Some properties of aqueous titanium isopropoxide–hydrogenperoxide solutions and their decomposition to produce titanium dioxide

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The preparation of aqueous titanium isopropoxide–hydrogenperoxide solutions, their light absorption spectra, optical density changes based on the transformation to colloids, thermal analysis of the dry colloids to titanium dioxide and the spontaneous explosions of the residues produced after vacuum evaporation of the solutions transforming titanium dioxide powders, were studied. The solutions were prepared by dissolving titanium tetraisopropoxide in an aqueous hydrogenperoxide solution. Component isopropanol was expelled from the mixture by vacuum evaporation. The presence of various H_2O_2/Ti ratios of residues produced by the evaporation, and the variation of absorption spectra with the concentration of hydrogen-peroxide suggested that the hydrogenperoxide content in the solute species was determined by the concentration of hydrogenperoxide in them. The thermal analysis of the dry colloids revealed that they suddenly decompose exothermally and consist of titanium, water and hydrogenperoxide. X-ray powder diffraction revealed that the dry colloid was amorphous and the heated product of the colloid at 440° C was in the anatase form and also that the explosion products were the same. SEM revealed that the fine dry colloid deformed above 609° C.

1. Introduction

Titanium hydroxide is precipitated in an aqueous solution by the action of hydrolysis on titanium salts. The titanium hydroxide precipitate must then be filtrated and washed for general uses. Titanium hydroxide can be converted to titanium oxide by heating [1]. Titanium salts are soluble in a strong acidic aqueous solution, usually in hydrochloric acid, sulphuric acid and in some organic complexing agents.

With addition of an aqueous hydrogenperoxide solution to the aqueous solutions of titanium salts, yellow titanium hydrogenperoxide complex is produced. This coloured complex has been used for analysis of titanium and hydrogenperoxide [2–15], and also its stability constant in the presence of other acids has been reported [16–22]. Solid titanium hydrogen peroxide containing coexisting salt is produced [23]. However, plain titanium hydrogenperoxide solutions have not yet been reported.

We have previously synthesized plain titanium hydrogenperoxide solutions and titanium isopropoxide-hydrogenperoxide solutions [24], and this paper deals with some properties of the latter solutions and the precise conversion processes to titanium dioxide. The solutions have the following characteristics: they are composed of titanium, hydrogen, oxygen and easily removable carbon: they can be converted to titanium dioxide only on heat treatment with no additives; they can be turned into sols or gels; and by vacuum evaporation they can solidify explosive solid titanium hydrogenperoxides that spontaneously become titanium dioxide powders.

2. Experimental details

The chemicals employed were titanium tetraisopropoxide (Ti(iOPr)$_4$ (Nippon Soda Co. Ltd, Japan), hydrogenperoxide (H_2O_2) solution (the purest grades of 30% and 60% aqueous solutions Santoku Chemical Industries Co. Ltd, Japan), sulphuric acid (analytical grade) and potassium permanganate (chemical grade).

The following instruments were used in the experiments: an ultra-sonic wave washer, a 500 W microwave oven, a spectrophotometer, a DTA–TGA apparatus, a gaschromatograph, a glass vacuum evaporator (10 cm diameter, 50 cm long, leading to a liquid nitrogen cold tap), a oil rotary vacuum pump (50 l min^{-1}), a transmission electron microscope (TEM 100 kV), a scanning electron microscope (SEM 20 kV), and an X-ray powder diffractometer.

A sample solution in a flask was first heated in a 500 W microwave oven; after a while, gas was vigorously evolved. At this point the flask was moved into a boiling water bath and kept in it. This moment is taken to be the starting time. In another case, a glass tube containing the different sample solutions was dipped into a water bath which was kept at a constant temperature.

Titanium was determined spectrophotometrically, using hydrogenperoxide and sulphuric acid at 410 nm, and/or estimated at a weight of Ti(iOPr)$_4$ given in the tables.

H_2O_2 in the samples acidified with sulphuric acid was titrated with a potassium permanganate solution and the amounts of H_2O_2 in the evacuated residues was estimated from the volumes of oxygen evolved in the explosions.

Measurements of the absorbances of the solutions and of the optical densities of the colloids were done using 10 mm light path quartz cells. The densities in Fig. 3AF which were higher than 1 were estimated from the measured values of suitably diluted samples.

3. Results and discussion

3.1. Dissolution of Ti(iOPr)₄ in an aqueous H₂O₂ solution

A cool 30% H_2O_2 solution was added to Ti(iOPr)₄ in a beaker cooled in an ice bath. After stirring the mixture slowly during cooling, a yellow titanium isopropoxide–hydrogenperoxide solution (Ti–iOPr–H_2O_2) and/or a red was produced. The H_2O_2 concentrations of the solutions were adjusted variously. After about 21 h from the adjustments at about 25° C, the absorption spectra were measured. The results are presented in Fig. 1. Their conditions were as follows: Equal concentrations of H_2O_2 solutions served as references for each sample. The concentrations (mol l^{-1}) of titanium salt were 1.28 × 10^{-4} for A to I, and 2.15 × 10^{-2} for J. The concentrations (%) of H_2O_2 were: in A, 0.001 42; in B, 0.054; in C, 0.107; in D, 0.277; in E, 0.808; in F, 1.37; in G, 2.75; in H, 6.88; in I, 20.6; and in J, 0.399. The following points are seen in Fig. 1. The solutions having higher concentrations of H_2O_2 (E < F < G < H < I) show longer wavelengths and lower absorbances at each their maximum absorbance above 0.8% H_2O_2. Above 330 nm wavelength, the absorbance increases slightly (A < E < F < G < H < I) as the concentration of H_2O_2 increases. The solution having the most diluted concentration of H_2O_2 (A) shows an absorption maximum at about 265 nm. The absorbance decreases as the wavelength gradually lengthens. Therefore diluted titanium salt solutions (A to I) appear yellow and concentrated ones (J) red in colour.

3.2. Dilution of Ti–iOPr–H₂O₂

On dilution of Ti–iOPr–H_2O_2, its colour gradually changes. The colour change processes were observed using absorption spectrophotometry and the results are presented in Fig. 2. The conditions were as fol-
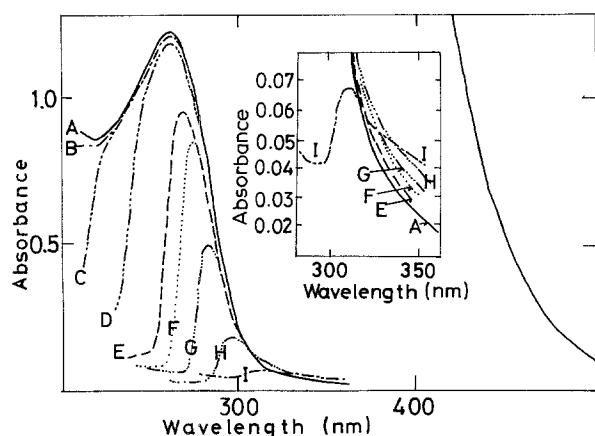
Figure 2 Absorption spectra of Ti–iOPr–H_2O_2 in the transient state. A, Ti–iOPr–H_2O_2 having 30% H_2O_2 was diluted to a 0.6% H_2O_2 and 8.57 × 10^{-4} mol l^{-1} Ti(iOPr)₄ solution. Duration: A, 9 min; B, 21 min; C, 35 min; D, 50 min; E, 100 min; F, 160 min; G, 4 h; H, 6 h; I, 23 h.

lows. The starting solution was prepared in 30% H_2O_2 and was diluted to 0.6% of examination's which was 8.57 × 10^{-4} mol l^{-1} titanium salt simultaneously. A pure 0.6% H_2O_2 solution served as reference. The temperature was maintained at 25° C for times (h) of: A, 9/60; B, 21/60; C, 35/60; D, 50/60; E, 100/60; F, 160/60; G, 4; H, 6; and I, 23. Sequential measurement was conducted in one instance for about 6 min. It appears that the change reaches a maximum after about 6 h and it then shifts back somewhat after 23 h.

3.3. Changes of optical densities of Ti–iOPr–H₂O₂ at 100° C

Ti–iOPr–H_2O_2 faded, and bubbles were evolved even at a few degrees, and became first a sol and then a gel at high concentrations. The sol then became viscous and turbid and produced a pale yellow precipitate which eventually turned white after more than a month at room temperature. The processes were accelerated by the presence of small amounts of acetic acid which are effective for syneresis.

Changes in the optical densities of Ti–iOPr–H_2O_2 were measured at 100° C. The results are presented in Fig. 3. The concentrations of Ti(iOPr)₄ (mol l^{-1}), and

Figure 1 Absorption spectra of Ti–iOPr–H_2O_2 with varying concentrations of H_2O_2 taken after 21 h from the adjustments at 25° C. Concentration of Ti (mol l^{-1}). A to I, 1.28 × 10^{-4}; J, 2.15 × 10^{-2}. Concentration of H_2O_2 (%): A, 0.001 42; B, 0.054; C, 0.107; D, 0.277; E, 0.808; F, 1.37; G, 2.75; H, 6.88; I, 20.6; J, 0.399.
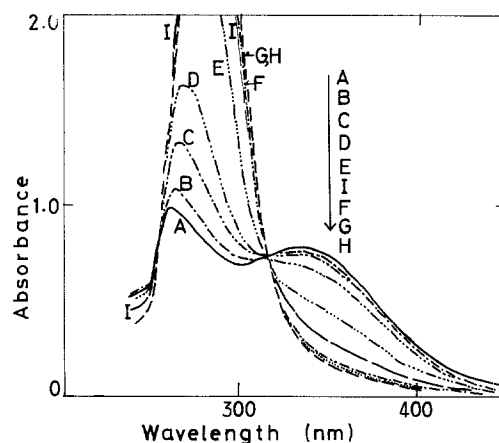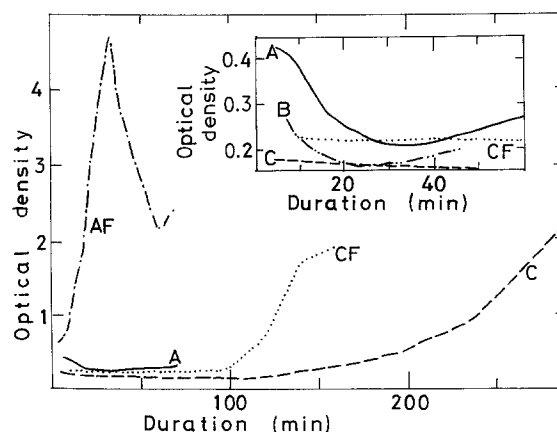
Figure 3 Changes of optical densities of Ti–iOPr–H_2O_2 at 100° C. (as mol l^{-1} Ti(iOPr)₄, % H_2O_2, nm light): A and AF, 0.0215, 1.2, 440; B, 0.0176, 0.5, 440; C and CF, 0.001 41, 0.04, 360. A, B and C, hot; AF and CF frozen once and melted.

of H_2O_2 (%), and in the wavelength of monochromatic light (nm) were as follows: A, $0.215\,mol\,l^{-1}$, 1.2%, 440 nm; AF, A with additional quick freezing and melting process, B, $0.0176\,mol\,l^{-1}$, 0.5%, 440 nm; C, $0.001\,41\,mol\,l^{-1}$, 0.04%, 360 nm, CF, C with additional quick freezing and melting process; others, $0.0704\,mol\,l^{-1}$, 2% gelatinized after 11 min, could not be measured. Monochromatic light at 440 nm was selected for the high concentration, and at 360 nm for the dilute concentration to produce suitable results. Measurements were made on the hot samples as soon as they were removed and on the once frozen samples that were held at room temperature, and melted after being dropped into liquid nitrogen to freeze. After quick freezing, the sols yielded dispersed irreversible hydrophobic particles which scatter the light; thus the scattering effect of sols is magnified by the freezing process. Solutions A, AF and B were used soon after each preparation, solutions C and CF were used one day later.

The optical densities of A, B and C initially decreased with increasing time, and continued to increase after each minimum. These decreases are considerable, as decomposition of H_2O_2 in the solutions proceeds, because the absorbance depends on the concentration of H_2O_2 in its solution, as predicted in Fig. 1. The increases are considered to be as the result of the scattering of light by the growing particles. AF shows an increase in density after a few minutes. This fact suggests that the production of the sol proceeds in the decreasing process of A after a few minutes. In the case of AF, the density shows a maximum after 30 min, and decreases gradually. It is suggested that after 30 min the sol AF has grown sufficiently to produce effective scattering. C and CF show an increase in density later compared with A and AF. This indicates that the solutions having higher concentrations of salt decompose sooner than those with lower concentrations. The densities of CF are a little larger than those of C during these periods of decrease. This could be caused by contamination during the freezing operations.

3.4. Freeze drying of colloids and their thermal analysis

As mentioned previously, the colloids have various growth states and concentrations. The solutions, sols and gels become red and solid on drying in air at room temperature. With quick freeze drying of the colloids, fine dry solids were obtained, similar to the case of silicic colloids [25]. The fine dry solids were measured with DTA, TGA and gas evolution. The results are presented in Fig. 4. The conditions were as follows. The sol of composition $0.119\,mol\,l^{-1}$ Ti(iOPr)$_4$, 13% H_2O_2, was kept at $70°C$ for several minutes, dipped into liquid nitrogen, and then dried in a vacuum. The dried sol (37.4 mg) was heated at $2°C\,min^{-1}$, in DTA and TGA. The other sol (composition $0.0644\,mol\,l^{-1}$ Ti(iOPr)$_4$, 5.9% H_2O_2), kept at $25°C$ for 24 h) was dropped on to a copper block partially dipped in a liquid nitrogen bath and dried in a vacuum. This sample was heated at a rate of $1°C\,min^{-1}$ in a flow of helium at a rate of $10\,ml\,min^{-1}$ in gas evolution
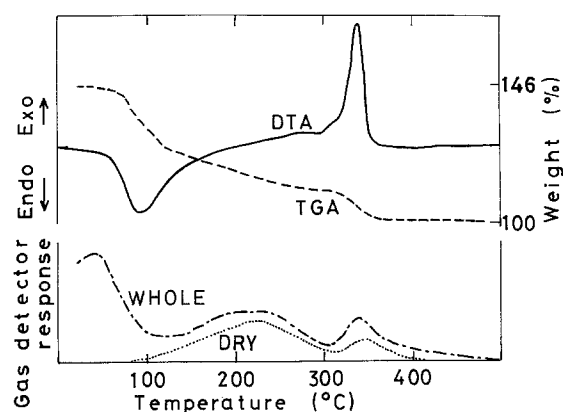

Figure 4 Thermal analysis of quick freeze-dried colloids. DTA and TGA: dry sample weight 37.4 mg at start, $0.119\,mol\,l^{-1}$ Ti(iOPr)$_4$, 13% H_2O_2, kept at $70°C$ for several min, dipped into liquid nitrogen, and dried in vacuum, heating rate $2°C\,min^{-1}$. Gas evolution: dry sample weight 6.01 mg (WHOLE) and 6.35 mg (DRY) at start, $0.0644\,mol\,l^{-1}$ Ti(iOPr)$_4$, 5.9% H_2O_2, kept at $25°C$ for 24 h, dropped on to a copper block partially dipped in liquid nitrogen, and dried in a vacuum, heating rate $1°C\,min^{-1}$ in a helium flow of $10\,ml\,min^{-1}$. WHOLE, whole gas; DRY, gas passed through a silica gel column.

analysis. The flow was introduced straight into a gas chromatograph (labelled WHOLE in Fig. 4), or introduced into it after the evolved water in the gas was absorbed by passing through a silica gel column (labelled DRY). The amount of each sample at the start was 6.01 mg in WHOLE and 6.35 mg in DRY. The difference between WHOLE and DRY suggests the presence of water in the evolved gas. DRY reveals oxygen. About 4 min were required for the gas to flow from the sample to the gas chromatograph.

Around $80°C$, an endothermic weight loss causing the escape of water occurs, and a sharp exothermic loss occurs at about $340°C$. Between 100 and $270°C$ gradual decomposition yields water and oxygen from the contained H_2O_2 radical. It is known that the decomposition of H_2O_2 into oxygen and water is exothermic. X-ray powder diffraction of the dry colloids showed an amorphous pattern with a slight halo peak around 0.3424 nm, and that of the sample heated at $440°C$ shows an anatase pattern. The anatase to rutile phase transition occurred at about $700°C$. The dry colloids may consist of titanium dioxide, water and hydrogenperoxide.

3.5. Vacuum evaporation of $Ti-iOPr-H_2O_2$

Unless heated, when $Ti-iOPr-H_2O_2$ was placed in an evaporator and evacuated with a rotary oil pump, water, H_2O_2 and isopropanol were distilled out and collected in a trap cooled with liquid nitrogen, and a yellow to red solid residue appeared in the bottom of the evaporator. Small amounts of isopropanol were detected in the residue by gas chromatography. When the solution was treated in a high concentration of H_2O_2, it quickly yielded a reddish explosive residue. During evaporation in the presence of liquid, its temperature was kept below $0°C$. When a liquid disappeared in the evaporator, evacuation was stopped and the evaporator was opened to the air. The temperature then shifted to near room temperature, and after a while the residue explosively converted to titanium

Experiment	Measurement					Calculation	
	Addition		Product		Distillate: H_2O_2	Solution,	O_2 or residue,
	Ti(iOPr)$_4$ (g)	30% H_2O_2 (ml)	TiO$_2$ (g)	O$_2$ (ml)	(m mol)	r/q	r/q
1	1.738	12.5	0.390	800	56.0	21.3	10.7
2	3.293	15.0	0.921	1450	30.8	13.5	10.2
3	1.445	10.4	unknown	460	50.2	21.3	7.4
4	2.587	17.0	0.604	800	74.2	19.5	7.2
5	1.452	10.4	0.252	300	54.0	21.2	4.8
6	1.960	14.1	0.461	340	69.1	21.3	4.0
7	1.437	10.3	0.313	200	52.3	21.3	3.2
8	0.761	5.5	0.147	90	29.4	21.3	2.8
9	0.345	9.7	0.350	90	54.4	21.3	1.6
10	1.515	10.9	0.272	90	49.3	21.3	1.4
11	0.914	6.6	0.185	40	33.4	21.3	1.0

oxide powders and gases. In the case of a violent explosion, an anatase type of titanium oxide was formed, accompanied by sound and a flash. The production of anatase may be considered to be the result of the heat produced in the decomposition of titanium hydrogenperoxides which momentarily increases its temperature. If necessary, to trigger the explosion, hot water could be poured on the outside of the evaporator. The conditions and the results of the explosive experiments are presented in Table I. The molar ratios of the residues vary, although the solutions are the same. The highest ratio is 10.7 and the lowest, 1.0. For a more precise determination of H_2O_2 in the residues, titrations were performed on them. To prevent the explosion, the residues were cooled by dipping the evaporator into a liquid nitrogen bath before opening it, and they were then dissolved in water. The dissolved residues were then titrated. The conditions and the results are presented in Table II. Evaporations were repeated twice by dissolving the first residues with H_2O_2 or water in experiments 2 and 3. Evaporations were repeated three times in experiment 1. The amount of additives, molar ratios H_2O_2/Ti of the solution, molar ratios of H_2O_2 distilled into the trap against the amount of titanium in the solution, and the molar ratios of H_2O_2/Ti of the residues are given for each distillation. The molar ratios of H_2O_2/Ti in the residues varied, and show the highest value of 10.9 in Table II, experiment 3, first residue. High concentrations of H_2O_2 in the solutions do not guarantee the production of a high ratio in the residue as shown in Table II, experiments 7 and 8. H_2O_2 was distilled out from even a low ratio solution which therefore gave a low ratio residue, as shown in Table II, experiment 1, third distillation. The evolutions of small bubbles in the solutions in 30% H_2O_2 were seen at a few degrees. This suggests that decomposition of H_2O_2 in a high concentration proceeds spontaneously during evacuation. It would appear that the main reason for the varying ratios in the residues is the uncontrollable decomposition of H_2O_2 during the evaporation of the solution.

3.6. Appearance of the products

Fig. 5a shows a scanning electron micrograph (SEM) of the freeze-dried colloid shown in Fig. 3, line B, kept at 100° C for 29 min, having a minimum optical density of 0.168 on 440 nm light. The products seem to be thin flakes. This colloid was gradually heated to 609° C over 1.5 h, and the SEM of this is shown in Fig. 5b. Small particles and slight shrinkages are shown on the hem of the flakes. The colloid shown in Fig. 5a was gradually heated to 775° C over 2 h, and the SEM of this is shown in Fig. 5c. Small vacancies in the films and fibres are seen. On heating the colloid shown in Fig. 5a gradually to 850° C over 3 h, the product obtained was as shown in Fig. 5d. Vacancies, small particles, lined particles and fibres are shown. Comparison of Figs 5a to d shows the shrinkage process and the sintering process of the dry colloid. Fig. 5e shows an SEM of the product, titanium dioxide powders, in Table I, experiment 1. Various shapes (not round) are seen in it; there are obvious differences from the usual round particles precipitated in a solution or in a gas phase. The right-hand photograph of Fig. 5f shows a transmission electron micrograph of the freeze-dried colloid that was used for the gas evolution analysis in Fig. 4, and its electron diffraction pattern is shown on the left. Its appearance is that of a thin film in a crumpled form. For TEM observation the sample was dispersed in carbon tetrachloride using an ultrasonic wave which may have crumpled the thin film.

4. Conclusions

Isopropanol can be distilled from Ti–iOPr–H_2O_2 in a vacuum, therefore this can be assumed to be the same as the solution that is composed of solute titanium hydrogenperoxides in a mixed solvent of isopropanol, H_2O_2 and water. As shown in Fig. 1, the spectra depend on the concentrations of H_2O_2, and the residues in Tables I and II show various ratios in H_2O_2/Ti. The results of thermal analysis show that the colloids consist of titanium dioxide, oxygen and water. These facts suggest that titanium hydrogenperoxides exist in the form of $Ti_q(H_2O_2)_r(H_2O)_t(OH)_z$ in the solute and solids.

Changes in the spectra on dilution shown in Fig. 2, proceed slowly and then reverse somewhat in the spectrum taken at 6 h to that taken at 23 h. This fact suggests that the substitution between the water radical and the hydrogenperoxide radical in the titanium complex occurs slowly and with vibration.
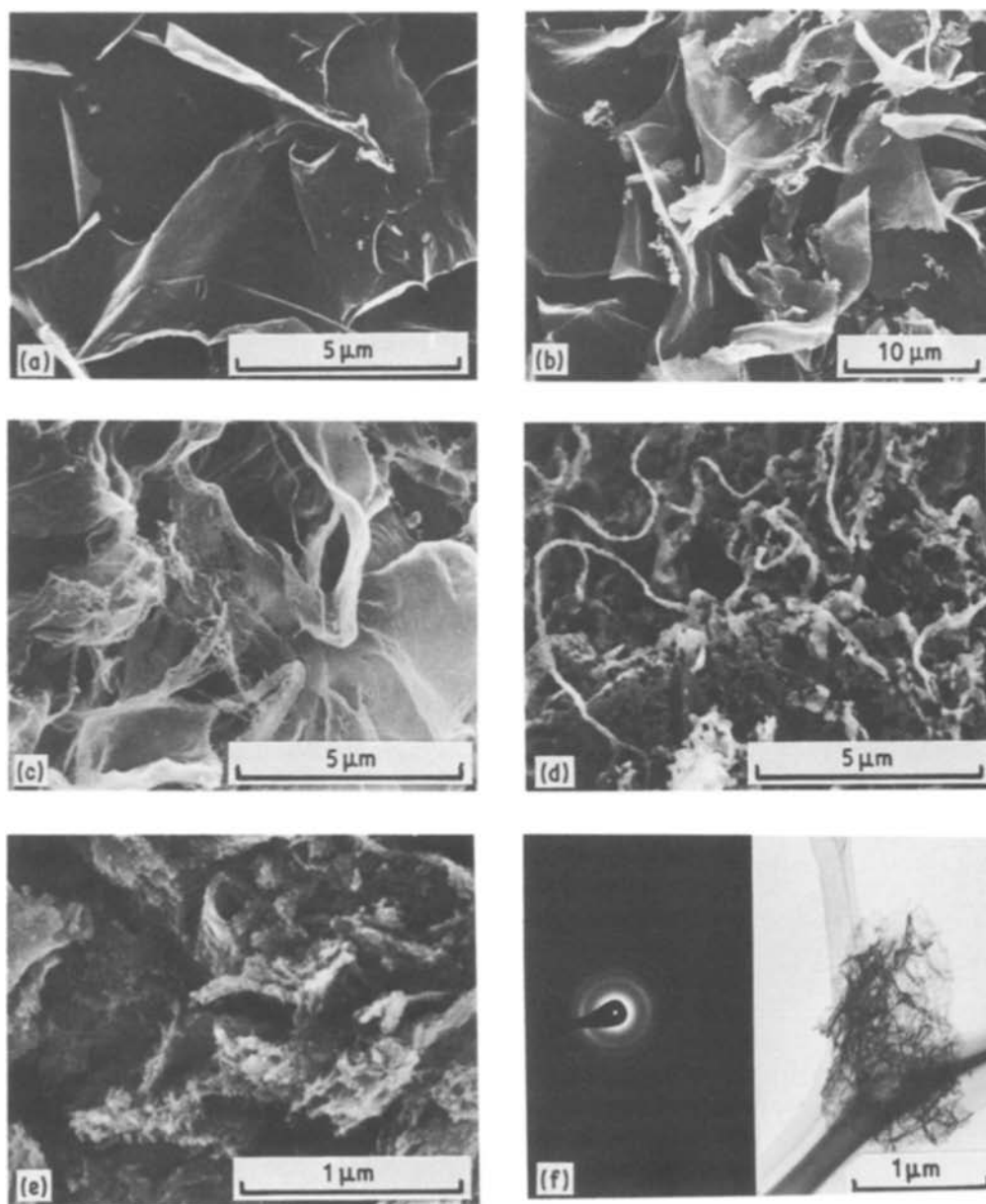
TABLE II Data of vacuum evaporations

Experiment	1st distillation					2nd distillation				3rd distillation			
	Addition		Solution	Distillation		Addition	Solution	Distillation		Addition	Solution	Distillation	
	Ti(iOPr)$_4$ (g)	H$_2$O$_2$ (% ml)	r/q	Distillate, r/q	Residue, r/q	H$_2$O (% ml)	r/q	Distillate, r/q	Residue, r/q	H$_2$O (ml)	r/q	Distillate, r/q	Residue, r/q
1	2.022	30–44	20.5	6.9	unknown	30–10	>15	10.6	5.0	25	5.0	2.7	1.5
2	2.438	30–22	26.8	unknown	unknown	30–20	>24	unknown	2.0				
3	1.651	30–22	39.5	unknwon	10.9	0–100	10.9	8.6	unknown				
4	1.507	30–14	27.5	14.4	6.2								
5	1.879	30–22	34.7	unknown	2.9								
6	2.552	30–22	25.6	unknown	7.3								
7	1.803	60–22	75.5	unknown	3.5								
8	1.991	60–25	77.7	64.8	3.4								

Figure 5 (a) SEM of quick freeze-dried colloid shown in Fig. 3B, kept for 29 min. (b) SEM of colloid shown in (a) heated at 609° C. (c) SEM of colloid shown in (a) heated at 775° C. (d) SEM of colloid shown in (a) heated at 850° C. (e) SEM of product shown in Table I, experiment 1, in explosion. (f) TEM of quick freeze-dried colloid used for Fig. 4 WHOLE and DRY and its electron diffraction pattern.

The ratios r/q in the compound are variable. Lower ratios would be more stable and higher ones would be unstable or explosive. To produce a high ratio r/q residue, it may be necessary for vacuum evaporation to be conducted below 0° C.

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