PRECIPITATION AND AGEING OF ANTIMONY(III) SULPHIDE

Elizabeth C. BROWN, D.R. GLASSON and S.A.A. JAYAWEERA
John Graymore Chemistry Laboratories,
Department of Environmental Sciences,
Plymouth Polytechnic
Plymouth PL4 8AA (UK)

ABSTRACT

Antimony(III) sulphide has been prepared by precipitation from aqueous solution, under different conditions of concentration, temperature, pH and ageing time. The phase composition, crystallinity and particle size of the precipitates have been studied by X-ray diffraction, electron microscopy and vacuum microbalance techniques, and correlated with conditions of precipitation.

The sulphide samples were prepared from 1 M, 0.5 M and 0.1 M antimony(III) chloride solutions through which hydrogen sulphide gas was passed at 20 $^{\circ}$C and 85 $^{\circ}$C. The precipitates were aged for different lengths of time, and examined by X-ray powder diffraction and electron microscopy. The surface area and porosity of selected samples were determined by the BET method from nitrogen adsorption isotherms recorded gravimetrically at -196 $^{\circ}$C on a vacuum microbalance.

However the above sulphide samples, precipitated at relatively low pH, contained impurities such as antimony chloride and oxychloride. Preparation of pure antimony sulphide was achieved best by precipitation from a dilute solution (0.015 M) of potassium antimonyl tartrate (tartar emetic) with hydrogen sulphide gas. Precipitation occurred then at the relatively higher pH of 4 - 5 in the presence of smaller concentrations of electrolytes, so that the product was very finely-divided and porous.

INTRODUCTION

Antimony(III) sulphide has important industrial applications, including many in the polymer and paint industries (ref. 1). It was used in large quantities for the dark pigment in camouflage paint, because it has the same infra-red reflectance properties as the surrounding green foliage (ref. 2).

The above applications are governed by the surface and solid state properties of the material, especially its particle size and crystallinity. In this

research, antimony(III) sulphide has been precipitated under different experimental conditions; the colour, surface area, porosity, crystallite and aggregate size, and crystallinity of the products have been correlated with conditions of precipitation. In earlier work on zinc and lead sulphides, it was found that such conditions governed these properties (ref. 3), which, in turn, affected the oxidation behaviour of the sulphides (ref. 4).

Mellor (ref. 5) has summarised early work on the preparation of antimony sulphide. Rose passed hydrogen sulphide gas through a solution of antimony(III) chloride and tartaric acid in hydrochloric acid until the warm solution was saturated. According to Duflos the reaction would not be complete if the tartaric acid were omitted, owing to the formation of a sulphochloride. Youtz reported that antimony sulphide precipitated from a solution containing hydrochloric acid is never pure, being contaminated with variable amounts of relatively volatile antimony oxychloride, which is difficult to remove. Mellor reported also that the action of hydrogen sulphide on a hydrochloric acid solution of antimony chloride is reversible.

Rose, Proust and Ditte (ref. 5) found that the red amorphous sulphide transformed to a black crystalline form on treatment with dilute acids, especially with hydrochloric acid. Lang reported that the change occurred rapidly with increasing concentration of the acid. According to Akerman and Pettenkorfer, the colour depends on the mode of preparation and is related to grain size of the material.

EXPERIMENTAL

Materials

BDH 'Analar' antimony(III) chloride and potassium antimonyl tartrate , $KSbO.C_4H_4O_6$, were employed as the antimony salts. Hydrogen sulphide gas was generated from a Kipps apparatus using iron(II) sulphide and dilute (2 M) hydrochloric acid. For precipitation from the tartrate solution, the gas was washed with water to remove traces of contaminating acid fumes. The commercial antimony sulphide was supplied by Bleiberger Bergwerks Union, Klagenfurt, Austria.

Procedure

Because of its deliquescent nature, antimony chloride was weighed in a silica gel-dried atmosphere. The salt was dissolved in hydrochloric acid (5 M) to prevent the formation of insoluble oxychloride. Hydrogen sulphide gas was bubbled continuously through the solutions with stirring for one hour to ensure complete precipitation.

Samples of the precipitate were removed after one hour, filtered and washed under suction, first with 100 cm^3 of distilled water and then with two 50 cm^3

aliquots of acetone, to arrest further ageing (ref. 3a). The remaining precipitate was left in the mother liquor and further samples removed after 10, 24, 50 and 80 hours, and treated as above.

Precipitations were carried out also at 85 $^{\circ}$C using a thermostatically controlled water bath. Evaporation losses from the reaction mixture were mini-mised by using a condenser.

Antimony sulphide was prepared also in practically neutral solution by passing hydrogen sulphide gas through potassium antimonyl tartrate (0.015 M). The precipitate was aged for one hour, and recovered as above.

For selected precipitations, the pH of the reaction mixture was monitored continuously. Complex salt formation was investigated by adding antimony(III) chloride (1 M) to sodium sulphide (0.1 M).

The antimony sulphide samples have been assigned three-figure code numbers. The first figure refers to the molarity of the antimony salt solution, the second to the temperature of precipitation and the final one to the ageing period. Thus, sample 0.5/20/80 is one prepared from 0.5 M antimony chloride at 20 $^{\circ}$C and aged for 80 hours.

The phase compositions of the precipitates were studied by recording their X-ray powder diffraction pattern, using copper $K\alpha$ radiation of wavelength 0.1542 nm. A Hilger and Watts Y90 X-ray generator fitted with a Philips sealed tube was used. The sample was mounted on a Berthold diffractometer.

The nitrogen adsorption isotherms were recorded gravimetrically (ref. 6) on a CI Mark 2B microforce balance (μg to mg sensitivity) at 77 K using 0.25 g samples with liquid nitrogen as the coolant. Hysteresis on the isotherms indicated any porosity present and the pore size ranges. Specific surface areas were calculated by the BET method. Prior to nitrogen adsorption the samples were outgassed at room temperature to remove any surface films of volatile contaminants.

A Jeol SEM 35C Scanning electron microscope was used to examine the microstructure of the samples. The materials were subjected to ultrasonic vibration for one minute to disperse the particles. Specimen preparation was achieved by vacuum deposition of a thin film of gold on the surface of the material.

RESULTS AND DISCUSSION

Colour

The samples of precipitated antimony(III) sulphide varied in their colour. The freshly precipitated crystals were orange and finely-divided, whereas, the aged crystals were black and more coarse. At the elevated temperature a similar trend was observed, the colour change being enhanced due to rapid ageing.

TABLE 1

Colour of the antimony(III) sulphide precipitates and the degree of contimination by antimony oxychloride.

| Sample | Colour | | Degree of Contamination SbOCl |
	Before Storage	After Storage	
1/20/1	orange	black	none
1/20/10	black	black	none
1/20/24	black	black	none
1/20/50	black	black	none
1/20/80	black	black	none
0.5/20/1	orange	black	none
0.5/20/10	black	black	none
0.5/20/24	black	black	none
0.5/20/50	black	black	none
0.5/20/80	black	black	none
0.1/20/1	orange	black	none
0.1/20/10	black	black	none
0.1/20/24	black	black	none
0.1/20/50	black	black	none
0.015/20/1	orange	orange	none
1/85/1	black/orange	black/bronze	large
1/85/10	black	black	trace
1/85/24	black/yellow	black/yellow	large
1/85/50	black	black	trace
1/85/80	black	black	trace
0.5/85/1	black	black	none
0.5/85/10	black	black	none
0.5/85/24	black/yellow	black/yellow	small
0.5/85/50	black/yellow	black/yellow	large
0.5/85/80	black/yellow	black/yellow	large
0.1/85/1	rust	rust	none
0.1/85/10	black/yellow	black/yellow	small
0.1/85/24	black	black	trace
0.1/85/50	black	black	small
0.1/85/80	black	black	small
commercial	–	black	none

There was also a yellow component in some samples, thought to be due to the presence of antimony oxychloride. During storage the colour of some precipitates changed from orange to black; this was assumed to be due to continued ageing of the samples. Table I shows the colour of the precipitates and the degree of contamination by antimony oxychloride. These observations confirm the earlier work of Akermann and Pettenkorfer (ref. 5).

Phase composition

All the samples gave X-ray diffraction patterns corresponding to antimony(III)

sulphide, showing that they were crystalline (ref. 7). The only exception was sample 0.015/20/1 precipitated from the tartrate; this gave no diffraction pattern indicating its amorphous nature.

Some samples precipitated at low pH (0 - 1) and at elevated temperatures, showed diffraction peaks corresponding to antimony oxychloride. This would account for the yellow colour of the materials (Table I). X-ray diffraction did not indicate the presence of sulphur in the samples. Any antimony chloride in the samples was not present in large enough quantities to be detected by X-ray diffraction.

TABLE II

Percent weight loss on outgassing in vacuo of antimony sulphide samples

Sample	Weight Loss %
commercial	0
0.015/20/1	0
1/20/1	7.4
1/20/24	0.5
1/20/80	2.1
0.1/85/1	0.6
0.1/85/24	0.4
0.1/85/80	-

Surface area

The specific surface areas of selected samples were determined by gas sorption. On outgassing in vacuo, those samples precipitated at low pH lost weight initially. This is attributed to the loss of a surface coating of antimony(III) chloride (b.p. 223 $^{\circ}$C). Table II shows the percentage of weight loss by each sample on outgassing. Samples precipitated from 1 M SbCl$_3$ solution at 20 $^{\circ}$C appear to contain more antimony chloride than those precipitated at the lower concentration and higher temperature. This is due to the partial reversal in more acidic media of the reaction:

$$2SbCl_3 + 3H_2O \rightleftharpoons Sb_2S_3 + 6HCl$$
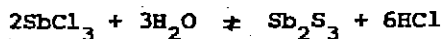
These observations are in agreement with those of earlier workers (ref. 5). Other methods of removing the contaminating antimony chloride, e.g. by washing with water, are difficult, since at higher pH and temperature hydrolysis occurs to antimony oxychloride.

Figure 1a - d show the nitrogen adsorption isotherms on the commercial sample and samples 0.015/20/1, 0.1/85/1 and 1/20/24 respectively. All the curves show a Type II isotherm. The first three curves show hysteresis indicating that these samples are porous. The commercial sample and sample

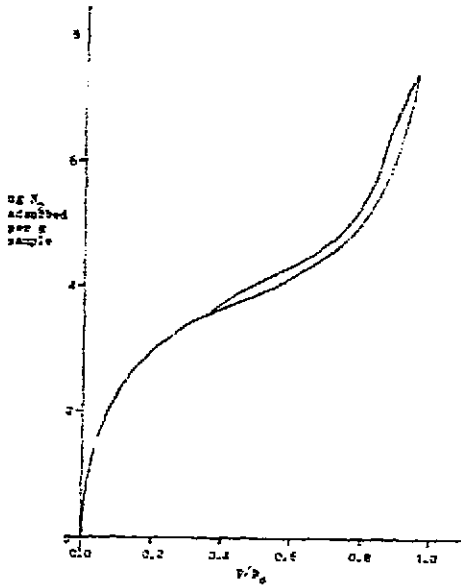Figure 1a. Adsorption of nitrogen on antimony (III) sulphide (commercial) at -196°C.

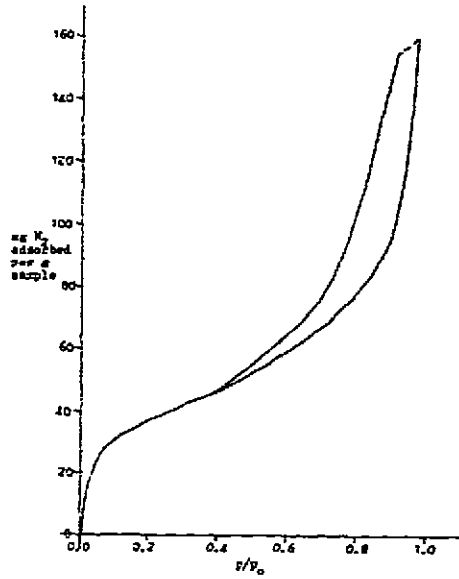Figure 1b. Adsorption of nitrogen on antimony (III) sulphide (tartrate) at -196°C.

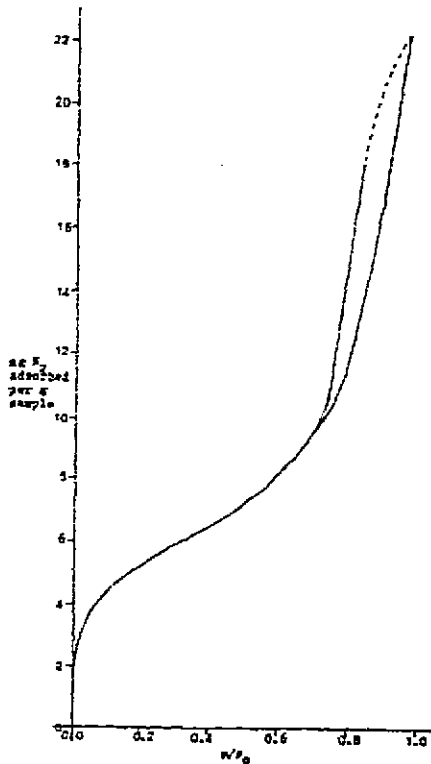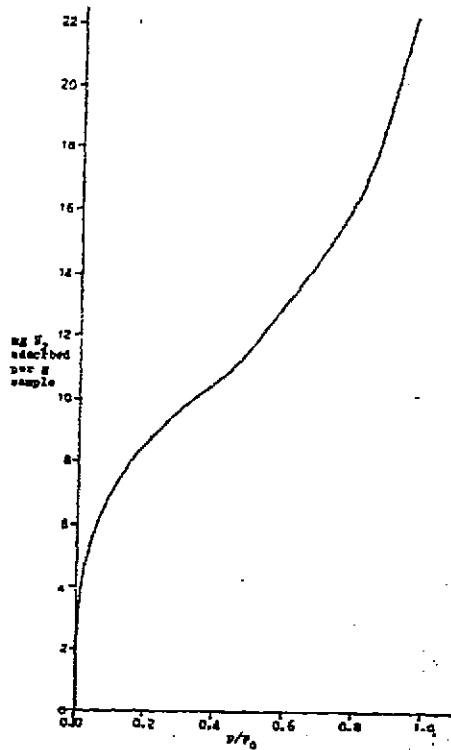Figure 1c. Adsorption of nitrogen on antimony (III) sulphide (0.1/85/1) at -196°C.

Figure 1d. Adsorption of nitrogen on antimony (III) sulphide (1/20/2x) at -196°C.

0.015/20/1 both contain the full range of mesopore sizes (2 - 50 nm) but with few micropores, whereas sample 0.1/85/1 contains macropores (ref. 8) and only the upper range of mesopore sizes (ca. 6 - 50 nm).

TABLE III

Crystallite size as calculated from gas sorption results and average particle size from electron microscopy data.

Sample	Gas Sorption		Porous?	Electron Microscopy	
	Specific Surface Area (m^2g^{-1})	Average Crystallite Size (μm)		Average Aggregate Size (μm)	Average Particle Size (μm)
commercial	8.7	0.15	✓	–	0.2 x 2 to 0.5 x 5
0.015/20/1	97.7	0.013	✓	20	submicron
1/20/1	2.8	0.46	x	2 x 2 to 8 x 9	0.5
1/20/24	2.5	0.52	x	2 x 2 to 8 x 9	0.5
1/20/80	2.3	0.56	x	1 to 3	0.5
0.1/85/1	15.3	0.085	✓	–	0.1
0.1/85/24	1.8	0.71	x	5 to 20	0.3 to 1
0.1/85/80	<0.1	>10	x	50	–

The gas sorption results have been used also to calculate average crystallite sizes (using an X-ray density of 4.63 for antimony(III) sulphide) for comparison with electron microscopy observations.

Table III summarises the specific surface areas and the calculated particle sizes (equivalent spherical diameter) of the samples. The variation of these with ageing time are shown in Figure 2. The crystallite size calculations of the porous materials do not take into account differences in external and internal surface areas. Thus the actual crystallite sizes are larger than indicated in Table III.

Electron microscopy

The scanning electron micrographs (Figures 3a - f) show a wide range of individual crystallite and aggregate sizes. An average value was estimated for these. Table III records these values and compares them with those calculated from surface areas. Reasonable agreement is found between the crystallite size measurements, except for the commercial sample. Agreement between such measurements is not always satisfactory as calculations are based on different distributions. Thus, for example, previous work on precipitated lead sulphides (ref. 3b) showed that the crystallite sizes obtained
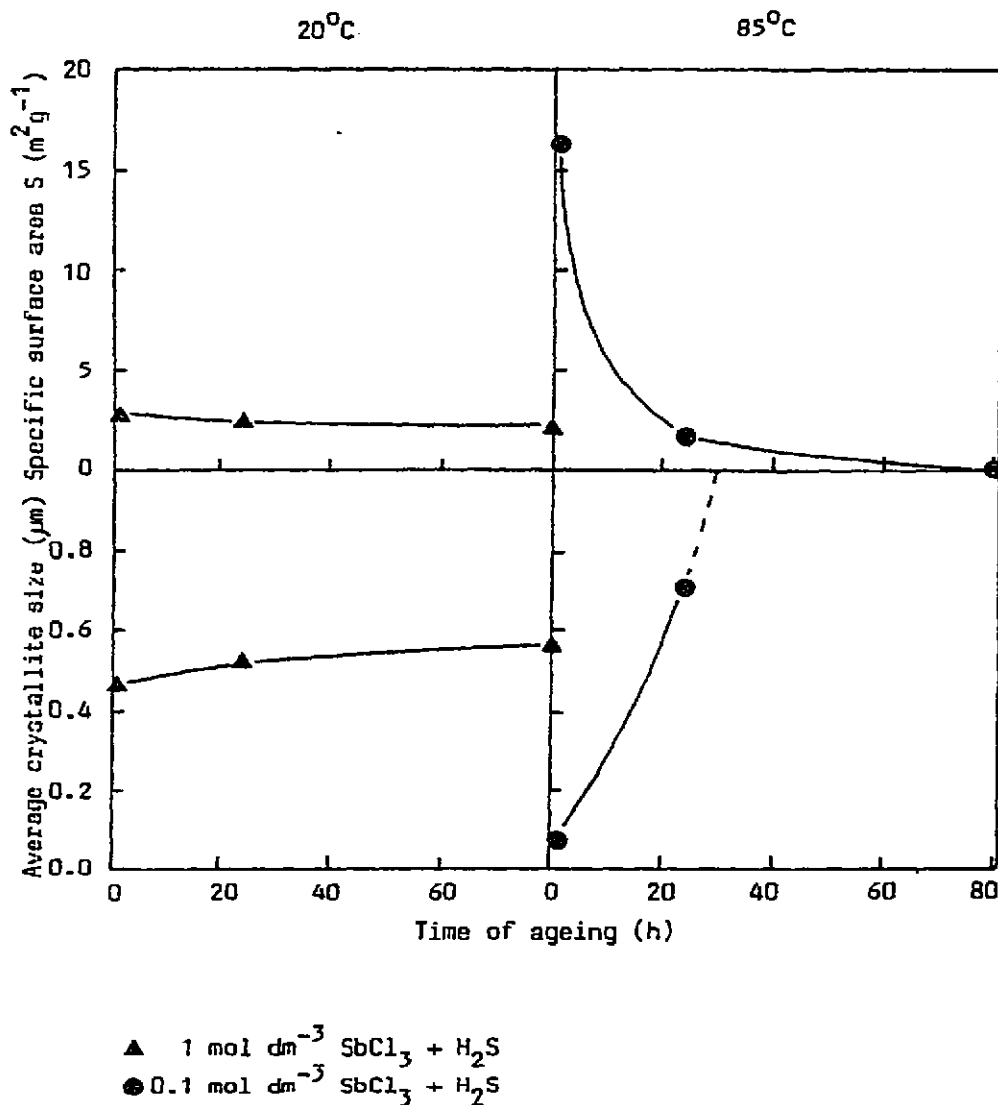
20°C   85°C

Figure 2. The effect of ageing at differing temperatures on the size and surface area of antimony(III) sulphide.

from electron microscopy gave values 2- to 3-fold lower than those obtained from other techniques.

Gas sorption data shows that the crystallite size of the commercial sample is 0.5 um, whereas electron microscopy indicates a much larger size, Figure 3a. However, calculation of crystallite size from surface area measurements assume a spherical or cubic shape for the particles. Electron microscopy shows that this is not so; the particles are needle-shaped with an aspect ratio of about 1/10. Recalculation of particle size on this basis gives better agreement between the two methods.
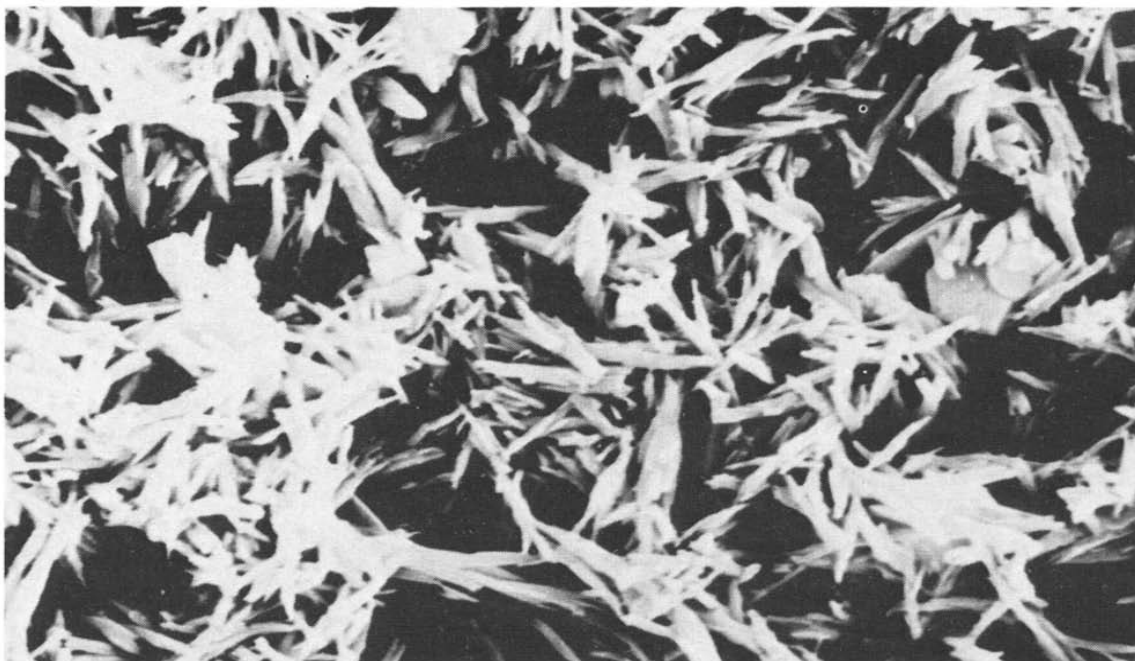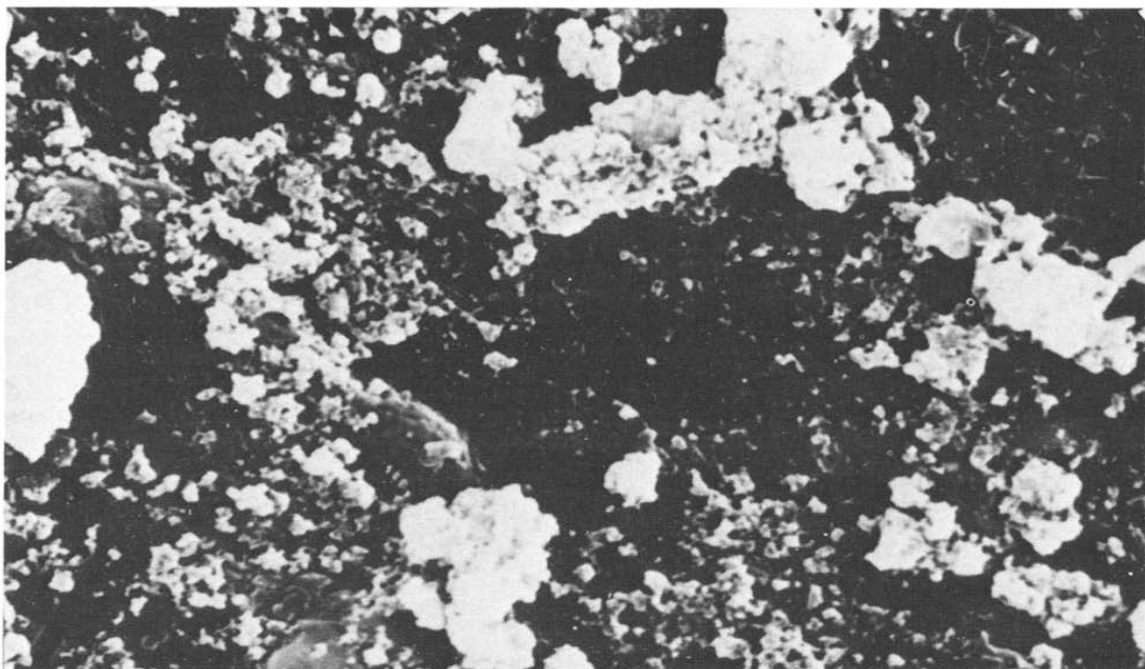
Fig. 3a (above) Commercial antimony sulphide.   Magnification x 6000

Fig. 3b (below) Antimony sulphide sample 0.015/20/1
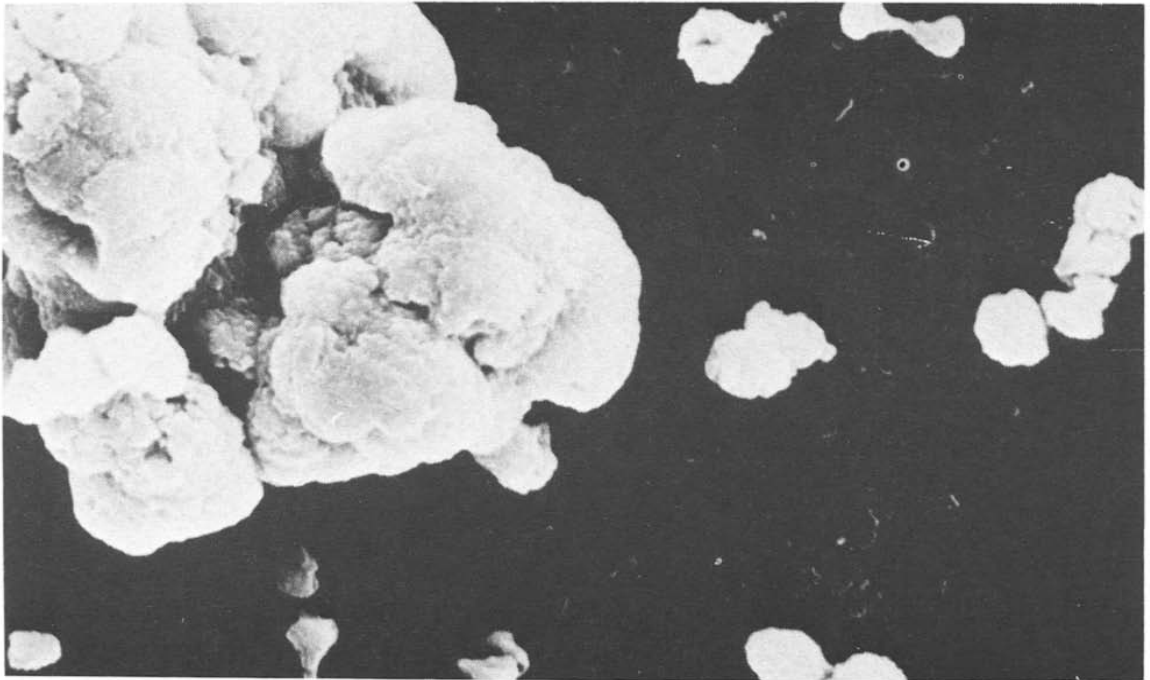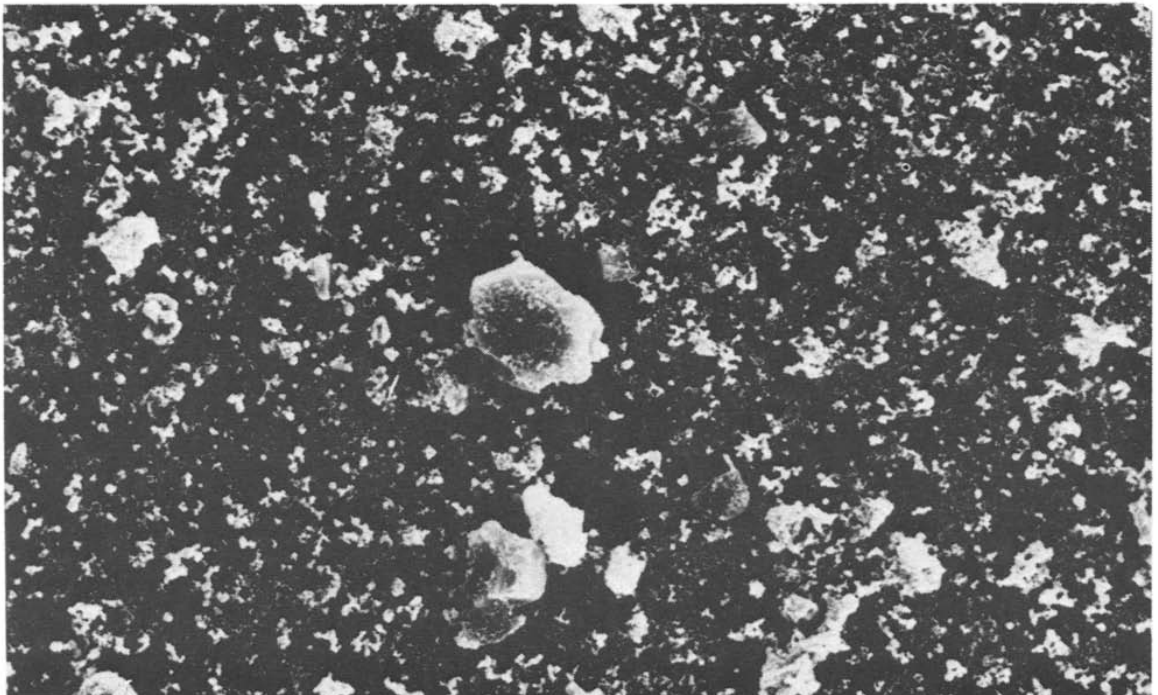   Magnification x 6000

Fig. A: above: Antimony Sulphide sample 1/20/1
        Magnification X 6000

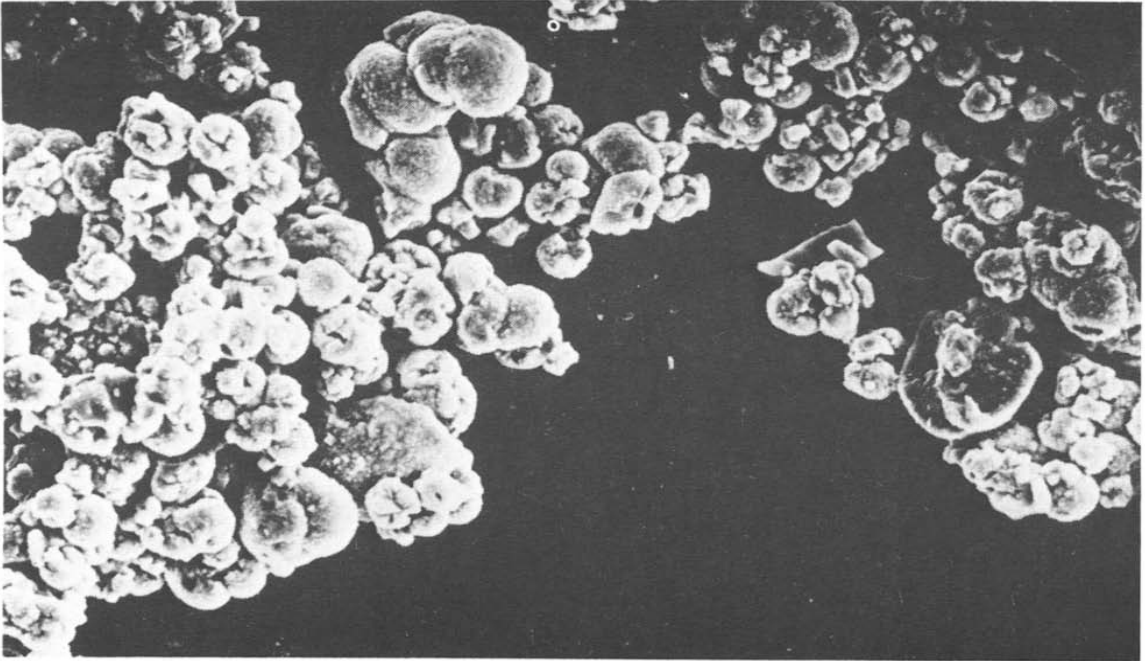Fig. B: below: Antimony Sulphide sample 0.1/85/1
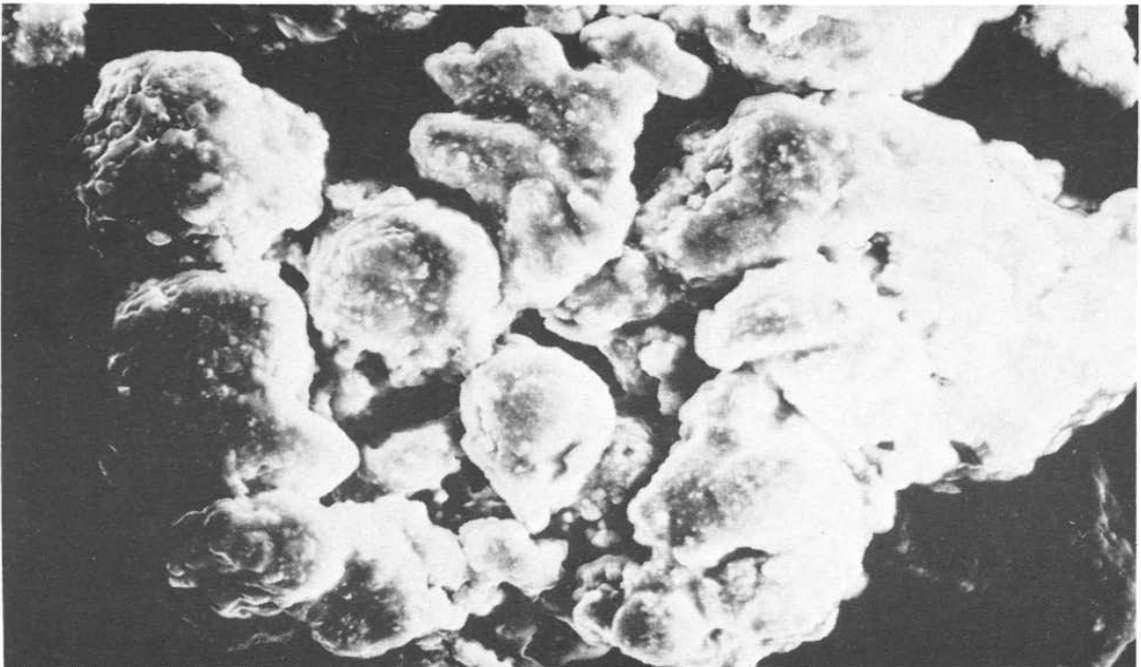   Magnification X 600

Fig. 3e (above) Antimony sulphide sample 0.1/85/24
                Magnification x 600

Fig. 3f (below) Antimony sulphide sample 0.1/85/80
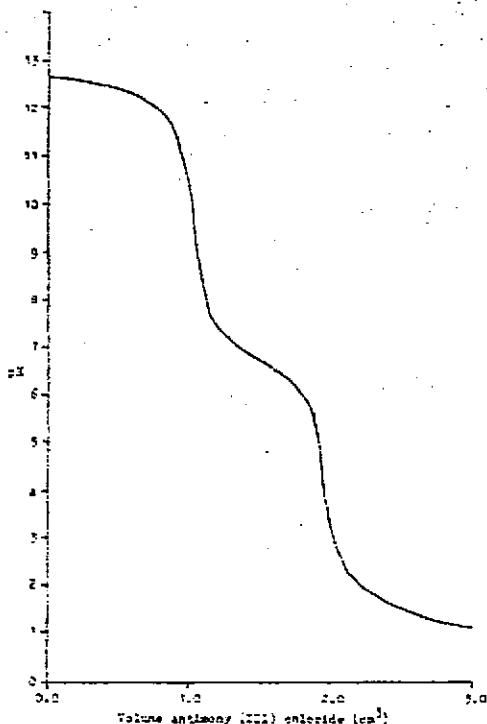   Magnification x 600

Figure 4. pH change for the addition of 1M antimony(III) chloride to 0.1 M
sodium sulphide at room temperature.

Figure 3b shows the material precipitated from the tartrate. No well-
formed crystallites can be seen and much sub-micron material is present, which
is probably porous and is of poor crystallinity.

Figure 3c shows the material precipitated at 20 $^{\circ}$C and aged for 1 hour. The
appearance is similar to that after 1 h and 24 h ageing, in accordance with the
small changes in surface area and average crystallite size. (See Table III and
Figure 2). The effect of ageing is more pronounced at the higher temperature;
compare Figures 3d – f, which are of a lower magnification (x 600).

Effect of pH

Figure 4 shows the variation of pH during the addition of antimony(III)
chloride to sodium sulphide. The graph shows two "end-points" for the
reaction, at 1.00 and 2.00 cm^3. The ratio of these volumes, 1/2, indicates
the formation of the complex Na_3SbS_3 with excess sodium sulphide. For the complex
$NaSbS_2$, to be formed (ref. 9), the ratio of the volumes would be 3/4.

CONCLUSIONS

The ageing of precipitated antimony(III) sulphides is promoted by increasing
the time of ageing, temperature and concentration of solution. At low pH the

product tends to be contaminated with antimony(III) chloride, whilst at higher temperatures and concentrations the contaminant is antimony oxychloride.

REFERENCES

1 (a) W.A. Larkin, German Patent 2 628 995. 27 January 1977 (b) J.R. Gregor
   and H.E. Van Orden, US Patent 2 940 841. 14 June 1960 (c) L. Csonka,
   F. Horkay, F. Szarto, J. Szerecz and J. Gonczy, Hungarian Patent 148 371.
   30 June 1961 (d) W. Budich, R. Krah and K.G. Scharf, German Patent 2 247 980.
   29 September 1972.
2 W.R. Jones, Minerals in Industry, Pelican, London, 1955, p. 33.
3 (a) B. Basak, D.R. Glasson and S.A.A. Jayaweera, in A.L. Smith (Ed.), Particle
   Growth in Suspensions, SCI Monographs No. 38, Academic Press, London, 1974,
   Ch. 10, 143 - 151 (b) P.J. Sleeman, PhD Thesis, Plymouth Polytechnic (CNAA),
   1976.
4 (a) B. Basak, P.H. Boothroyd, D.R. Glasson and S.A.A. Jayaweera, Proc. Journées
   de Calorimétrie et d'Analyse Thermique, Rennes, May 9 - 10, 1974, Vol. 4,
   pp. 35 - 58 (b) S.A.A. Jayaweera and P.J. Sleeman in D. Dollimore (Ed.), Proc.
   1st European Symp. Thermal Analysis, Salford, September 20 - 24, 1976, Heyden
   & Son, London, pp. 287 - 290 (c) B. Basak, D.R. Glasson and S.A.A. Jayaweera,
   Proc. 2nd Anglo-French Symp. Thermal Analysis and Calorimetry, Plymouth,
   September 19 - 21, 1977, pp. 47 - 50 (d) D.R. Glasson and S.A.A. Jayaweera,
   in D. Dollimore (Ed.), Proc. 2nd European Symp. Thermal Analysis, Aberdeen,
   September 1 - 4, 1981 (in press).
5 J.W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry,
   Longmans, London, Vol IX, 1946, p. 512 - 518.
6 D.R. Glasson, J. Chem. Soc. (1956), 1506 - 10.
7 X-ray Powder Diffraction File, American Society for Testing and Materials,
   Philadelphia, 1960, Sets 1 - 5; 1967, Sets 6 - 10.
8 E. Robens, in A.W. Czanderna and S.P. Wolsky (Ed.), Microweighing in Vacuum
   and Controlled Environments, Elsevier, Amsterdam, 1980, Ch. 4, 127 - 173.
9 G. Svehla, Vogel's Textbook of Macro and Semimicro Qualitative Inorganic
   Analysis, 5th Edition, Longman, London, 1979, p. 232.