Formation and Aging of Precipitates. II. Electron Microscopic Studies of the Aging of Barium Sulfate Precipitate

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Introduction

The aging of the precipitate is not only significant for the study of its properties, but also interesting from the view-point of the production of powdered materials in the chemical industry. The aging of barium sulfate precipitate has been studied by many investigators by means of various methods. Nowadays, as the electron microscope has made it possible to observe the colloidal dimension, the aging process can be studied in detail.

The authors previously described the shape and size of freshly precipitated barium sulfate[1]. In this paper the aging of the precipitates and the process of the growth of the crystals are described.

I. Aging Process in various Concentrations.

Barium sulfate precipitates produced as described in the previous paper[1] were kept in mother liquor and they were sampled out for electron microscopy at various intervals of time.

1) E. Suito and K. Takiyama, This Bulletin, **27**, 121 (1954).

(*a*) *Crystallization of Gel* In the range of the total concentrations, 1.0∼0.5 M, the fresh precipitates were colorless and transparent jellies and seemed to be amorphous. These jellies changed to a white gelatinous mass in a few minutes and settled down after a few days. These sedimented precipitates were composed of spherical particles, which were crystalline, as shown in Photo 2.

(*b*) *Precipitates uniform in Shape and Size* In the range of the total concentrations from 0.10 to 0.01 M the freshly precipitated particles were spindle shaped, cross spindle shaped and diamond shaped and each precipitate had homodisperse or uniform size distribution[1]. In these cases no change of the shape and size was observed for a few months. But the particles precipitated over the range 0.10 to 0.02 M, which had been dendritic and spindle shaped, changed to smooth spindle or hexahedron (rectangle in cross section) shaped ones after about 2 years as shown in Photo 6. Nevertheless, the size of the particles was almost unchanged as shown in Photos 5 and 6. The dendritic particles, which were probably unstable, reoriented to ideal crystals, which were rectangular and stable, during the digestion in the mother liquor.

(*c*) *Precipitates not uniform in Shape and Size* At the total concentration of 0.001 M the freshly precipitated particles consisted of two different sizes and shapes, i. e. large diamond shaped particles of about 2 μ and small spindle shaped ones of about 0.2 μ as shown in Photo 8. These smaller ones disappeared after several hours as shown in Photo 9. Two kinds of particles must have appeared by heterogeneous mixing of the reagents. The disappearance of the smaller particles is explained by recrystallization, that is to say, the smaller particles, which were more soluble than the larger ones, dissolved and were deposited on the larger ones.

In the range of the total concentrations below 0.0003 M, the precipitates, which were sampled out immediately after mixing the reagents, consisted of various sizes. In this case the size of the particles changed to uniform as shown in Photo 11 and Ostwald's ripening theory was proved to be valid.

II. Growing Process of Crystal.

In order to study the process of growth of the crystal, the changes of the electric conductivity and the turbidity were measured during the formation of the ideal crystal, whose shape was rectangular.

(*a*) *Change of Conductivity* 10 cc. of barium hydroxide solution and sulfuric acid, whose concentrations were both 0.0021 M, were added simultaneously in to 40 cc. of water. The conductivity of the suspension was measured at ten seconds intervals. The change of the conductivity is indicated by curve 1 in Fig. 1. A rapid change occured about forty seconds after mixing.

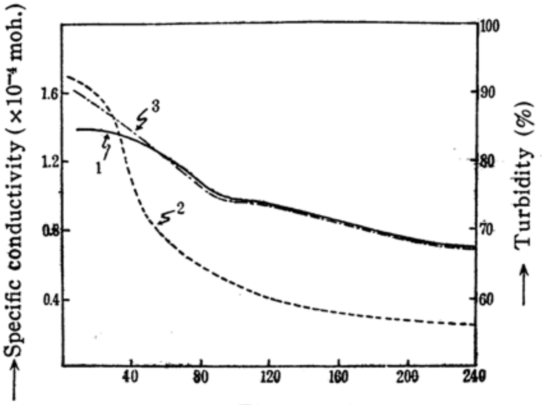

Fig. 1. The change of conductivity and turbidity during the formation of the precipitate.

(*b*) *Change of Turbidity* 2 cc. of barium hydroxide solution and sulfuric acid, whose concentrations were both 0.0021 M, were added into 8 cc. of water. The intensity of the light that passed through the specimen was compared with the intensity of the light that passed through water by means of photocolorimeter. In Fig. 1, curve 2 indicates the intensity of the passed light in percentage. The turbidity changed rapidly about thirty seconds after mixing the reagents.

As indicated in Fig. 1, the curve of the conductivity and the turbidity have a similar form. From these curves, a certain induced period, ten to sixty seconds, is considered to be needed for the formation of the nucleus which grew slowly to the perfect crystal.

(*c*) *Change of Conductivity during the Crystallization in the Presence of Nucleus* 20 cc. of barium hydroxide solution and sulfuric acid, whose concentrations were both 0.0021 M, were added into 40 cc. of the suspension described in (a). The change of the conductivity is indicated by curve 3 in Fig. 1. When the nucleus is present, the crystallization does not require the induced period.

III. Morphology of the Crystals slowly formed and in the Presence of Nucleus.

(*a*) *Crystals slowly formed* The precipitated particles of barium sulfate described above in (II. a) are rectangular as shown in Photo 12, and this shape is ideal for barium sulfate. The ratio of the length of the two edges was almost constant, namely, 2 : 1. Occasionally twin crystals appeared besides these rectangular single crystals. As marked in Photo 12, two twins are observed from different directions by shadowing. As the facet of the twin of orthorhombic crystal is (110), the angle between the two crystals of the twin ought to be about 63°11', but the angle of the twin shown in Photo 12 is 70° because of the inclination of the crystal to the specimen holder.

(*b*) *Precipitates formed in the Presence of Nucleus* As mentioned above the deposition of the precipitate was promoted by the addition of nucleus. The precipitated particles, which were prepared in the presence of the nucleus as described in (II. c), contained two kinds of rectangular particles, large and small.

The rectangular particles shown in Photo 13 appeared a few minutes after mixing dilute reagents. Before mixing reagents the nuclei, which were diamond shaped as shown in Photo 14, were added to barium hydroxide solution. Immediately after mixing the reagents, the precipitate shown in Photo 15 appeared. The nuclei grew to angular edged particles and many new rectangular particles appeared. It seems that the nuclei accelerate the separation of the crystals and do not affect the shape of the precipitated particles.

Summary

1. The amorphous precipitate of barium sulfate changed to a crystalline state by aging.
2. The precipitated particles produced in uniform size remained almost unchanged for a few months, but they became perfect for a long period (i. e. a few years).
3. When the particles of two different sizes formed directly after mixing the reagents, the smaller particles went into solution and the larger particles grew at the expense of the small ones.
4. In the case of dilute reagents the rapid change of conductivity was observed in an early stage of the reaction. The nucleus probably formed during this stage.
5. The precipitation was promoted by the nucleus added before the reaction, but the presence of the nucleus did not affect the shape of the precipitated particles.

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