during the synthesis process in the anatase structure to form a complete solid solution in which the dopants are well dispersed into the particles. The pigment formation is complete through the transformation of the anatase structure into rutile. The complete dispersion of dopants ensures a unique optical quality.

In the case of sample A, we suggest that when the rutile appears at lower temperature (650°C) the thermal diffusivity of the dopants is too low. In the 650–900°C temperature range rutile doped particles are formed, in which the dopant amount depends on the temperature at which the structure modification (anatase–rutile) is observed. Finally the pigment is composed of particles with various amounts of dopants and thus inhomogeneous optical properties. Among them, particles with high chromium content strongly absorb light for wavelengths greater than 600 nm, which might explain the

lower reflectance observed in sample A compared to B for the long wavelengths.

CONCLUSION

Through these investigations we have identified the need to control the thermal behaviour of the precursor (rutilisation kinetic) to ensure the formation, during the pigment synthesis process, of a homogeneous colored solid solution.

From these data we have prepared at the industrial scale two grades of titanium dioxide:

— powder: G5; and
— colloidal suspension: Sol S-5-300.

These two precursors are now available and will allow pigment manufacturers to get a perfect buff color.

The physical characteristics of the available products are listed below:

— anatase phase (100%);
— large surface area (S.A. $> 250\,m^2\,g^{-1}$);
— high purity (main impurity is sulfate is lower than 0.6% in weight); and
— low anatase–rutile kinetic transformation rate.

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