NOTATION

H = height of bed
ΔP_b = pressure drop through the bed
$\Delta P_{b,mf}$ = pressure drop through the bed at the minimum fluidization velocity
ΔP_d = pressure drop through the distributor
$\Delta P_{d,mf}$ = pressure drop through the distributor at the minimum fluidization velocity
ΔP_t = overall pressure drop
R = distributor-to-bed pressure drop ratio
Re_t = Reynolds' number at the particle terminal velocity
r_b = static bed resistance
r_d = distributor resistance
$r_{d,mf}$ = distributor resistance at the minimum fluidization velocity
u = superficial fluid velocity
u_{mf} = minimum fluidization velocity
u_t = particle terminal velocity
ϵ = void fraction of the bed
ϵ_{mf} = void fraction of the bed at the minimum fluidization velocity
ρ_f = density of fluid
ρ_s = density of particles
ζ = orifice coefficient

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Formation of Inclusions in Terephthalic Acid Crystals

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INTRODUCTION

In recent years improved processes for the manufacture of terephthalic acid (TPA) have led to the development of processes for the direct esterification of TPA with ethylene glycol. This route to the formation of polyethylene terephthalate (PET) has significant economic advantages (Hizikata (1977)) when compared with the route employing dimethyl terephthalate (DMT). A requirement of the direct esterification route is a pure grade of TPA virtually free of impurities which cause unwanted coloring of the product PET. The impurities in TPA manufactured by the oxidation of paraxylene are typically intermediate and byproducts of the oxidation such as 4-carboxybenzaldehyde (4-CBA), o- and m-phthalic acid, p-toluic acid and p-acetylbenzoic acid. 4-CBA is probably the most difficult of these impurities to remove and its concentration in TPA serves as a practical criterion of TPA purity.

Purification of TPA has been the subject of intensive research of the years and a multitude of techniques have been proposed. A summary of these techniques appears as Table 1. A large number of the TPA purification techniques employ crystallization (from the vapor or from the liquid) as a purification step (Maclean, 1960; Kurtz, 1965; Olsen, 1970). It has been reported (Fujita et al., 1968) that recrystallization alone does not normally reduce 4-CBA concentrations in TPA crystals to the desired level. In a recent paper Myerson and Gaines (1982) reported that TPA crystals underwent an irreversible change of habit (known as crystal aging) when immersed in their own saturated solution. The rate of this change of shape was reported to be a strong function of temperature and resulted in an increase in crystal purity. It is the purpose of this study to present several observations which may explain the limitations of crystallization or aging as a purification method.

TPA RECRYSTALLIZATION AND AGING

Recrystallization and aging experiments were conducted in a batch suspension crystallizer shown in Figure 1. It consists of a

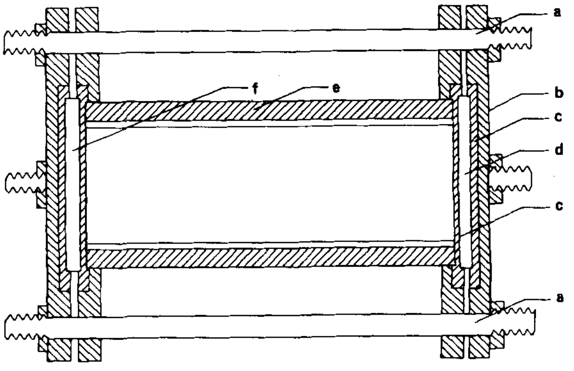

Figure 1. Batch suspension crystallizer: (a) 6.4 × 10^{-3} m connecting rod; (b) 1.016 × 10^{-1} m diameter by 6.4 × 10^{-3} m thick steel frame plate; (c) teflon gasket; (d) 5.08 × 10^{-2} m diameter by 6.4 × 10^{-3} m thick tempered sight glass; (e) 3.81 × 10^{-2} m nominal diameter schedule 80 stainless steel pipe; (f) 3.81 × 10^{-2} m OD tempered sight glass.

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Table 1. Proposed Methods of TPA Purification

Phase	Method		Comments
Vapor Phase	Sublimation	Maclean (1960)	Fluidized Bed
	Sublimation, oxidation/hydrogenation	Bryant et al. (1970)	Metal Catalyst
Liquid Phase	Oxidation	Tate (1962) Wise and Meyer (1963)	Activated Carbon Treatment
		Shigeyasu et al. (1968)	Ion Exchange Treatment
		Taylor et al. (1971)	In Acetic Anhydride Solution
		Stautzenberger and Maclean (1971)	Weak Acid Solution
		Ichikawa and Suzuki (1969)	Aqueous Pyridine Solution
	Other	Ringwald (1963)	Sulfuric Acid Treatment
		Kurtz (1965)	Recrystallization
		Swakon (1963)	CO treatment, activated carbon
		Olsen (1970)	Controlled Continuous Crystallization
		Hensley and Towle (1967)	Activated Carbon
		Witt and Blay (1972)	Iodine or Bromine Catalyst
		Blay (1973)	Mixtures of Acids and Catalysts

glass-lined stainless-steel tube with flat glass windows at each end and held in place by a cover plate and bolts. The chamber is equipped with a magnetic stirrer. Temperature is controlled in the crystallizer by immersion in a constant temperature bath or through controlled resistance heating. Observation and photography of the growing or aging crystals was possible through the use of a stereo-zoom microscope.

Pure and fiber grade TPA supplied by the Amoco Oil Co. was slowly recrystallized in the batch suspension from aqueous solutions at temperatures ranging from 423 to 473 K. The resulting crystals were rod shaped, bound mostly by three or four planes parallel to the long dimensions of the crystals. Frequent twinning was observed along the long axis parallel to the crystallographic c-axis. The crystals ranged in size from 1×10^{-3} m to 5×10^{-3} m (measured along the long axis) with the average being 2×10^{-3} m.

Aging experiments were carried out in the same apparatus holding the temperature constant. Aging experiments showed a gradual transformation of the initial globular crystals to needles indistinguishable from those obtained from crystallization experiments. The transformation of the particles took approximately 15 hours at 473 K. These results are similar to those reported by Myerson and Gaines (1982) in their study of TPA aging.

The crystal structure of two polymorphic forms of TPA was described by Bailey and Brown (1967). The crystal structures of the crystals obtained experimentally in this work were investigated employing X-ray diffraction of both polycrystalline and single crystal samples. Results of the X-ray analysis were consistent with polymorphic form I as reported by Bailey and Brown. The unit cell parameters determined along with those reported by Bailey and Brown appear in Table 2. No form II was detected in polycrystalline species. The crystals were also examined employing scanning electron microscopy (SEM). SEM photographs of the crystals viewed along their long dimension revealed the frequent occurrence of large longitudinal cavities often positioned close and parallel to the twinning plane. Two such crystals appear in Figures 2 and 3.

Quantitative determination of the volume of the inclusions observed in the SEM photography was accomplished through density measurement. The theoretical density of TPA (polymorphic form I) was calculated from the unit cell parameters given in Table 2 and yielded a value of 1.573×10^3 kg/m^3. The volume of the inclusions filled with solution will result in a decrease in the density of the crystal proportional to the included volume. At 298 K the density of TPA as a function of the volume of included solution can be expressed by the relation:

$$\rho = (1.573 \times 10^3 - 5.73I)$$

where ρ is the density in kg/m^3 and I is the percent-included volume in the crystal.

Table 2. Unit Cell Parameters of TPA Form I

	Measured	Bailey and Brown (1967)
a_o	7.736×10^{-10} m	7.730×10^{-10} m
b_o	6.444×10^{-10} m	6.443×10^{-10} m
c_o	3.7504×10^{-10} m	3.749×10^{-10} m
α	91.51°	92.75°
β	109.12°	109.15°
γ	95.77°	95.95°

The density of the grown and aged TPA crystal was measured employing 2×10^{-6} m^3 pycnometers at 298 K with water as the liquid media. Considering the low TPA solubility in water at room temperature (approximately 1×10^{-3} wt. %, Stautzenberger and Maclean, 1971) no correction on solubility was applied. The average density obtained for aged and crystallized TPA was 1566 ± 6 kg/m^3 which results in an average calculated value of the included volume of 1.2%.

The presence of solvent inclusions in TPA crystals purified by crystallization or by crystal aging, puts a limit on the degree of purification that can be obtained by these processes. The final concentration of impurities in TPA purified by these processes will, therefore depend on both the concentration of the impurity in the included solution and the size of the inclusion. In previous studies of solvent inclusions (Myerson and Kirwan, 1977; Slaminko and Myerson, 1981; Senol and Myerson, 1982) it has been demonstrated that the degree of solvent inclusion increases with increasing crystal growth rate and is a function of crystal size and the impurities present in solution. The effect of these variables on the formation of solvent inclusions in TPA will require a carefully controlled experimental study. The results of this work indicate, however, that under both slow (aging) and rapid (recrystallization) growth con-

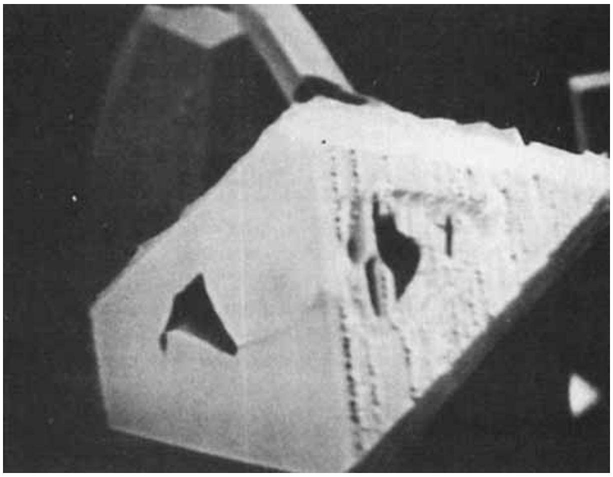

Figure 2. SEM photograph (500×) of aged TPA.

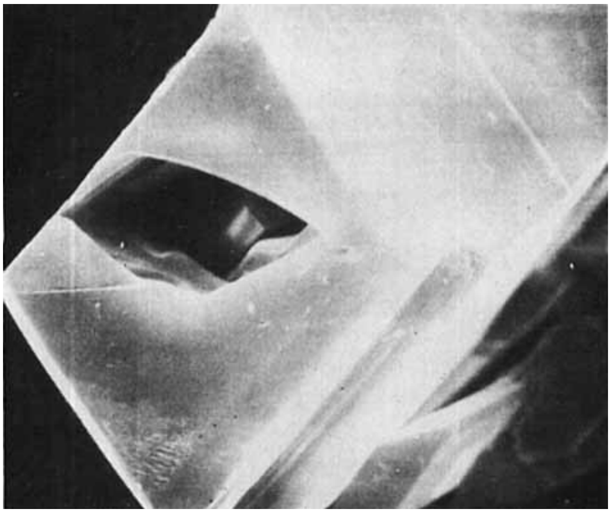

Figure 3. SEM photograph (420×) of aged TPA.

ditions the degree of inclusions in TPA crystals are identical. This suggests that extremely slow growth conditions might be required for the preparation of inclusion-free TPA.

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Calculation Method for Vapor-Liquid Equilibrium in the Critical Region

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The purpose of this work was to test a new prediction method for vapor-liquid equilibrium (VLE) in the critical region. The vapor-liquid equilibrium calculation method used in this study was that due to Leung and Griffiths (1973), which treated composition as a dependent variable. We also followed the work of Moldover and Gallagher (1978), in regard to the power law equations used with the Leung-Griffiths' method.

The input data for the method included the densities of the coexistent phases and the vapor pressure of the pure components along with the critical locus for the binary mixture. Since there are few systems for which the critical locus has been measured thoroughly, the use of the Peng-Robinson (1976) equation of state is investigated for calculation of the critical locus for the mixture in conjunction with this VLE calculational method.

When an equation of state of the van der Waals type is used to calculate VLE near the critical point of binary mixtures, the errors are usually greater than in the other parts of the phase diagram

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