

An X-ray Diffraction Study to Determine the Effect of the Method of Preparation upon the Crystal Structure of TiO_2

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The existence of different polymorphic forms of hydrolytically prepared TiO_2 is reviewed briefly. A quantitative X-ray diffraction technique by means of a recording spectrometer for determination of rutile and anatase in mixtures of the two is described.

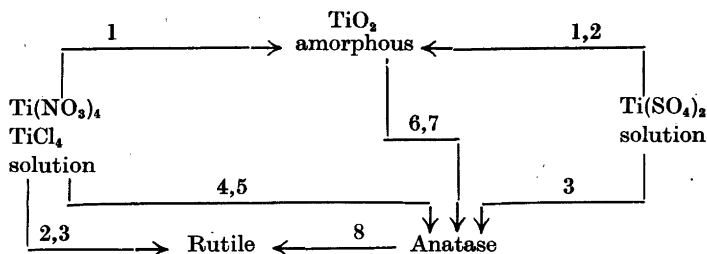
Precipitation, drying, and calcination of TiO_2 samples were carried out under varying conditions. Both sulfate and chloride solutions of titanium were used, and the products were examined by X-ray diffraction. It was observed that the initial partially dehydrated product always was amorphous, even after drying at 110°C in practically all cases. At elevated temperatures the first crystalline form of samples originating from sulfate solutions always was anatase. Direct boiling of chloride solutions produced rutile as initial crystalline product, other methods of hydrolysis resulted either in anatase or in mixtures of the two. All samples from both sulfate and chloride solutions were converted into rutile at last between 700 and 920°C , the rate of conversion being somewhat depending on the origin of the sample. No brookite was found at any step.

As is well known, titanium can be precipitated from aqueous solutions where it exists as sulfate, chloride, or nitrate either by alkaline or acid hydrolysis, the latter being usually effected by boiling. It has been observed by different workers that the appearance, physical and chemical behaviour of the precipitate largely depend on the previous treatment. The present work deals with the correlation between the crystal form of the hydrolyzed product (TiO_2) and the method of hydrolytic precipitation.

This problem has been studied by Parravano¹, among others, and he has given the following schema which outlines the different methods and resulting products.

According to Schossberger² sulfate solutions of titanium always give products which show the crystal form of anatase. This can be converted at temperatures between 600° and 1000°C into rutile. Instead of that, chloride solutions produce rutile directly; if sulfuric acid is added, an increasing amount

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1. Precipitation (alkaline hydrolysis)
2. Hydrolysis at room temperature
3. Hydrolysis by boiling
4. Hydrolysis in the presence of SO_4^{2-} or PO_4^{3-} ions
5. Hydrolysis in the presence of excess Cl^- ions
6. Dehydration
7. Moderate heating
8. Igniting

of anatase is formed. If titanium oxyhydrate was precipitated with ammonia, redissolved in HCl and precipitated again, anatase was formed. If aged in the mother liquor for a longer time and then dried at 300° , the resulting product showed a rutile crystal form. Schossberger also states that no brookite was found in any product.

Weiser *et al.*³ obtained amorphous or anatase type products by using ammonia precipitation from both sulfate, chloride, and nitrate solutions of titanium. If the hydrolysis was carried out by boiling, the precipitate from sulfate solutions was found to be anatase, and that from chloride or nitrate solutions rutile, if no excess Cl^- or NO_3^- ions were present in the latter case. Otherwise the resulting product was anatase also in this case. These workers explain that the rate of transformation of the more soluble and less stable anatase modification into the less soluble and more stable rutile modification is influenced by two opposite factors, *viz.* retardation of the transformation by an adsorbed layer of ions on the anatase which reduces its rate of solution, and acceleration of the transformation by an ionic environment in which anatase is more soluble. Anatase formed by hydrolysis of titanium chloride or nitrate solutions is transformed fairly rapidly into rutile at 100° . The change is slowed down by the presence of alkali chloride or nitrate, speeded up in the presence of excess hydrochloric or nitric acid. Further they state that anatase formed by the hydrolysis of titanium sulfate solutions is not transferable into rutile in any reasonable time even in strong sulfuric acid solution.

It is of interest to mention an inconsistency concerning this matter which can be found in the latest monograph about titanium, edited by Skinner *et al.*⁴: "Alkaline hydrolysis of TiCl_4 yields a precipitate which on drying shows the anatase structure. If hydrolysis of $\text{Ti}(\text{SO}_4)_2$ or of TiCl_4 in presence of the sulfate ion is carried out, the oxide formed on drying is rutile." — As can be easily seen, the whole matter has been reversed; in addition to that, the statement is confusing and oversimplified. The same book claims that Lashchenko

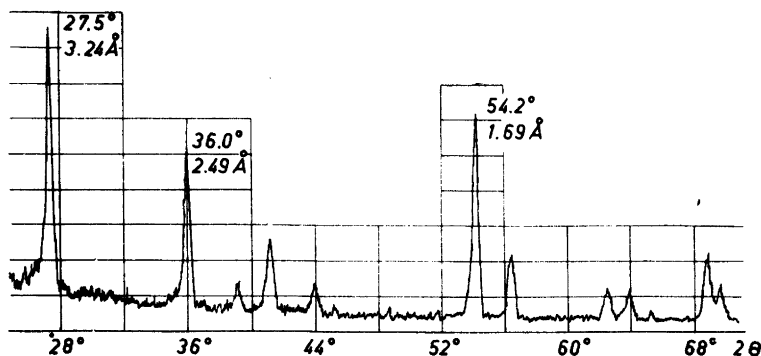


Fig. 1. A typical rutile X-ray diffraction pattern obtained by a Geiger-counter recording spectrometer using Cu K α -radiation and Ni filter. The curve is shown between the 2θ -values 25° and 70°. The 2θ -angles and corresponding values of the d-spacings are given for the principal diffraction lines of rutile.

and Kompanski⁵ have prepared brookite by dehydrating metatitanic acid. Unfortunately, we were not able to check this matter in the original paper, but the *Chem. Abstracts* reference, used also by the editors of the monograph, did not know anything about a possible brookite formation.

Inuzuka⁶ reports the formation of brookite on glass surface dipped into aqueous solution of TiCl₄ containing HCl, dried at 100° C and heated at 300–400° C for an hour.

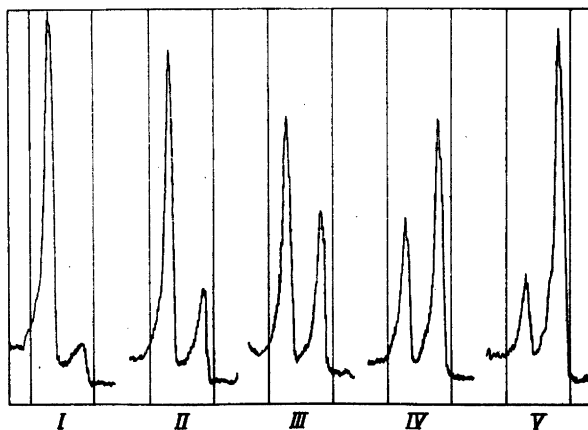


Fig. 2. X-ray diffraction records obtained from different standard mixtures. I. 12.5 % rutile, 87.5 % anatase; II. 25 % r., 75 % a.; III. 50 % r., 50 % a., IV. 75 % r., 25 % a., and V. 87.5 % rutile, 12.5 % anatase. Only the main peaks are shown, 3.51 Å for anatase (left peak), and 3.24 Å for rutile (right peak).

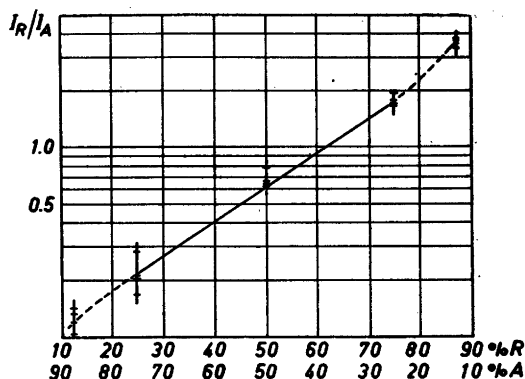


Fig. 3. Working curve for quantitative determinations of rutile and anatase in mixtures of the two. I_R intensity (height) of the rutile peak at 3.24 Å, I_A intensity of the anatase peak at 3.51 Å.

Various methods of "seeding" sulfate solutions for producing rutile directly exist in patent literature only, and they seem to lack any broader scientific basis. This author has not been able to effect a direct rutile hydrolysis from sulfate solutions by any of the numerous recommended seeding agents he tried; the moderately heated product was always anatase and changed into rutile by further ignition.

EXPERIMENTAL

In this work several methods of preparation of titanium dioxide were employed, and the calcination was carried out stepwise thus allowing the checking of the crystal form produced at the respective temperature. Ammonia precipitation was used for both chloride and sulfate solution; sodium hydroxide precipitation for chloride solution, and hydrolysis at boiling temperature for both solutions. One experiment was made using dilution technique. Table 1 contains additional information about these experiments.

X-ray technique

A North American Philips' Geiger-counter X-ray diffraction spectrometer with a strip-chart recorder was used for the anatase-rutile determinations. Cu $K\alpha$ -radiation, 30 kV, 6 mA, with a nickel filter was employed. The sample was packed into a rectangular cavity in a plastic slide, and a flat and smooth surface was formed with a spatula. The plastic slide was placed in position on the spectrometer, the goniometer arm was set to $2\theta = 72^\circ$, if the whole characteristic diffraction pattern of rutile and/or anatase was desired. For the strongest peaks only, the goniometer arm was set to 32° . In both cases, the apparatus was run at a speed of 2° per minute to about 23° . A typical rutile diffraction pattern is shown in Fig. 1.

According to Klug⁷ the degree of precision and reproducibility in a quantitative analysis of powder mixtures with the Geiger-counter spectrometer is dependent upon different factors: instrument stability and reproducibility, crystallite size of the powder, mounting of the specimen, mixing of the internal standard with the sample, etc. Absorption effects are present which usually prevent one from directly comparing line intensities of a component in a mixture with the pattern of the pure component prepared under identical conditions. This is always the case if the mixture contains components with

Table 1. Results from different hydrolysis experiments

Method of precipitation	Crystal form found at different drying or calcination temperatures						
	Room temp. Dehydrated with alcohol	110° C, 2 hrs	300° C, 1 h	500° C, 1 h	700° C, 1 h	800° C, 1 h	920° C, 1 h
Alkaline precipitation. 10 % aqueous solution of TiCl_4 added to a 1:1 diluted NH_4OH at room t.	amorphous	amorphous	anatase fairly well developed	anatase	57 % anatase 43 % rutile	rutile with tra- ces of anatase	rutile
Alkaline precipitation. 10% aqueous acid solution of $\text{Ti}(\text{SO}_4)_2$ added to a 1:1 diluted NH_4OH at room t.	amorphous	amorphous	anatase poorly developed	anatase	anatase, with tra- ces of rutile	rutile with tra- ces of anatase	rutile
Alkaline precipitation. 10 % aqueous HCl-acid solution of TiCl_4 added to a 20 % NaOH solution. Room temperature.	amorphous	amorphous	72 % rutile 28 % anatase	rutile with tra- ces of anatase	rutile	—	—
Hydrolysis by boiling a 10 % aqueous HCl-acid solution of TiCl_4 .	amorphous	amorphous, traces of rutile	rutile poorly developed	rutile	—	—	—
Hydrolysis by adding a 10 % aqueous HCl-acid solution of TiCl_4 to a large volume of boiling water.	amorphous	—	68 % rutile 32 % anatase	rutile	—	—	—
Hydrolysis by boiling a 10 % aqueous acid solution of $\text{Ti}(\text{SO}_4)_2$.	amorphous	amorphous, traces of anatase	anatase, poorly developed	anatase	anatase	—	rutile

different X-ray absorption. Mixtures of two polymorphic components, however, like anatase and rutile, usually can be analyzed directly, the intensity of the line being proportional to the concentration.

In this work standard mixtures of pure rutile and pure anatase were prepared, by milling, containing 12.5, 25, 50, 75 and 87.5 % of rutile, the rest being anatase in each case. No internal standard was added. The principal peaks of the diffraction curve representing d -spacings of 3.51 Å for anatase and of 3.24 Å for rutile are shown in Fig. 2 for all these five cases.

A working curve, presented in Fig. 3, was prepared by measuring the height of the peak from the base line using arbitrary units, here millimeters. The relation I_R/I_A (I_R intensity (height) of the rutile peak, I_A intensity of the anatase peak, respectively) was plotted against concentration on semilogarithmic paper. The curve with its evidently straight middle portion was drawn on the paper based on four different I_R/I_A values, representing four different runs, the specimen being remounted in each case. These values have also been marked on the paper. The analysis of an unknown mixture is carried out in the same way: after making a run, the peak heights are measured, I_R/I_A calculated, and the working curve gives the sought composition. As can be seen in Fig. 2, the principal peaks of these polymorphic forms are very favorably located, rather close, but not so close that they would interfere with each another. Hence, the X-ray operation itself takes only about 5 minutes.

RESULTS AND DISCUSSION

As can be seen in Table 1, an alkaline precipitation with NH₄OH gave anatase initially from both sulfate and chloride solutions. The crystal structure, however, was developed faster in the latter than in the former case with the increasing temperature, and the change into rutile took place earlier. If alkaline precipitation was carried out with NaOH, the main part of the precipitate dried at 300° C consisted of rutile, and a complete change into rutile was effected at 700° C. Hydrolysis by boiling a rather concentrated solution of TiCl₄ produced rutile directly after the amorphous state without any anatase formation. If dilution technique was used, anatase also was present at lower heating temperatures. Normal acid hydrolysis of a sulfate solution produced first anatase (after the amorphous state), a complete conversion into rutile took place between 700° and 920° C. In all cases the product partly dehydrated with alcohol and dried at room temperature was completely amorphous, and even at 110° only a very weak crystallization could be observed in a couple of cases.

The main tendency of the anatase-rutile polymorphism observed in these experiments agrees with that presented by Parravano and Schossberger (*cf.* p. 1796). It has been shown, however, that an amorphous phase always exists before any crystallization takes place, even in the case of direct rutile formation. Other deviations from this schema were also observed, such as the difference between products if the alkaline hydrolysis was carried out with ammonia or sodium hydroxide, or the existence of mixtures of both crystal forms at different calcination temperatures.

As far as the third polymorphic form of TiO₂, brookite, is concerned, all specimens prepared during this work and also during another of the same nature, described elsewhere⁸, representing a great variety of methods of hydrolysis and calcination temperatures were checked carefully for the characteristic X-ray diffraction lines of this particular substance. No traces of brookite could be found in any case, however.

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