

244. *The Production of Active Solids by Thermal Decomposition.*
*Part XIII.*¹ *The Calcination of Ion-free Hydrous Titania.*

By S. J. GREGG and M. I. POPE.

Two batches of hydrous titania have been prepared by hydrolysis of *n*-butyl titanate, one contaminated with vanadium ions but the other virtually free from foreign metal ions. Separate portions of each batch were calcined for five hours, at a succession of temperatures, and the following properties of the cooled product were determined: the specific surface by the sorption of nitrogen, the pore volume by the sorption of benzene, and the percentage of rutile and of anatase by *X*-ray examination. In both batches an accelerated rate of sintering (as indicated by loss of surface area and of pore volume) and the inception of the phase change from anatase to rutile both occur at about 650° which is probably close to the Tammann temperature of titania. This behaviour contrasts with that of the titania of Part XII (contaminated with sulphate ions) where an acceleration in sintering still occurred at the Tammann temperature but the phase change did not start till about 1050°.

In Part XII¹ the effect of heat on the activity of hydrous titania was reported. The starting material, which simulated the hydrous titania used in the industrial preparation of titania pigments, contained an appreciable percentage of ionic impurities. In view of the known effect of such impurities both on sintering behaviour and on the temperatures at which the transformation from the anatase to rutile occurs, a similar investigation has been made with a virtually ion-free titania made by hydrolysis of an alkyl titanate.

Results show that, whereas at temperatures below the Tammann region the sintering behaviour is only slightly different whether foreign ions are absent or present, yet in the absence of ions both the inception of the phase change and an acceleration of sintering—as measured by the fall in specific surface and in pore volume—take place in the region of the Tammann temperature.

EXPERIMENTAL

Materials.—Two batches of hydrous titania were prepared, the first (A) being used for some preliminary experiments, and the second (B) for the main study. Batch A was prepared from a sample of *n*-butyl titanate (containing 0.2% of vanadium) which was purified by distillation under 4 mm. pressure, the fraction boiling at 146° being collected. A 50% solution of the distillate in *n*-butyl alcohol was then hydrolysed by running it dropwise into a 5% solution of water in ethyl alcohol under nitrogen, with stirring. The gel-like precipitate was separated by decantation and washed with a large excess of distilled water; it had a pale cream colour (attributable to vanadium ions), but neither iron nor butyl alcohol was present in detectable quantities.

Batch B was prepared from a specimen of specially purified *n*-butyl titanate (Laporte Titanium Ltd.), containing less than 10 p.p.m. of vanadium, the main metallic impurity. It was hydrolysed by being added dropwise to distilled water, precautions being taken to avoid change in pH by atmospheric contamination: the water had been boiled out and cooled under nitrogen, and it was mechanically stirred in an atmosphere of nitrogen whilst the alkoxide was being added. The white gelatinous precipitate was separated by decantation and air-dried at 25°.

A "calcination series" was then prepared from each batch of hydrous titania: separate samples were heated in a silica crucible at a series of fixed temperatures (*T*) in a vertical electric furnace ($\pm 4^\circ$), the furnace being raised to *T* during 30 min. and kept there for 5 hr.; the crucible was then removed and allowed to cool in air.

The following properties of the calcined samples were examined: (1) specific surface by nitrogen adsorption at -183° , (2) phase composition and crystallite size by *X*-ray analysis,

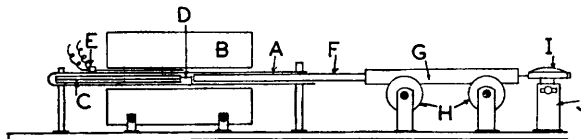
¹ Part XII, Asher and Gregg, *J.*, 1960, 5057.

(3) pore structure by benzene sorption isotherms at 25°, and (4) electron micrographs. In addition, a sample of the starting material of each batch, made into a pellet under pressure, was subjected to a steadily rising temperature, and its length measured at frequent intervals in an extensometer.

The measurements of the sorption of nitrogen at -183°, and of benzene at 25°, were carried out gravimetrically on an electromagnetic sorption balance,² housed, together with the arrangements for storing and manipulating the adsorbate, in an air thermostat kept at 25°; the sample (1–2 g.) was outgassed at 100° until the fractional rate of loss in weight fell to less than 0.1% per hour.

The proportions of anatase and of rutile were determined by means of an automatically recording X-ray diffraction apparatus described by Richmond and Watson,³ which gave direct readings of the percentages of the two forms. A modification of the apparatus permitted the broadening of the X-ray diffraction lines to be determined, and hence the mean apparent crystallite sizes of the samples to be estimated.

FIG. 1.—*The extensometer.*



For the extensometric examination, the air-dried material, in powder form, was compressed at 32,000 lb. in.⁻² in a die $\frac{3}{8}$ " in diameter, for 5 min., to give a pellet 20–30 mm long. The pellet was subjected to a temperature rising at 200° per hr. in an extensometer (Fig. 1) consisting of a Mullite tube *A* (15 mm. internal diameter) closed at one end and mounted horizontally in a tubular electric furnace (*B*). A fluted silica spacer (*C*) kept the compact sample (*D*) in a fixed position near the centre of the furnace and directly below the junction of a platinum–rhodium thermocouple (*E*). The Mullite rod (*F*), 12 mm. in diameter, had one end inserted concentrically into a silver-steel rod (*G*) balanced so as to move freely on two low-friction pulley wheels (*H*). The rod (*F*) was pressed against the pellet by the spring-loaded probe of the dial indicator gauge (*I*), which was bolted securely in position on the slotted bracket (*J*) with the probe fully depressed against the steel rod (*G*). In this way changes in length of as little as 0.002 mm. can be measured with a total range of 13 mm. Corrections were made for the slight lag in the temperature of the sample from that of the furnace.

RESULTS AND DISCUSSION

We now compare the results from the two batches with those for the titania (hereafter called batch XII) described in Part XII.¹ Below 600° the plots of specific surface against temperature are broadly similar for all three batches (Fig. 2), the maximum in the curve for batch A being explained in terms of the removal of water from previously blocked pores in the manner suggested in Part XII. The absence of the maximum in the curve for batch B is probably attributable to the removal of such water during preparation and storage, for this material was air-dried at 27° and stored in a well-stoppered bottle, whereas batch A had been stored in a desiccator at a relative humidity of 50%. The loss of area with increasing temperature of calcination is the result of sintering. As in Part XII, any increase in specific surface *S* of the kind to be expected if chemical decomposition occurs is again absent, in accordance with the fact that titania is a hydrous oxide, so that no change in lattice structure occurs when water is expelled.⁴

Commencing at a temperature between 600° and 700°, say *ca.* 650°, the loss of area by sintering accelerates, as is again brought out by plotting log *S* against 1/*T* (*T*° K is the temperature of calcination). For batch B (the ion-free material), indeed, the break

² Gregg, *J.*, 1955, 1438.

³ Richmond and Watson, *J. Oil Colour Chemists Assoc.*, 1952, **35**, 162.

⁴ Weiser and Milligan, *Chem. Rev.*, 1939, **25**, 1.

in the curve (Fig. 3) is quite sharp if the point for 700° is ignored, and there can be little doubt that a new mechanism of sintering has come into operation at about 650°; and, as pointed out in Part XII, this temperature could well lie close to the Tammann temperature of titania. The curve for the total pore volume V (Fig. 4) for batch B (that for

FIG. 2. Plot of specific surface, S (surface area in $m.^2 g.^{-1}$) (by sorption of nitrogen at -183°) against temperature of calcination for batches A (dotted line), B (broken line), and XII (full line). (Inset: Enlarged high-temperature region of curve for batch B.)

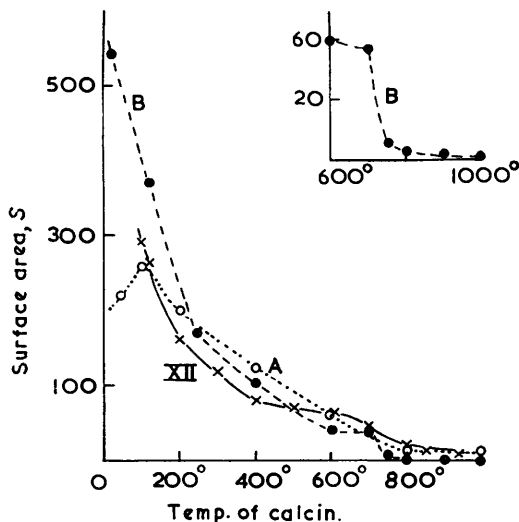


FIG. 4. Plot of $100(l_T - l_{1000})/l_{1000}$ against temperature of calcination (where l_T is the length at temperature T) for pellets from batches A and B. Curve C illustrates the total pore volume ($cm.^3/g.$) plotted against temperature of calcination for batch B.

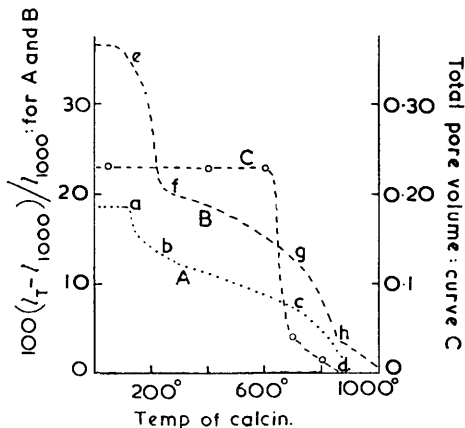


FIG. 3. Plot of $\log_{10} S$ ($S =$ surface area in $m.^2 g.^{-1}$) against the reciprocal of the temperature of calcination (in $^\circ K$) for batches A and B.

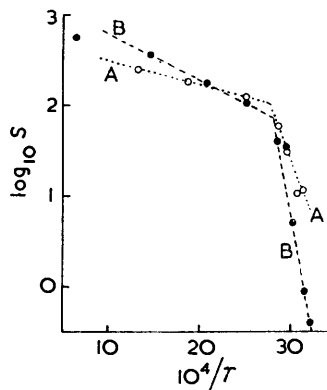
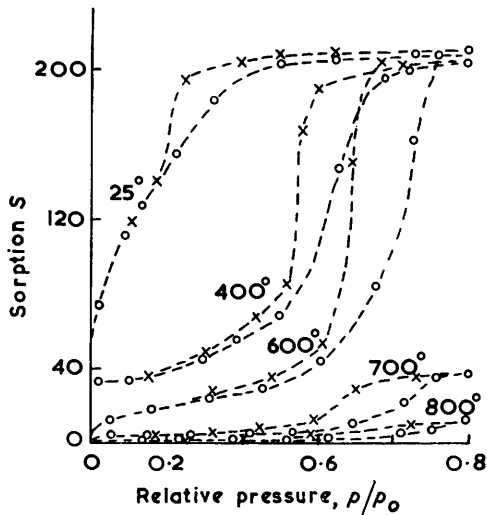


FIG. 5. Sorption isotherms ($mg./g.$) of benzene at 25° on batch B (ion-free) titania. (The temperature of calcination is marked on each isotherm.)



batch A was not measured) is also similar to that for batch XII, with the interesting difference that V remains sensibly constant to 600° and then falls, whereas with batch XII the curve was somewhat rounded off in the region 400—600°. The concept of a framework which undergoes progressive and fairly rapid collapse once the Tammann temperature

has been passed is again apposite, the onset of the collapse being sharper in the ion-free material of batch B than with the contaminated material of batch XII. The adsorption isotherms of benzene (Fig. 5) indicate that the pore-size distribution changes in favour of the larger pores at temperatures up to 600° even though the total pore volume is virtually unchanged, again in accordance with the framework model.

With batch XII the phase change of anatase to rutile commenced at about 950°, corresponding to $0.58T_m$ (where T_m °K is the m. p. of rutile) and so is well above the Tammann range⁵ ($0.37-0.52 T_m$)—particularly if, as seems probable from the sintering results, the Tammann temperature is at 650°. In the case of batch B the phase change (Fig. 6) begins slightly below 600° and is almost complete in the 800° specimen; with batch A the change occurs over a somewhat wider range of temperature, the proportion of rutile being greater at the low-temperature end and somewhat smaller at the high-temperature end than with batch B. It thus seems that with both batches the inception of the phase change and an acceleration of sintering each occur at a temperature near to the Tammann temperature.

Electron micrographs furnished interesting confirmation of the accelerated sintering above 600°. They showed a marked increase in particle size between 600° and 750°,

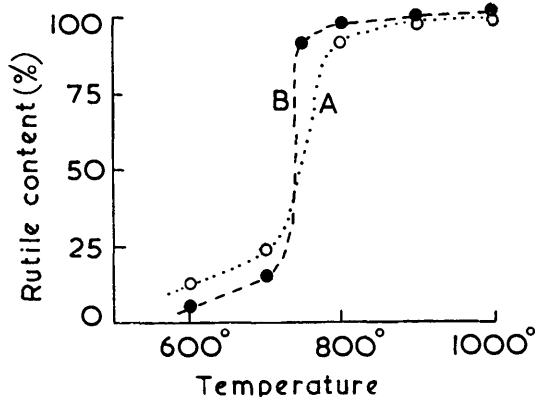


FIG. 6. Plot of the percentage of rutile against temperature of calcination for batches A and B.

and also the very rounded appearance of the particles and the paucity of very fine particles at 1000°. Other workers⁶ have also noted that, on calcination of hydrous titania, growth in crystallite size commences at about 600°.

There is thus a significant difference between the behaviour of the batches A and B on the one hand and batch XII on the other, for in batch XII there was an acceleration of sintering at about 600° but the onset of the phase change was delayed till 950°. It thus seems that the impurities in batch XII did not noticeably shift the Tammann temperature but prevented the phase change at this temperature. Since the phase change would require, not only the mobility of the constituent ions, but also the formation of growth nuclei,⁷ one infers that the impurities have inhibited the formation of such nuclei without adversely affecting the ionic mobility. This state of affairs does not seem unreasonable inasmuch as suitable impurities could promote the formation of defects and thus enhance ionic mobility, whereas the formation of nuclei could be hindered by the accumulation of impurities in positions, *e.g.*, along dislocation lines,⁸ where nuclei might otherwise be formed.

The specific surface for 700° at first sight seems anomalously high (Fig. 2, inset, and

⁵ Finch and Sinha, *Proc. Roy. Soc.*, 1957, A, **239**, 145.

⁶ Sullivan and Cole, *J. Amer. Ceram. Soc.*, 1959, **42**, 127.

⁷ Czanderna, Rao, and Honig, *Trans. Faraday Soc.*, 1958, **54**, 1069.

⁸ Cottrell, "Dislocations and Plastic Flow in Crystals," Oxford Univ. Press, 1953.

Fig. 3); but, as already pointed out,⁹ an increase in area might well be expected when a phase change occurs, but it is opposed by the accelerated sintering, so that the areas actually registered along the curve result from the balance between the two processes. A high value at a particular temperature then merely implies that the loss of area by sintering was at that temperature less important relative to the gain of surface by activation than it was at neighbouring temperatures.

The extensometric data (Fig. 4) broadly support these interpretations. For each of the batches there is an increased rate of contraction commencing between 700° and 750°. To verify that this contraction accompanied the phase change from anatase to rutile, two pellets of batch B were subjected to the same rate of rise of temperature as in Fig. 4 and were removed from the furnace at a temperature corresponding to points "g" and "h" respectively; the rutile contents were found to be 2% and more than 98%, respectively, showing that the phase change occurs almost entirely between these two temperatures in batch B. The contractions *ab* and *ef* are caused largely by loss of adsorbed water, and *bc* and *fg* by sintering: with a steadily rising temperature any features are likely to be spread over a wider range of temperature and to be displaced towards the high-temperature side.

As will be noted, however, the volume of the pellet, unlike the pore volume, was diminishing steadily even at temperatures below the Tammann temperature, so that at no temperature was there evidence of the kind of stable framework which seemed to be present in the uncompressed samples. This is not altogether unexpected: the very high pressure used for compression would largely break up the framework and bring the particles within the grains into much closer contact; this would promote sintering by adhesion, which can occur at temperatures much below the Tamman temperature (cf. Part I⁹).

Finally, a comparison of the value of the crystallite size (l_s) calculated from the specific surface with that (l_x) calculated from the X-ray line broadening is interesting ($l_s = 6/S$, if particles are assumed to be isodimensional). l_x corresponds to regions of crystal perfection, whereas l_s merely measures the size of particles into which nitrogen molecules cannot penetrate; such particles could include several perfect crystallites, imperfectly aligned with respect to each other, any gaps between the crystallites being too small to admit nitrogen molecules. l_x should therefore never exceed l_s and, as is seen (Table), this is actually found.

Mean apparent crystallite sizes (in Å) of samples of batch B titania, calculated (1) from X-ray line broadening and (2) from nitrogen adsorption at -183°.

Temp. of calcin. ...	25°	250°	400°	600°	700°	750°	800°	900°	1000°
(1) l_x	—	—	92	134	269*	523	523	864	—
(2) l_s	27	91	146	385	417	2850	6400	12,700	35,300

* This figure refers to anatase; for rutile it is 393.

Conclusion.—In ion-free titania the phase change from anatase to rutile and accelerated sintering both commence at approximately 600°, close to the probable Tammann temperature of titania. Comparison with the results of Part XII suggests that the presence of certain impurities considerably raises the temperature at which the phase change commences without greatly influencing the temperature at which accelerated sintering (which in particular leads to a rapid reduction in pore volume) sets in.

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WASHINGTON SINGER LABORATORIES,
THE UNIVERSITY, EXETER.

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⁹ Gregg, *J.*, 1953, 3940.