JOURNAL OF MATERIALS SCIENCE 16 (1981) 1680–1688

Surface properties of TiO_2 modified with zinc ions

FABIO GARBASSI, EMILIANO MELLO CERESA
Istituto G. Donegani SpA, Via G. Fauser, 4 - 28100 Novara, Italy
MARIO VISCA
Centro Ricerche SIBIT, Piazza Donegani 5/6 15047 Spinetta Marengo, Italy

The surface properties of TiO_2 modified with zinc ions have been studied. Zinc ions mainly segregate at the surface and their removal occurs at acid pH, while at basic pH both the bulk and the surface zinc contents are not affected. Different surface oxygen species were observed and identified: the species at 529.7 eV, is attributed to lattice oxygen ions, the others, at higher energies, are oxygen-containing groups due to surface hydration. A direct correlation was found between the surface zinc concentration and the photostability of the TiO_2 samples.

1. Introduction

The rutile form of titanium dioxide is the most important white pigment. Two different industrial processes, the sulphate and the chloride one, are used in manufacturing TiO_2 bases which, generally, are modified during the process with alumina, silica or other materials. These materials, in the form of coatings, are used to improve the optical and rheological performances of the products.

Knowledge of the surface characteristics of TiO_2 bases is of particular importance because these properties play an important role in determining the interactions between the surface and the aqueous medium into which TiO_2 must be dispersed for the deposition of the coatings. Furthermore, the properties of the surface species influence the physical behaviour of the base material as regards the photo-activity. In fact, it is well known that TiO_2 exposed to light of certain wavelengths exhibits phototropy, i.e. darkening in sunlight, returning to white in the dark [1]. Such photo-activity produces photochemical reactions in paint media and films, involving the pigment and the vehicle which are responsible for the degradation of finished products [2].

The present investigation deals with the surface behaviour of different commercial "sulphate base" titanium dioxide pigments, modified with zinc ions. The zinc ions are added before calcination; they enhance the rutile formation rate, prevent the reduction of titanium dioxide during calcination and reduce the photo-activity of the material [3, 4].

Within this framework, particular attention has been paid to the determination of the surface characteristics of TiO_2 using X-ray photoelectron spectroscopy (XPS) and to the role of the zinc species on the enhancement of the TiO_2 photostability.

2. Experimental Procedures

2.1. Materials

Three different commercial uncoated rutile samples (Samples A, B and C) were studied. They were obtained via the sulphate process starting from different ores.

The preparation process consists of the digestion of the starting ore in concentrated sulphuric acid, to obtain soluble iron and titanium sulphates. After iron sulphate removal by crystallization, titanium dioxide was obtained by thermal hydrolysis of the titanium (IV) ions in a highly acidic solution. Before calcination, seed nuclei with a rutile structure were added to the anatase pulp together with zinc and potassium salts and phosphoric acid. The system was then heated in air at about 900° C to form rutile particles of suitable size and morphology. The main characteristics of titania bases are shown in Table I.

0022–2461/81/061680–09$02.90/0

TABLE I Characterization of titanium dioxide samples

Sample	Specific surface area ($m^2 g^{-1}$)	X-ray diffraction	Average particle diameter (μm)	ZnO content (wt%)
Rutile A	5.9	R* + $ZnTiO_3$ (~ 1.5 wt%)	0.21	1.06
Rutile B	6.0	R + $ZnTiO_3$ (~ 2.0 wt%)	0.23	1.41
Rutile C	6.0	R + $ZnTiO_3$ (~ 1.5 wt%)	0.26	1.05

*R ≡ rutile.

X-ray diffraction (CuKα radiation) indicated the presence of two crystalline phases in the samples: rutile and zinc metatitanate ($ZnTiO_3$) with an ilmenite type structure [5]. Since the high concentration of Nb in Sample B, due to the particular starting ore, could cause a darkening effect in the final product, zinc oxide was added to it in a higher amount [6].

Specific surface areas were determined by low-temperature N_2 adsorption using the BET technique. Electron micrographs, obtained using a Philips EM-300 microscope, showed that all the particles have an ellipsoidal shape. The mean diameter of the particles, measured using a Zeiss TGZ-3 particle size analyser, was found to be about 0.2 μm, with a rather broad size-distribution. The bulk zinc content was determined by atomic absorption spectroscopy with a model 503 Perkin Elmer spectrophotometer after dissolution of the materials.

Rutile powders were subjected to leaching treatment at different pH values in order to obtain three series of samples characterized by different amounts of Zn (Table II). These samples were labelled A, B and C with a figure representing the specific leaching treatment. 25 g of titanium dioxide were suspended in 1 l of double-distilled water; HNO_3 or NaOH (AR grade solutions) were used for pH adjustment. The slurries were shaken for 30 min at 25° C, filtered and washed with double-distilled water. Samples were then dried at 110° C for 8 h.

Zinc concentrations were measured both in the dried samples and in the filtered solutions. The slight increase in the specific surface area observed with the decrease of leaching pH was presumably associated with the roughness of the oxide surface induced by the leaching treatment [4].

2.2 XPS measurements

A Physical Electronics, Inc. (PHI) system equipped with a Douple-pass Cylindrical Mirror Analyser Model No. 15-255G was used for XPS measurements. Powder samples were inserted in In foil (Goodfellow, 99.999%) before analysis [7]. O1s, Ti2p and Zn2p photoemission peaks were collected under high resolution conditions (pass energy 50 eV), using a MgKα source at a power of 400 W. A flood electron gun was used in order to correct electrostatic sample charging.

Data acquisition and storage were carried out using a PDP 11/50 computer (Digital Equipment Corp.) connected to the spectrometer. 10 to 30 runs were averaged for each spectrum depending on its intensity and background noise. Background subtractions were performed using a non-linear background function [8], while smoothing was carried out using a band-pass filter system. More details on these procedures are reported elsewhere [9].

Smoothed peaks were fitted by means of one or more Gaussian curves (a peak shape which satisfactorily describes the experimental profiles), by using a routine which optimizes the position in the energy scale, the intensity (height) and the full width at half maximum (FWHM). Atomic surface concentrations, C_x, were determined by correcting the peak intensities, I_x, obtained by numerical integration, for the corresponding elemental sensitivity factors, f_x [10], which take into account the photoelectric cross-section and the dependence on the kinetic energy of the escape depth of electrons and of the analyser efficiency:

$$C_x = \left(\frac{I_x/f_x}{\Sigma I_n/f_n}\right) \times 100. \qquad (1)$$

2.3. Photo-activity measurements

The photochemical reactivities of TiO_2 samples were determined by evaluating their relative darkening, in comparison with a commercial weather-stable TiO_2 pigment (Montedison RS52), using an original Hanau Quarzlampen Xenotest 150, equipped with a Xenon arc lamp of 1 500 W and 180 000 Lux of radiant intensity, whose spectral energy distribution corresponds well with that of direct sunlight.

TABLE II Bulk properties of titanium dioxide samples obtained after leaching treatments

Sample	pH	ZnO content (wt%)	Zn/Ti (atoms)	X-ray diffraction	Specific surface area ($m^2 g^{-1}$)
Rutile A					
A1	10.5	1.06	0.0105	R* + $ZnTiO_3$ (traces)	5.7
A2	8.0	1.04	0.0103	R + $ZnTiO_3$ (traces)	5.9
A3	6.5	0.82	0.0081	R + $ZnTiO_3$ (~ 1.5 wt%)	6.1
A4	4.5	0.60	0.0059	R + $ZnTiO_3$ (~ 1.5 wt%)	6.4
A5	2.0	0.47	0.0046	R + $ZnTiO_3$ (< 1.5 wt%)	6.5
A6	1.0	0.40	0.0036	R + $ZnTiO_3$ (traces)	6.5
Rutile B					
B1	10.5	1.41	0.0140	R + $ZnTiO_3$ (traces)	5.9
B2	8.0	1.36	0.0135	R + $ZnTiO_3$ (traces)	6.2
B3	6.5	1.08	0.0107	R + $ZnTiO_3$ (~ 2.0 wt%)	6.2
B4	4.5	0.80	0.0079	R + $ZnTiO_3$ (~ 1.5 wt%)	6.3
B5	2.0	0.66	0.0065	R + $ZnTiO_3$ (< 1.5 wt%)	6.3
B6	1.0	0.62	0.0061	R + $ZnTiO_3$ (< 1.5 wt%)	6.5
Rutile C					
C1	10.5	1.05	0.0104	R + $ZnTiO_3$ (traces)	6.0
C2	8.0	1.03	0.0102	R + $ZnTiO_3$ (traces)	6.0
C3	6.5	0.87	0.0086	R + $ZnTiO_3$ (~ 1.5 wt%)	6.0
C4	4.5	0.59	0.0058	R + $ZnTiO_3$ (~ 1.5 wt%)	6.4
C5	2.0	0.49	0.0048	R + $ZnTiO_3$ (< 1.5 wt%)	6.4
C6	1.0	0.45	0.0044	R + $ZnTiO_3$ (< 1.5 wt%)	6.8

*R = rutile.

The samples were prepared as follows: TiO_2 powders (0.5 wt%) were mixed and dispersed in 70 g of stabilized PVC and 30 g of dioctylphthalate at 150° C for 5 min. The paste obtained was pressed and moulded into plasticized opaque sheets from which samples of uniform thickness, 3.0 cm × 1.2 cm in size were cut.

Samples were exposed to Xenon radiation for 500 h, corresponding to an exposure to sunlight of about 1 000 h at 45° C and 60% relative humidity.

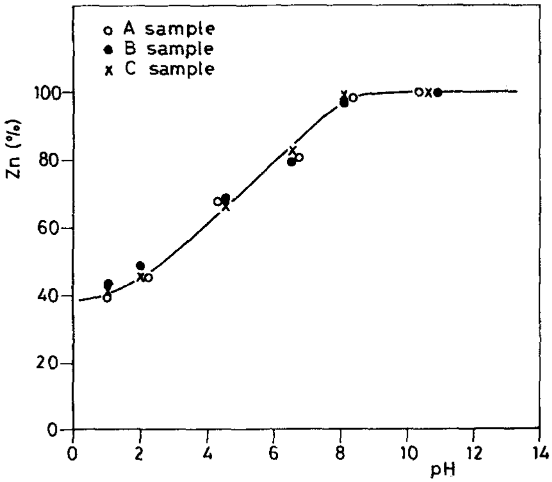

Figure 1 Bulk zinc content of the TiO_2 samples after different leaching treatments.

Samples were then kept in the dark for 6 months and the evaluation was successively performed by considering the colour changes using a visual classification.

Due to the method used, a comparison of the different samples could be made which was not affected by the influence of the components of the material (wetting agents, plasticizers, light stabilizers, etc.) other than the TiO_2 base.

3. Results

The effect of the leaching treatments on the Zn content of the products, Samples A, B and C, is shown in Fig. 1. The amount of zinc remaining in the bulk at different pH values was referred to as a percentage of the original content of the untreated samples. The initial bulk zinc content did not change at high pH, while it dramatically decreased on increasing the acidity of the treatment up to pH = 1, at which point only 40% of the initial zinc content was still in the TiO_2 samples. In this way three series of samples, from the same base products were obtained containing decreasing amounts of zinc.

In Table III the surface compositions (at %) in the three different TiO_2 series are reported. For the sake of simplicity the carbon contamination was neglected from the calculation, as well as the

TABLE III Surface chemical analyses (at%) for the three series of TiO_2 samples

Sample	O1s	Ti2p	Zn2p	Zn/Ti (atoms)
A	74.4	15.6	10.0	0.64
A1	70.5	18.0	11.5	0.64
A2	67.4	19.9	12.7	0.64
A3	72.8	20.0	7.2	0.36
A4	77.6	19.3	3.1	0.16
A5	80.3	17.9	1.8	0.10
A6	81.6	17.9	0.5	0.03
B	73.0	14.8	12.2	0.82
B1	70.4	16.8	12.8	0.76
B2	67.3	16.2	16.5	1.02
B3	70.9	17.7	11.4	0.64
B4	72.3	21.7	6.0	0.28
B5	74.8	23.0	2.2	0.10
B6	75.6	23.6	0.8	0.03
C	73.4	16.6	10.0	0.60
C1	68.1	16.9	15.0	0.89
C2	67.5	16.9	15.6	0.92
C3	71.6	18.4	10.0	0.54
C4	76.4	19.9	3.7	0.19
C5	77.1	21.8	1.1	0.05
C6	76.3	22.9	0.8	0.03

observed small quantities of K (not more than 1%). No other elements were found in all samples.

It appears that the surface content of Zn is definitely higher than that found in the bulk and that leaching treatment, in increasingly acidic media, progressively reduces the surface Zn content. This result, which correlates well with the chemical analysis (Table II), is reported in Table III as the Zn/Ti ratio and is illustrated in Fig. 2, where the Zn/Ti surface atomic content ratio is displayed as a function of the pH level of the leaching solution. The treatment at high pH values does not affect, albeit it sometimes increases, the zinc content on the surface with respect to that found on untreated samples. To a first approximation the behaviour of the three series of samples is very similar.

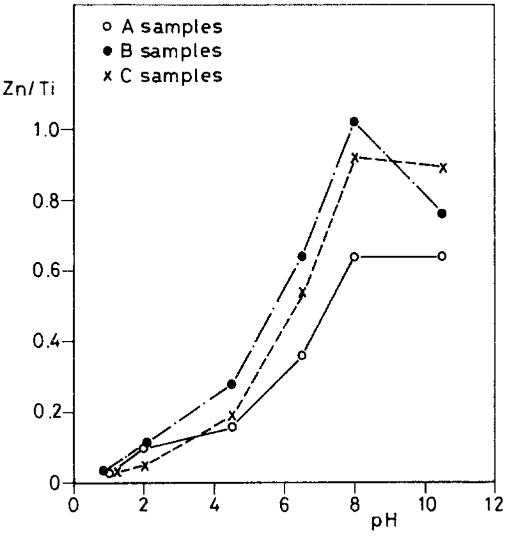

Figure 2 Zn/Ti surface atomic ratio against pH of the leaching solution for the three series of TiO_2 samples. Values for the untreated samples: A–0.64, B–0.82 and C–0.60.

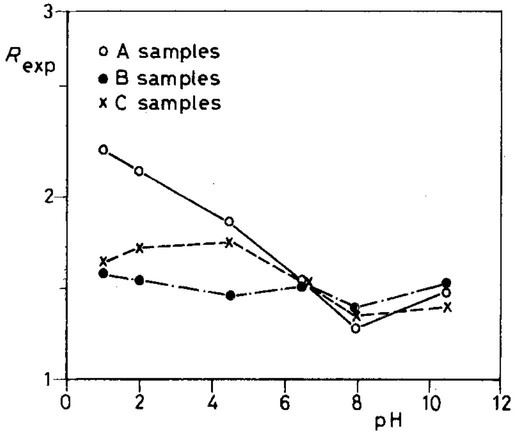

Figure 3 R_{exp} surface atomic ratio against pH of the leaching solution for the three series of TiO_2 samples. Values for the untreated samples: A–1.81, B–1.75 and C–1.70.

Surface oxygen concentrations were always found to be higher than expected on the basis of stoichiometric considerations. In Fig. 3 the experimental ratios $R_{exp} = (n_0 z_0 q)/(\Sigma n_i z_i q)$ of the surface oxygen ion charge ($n_0 z_0 q$) and that of cations ($\Sigma n_i z_i q$) are reported as a function of pH, n_0 and n_i being the concentrations (at%) of surface oxygen ions and cations, respectively, and $z_0 q$ and $z_i q$ their charges.

Results, from various TiO_2 bases, were very similar at a pH > 6.5, while in more acid solutions the pigments behaved differently. A minimum was also found at pH = 8.0 with respect to the untreated samples (Samples A, B and C), which show very similar values. The constancy of R_{exp} in Samples of B must also be noted. Values of R_{exp} higher than 1 suggest the presence of O-species on the surface other than the oxide species belonging to TiO_2 or ZnO [11]. The presence of several O-containing species, due to the hydration of TiO_2 surfaces has already been demonstrated by infrared (i.r.) spectroscopy [12–14] and XPS studies [15].

The experimental profiles of the O1s peaks can be considered as the sum of various contributions at several binding energy values. The modification of the peak profiles in samples subjected to different leaching treatments suggested also that the relative contributions of the different oxygen species to the whole peak should vary as a function of the "history" of each sample. Oxygen 1s photoemission peaks were submitted to a very accurate analysis, dissociating each experimental profile into several Gaussian components. No constraints were introduced into the fitting procedure, with the aim of limiting operator influence. In this way, all peaks (except for three) were found to originate from three Gaussian contributions. Some examples of such fittings are reported in Fig. 4.

Average binding energies, E, and FWHM values of the various components, with their estimated errors, are shown in Fig. 5. The occurrence in the different samples is also reported.

A peak at $E = 529.65$ eV is always present, generally associated with other peaks exhibiting a chemical shift of $+1.8$ and $+3.2$ eV. On all samples leached at $\mathrm{pH} = 1$ such chemical shift values are reduced to $+0.85$ and $+2.5$ eV, respectively, while on some samples treated in a basic medium a component at lower binding energy appears (-1.0 eV). This behaviour is typical of Samples A and B only. The abundance of each O1s component after the different treatments is shown in Fig. 6.*

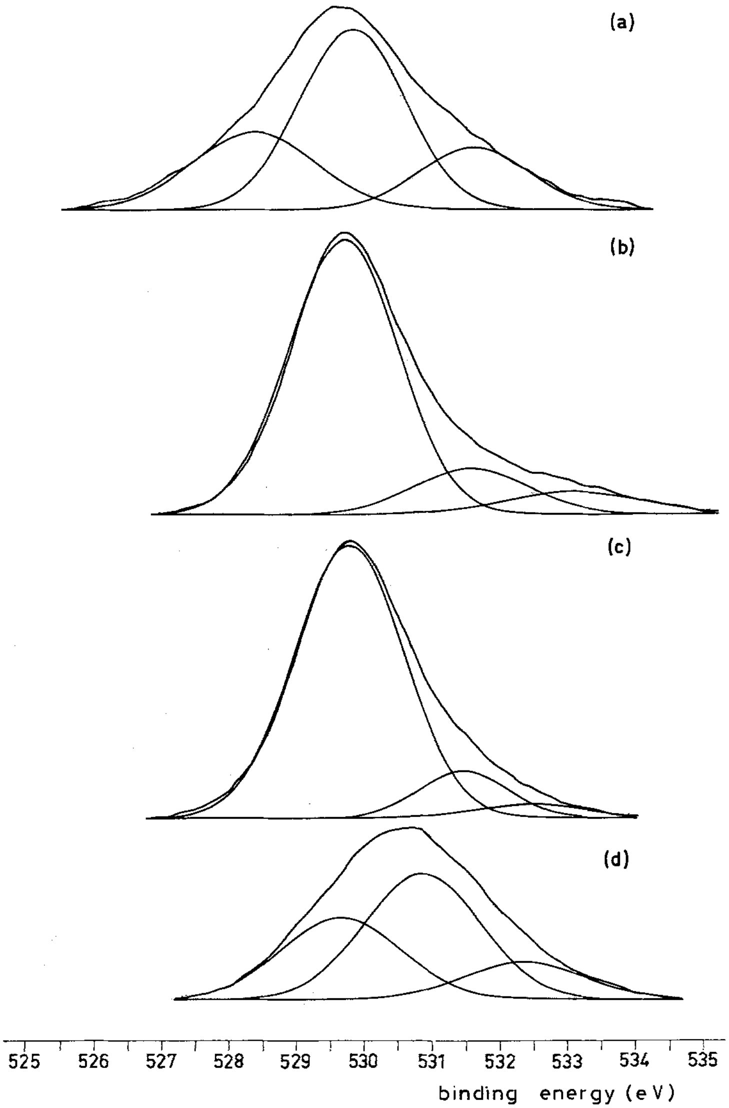

Figure 4 Some examples of O1s photoemission peaks of TiO_2 samples, dissociated into different components by a computer technique: (a) A1 sample, (b) A4 sample, (c) A5 sample, (d) A6 sample.

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* The amount of the species which sometimes appeared under basic conditions, at 528.65 eV, was summed, for reasons that will be explained in the discussion section, to that of the main species at 529.65 eV.

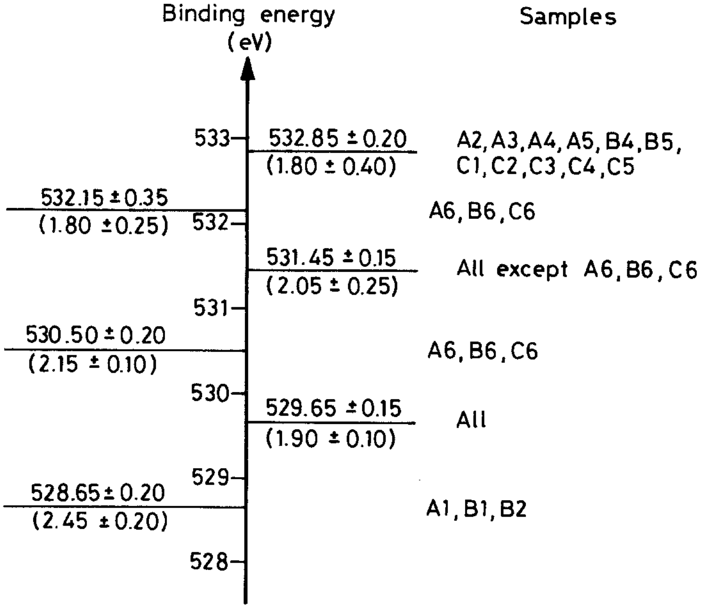


Figure 5 Binding energies and FWHM of the various components of O1s peak and their occurrence in the different TiO_2 samples.

The greatest variation in the relative amount of oxygen species occurs when the acidity of the leaching solution is changed from pH2 to pH1. It must however be noted that in this case the two oxygen species at higher binding energies move to a lower energy value. Another point that can be observed here is the remarkable stability of the oxygen on the surface of Samples C.

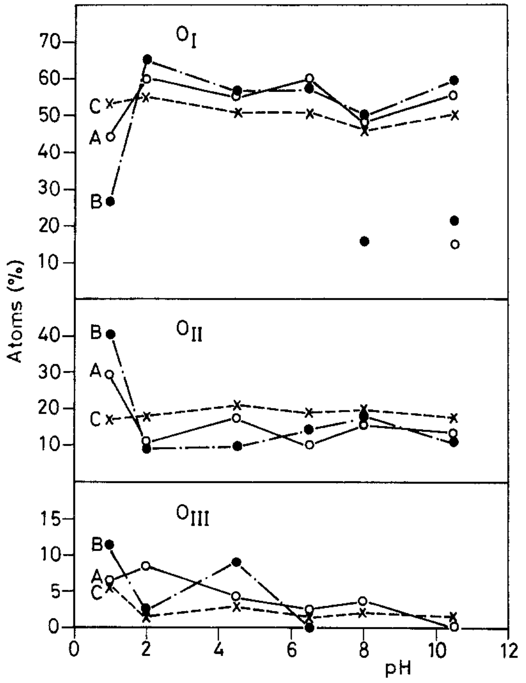


Figure 6 Abundance of each O1s component against pH of leaching solution for the three series of TiO_2 samples O_I (b.e. 529.7 eV), O_{II} (b.e. 531.5 eV), O_{III} (b.e. 532.9 eV).

$Ti2p_{3/2}$ peaks occurred in all samples at 458.5 ± 0.1 eV with a spin–orbit splitting of 5.67 ± 0.05 eV, in good agreement with previous measurements [10]. Full widths at half maximum (FWHM) of 1.89 ± 0.05 and 2.62 ± 0.12 eV were found for the $2p_{3/2}$ and $2p_{1/2}$ components, respectively. Meaningfully larger values for $2p_{3/2}$ were found in some B samples treated in basic (B1 = B2 = 2.02 eV) or strongly acidic media (B6 = 2.57 eV). Good fits were generally obtained only when the presence of a small peak between the two main ones, and a shoulder in the low-energy side of $Ti2p_{3/2}$ were included. A typical four-Gaussian fitting is compared with the experimental profile in Fig. 7. Due to their low intensity, which probably increases background subtraction errors, the calculated parameters of such peaks have a larger uncertainty than the previous ones. They have a binding energy (b.e.) of 456.75 ± 0.20 and 461.05 ± 0.35 eV, respectively, with FWHMs of 1.84 ± 0.43 and 2.70 ± 0.40 eV. They contribute to the total intensity by a fraction of 3 to 9% each. The higher b.e. species occurs more frequently and has a larger intensity than the other.

$Zn2p_{3/2}$ peaks were found at 1021.8 ± 0.20 eV in good agreement with literature data [10]. Its FWHM was 2.28 ± 0.10 eV.

Photostability results, determined by examining the colour of the pigmented plastic films after set

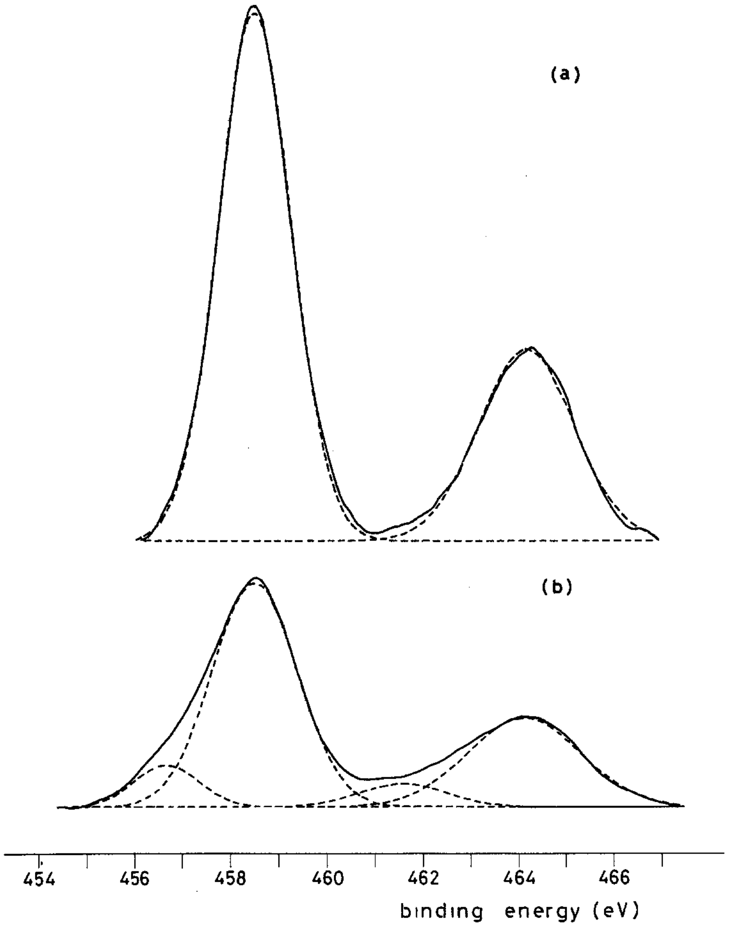


Figure 7 Ti2p$_{3/2}$ photoemission peaks of TiO$_2$ samples: (a) typical experimental profile, (b) four-Gaussian fitting (Sample B6).

periods of time by a visual classification, are shown in Table IV.

4. Discussion

It is well known that metal oxide surfaces, TiO$_2$ among them, hydrate under normal conditions, and show both physisorbed water, via hydrogen bonding, and different OH groups resulting from water chemisorption [16]. This hypothesis is confirmed by the R_{exp} surface values, reported in Fig. 3, which, since they are always greater than 1, indicate that the surface oxygen is in excess of the amount required by the stoichiometry of the surface when considered as a mixed TiO$_2$–ZnO oxide.

The fact that the curves for Samples A, B and C exhibit essentially the same trend at pH values greater than 6.5 could be explained by considering that, at high pH values, ZnTiO$_3$ (whose presence at the surface is confirmed by X-ray diffraction analysis of the samples, see Table II) dissolves, inducing structural rearrangements. The solubilized zinc species reprecipitates, as could be inferred from examination of Fig. 1, which indicates that the bulk zinc content remains constant by varying the pH, and Fig. 2 which shows a shallow maximum in the Zn/Ti ratio at pH = 8. This conclusion is supported by the known solubility relationships of ZnO [17], which show a solubility minimum in the pH range 8.5 to 11.5. This fact gives rise to a thin layer of hydrous zinc oxide, which should modify all the physicochemical and electrokinetic surface properties of the products. The reaction model agrees with that of James and Healy [18] for the adsorption of hydrolysable metal ions at the oxide–water interface.

Although it could merely be a coincidence, it is worth mentioning that a R_{exp} value of about 1.33, observed at pH = 8, corresponds well with the theoretical value expected for a TiO$_2$–Zn(OH)$_2$ surface phase.

At pH values lower than 8, the main reaction involving the system has been shown to be the removal of zinc (see Fig. 1) paralleled by a slight increase in the surface oxygen content (see Fig. 3)

TABLE IV Degree of darkening of PVC sheets containing TiO_2 samples, after 500 h of exposure to the xenon arc lamp

Sample	Visual darkening degree
A	++
A1	+
A2	+
A3	+++
A4	+++
A5	++++
A6	++++
B	+
B1	+
B2	+
B3	++
B4	+++
B5	++++
B6	++++
C	++
C1	+
C2	+
C3	++
C4	+++
C5	++++
C6	++++
Photostable pigment RS 52	++

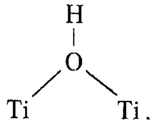
Note: + –very light brown.
++ –light brown.
+++ –brown.
++++–dark brown.

which could indicate that zinc leaching induces changes in the population of surface sites, which react with water. Apparently, the starting ore can influence the surface properties of TiO_2, as the coverage of the surface with the oxygenated species is more important in the case of Samples A than for Samples B and C.

A deeper insight into the configuration of the surface can be obtained by discussing the nature of the different oxygen species, which have been identified by dissociating the asymmetric O1s peak and are indicated by O_I (b.e. 529.7 eV), O_{II} (b.e. 531.5 eV) and O_{III} (b.e. 532.9 eV), respectively. However, the fact that both Ti and Zn species are present at the surface must be taken into account. Therefore, the surface oxygen atoms may be bound to different cationic species. Moreover, as a slight influence has been observed on the results depending on the preparation procedures, the binding energies corresponding to O_I, O_{II} and O_{III} have been averaged over all the samples examined.

In good agreement with literature data, the 529.7 eV oxygen peak must be attributed to the lattice oxygen ions O^{2-}, which are associated both with Ti^{4+} and Zn^{2+}, as true oxide oxygen species [19, 20].

The higher binding energy forms are due to surface hydration. The 531.5 eV form, representative of a looser bound state than the ordinary lattice oxygen, can be attributed to adsorbed species (O_{ads}). Consistent with the presence of water layers and OH groups on the surface, these are assigned to –Ti–OH and –Zn–OH species [20, 21]. According to Sham and Lazarus [15] this –Ti–OH species shows acid character which most likely originates from the surface oxide



Our results cannot however confirm this observation as the presence of zinc, which also contributes to the O_{II} XPS peak, makes it difficult to distinguish between the two different species which may possibly be present, one bound to titanium and the other to zinc. In the literature there is no reliable data about the acid or basic character of surface –Zn–OH groups. The third peak observed (O_{III}) must represent another adsorbed oxygen species, probably OH groups belonging to a different chemical environment. This has been previously attributed to adsorbed oxygen-containing species [22], to basic Ti–OH groups [15] and to water contamination [20]. It is difficult however to define with sufficient accuracy the relative contributions of each of the mentioned oxygen species.

Evidence for the existence of an oxygen species more strongly bound than the bulk oxygen can be inferred from the O1s peaks of the Samples A1, B1 and B2 which are asymmetrically shifted towards lower binding energy. About this oxygen species (b.e. 528.7 eV), which has never been reported before, it is impossible to tell whether it originates from a surface structure developed by interaction between ZnO and TiO_2 or whether it is due to surface impurities present on the samples. This form was considered to be a more strongly bound type of lattice oxygen, so it has been computed together with O_I species.

The binding energy shift of the minor species O_{II} and O_{III}, relative to the main O1s signal, observed in Samples A6, B6 and C6, can be attributed to composition changes caused by the decrease of the zinc surface concentration due to the leaching treatment.

The existence of the oxygen-containing surface groups bound to Ti^{4+} can also be seen from the $Ti2p_{3/2}$ peak which shows a shoulder at lower b.e., representing the hydroxylated surface Ti atoms, less positively charged than the bulk Ti species [15].

The zinc ions present in the TiO_2 lattice as solid solution do not seem to influence photostability. In fact, this species was unaffected by the surface leaching treatment whereas the photostability was found to be dependent on the pH at which the treatment was carried out. A direct relation between Zn surface concentration in the samples and photostability was found. The darkening effect was greater (minimum of stability) when the zinc removal from the surface was a maximum (samples treated at lower pH) and less (maximum of stability) when the surface concentration increased (samples treated at higher pH) with respect to the untreated products, due to the previously described mechanism of reprecipitation.

It is also worth noting that adsorbed molecular water and surface hydroxyl groups play a decisive role in the degradation process, since they allow the formation of OH^0 radicals responsible for the photocatalytic reaction at the TiO_2 surface, on exposure to ultra-violet radiation [23, 24]. A fairly good agreement has been found with such a description, in fact samples with lower R_{exp} values (smaller hydration) are less reactive to participation in the photoprocess.

Acknowledgements

The present work has been carried out with the financial support of SIBIT SpA, Milan. The authors acknowledge Professor S. Pizzini for his highly appreciated comments.

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Received 8 September and accepted 9 December 1980.