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Preparation of colloidal Sb_2O_5 and its stability①

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Abstract: Colloidal antimony pentoxide was prepared by oxidation of antimony trioxide with hydrogen peroxide as oxidant and phosphoric acid as stabilizer. Effects of stabilizer, oxidant amount and reaction temperature on the diameter of colloidal particles and their size distribution were discussed. And static electricity effects on colloidal stability were studied by measurement of Zeta potential. Results show that Zeta potential of colloidal Sb_2O_5 moves from －30 mV to －56.8 mV with the addition of H_3PO_4 as the stabilizer, zero point of charge of colloidal H_3PO_4-Sb_2O_5 moves from pH＝1.85 to more acidic regions, and colloidal H_3PO_4-Sb_2O_5 is stable in wider pH range. The stable time of colloidal H_3PO_4-Sb_2O_5 particles without coagulation is more than six months. The size of colloidal particles is smaller and their distribution is narrower by adding H_3PO_4 as the stabilizer and decreasing reaction temperature, and the average diameter of H_3PO_4-Sb_2O_5 particles prepared is 30 nm.

Key words: clloidal antimony pentoxide stability; Zeta potential; zero point of charge

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1 INTRODUCTION

Colloidal antimony pentoxide is a new inorganic flame retardant. It can be used in rubber, plastics, fiber, textile, carpet, paint, paper and printed circuit board because of its flame retarding ability and other excellent properties such as high dispersion, low coloring intensity and high heat-stability[1－5]. Although more and more applications of colloidal antimony pentoxide are found in the industry, there are lack of detailed studies on preparation and stability of colloidal antimony pentoxide except some patents about technological process at present[6－10]. Purpose of this paper is to analyze the factors concerning with sizes of colloidal particles and their distribution, and to discuss the colloid stability from the view of Zeta potential.

2 EXPERIMENTAL

2.1 Preparation of colloid antimony pentoxide

According to the reaction,

$$Sb_2O_3 + 2H_2O_2 = Sb_2O_5 + 2H_2O$$

antimony pentoxide sol was prepared by admixing antimony trioxide, stabilizer with water. Hydrogen peroxide was added slowly into the mixture after reflux for enough time. Antimony trioxide was oxidized to antimony pentoxide by hydrogen peroxide. When the concentration of antimony pentoxide produced exceeds its solubility, it precipitates and forms colloidal sol.

2.2 Measurement of Zeta potential of colloid

The colloidal sol was diluted to contain 0.5% antimony pentoxide. Then its pH was regulated by 0.1 mol/L NaOH or 0.1 mol/L HCl. Under different pH values, the Zeta potential(ζ) was measured.

2.3 Measuring apparatus

The distribution and average particle size of the colloidal particles and Zeta potentials were measured by a DELSA 440SX particle analyzer (made by COULTER Company of America).

3 RESULTS AND DISCUSSION

3.1 Size of colloidal particles and their distribution

3.1.1 Effects of stabilizer on size distribution of particles

The average diameter of colloidal particles is often from 10^{-9} m to 10^{-7} m(1－100 nm)[11]. Effects of additive H_3PO_4 on the size distribution of particles of colloidal antimony pentoxide were studied. The results are listed in Table 1 and shown in Fig. 1. From Table 1, it can be seen that H_3PO_4 had strong effect on the stability of colloidal antimony pentoxide. The coagulation of colloidal particles was postponed with increasing amounts of H_3PO_4. The transparency of colloidal dispersion was promoted from milky white to clear with the addition of H_3PO_4. According to light scattering theories[12], the smaller the colloidal particles, the better the dispersion and the higher the transparency of colloid.

From Fig. 1, it was obviously observed that the addition of H_3PO_4 resulted in smaller average

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Table 1 Effects of H_3PO_4 on color and stability of colloidal antimony pentoxide

Content of H_3PO_4, $x(H_3PO_4)/x(Sb)$	Phenomenon of colloid
0	Milkly white, coagulated in 2 h
0.04	Yellow green, coagulated in 3 d
0.1	Clear yellow green, stable in 15 d
0.2	Clear blue, stable after 100 d
0.4	Clear blue, stable after 100 d
1.0	White, coagulated in 3 h

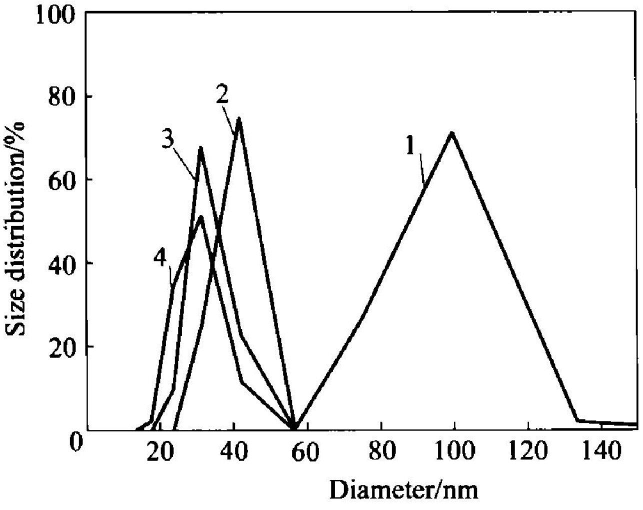

Fig. 1 Effects of H_3PO_4 on size-distribution of particles

($m(Solid)/V(Liquid) = 0.2$ g/mL, $x(H_2O_2)/x(Sb_2O_3) = 2.5$, 95 ℃, 90 min)
1 —$x(H_3PO_4)/x(Sb) = 0$; 2 —$x(H_3PO_4)/x(Sb) = 0.1$; 3 —$x(H_3PO_4)/x(Sb) = 0.2$; 4 —$x(H_3PO_4)/x(Sb) = 0.3$

diameter of colloidal particles and narrower size distribution. Without H_3PO_4 colloidal particles were larger with wider size distribution. The average particle diameter was (94 ± 17) nm. When molar ratio of H_3PO_4 to Sb was 0.1, 0.2 and 0.3, the average diameter of colloidal particles was (40 ±13) nm, (33 ± 5.8) nm and (30 ±6.6) nm respectively. According to colloid theories[11], the formation of colloid includes nucleation and growth. The size of colloidal particles depends on comparative rates of both processes. If the nucleation rate is higher than the growth rate, the colloidal particles become smaller. During the oxidation of antimony trioxide to antimony pentoxide, once the molecular antimony pentoxide precipitates and forms colloidal nucleus, H_3PO_4 is adsorbed on the colloid surface. The static electricity repulsion among the particles inhibits the growth of nucleus, which leads to smaller average diameter and narrower size distribution.

However, the colloid stability deteriorates and coagulation takes place when the molar ratio of H_3PO_4 to Sb is more than 1.0. Because positive ions in H_3PO_4 repulse the same ions of diffusion layer into the adsorption layer of colloidal particles[11, 13], the charge intensity and Zeta potential of colloidal particles decreases, and colloid stability deteriorates.

According to Table 1 and Fig. 1, suitable molar ratio of H_3PO_4 to Sb ranged from 0.2 to 0.4.

3.1.2 Effects of oxidant on size distribution of particles

Difference between the formation rate of new nucleus and the growth rate of existing nucleus leads to different size-distribution of colloidal particles. If most nucleuses form in very short time, the size-distribution is narrow[5]. Effects of oxidant amount on size distribution of particles were studied and the result is shown in Fig. 2.

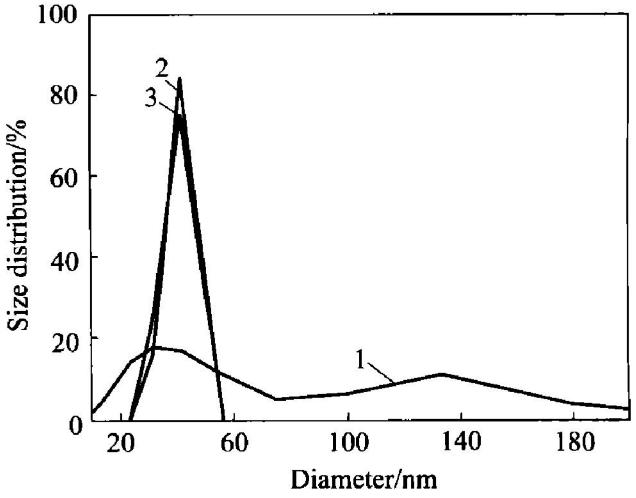

Fig. 2 Effects of H_2O_2 content on size-distribution of particles

($m(Solid)/V(Liquid) = 0.2$ g/mL, $x(H_3PO_4)/x(Sb) = 0.1$, 95 ℃, 90 min)
—$x(H_2O_2)/x(Sb_2O_3) = 2.0$; 2 —$x(H_2O_2)/x(Sb_2O_3) = 2.5$; 3 —$x(H_2O_2)/x(Sb_2O_3) = 3.0$

It can be seen from Fig. 2 that when the oxidant was added according to stoichiometric relation that was $x(H_2O_2)/x(Sb_2O_3) = 2.0$, the produced colloidal particles of antimony pentoxide were relative large with wide distribution, in which the average size of 76% particles was (35 ±16) nm and others was (126 ±33) nm. When the molar ratio of H_2O_2 to Sb_2O_3 was increased to 2.5 and 3.0, the average particle diameter decreased to (40 ±13) nm and (37 ±6) nm. Reaction rate for the oxidation increases with rising amounts of hydrogen peroxide. It can increase the supersolubility of antimony pentoxide in the same reaction period. Generally, when the supersolubility increases, both the nucleation rate and growth rate increase, but the former increases more significantly, which results in smaller particles[5, 11]. During the preparation of colloidal antimony pentoxide the suitable molar ratio of H_2O_2 to Sb_2O_3 ranged from 2.5 to 3.0.

3.1.3 Effects of temperature on size distribution of particles

Effects of reaction temperature on the size-distribution of particles are shown in Fig. 3. It indicated that lower reaction temperature led to smaller particles of antimony pentoxide with narrower size distribution. The average diameter was (37 ±6) nm at 95 ℃, (32 ±4.1) nm at 80 ℃ and (29 ±6.4) nm at 70 ℃, respectively.

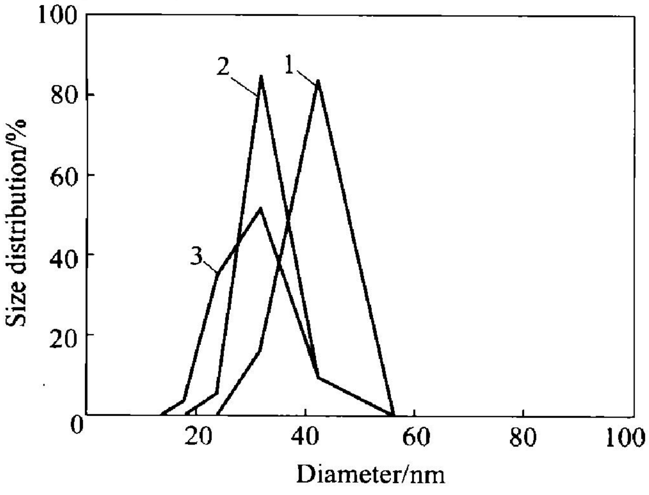

Fig. 3 Effects of reaction temperature on size-distribution of particles
(m(Solid)/V(Liquid) = 0.2 g/mL, $x(H_2O_2)/x(Sb_2O_3)$ = 3.0; $x(H_3PO_4)/x$(Sb) = 0.1)
1—95 ℃; 2—80 ℃; 3—70 ℃

By lowering the reaction temperature the kinetic energy of antimony pentoxide decreases and molecular attraction force relatively increases. Antimony pentoxide coagulates easily and nucleuses form. So nucleation rate increases at lower temperature. Meanwhile viscosity of dispersion increases at low temperature. It dose not benefit the diffusion of new moleculae onto the surface of existing colloidal nucleuses and thus the growth of nucleus is inhibited. Increasing nucleation rate and decreasing growth rate result in smaller colloidal particles at low reaction temperature[11]. On the other hand, solubility increases at high temperature, so small particles dissolve and large particles grow up. It is disadvantageous for the formation of colloidal sols.

However, the yield decreased because of the slow reaction rate at low temperature. At 95 ℃, 80 ℃ and 70 ℃, the yield was 98%, 86.5% and 43.2% respectively. Considering the diameter distribution of colloidal particle and output synthetically, 95 ℃ was the suitable reaction temperature.

The suitable reaction condition was summarized as the following: m(solid)/V(liquid) = 0.2g/mL, $x(H_2O_2)/x(Sb_2O_3)$ = 3.0 and $x(H_3PO_4)/x$(Sb) = 0.2. The colloid antimony pentoxide was prepared at 95 ℃ for 90 min. Its particle distribution is shown in Fig. 4. The average diameter of the antimony pentoxide was (30 ±4.2) nm and the colloid existed for at least six months.

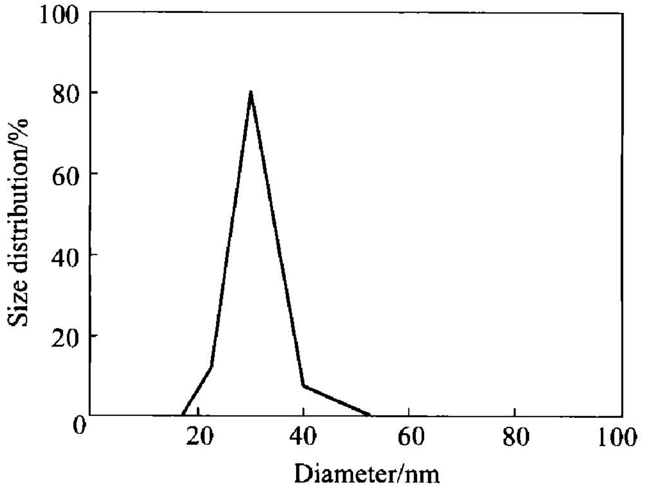

Fig. 4 Size-distribution of colloidal H_3PO_4-Sb_2O_5 particles

3.2 Colloid stability

Colloid stability usually depends on the charge of colloidal particles and their static electricity repulsion. Zeta potential(ξ) reflects not only the charge of colloidal surface but also colloid stability. Most of colloidal suspensions are stable at $|\xi|$ = 30 mV[11, 13]. In this paper H_3PO_4 was chosen as the stabilizer and the colloid stability was studied from the view of Zeta potential. The result is shown in Fig. 5.

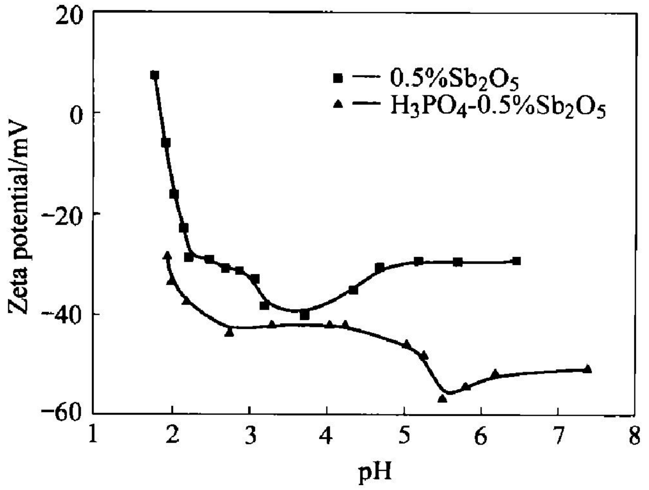

Fig. 5 Effects of H_3PO_4 on Zeta potential of colloidal particles

From Fig. 5, it was shown that the zero point of charge (ZPC)[14, 15] of the colloid antimony pentoxide was at pH= 1.85 if no stabilizer was added. The colloidal particles were negatively charged at pH> 1.85 while positively charged at pH< 1.85, and $|\xi|$ was less than 30 mV at pH< 2.8. The lower Zeta potential indicated instability of colloid antimony pentoxide without the addition of H_3PO_4.

When H_3PO_4 was added as the stabilizer, ZPC of colloid antimony pentoxide moved to more acidic regions. In wider pH regions colloidal particles were negatively charged and $|\xi|$ was higher than 30 mV. The maximum potential was about − 56.8 mV at pH = 5 − 7.

Antimony trioxide is oxidized to antimony pentoxide by hydrogen peroxide. When the concentration is higher than its solubility, the antimony pentoxide precipitates and colloidal nucleus forms. The nucleus has strong adsorbing ability because of its larger surface and higher energy. Negative ions in water were more easily adsorbed than positive ions were. They covered the surface of colloidal nucleuses to form diffusion double layer. So colloidal particles are negatively charged. When H_3PO_4 is used as the stabilizer in the reaction, the same negative ions are released because of ionization of H_3PO_4 and they are also adsorbed onto the surface of colloidal nucleuses. The charge intensity increases, the thickness of double layer and Zeta potential increases. So the state of colloid antimony pentoxide is switched from thermodynamic instability to kinetic stability by adding H_3PO_4 as the stabilizer.

4 CONCLUSIONS

1) A stable colloidal dispersion of antimony pentoxide is prepared by reflux oxidation method with H_3PO_4 added as the stabilizer. The average particle diameter is (30 ±4.2) nm and the colloid exists at least six months.

2) The suitable reaction parameters are selected by conditional experiments: $x(H_2O_2)/x(Sb_2O_3) = 2.5 - 3.0$, $x(H_3PO_4)/x(Sb) = 0.2 - 0.4$ and 95 ℃.

3) Colloid antimony pentoxide is stabilized by static electricity. When adding H_3PO_4 as stabilizer, colloidal dispersion is stable in wider pH regions, its zero point of charge of colloid H_3PO_4-Sb_2O_5 moves from pH = 1.85 to more acidic regions, and its Zeta potential moves from − 30 mV to − 56.8 mV.

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