

## HYGROSCOPIC AEROSOLS

by

G. R. Gillespie, Research Assistant

Aerosols, such as smoke, dusts, and fume, present important problems in industrial operations. In metallurgical processes, dusts and fumes are collected and recovered for economic reasons or for the protection of the health of the workers; in chemical manufacturing, waste gases containing injurious aerosols must be cleaned before discharge to the atmosphere.

Filters, scrubbers, cyclones, electrostatic precipitators and other devices are used for cleaning gases. Since hygroscopic aerosols often exist as droplets in the submicron range, their collection becomes difficult. For these, filtration through porous media, impaction at high velocities and agglomeration by means of sound waves have been used, in addition to electrostatic precipitation which has been standard in the past. The selection and design of these devices depend to a large extent on knowledge of the particle size distribution in the aerosol. It is seldom that such information is available. Even in the case of sulfuric acid mist, no accurate information exists on particle sizes, or on the effect of the operating conditions and the nature of the source.

Recently the high velocity jet impactor has been developed as a reliable and convenient instrument for measurement of the particle size distribution in non-homogeneous aerosols. This device was used to determine the effect of various factors on the distribution of droplet size in several hygroscopic aerosols. The mists were made under closely controlled conditions in the laboratory. Some data, which corroborate those obtained in

the laboratory, have been taken from measurements on stack gases from a commercial sulfuric acid plant.

### Sulfuric Acid Aerosols

In the laboratory sulfuric acid aerosols were produced by reacting sulfur trioxide vapor with moist air to form sulfuric acid vapor which immediately condensed into small liquid droplets. A schematic diagram of the equipment used to carry out this reaction is shown in Figure 1. The concentration of the aerosol was varied from 0.05 to 2.9 grains per cubic foot, and the moisture content of the air was varied from 10 to 90 per cent relative humidity. After formation, the aerosol entered a horizontal lucite tube 14 feet long and tapered from 1 inch to 6 inches in diameter, in which it was allowed to age for a period of time up to five minutes. At various intervals along the tube were placed ports from which samples of the aerosol could be withdrawn through an impactor for particle size determination.

The four-stage cascade impactor used was patterned after that of Ranz and Wong (3) and was equipped with 12 interchangeable jets giving nearly any particle size cut desired between 0.2 and 3.0 microns diameter. At each stage the largest droplets were impacted in a glass cup, and the smaller droplets still entrained in the gas stream were carried to the following stage where the next largest size range of droplets was collected. The droplets not impacted in any of the four stages were collected in a three-stage glass wool filter train. Sampling was continued until a weighable quantity of acid was collected in the small cups at each stage. The concentration of the acid samples was determined by titration against standard base.

From the data the weight fraction smaller than the characteristic diameter of each jet was calculated and the results expressed as a particle size distribution curve on log-probability paper. Representative plots for sulfuric acid aerosols of concentration of 1.2 and 0.3 grains per cubic foot are shown in Figures 2 and 3, respectively. On these graphs each line represents the particle size distribution of the aerosol at a given time after its formation.

The most apparent conclusion to be drawn from the data is the increase of the droplet size with time. This growth in size may occur in two ways: (1) by condensation of water vapor on the surface of the droplet until chemical equilibrium exists between the particle and the surrounding air, and (2) by coagulation of the particles formed. That any growth of the particles by condensation of water vapor must take place before the aerosol could be sampled (that is, within 0.2 seconds after its formation) is shown conclusively by the experimental data. If, for example, growth of the particles in the retention chamber were by condensation, then the larger droplets would necessarily show a lower acid content than the smaller ones. Also the weight per cent acid of the aerosol would decrease with time. Analysis of the acid in each size range showed that the acid content did not vary appreciably with size nor did the average acid content in the aerosol decrease with time.

Further evidence against condensation is shown by the fact that the weight of the aerosol per unit volume of air did not increase with time as would be expected if the droplets were absorbing water vapor from the air. Finally, it was found that, even at the earliest sampling point, the aerosol was already nearly in equilibrium with the surrounding air. Therefore,

it must be concluded that within a fraction of a second the reaction of  $\text{SO}_3$  and  $\text{H}_2\text{O}$  takes place, the sulfuric acid vapor condenses into primary particles, and these particles absorb sufficient water vapor to come into equilibrium with the air.

Having ruled out condensation as a growth mechanism in the tube what support is there that the growth is by coagulation? Recalling that the coagulation theory of Smoluchowski and Whytlaw-Gray states that the change in the number of particles per unit time is directly proportional to the square of the particle concentration, a plot of the reciprocal of the number of particles per unit volume against time should result in a straight line, the slope of which is called the coagulation constant.

Although number concentrations of the aerosols were not determined directly in this work, a method exists for calculating them. Since the size distributions fell on straight lines on a log-probability plot, they can be represented mathematically by the log-probability distribution function which permits the calculation of various mean and median diameters. Thus the number median diameter may be calculated by

$$\ln D_{nmd} = \ln D_{mmd} - .3 \ln^2 \sigma_g$$

and the mean volume diameter by

$$\ln D_v^3 = \ln D_{nmd}^3 + 9/2 \ln^2 \sigma_g$$

The volume of a droplet having this mean volume diameter when divided into the total volume of the aerosol gives the number of particles,  $N$ , per unit volume of air. The total volume of aerosol collected per unit volume of air may be determined from a knowledge of its weight and density.

Having thus obtained a value for the particle concentrations at various points in the retention chamber, plots of the reciprocal of this value against time were then made. These data are shown in Figure 4; the curve drawn represents the average slope,  $K = 16 \times 10^{-10}$  cc. per second, obtained from experiments with varying concentrations of aerosol and relative humidities of the air stream. This value compares favorably with that of  $15 \times 10^{-10}$  cc. per second predicted by Fuchs (1).

After obtaining satisfactory results in the laboratory, measurements were made on the exit stack gases of two commercial contact acid units. The particle size and particle size distribution of the mists contained in these gases were nearly identical with those produced under similar conditions in the laboratory. A mass median diameter of 0.6 microns and a standard geometric deviation of 1.3 were found. We believe that this is the first time that accurate measurements have been made on the particle size of sulfuric acid mist from a commercial plant.

#### Phosphoric Acid Aerosols

An aerosol of phosphoric acid was produced by vaporization of solid phosphorus pentoxide into a stream of nitrogen which was then mixed with moist air. The  $P_4O_{10}$  molecules reacted with the water vapor to form  $H_3PO_4$  which then condensed into small liquid droplets. As in the case of sulfuric acid, the aerosol immediately came into chemical equilibrium with the surrounding air.

The particle size was more than twice as large as that of sulfuric acid when produced under similar conditions of mist loading and relative humidity. This fact, resulting in a large decrease of the number of

particles per unit volume, reduced the rate of coagulation of the aerosol. In fact, even after seven minutes, no growth in the particle size could be detected by the impactors. These results are shown in Figure 5.

- A partial explanation of the differences in size of these two aerosols may be found in their relative self-nucleating powers: sulfuric acid and sulfur trioxide have been reported as strongly self-nucleating by LaMer (2). An indirect verification of the relative nucleating powers of sulfuric and phosphoric acid has been carried out in the laboratory. Foreign nuclei in the form of sodium chloride ions were added to the moist air stream. In the case of sulfuric acid no change in the particle size or number was found, indicating that additional nuclei had no effect on the physical properties of the aerosol. In the case of phosphoric acid, however, the addition of foreign nuclei increased the number concentration and decreased the size of the droplets. This fact indicates that phosphoric acid does not supply an excess of nuclei from which the droplets grow, which results in fewer but larger droplets. Figure 6 graphically represents these experiments.

Work on other hygroscopic aerosols is in progress, including those of hydrochloric acid, nitric acid, titanium tetrachloride, and silicon tetrachloride.

#### Conclusions

1. The high velocity cascade impactor has been shown to be a convenient instrument for determining the particle size distribution of hygroscopic aerosols in the micron and submicron range in both laboratory and field work.

2. Data have been presented showing the effect of aging on the particle size distribution of sulfuric and phosphoric acid mists.

## Bibliography

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2. LaMer, V. K., Inn, E. C. Y., Wilson, J. B., J. Colloid Sci. 5, 471-96 (1950).
3. Ranz, W. E., and Wong, J. B., "Jet Impactors for Determining the Particle Size Distribution of Aerosols". T. R. No. 4 SO-1005 E. E. S. Univ. of Illinois (1951) (Obtainable from Tech. Information Service, U. S. A.E.C., Oak Ridge, Tennessee).

## Nomenclature

$D_{mmd}$  = Mass median diameter

$D_{nmd}$  = Number median diameter

$D_v$  = Mean volume diameter

$N$  = Number of particles per cc of air

$K$  = Coagulation coefficient, cc per second

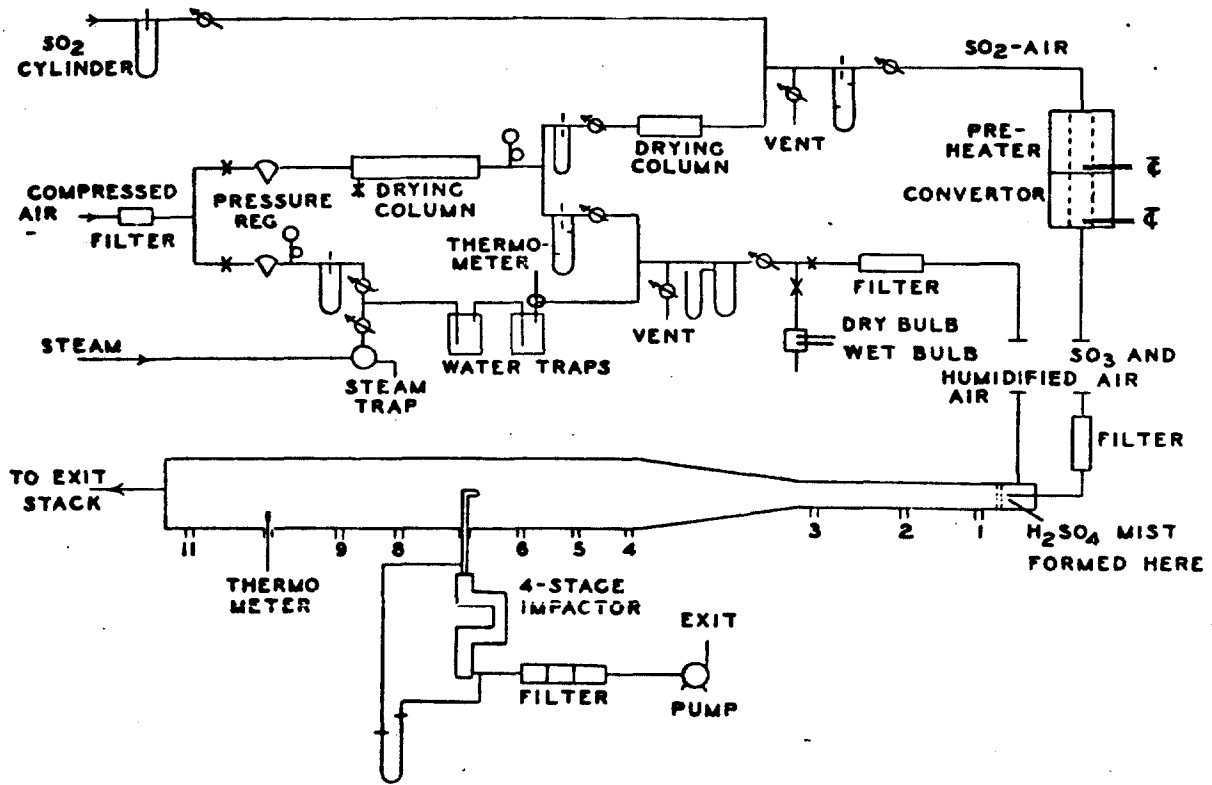


Fig. 1—Schematic diagram of equipment.

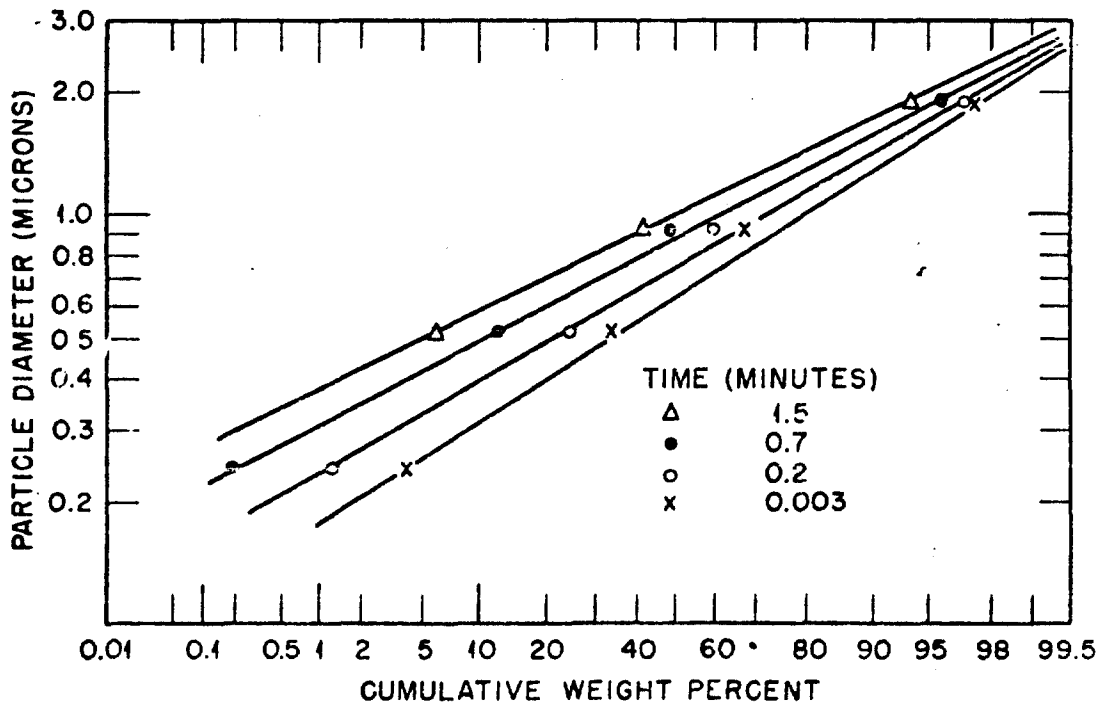


Fig. 2—Particle size distribution of sulfuric acid aerosol.



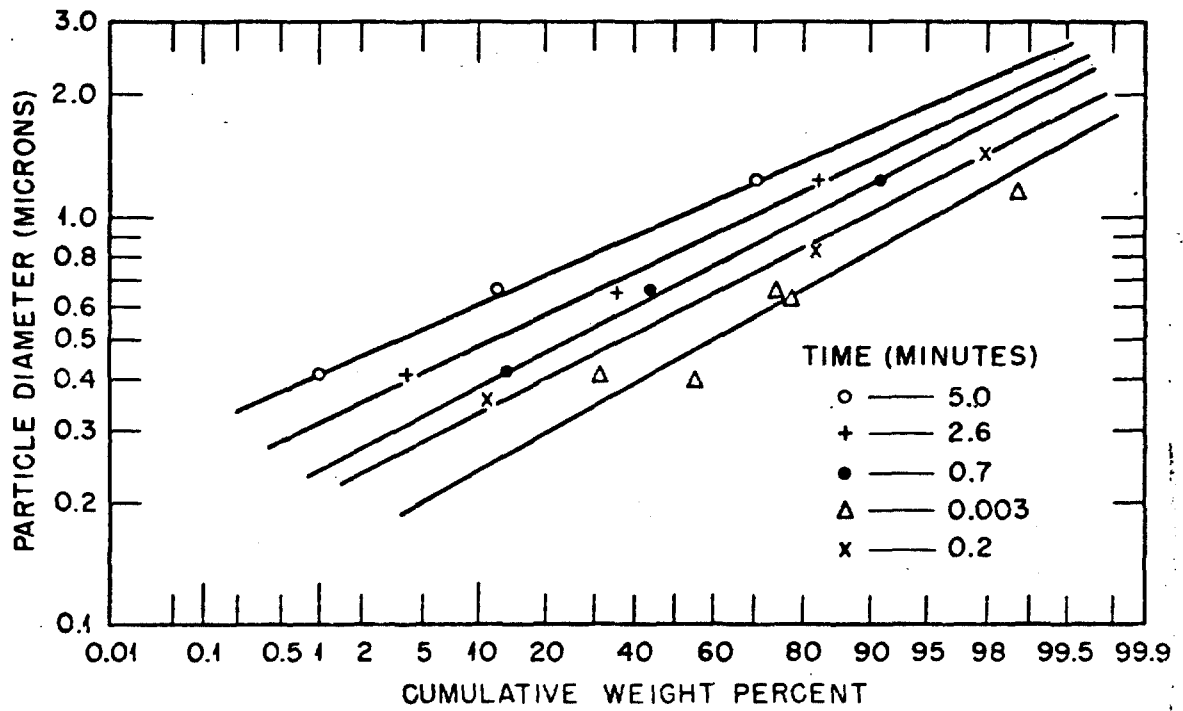


Fig. 3—Particle size distribution of sulfuric acid aerosol.

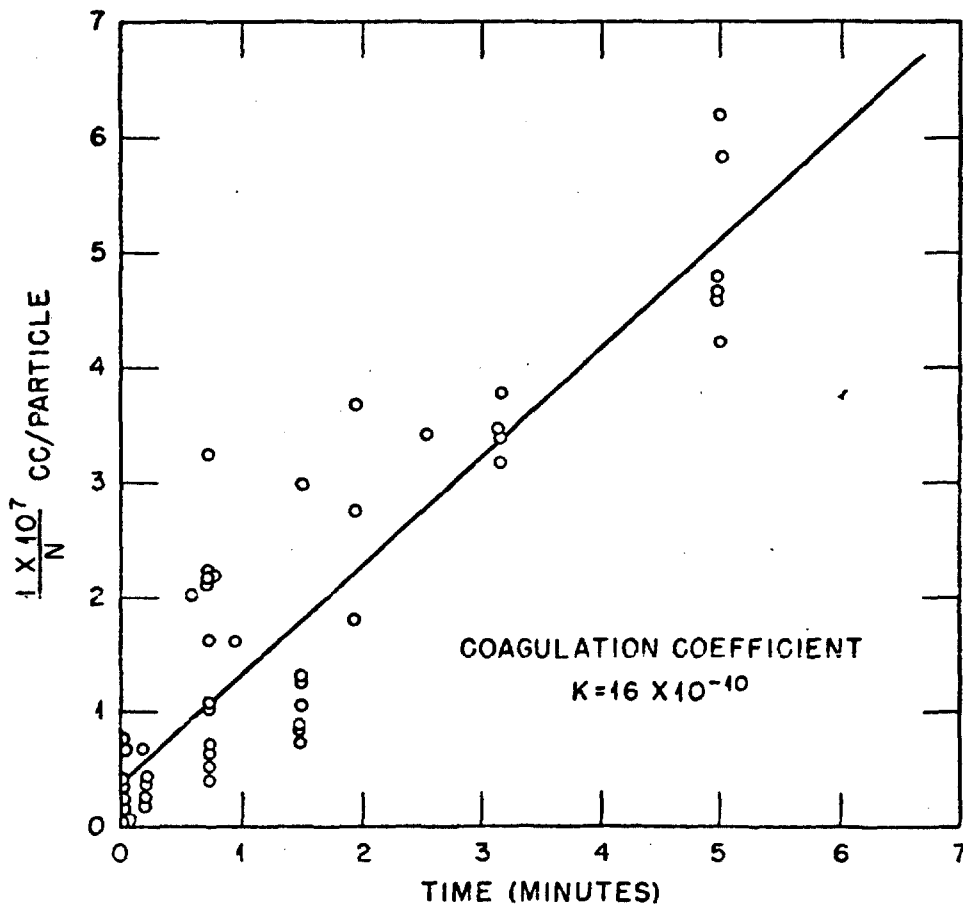


Fig. 4—Rate of coagulation of droplets sulfuric acid.

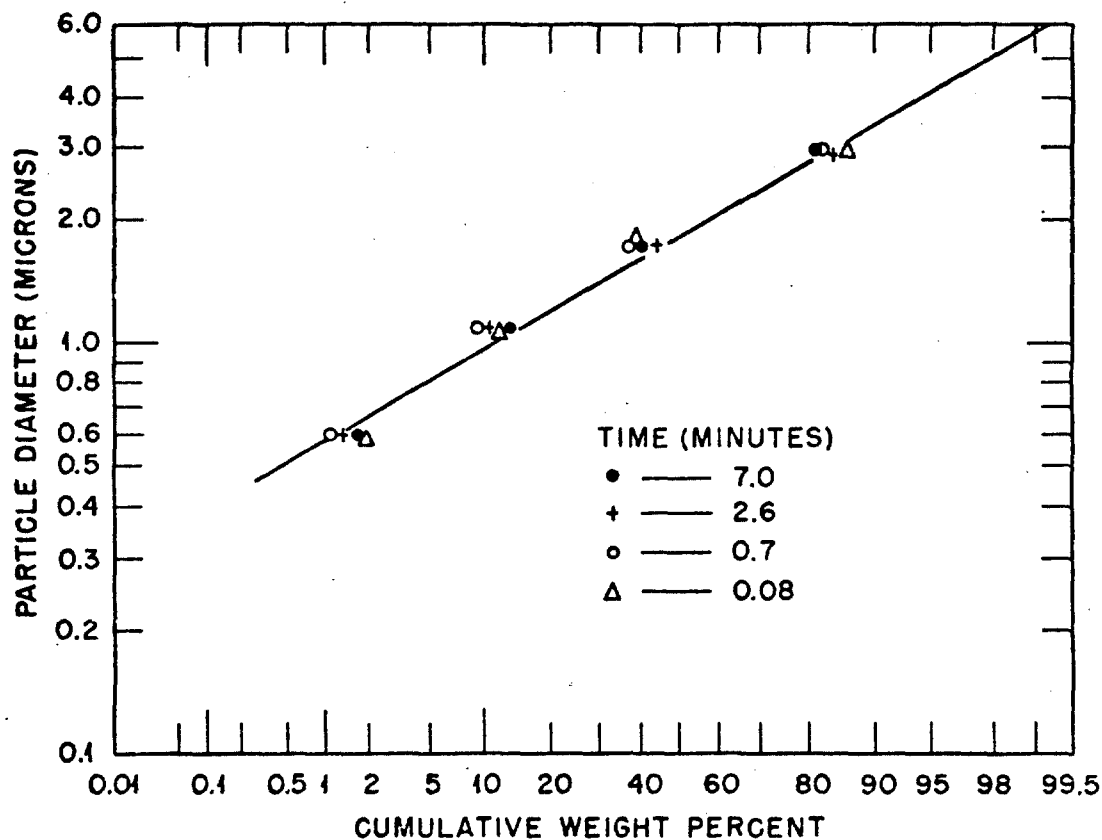


Fig. 5—Particle size distribution of phosphoric acid aerosol.

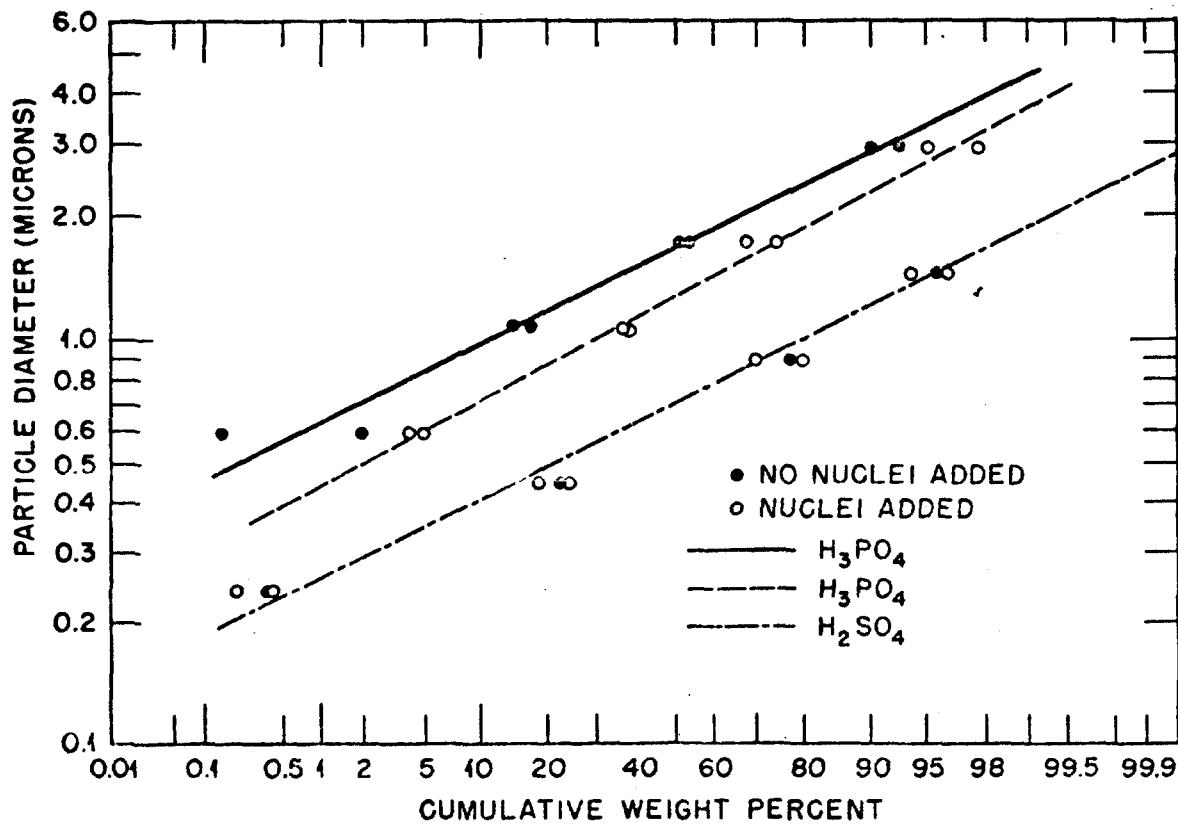


Fig. 6—Effect of foreign nuclei on particle size.