

PREPARATION OF FINE AMMONIUM PERCHLORATE CRYSTALS BY A "SALTING OUT" PROCESS*

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The precipitation of ammonium perchlorate (AP) from methanol solutions of AP by a salting out method has been studied. The organic solvents studied as precipitants were : chloroform, ether, isobutyl alcohol and methylene chloride. The characteristics of the precipitated AP crystals were investigated by means of scanning electron micrograph, X - ray diffraction, differential scanning calorimetry and thermogravimetric analysis. When ether, chloroform and methylene chloride were the precipitants, the product crystals had a particle size less than 5 μm . On the other hand, the crystals obtained with isobutyl alcohol as the precipitant had a orthorhombic shape and the mean crystal size was larger than 10 μm . Diffraction angles for AP crystals obtained with isobutyl alcohol as the precipitant coincided with those obtained with other precipitants used in this work, though the intensity in the X - ray diffraction changed.

Introduction

Solid ammonium perchlorate (AP) is a major oxidizing agent with a high oxygen content (~ 54 % by weight). By far, the most predominant use of AP is as an ingredient in propellant compositions for solid fuel rockets. For this use, it is necessary that AP meet rigid requirements for chemical purity and physical properties. It is well known that the efficiency and rate of combustion of a solid propellant can be maximized by increasing the area of contact between the oxidizer and other ingredients of the propellant composition and that this area of contact can be increased by reducing the particle size of the oxidizer.

Fine AP has hitherto been obtained by attrition of larger particles, as by milling or grinding. However, disadvantages include jagged, asymmetrical surfaces, high production hazards due to local hot spots produced by the violent friction, and contamination from the grinder and grinding media.

In this paper, we describe a method for preparation of fine crystals of AP, where the process involves precipitation of AP from a methanol solution by addition of organic solvents. This process is often referred to as "salting out"⁵⁾. Although salting out technique is widely employed in industry, relatively few published data are available regarding its use in crystallization and there is a noticeable lack of data on the specific AP crystallizing systems. The organic solvents studied as the precipitants were : chloroform, ether, isobutyl alcohol and methylene chloride. In addition, the solubility of AP in methanol was measured in order to determine the maximum expected yield of AP in the salting out process. The characteristics of the precipitated AP crystals were also investigated by means of scanning electron micrograph, X-ray diffraction,

differential scanning calorimetry and thermogravimetric analysis to observe the influence of the precipitants on the properties of solids.

1. Experimental Procedure

1.1 AP solubility in methanol

A common experimental method for the solubility determination was used. The chemical composition of AP used in this work is shown in **Table 1**. A saturated methanol solution of AP was prepared at some known temperatures by stirring excess solid and methanol for 24 h. The solubility was measured in the temperature range of 293~308 K. The equilibrium mixture was allowed to stand still for 1 h at a constant temperature to enable any finely dispersed solids to settle down, which was easily carried out due to the large difference between the densities of AP crystals and methanol (respectively 1.95 and 0.79 g/cm³)⁷⁾. Samples of the clear supernatant liquid were carefully withdrawn by means of pipets slightly hotter than the solution in order to avoid precipitation, after which the concentration of the solution was measured by drying of an aliquot from the solution and weighing.

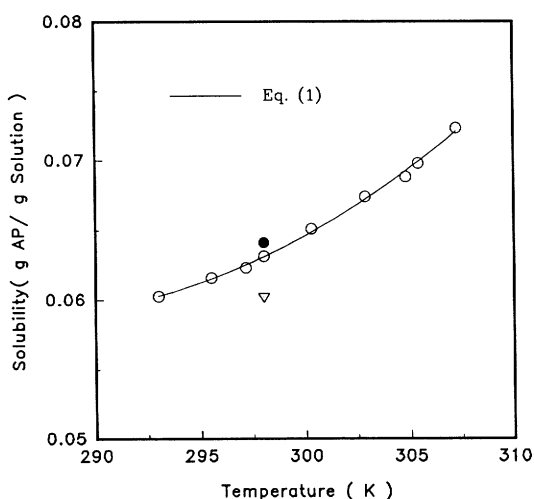
1.2 Crystallization

A 1500 ml cylindrical jacketed glass vessel (ϕ 100 \times 200 mm) equipped with a teflon paddle impeller of 55 mm diameter and 20 mm width was used as a crystallizer. Increasing quantities of the respective organic liquid were rapidly added with agitation to 100 g portions of the methanol solutions saturated at 298 K. The adding process took about 2 seconds. All experiments were carried out under the same conditions of temperature (298 K), agitation (600 rpm), and operation time (30 min). The temperature of the water bath was controlled with an accuracy of 0.05 K. The amount precipitated was measured by

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Table 1 Chemical composition of AP used in this work (weight %)

| | |
|---|----------|
| NH ₄ ClO ₄ | 99.3 |
| NH ₄ Cl | 0.005 |
| NH ₄ ClO ₃ | 0.002 |
| NaClO ₄ | 0.045 |
| (NH ₄) ₂ SO ₄ | 0.003 |
| Fe ₂ O ₃ | < 0.0001 |
| NH ₄ Bromate | < 0.001 |
| Na and K | 0.004 |
| Moisture | 0.025 |
| Insoluble matter | 0.002 |

**Fig. 1** Solubility of AP in methanol solutions (○): this work; (▽): Bircumshaw's data¹⁾ (●): Seidell's data⁶⁾

filtering the slurry through a 0.5 μ m Millipore filter, drying of the precipitate and weighing.

1.3 Analyses of samples

A scanning electron microscope (JEOL, JXA 840A) was used to observe the particle shape and size of the precipitated solids. Particle size distribution was measured by a Malvern Particle Sizer. The samples were subjected to X-ray diffraction analysis using CuK α radiation in the angle range from $2\theta = 10^\circ$ to 60° (Rigaku).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out with the heating rate of 10 K/min up to a maximum temperature of 773 K in a nitrogen atmosphere (DuPont Thermal Analyzer). The sample sizes were about 5 mg for DSC and about 15 mg for TG experiments, respectively. The nitrogen flow was kept at 80 ml/min for all the experiments.

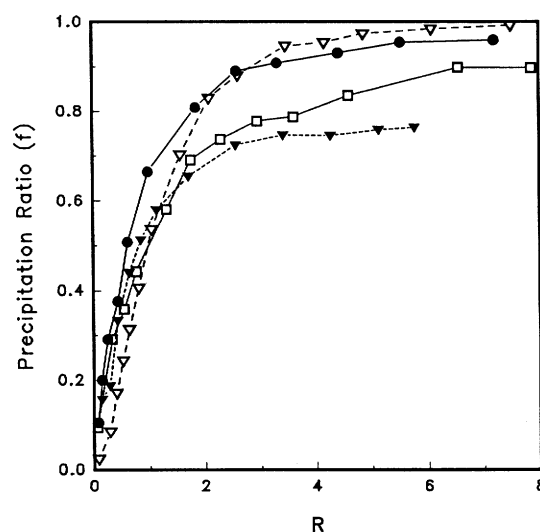
2. Results and Discussion

2.1 Solubility of AP

The solubility of AP in methanol is shown as a function of temperature in **Fig. 1** together with the results at 298 K in earlier papers^{1, 6)}. According to the equilibrium data obtained within our experimental range of temperature (293 ~ 308 K), the solubility of AP, C^* , in methanol solutions varies as follows :

Table 2 Solubility of AP in various solvents at 298 K (g AP/100g solution)

| Solvent | Solubility |
|--------------------|------------|
| Ether | 0 |
| Chloroform | 0 |
| Isobutyl Alcohol | 0.1268 |
| Methylene Chloride | 0 |

**Fig. 2** Precipitation ratio, f , for methanol solutions of AP at 298 K with various organic liquids as precipitants (▽): Ether; (●): Chloroform (□): Methylene Chloride; (▼): Isobutyl alcohol

$$C^* = 2.9145 \cdot 10^{-5} T^2 - 1.6665 \cdot 10^{-2} T + 2.4412 \quad (1)$$

The curve in **Fig. 1** was calculated from Eq.(1). At 298 K a saturated AP solution contains 0.0632 g AP / g solution. **Table 2** shows the solubility of AP measured by the method mentioned in 1.1 in four organic precipitants used in this work at 298 K.

2.2 Crystallization and Analyses

In **Fig. 2** the measured precipitation curves for the various organic solvents as precipitants are presented. The x - coordinate of **Fig. 2** is the mass ratio, R , defined as the added mass of a precipitant per unit mass of the methanol solution of AP. The precipitation ratio, f , is defined as the ratio of the mass of the precipitated salt by the addition of an organic precipitant to the mass of the salt in the methanol solution. It is shown that the presence of chloroform, ether, isobutyl alcohol and methylene chloride greatly reduces the solubility of AP in methanol. Precipitation of the salt as a function of the organic precipitant/methanol solution ratio exhibits an initial rapid rise followed by a slower approach to a maximum value. It is shown that yields are almost directly proportional to the amount of organic solvents added below a ratio of 1:1. The activity in precipitation decreases as follows:

ether > chloroform > methylene chloride > isobutyl alcohol

As expected, this sequence indicates that solvents with a

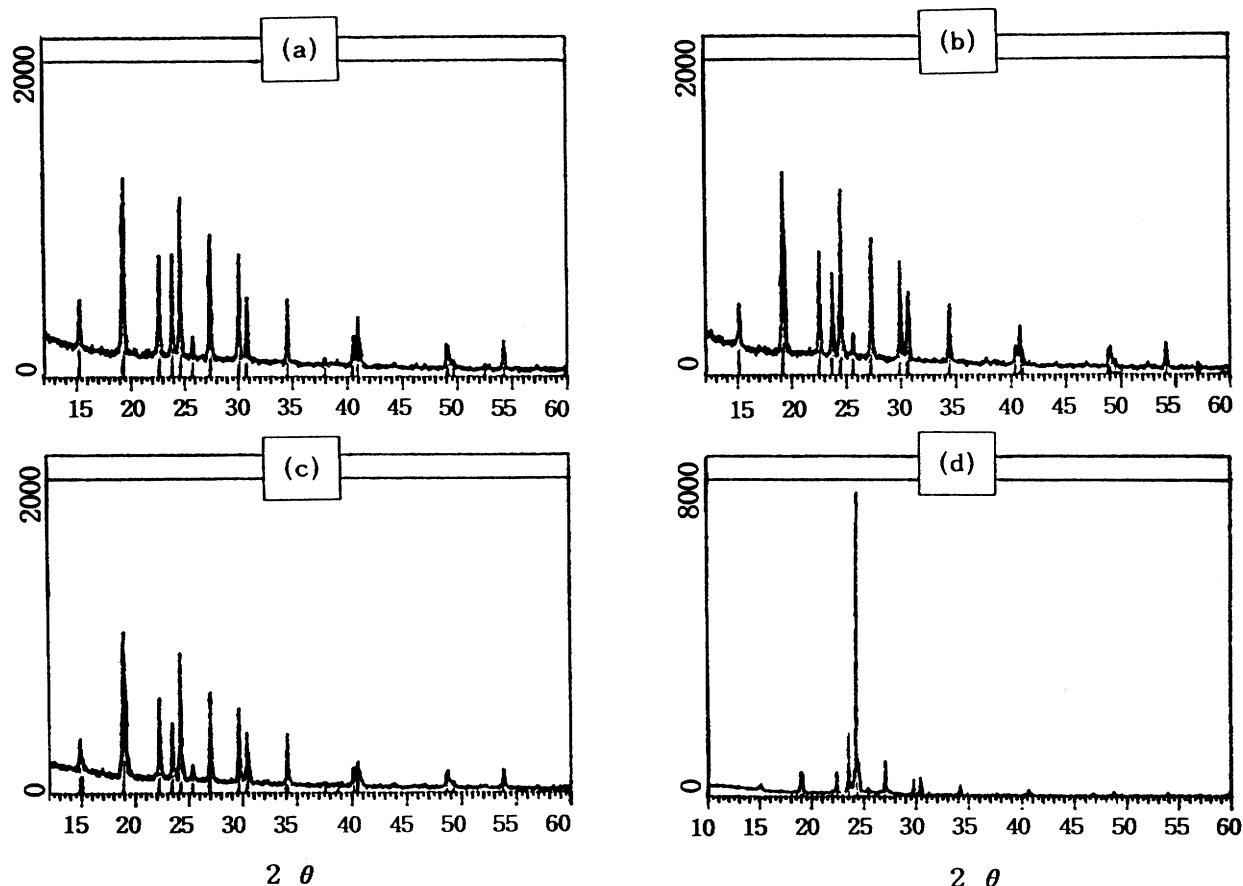


Fig. 4 X-ray diffraction patterns of AP crystals obtained with various organic liquids as precipitants
(a): Ether;
(b): Chloroform
(c): Methylene Chloride;
(d): Isobutyl alcohol

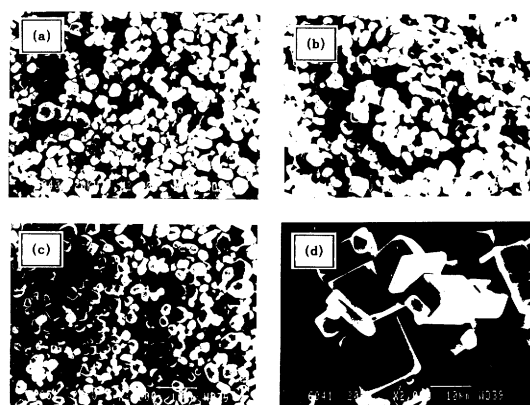


Fig. 3 Scanning electron micrographs of AP crystals obtained with various organic liquids as precipitants
(a): Ether; (b): Chloroform
(c): Methylene Chloride; (d): Isobutyl alcohol

smaller solubility parameter value prove to be more effective as precipitants.

Figure 3 shows SEM photographs, same magnification, of AP crystals obtained at $f = 0.6$ and $t = 30$ min with ether, chloroform, methylene chloride and isobutyl alcohol as the precipitants. It can be seen that except for the AP – methanol – isobutyl alcohol system, the crystal sizes obtained by the salting out method are less than $5 \mu\text{m}$. Moreover, a relatively high proportion of substantially

Table 3 Variation in the crystal size distribution as a function of time, t (min). Experimental conditions: $f = 0.6$, temperature = 298 K

| t | Precipitant | | | | | | | |
|------------------------|-------------|------|------------|------|--------------------|------|------------------|------|
| | Ether | | Chloroform | | Methylene Chloride | | Isobutyl Alcohol | |
| | d_{50} | C.V. | d_{50} | C.V. | d_{50} | C.V. | d_{50} | C.V. |
| 5 | 2.3 | 0.35 | 3.0 | 0.31 | 2.9 | 0.28 | 8.5 | 0.49 |
| 10 | 2.3 | 0.33 | 3.2 | 0.32 | 2.8 | 0.27 | 10.9 | 0.44 |
| 15 | 2.1 | 0.35 | 3.2 | 0.30 | 3.1 | 0.26 | 12.1 | 0.43 |
| 20 | 2.3 | 0.35 | 3.1 | 0.31 | 2.8 | 0.26 | 12.3 | 0.39 |
| 25 | 2.4 | 0.34 | 3.1 | 0.31 | 2.7 | 0.28 | 12.5 | 0.40 |
| 30 | 2.2 | 0.34 | 3.2 | 0.30 | 2.8 | 0.27 | 12.4 | 0.38 |
| Induction Period (sec) | 0 | | 0 | | 0 | | 4 | |

spherical particles was obtained. In the propellant industry, high solids loading is highly desirable. Bulk density can be increased by homogeneously mixing different average sizes of spherical particles. On the other hand, the crystals obtained with isobutyl alcohol as the precipitant had a shape which was almost orthorhombic with plane surfaces bounded by straight edges (see Fig.3 (d)) and the mean crystal size was larger than $10 \mu\text{m}$. It was invariably found that instantaneous precipitation of AP occurred as mixing of the two solutions (methanol solution of AP and a organic precipitant) when ether, chloroform and methylene chloride were the precipitants. Furthermore, there was no significant influence of f on both morphology and crystal

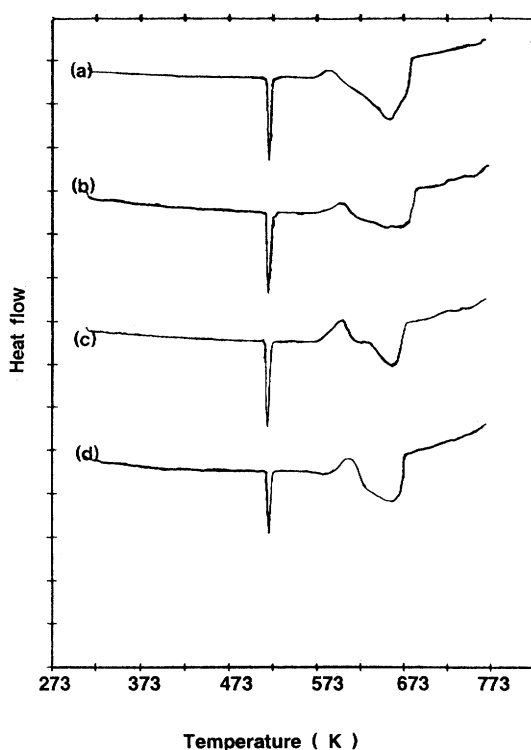


Fig. 5 DSC curves of AP crystals obtained with various organic liquids as precipitants
(a): Ether; (b): Chloroform
(c): Methylene Chloride; (d): Isobutyl alcohol

sizes. However, with isobutyl alcohol as the precipitant, the solid particles appeared several seconds later and the precipitation rate was slower. A typical set of experimental results of the change in the crystal size distribution with time, t , is shown in **Table 3**. The induction period was measured from the time of complete addition of the precipitant until the first nuclei became visible in each run. The coefficient of variation, C.V., was given by

$$C.V. = (d_{84} - d_{16}) / (2 d_{50}) \quad (2)$$

The values d_{16} , d_{50} and d_{84} were obtained from the cumulative undersize weight distribution by reading crystal sizes corresponding to 16%, 50% and 84%, respectively. With ether, chloroform and methylene chloride as the precipitants, the values of the median size, d_{50} , were observed to be almost independent of the operation time after the occurrence of nucleation. In contrast, with isobutyl alcohol as the precipitant, the d_{50} values increased with operating time and become constant after about 15 minutes. It is shown that the coefficient of variation was reduced from about 0.49 to 0.38 with increase in the operation time. From the results, it is certain that the increase in the median size occurred because of the reduction in the nucleation rate. These results mean that the nucleation process in the early stage of crystallization determines the size of the product crystals. Since, according to the classical theory of nucleation, the particle volume is inversely proportional to the nucleation rate, our results are consistent with theoretical predictions.

Figure 4 shows the X-ray diffraction patterns

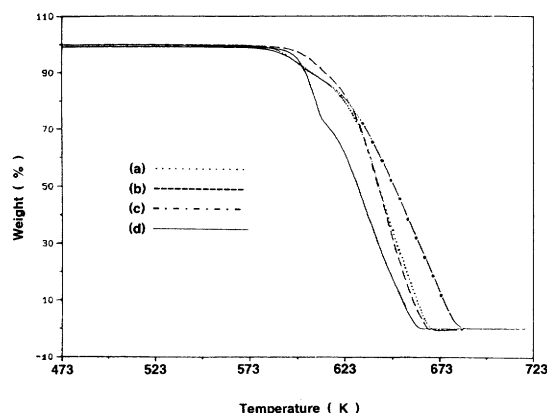


Fig. 6 TG curves of AP crystals obtained with various organic liquids as precipitants
(a): Ether; (b): Chloroform
(c): Methylene Chloride; (d): Isobutyl alcohol

obtained with the crystals shown in **Fig. 3**. Vertical axis represents intensity. Comparison of the X-ray diffraction patterns between crystals shown in **Fig. 3** (a, b and c) indicates identical structure and retention of crystallinity. On the other hand, the X-ray diffraction pattern in **Fig. 4** (d) is apparently different from those in **Fig. 4** (a, b and c). In this case, the intensity decreased at $2\theta = 19.3^\circ$ but at $2\theta = 24.5^\circ$ the intensity increased highly. The reasons for the difference in the X-ray diffraction pattern may be complex. However, it has long been known that variations in solvent can effect crystal growth and habit through changes in the physical properties of the solution and through changes in the solid – liquid interfacial energy. The kinetics of crystallite coarsening in a given atmosphere are affected by the surface energy, and by linkage to neighboring crystallites, which in turn depends on the size, shape and orientation of the parent crystal. Ito and Hikita³⁾ showed that the crystal habit of AP crystals affects the intensity of diffraction. Therefore, the difference in the X-ray diffraction was thought to be caused by the different shape of AP crystals obtained with isobutyl alcohol as the precipitant.

Figures 5 and 6 show the results of DSC and TG obtained with the crystals shown in **Fig. 3** respectively. It can be seen from **Fig. 5** that there is a crystallographic transition from the orthorhombic structure to a cubic structure at about 513 K, which agrees with the result reported by Jacobs and Whitehead⁴⁾. The TG curves in **Fig. 6** did not show appreciable changes in weight loss until 573 K. However, at a temperature above this, detectable changes appeared due to the decomposition and sublimation of AP. In **Fig. 6**, the differences in thermal decomposition patterns were also observed. Bircumshaw and Newman²⁾ showed that AP with its larger particle size had a smaller thermal decomposition rate. However, it can be seen from **Fig. 6** that above 573 K, the thermal decomposition rate of crystals obtained with isobutyl alcohol as the precipitant is faster than those obtained with other organic precipitants used in this work. It is well known that the thermal decomposition is greatly influenced not only by the particle size, but also by its shape and surface conditions. This indicates

that the preparation conditions of crystals play an important role in the properties of solids. It is necessary to remember that the crystallization behaviours obtained with isobutyl alcohol as the precipitant were considerably different from those obtained with other precipitants used in this work. Thus any difference in the crystallization behaviours during the preparation would appear to result in different defect levels. Although thermal decomposition and sublimation of AP have extensively been studied in the past, there is still relatively little information available on the thermal characteristics of AP crystals formed under different conditions. Clearly, further work on this area is needed.

Conclusions

The crystallization behavior of AP from methanol solutions by the salting out method was investigated and the following results were obtained.

- (1) When ether, chloroform and methylene chloride were the precipitants, the product crystals had a particle size less than $5\text{ }\mu\text{m}$ and a relatively high proportion of substantially spherical particles was obtained.
- (2) The crystals obtained with isobutyl alcohol as the precipitant had a orthorhombic shape and the mean crystal size was larger than $10\text{ }\mu\text{m}$.
- (3) Diffraction angles for AP crystals obtained with isobutyl alcohol as the precipitant coincided with those obtained with other precipitants used in this work, though

the intensity in the X-ray diffraction changed.

- (4) Above 573 K, the thermal decomposition rate of crystals obtained with isobutyl alcohol as the precipitant was faster than those obtained with other organic precipitants used in this work.

- (5) In the temperature range of 293~308 K, the solubility of AP in methanol solutions was expressed by Eq. (1).

Nomenclature

| | | | |
|-----------|---|---|--------------------|
| C^* | : | solute concentration at saturation | [g AP/ g solution] |
| $C.V.$ | : | coefficient of variation | |
| d_{50} | : | median size | [μm] |
| f | : | precipitation ratio | |
| R | : | added mass of an organic precipitant per unit mass of the methanol solution | |
| T | : | temperature | [K] |
| t | : | operation time | [min] |
| 2θ | : | reflection angle of X-ray | [$^\circ$] |

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