

## Powder Densities—Specific Surface Relations for PVC Resins

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### Synopsis

The bulk and tap densities of a series of PVC resins were found to be related linearly to each other and hyperbolically to the resin specific surface.

### INTRODUCTION

PVC produced by the suspension process consists of porous particles. The morphology of these particles, which is determined to a large extent by the polymerization process parameters, has a profound effect on the subsequent processing behavior.<sup>1</sup> Wallace et al.<sup>2</sup> have studied properties reflecting the particle morphology of a number of PVC resins and related them to the processing behavior of the resin. The properties studied by them included the porosity, pore size and distribution, bulk density, and surface area.

We have found that some of the properties reflecting the particle morphology can be correlated. The bulk (apparent) and tap densities of PVC suspension resins were found to exhibit a linear relationship with respect to each other. A similar relation was also found for a number of other types of solid particles. Both bulk and tap densities of a series of PVC resins prepared in these laboratories were found to be related to their specific surface by hyperbolic relations. These latter two relations were not as general as the densities relation, and it is believed that the hyperbolic relations are affected by process parameters.

### BULK DENSITY (BD)—TAP DENSITY (TD) RELATION

Figure 1 presents a plot of the bulk–tap densities relation for a number of PVC suspension polymers prepared in these laboratories as well as several commercial materials. It will be seen that all the data points fall on, or very close to, a straight line which can be described by the relation

$$TD = 1.2BD + 0.045 \quad (1)$$

This included a material, precipitated from tetrahydrofuran solution by methanol, which had a specific surface of 27 m<sup>2</sup>/g. Although no such cor-

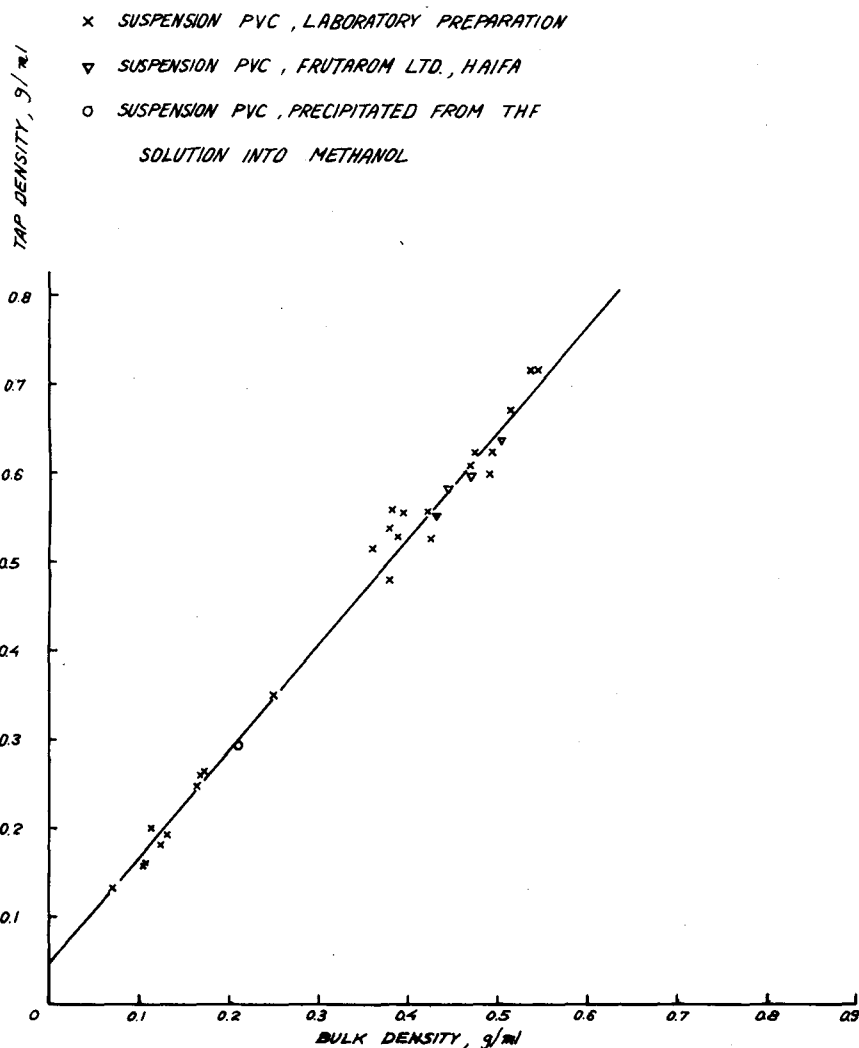


Fig. 1. Bulk density-tap density relation.

relation for PVC could be found in the literature, Hausner<sup>3</sup> reported a straight-line correlation between the bulk and tap densities for three copper powders of different morphologies—spherical, flakes, and irregular. Hausner's data lead to the following relation:

$$TD = 1.13BD + 0.3 \quad (2)$$

Neumann,<sup>4</sup> Brown and Richards,<sup>5</sup> as well as Graton and Frazer<sup>6</sup> determined, but did not correlate, these two densities for a number of mostly inorganic powders. Neumann found a difference in behavior between free-flowing and cohesive powders. Brown and Richards did not use the tap and bulk densities directly but rather the fractional solids contents.

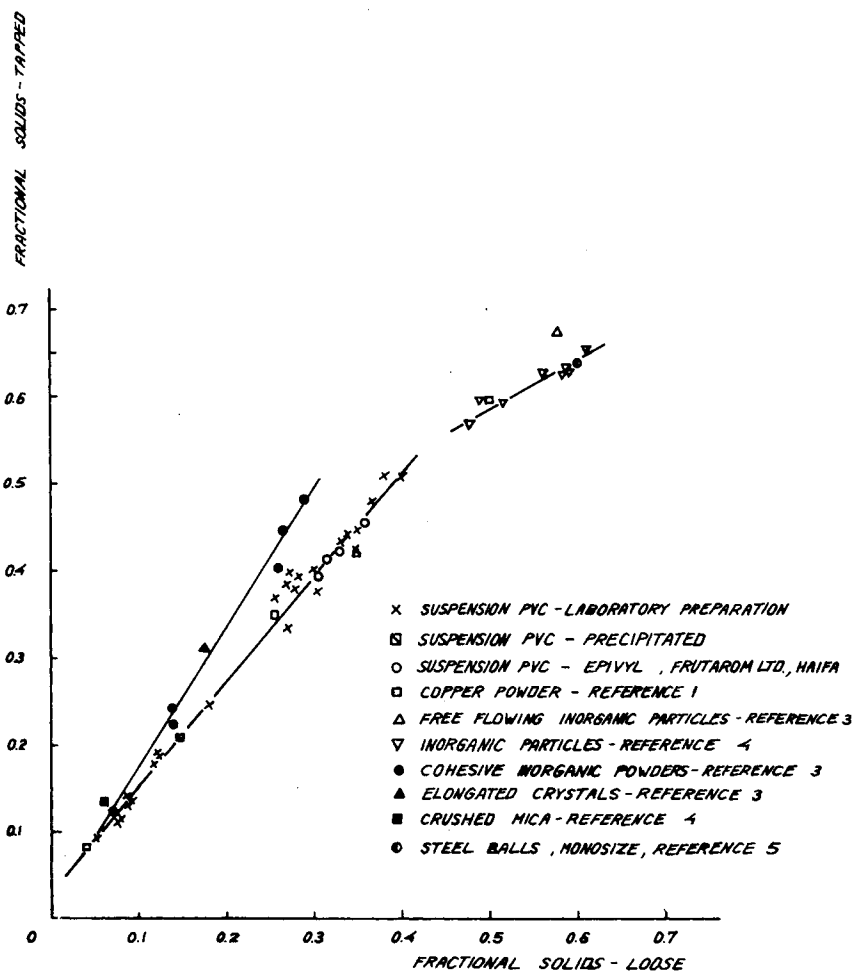


Fig. 2. Fractional solids loose-tapped relation.

The loose fractional solids content is the bulk density divided by the true density of the material. Similarly, the tapped fractional solids content is the tap density divided by the true density. This form permits comparison of different materials on the same basis. As not all the true densities of the materials examined by Brown and Richards were available to us, we converted our results as well as those of Hausner and Graton and Frazer to the fractional solids contents. The results are given in Figure 2. The materials can be divided into three groups. All the PVC resins fall on one line (as in Fig. 1). Two of the copper powders<sup>3</sup> also fall on this line. The cohesive particles<sup>5</sup> together with the crushed mica<sup>6</sup> and elongated crystals<sup>5</sup> form a separate line which crosses the PVC line at the data point for the copper flakes,<sup>3</sup> which is therefore common to both lines. The third

line is for inorganic particles,<sup>6</sup> most of which are spherical, as well as for copper spheres<sup>3</sup> and steel balls.<sup>7</sup>

It would therefore appear that, in general, the fractional solids loose-tapped relation is linear, the slope and intercept depending on the type and morphology of the material.

### SPECIFIC SURFACE (S)-TAP DENSITY (TD) RELATION

A plot of the reciprocal tap density, or tap volume,\* versus the reciprocal specific surface of the suspension PVC resins prepared in these laboratories, gives a hyperbolic type of curve (Fig. 3). With the aid of the graphic technique of Hohmann and Lockart,<sup>9</sup> the following relation was found:

$$S^{-1} = \frac{-0.127 - 0.12TD^{-1}}{1 - 0.66TD^{-1}} \quad (3)$$

- x SUSPENSION PVC LABORATORY PREPARATION  
 o SUSPENSION PVC, ERIVYL, FRUTAROM LTD., HAIFA

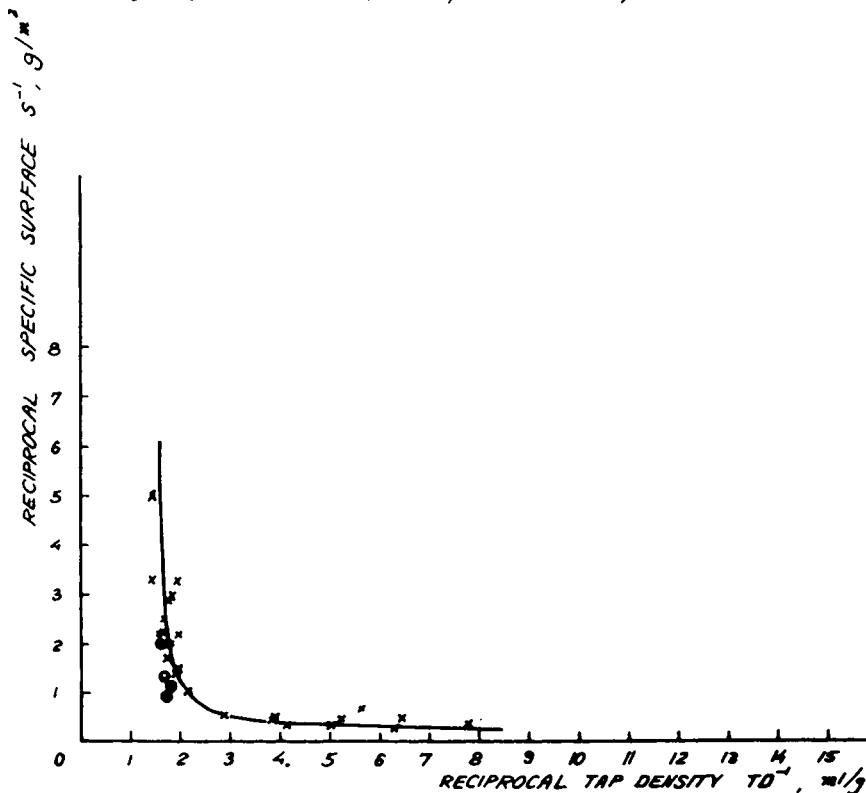


Fig. 3. Relation between reciprocal specific surface and reciprocal tap density.

\* The reciprocal bulk density has been called the bulk volume.<sup>8</sup> The reciprocal tap density can therefore be called the tap volume.

where  $S^{-1}$  is the reciprocal specific surface, in  $\text{g}/\text{m}^2$ , and  $TD^{-1}$  is the tap volume, in  $\text{ml}/\text{g}$ . This gives the hyperbola plotted in Figure 3. The asymptotic values derived from this relation give a maximum tap density of  $0.66 \text{ g}/\text{ml}$  and a maximum specific surface of  $5.5 \text{ m}^2/\text{g}$ . This relation, on converting to the direct functions of tap density and specific surface, should also be hyperbolic; however, when the data are plotted in this form, considerable scatter is found.

### SPECIFIC SURFACE (S)-BULK DENSITY (BD) RELATION

Figure 4 shows a plot of the reciprocal specific surface as a function of the reciprocal bulk density, or bulk volume,<sup>8</sup> for the suspension PVC resins prepared in these laboratories. This, too, appears to be hyperbolic, although there is somewhat more scatter here than in Figure 3. Combining eqs. (1) and (3) gave the relation

$$S^{-1} = \frac{-0.127 - 0.105BD^{-1}}{1 - 0.51BD^{-1}} \quad (4)$$

where  $BD^{-1}$  is the bulk volume in  $\text{ml}/\text{g}$ , which is plotted on the figure as a continuous line. In this case, too, a plot of the specific surface versus the bulk density shows considerable scatter. The asymptotes of relation (4)

- x SUSPENSION PVC LABORATORY PREPARATION
- o SUSPENSION PVC EPIVYL, FRUTAROM LTD, HAIFA
- Δ PVC DATA FROM REFERENCE 2

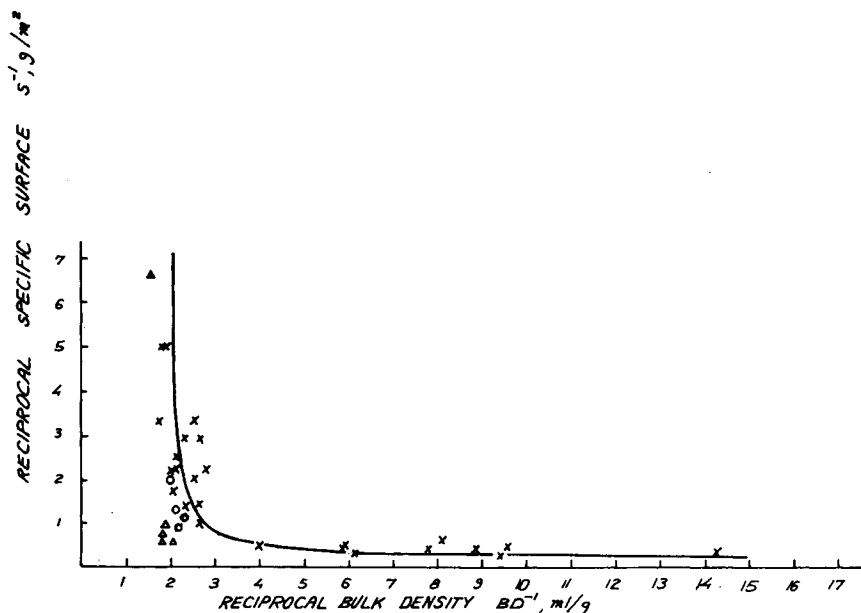


Fig. 4. Relation between reciprocal specific surface and reciprocal bulk density.

give the maximum bulk density as 0.51 g/ml and the maximum specific surface as 4.9 m<sup>2</sup>/g.

Data for several commercial materials (Electro-Chemical Industries, Ltd., Haifa) are given on these two figures and fall close to the curves representing the average values of the laboratory-prepared materials. The data given by Wallace et al.<sup>2</sup> are also plotted in Figure 4 and can be seen to be further off the curve than the commercial materials. The precipitated material does not fit on either of these curves, as its specific surface (27 m<sup>2</sup>/g) is far above the range of these graphs. These facts may indicate the constants of the hyperbolic relations to be specific to the polymerization process, probably depending on such parameters as temperature, reaction rate, stirring suspending agents type and concentration, and initiator type and concentration.

### EXPERIMENTAL

Polymerizations were run at 60°C using lauryl peroxide as initiator in suspension in a glass autoclave (Ingenieurbuero SFS, Zürich, Switzerland). Suspending agent type and concentration as well as the stirring conditions were the same for all experiments. Materials ranging from 12% to 90% conversion were examined. The low-conversion materials showed low bulk and tap densities. The specific surface-conversion relation will be reported separately. Specific surfaces were determined by the dynamic BET method<sup>10</sup> using nitrogen. Degassing of the samples was for 2 hr at 60°C under helium flow. In order to examine the effect of drying and degassing of the materials on the specific surface, a low-conversion, high-specific surface material was divided into two parts after removal from the autoclave. One part was dried and degassed as usual, drying by fluidized bed with air at 60°C for 2 hr. The other part was dried to constant weight at ambient temperature by means of a mechanical vacuum pump and degassed for 2 hr under helium flow at ambient temperature. The specific surfaces obtained differed by only 5%.

Bulk (apparent) densities were determined by ASTM D 1895-65T, Method A. Tap densities were determined by placing the resin in a 100-ml measuring cylinder, tapping on the bench, and making up with resin to the mark until further tapping produced no further volume reduction. The cylinder contents were then weighed.

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