# A Generalized Model to Predict the Viscosity of Solutions with Suspended Particles. IV. Determination of Optimum Particle-by-Particle Volume Fractions

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## SYNOPSIS

A new approach has been introduced to establish the optimum composition for all particles within a mixture or suspension to achieve the optimum packing fraction, $\varphi_n$, and/or the minimum viscosity, $\eta$. The derivation to obtain the optimum particle volume fraction assumed that a previously developed optimum composition for binary particles applied to any two particle volumes $V_i$ and $V_j$ in the mixture. The composition of the maximum packing fraction for a mixture of more than two particles was then assumed to be calculable from the optimized relationship of each separate binary pair of particle volumes $V_i$ and $V_j$ in the mixture. This derived equation was successfully shown to predict the optimum particle-to-particle composition of McGeary's experimentally measured binary, tertiary, and quaternary mixtures. The difference between the calculated and measured volume fractions was no greater than 3.85% and, in most instances, was significantly less than 3.85%. The maximum packing fractions, $\varphi_n$, determined experimentally by McGeary, were also successfully predicted to better than 3.26%. Theoretical particle-to-particle volume fractions evaluated for an example pressure-agglomerated latex appeared to predict the particle-size distribution only within a narrow range of particle sizes. However, when the theoretical and experimental results were evaluated as a function of the number of particles for each particle diameter, it was apparent that the agglomerated distribution closely approximated the theoretical optimum distribution above 600 Å. Agreement with theory below 600 Å was unsatisfactory. The decrease in viscosity of the example agglomerated latex appeared to have been enhanced as the optimum theoretical particle-size distribution was approached.
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## INTRODUCTION

Viscosity applications for liquids with suspended particles cross many disciplines. For example, the viscosity of spherical particle suspensions has been evaluated for synthetic rubber,[1-4] paint and coatings latexes,[5,6] milk,[7] bitumen emulsions,[8] and filled thermoplastics.[9,10] An extensive survey of the viscosity-concentration literature was made by Rutgers in 1962.[11,12] By comparing the experimental data with the equations, he concluded that the many literature equations could be reduced to five useful ones. These primary equations each incorporated some measure of suspension particles to pack efficiently as defined by a particle packing fraction, $\varphi_n$. More recently, it was shown[13] that the primary viscosity concentration equations identified by Rutgers can be combined into one generalized viscosity concentration equation. In a succeeding paper,[14] it was shown that combinations of binary particles go thorough a maximum packing fraction, $\varphi_n$, and that the minimum viscosity, $\eta$, for binary particle suspension blends can be predicted as a function the $D_5/D_1$ ratio of average particle diameters. The maximum value of the average particle-size ratio $D_5/D_1$ was shown by derivation to go through a maximum at a specific volume fraction composition for a binary mixture of particles. The location of this optimum binary composition was specified by the ratio of the

large to small particle diameters, $R_{12}$. In the last article in this series,[15] it was shown that an optimum composition and minimum viscosity can also be found for combinations of two latexes, each with a broad particle-size distribution. The optimum pseudobinary volume blend of two broad distribution latexes was found to occur at a specific composition[15] that again depended on the evaluation of the optimum packing fraction, $\varphi_n$. However, the optimum particle-by-particle composition within a given latex or particle mixture that yields the optimum packing fraction for a mixture of more than two particle sizes was not addressed. Such an optimum composition should also yield the minimum viscosity for a suspension of these particles. The identification of this specific particle-by-particle composition for a mixture or suspension of more than two particle sizes is the subject of this article.

The particle-by-particle composition that gives the maximum packing efficiency for a mixture of different particle sizes will apply equally well to both liquid suspensions as well as to dry mixtures of particles. Several applications of dry blends of particles have industrial importance. The wide diversity in dry packing applications of particles includes the concrete industry, makers of quality ceramic ware and refractories,[16,17] packed tower and bed hydraulics engineering,[18,19] industrial handling and packing,[20] soil geology,[21,22] and the packing of uranium oxide in long tubes for the nuclear industry.[23]

Several experimental investigations[23-25] have revealed that the packing fraction of binary mixtures of spheres exhibits a maximum value that is a function of the diameter ratio. Probably the most definitive experimental work on binary, tertiary, and quaternary packing of spherical particles was done by McGeary.[23] Several authors[26-28] attempted to analytically predict the optimum packing fractions found for these blends of spherical particles. These approaches attempted to describe the composition curves for these mixtures using different sets of equations for different parts of the composition curve even for binary mixtures. More recently, it was shown[14] that the maximum packing fraction and the location of this maximum composition for McGeary's binary blends could be predicted using only one equation. This article will extend this analysis to include the prediction of the optimum particle-to-particle composition of McGeary's tertiary and quaternary mixtures. This method will then be extended to the prediction of the optimum particle-to-particle composition for an undefined number of particles in a dry mixture or a latex blend.

## THEORETICAL OPTIMUM PARTICLE-TO-PARTICLE VOLUME FRACTION FOR A TERTIARY MIXTURE

McGeary[23] found that the packing fraction for binary mixtures of spherical particles goes through a maximum packing fraction as shown in Figure 1. McGeary's maximum binary packing fractions have been shown by this author[14] to be very successfully predicted using the following equation:

$$\varphi_n = \varphi_{\text{nult}} - (\varphi_{\text{nult}} - \varphi_m)e^{\alpha[1-(D_5/D_1)]} \quad (1)$$

$$\varphi_{\text{nult}} = 1 - (1 - \varphi_m)^n \quad (2)$$

$$D_5 = \frac{\sum\limits_{i=1}^{n} N_i \mathcal{D}_i^5}{\sum\limits_{i=1}^{n} N_i \mathcal{D}_i^4} \quad (3)$$

$$D_1 = \frac{\sum\limits_{i=1}^{n} N_i \mathcal{D}_i}{\sum\limits_{i=1}^{n} N_i} \quad (4)$$

where $D_x$ is the $X$th average particle diameter; $n$, the number of different particle diameters in a batch combination; $N_i$, the number of particles of the $i$th particle diameter; $\mathcal{D}_i$, the diameter of the $i$th particle size; $\alpha$, a constant = .268; $\varphi_n$, the packing fraction; $\varphi_{\text{nult}}$, the ultimate packing fraction for a specific number of particle sizes; and $\varphi_m$, the monodisperse packing fraction.

Utilizing this calculation procedure, the value of $\varphi_n$ can be evaluated for any ratio $D_5/D_1$. It can easily be shown that the maximum value of $\varphi_n$ for a binary mixture occurs at the same composition in which the value of $D_5/D_1$ goes through a maximum. The maximum value of the $D_5/D_1$ for a binary mixture of particles has been derived[14] to occur at the following large diameter particle volume fraction, $f_1$:

$$f_1 = \frac{\sqrt{R_{12}}}{\sqrt{R_{12}} + 1} \quad (5)$$

and

$$R_{12} = \frac{\mathcal{D}_1}{\mathcal{D}_2} \quad (6)$$

where $R_{12}$ is the ratio of the large-particle diameter to the small-particle diameter; $f_1$, the volume fraction of the large particle; $\mathcal{D}_1$, the diameter of the
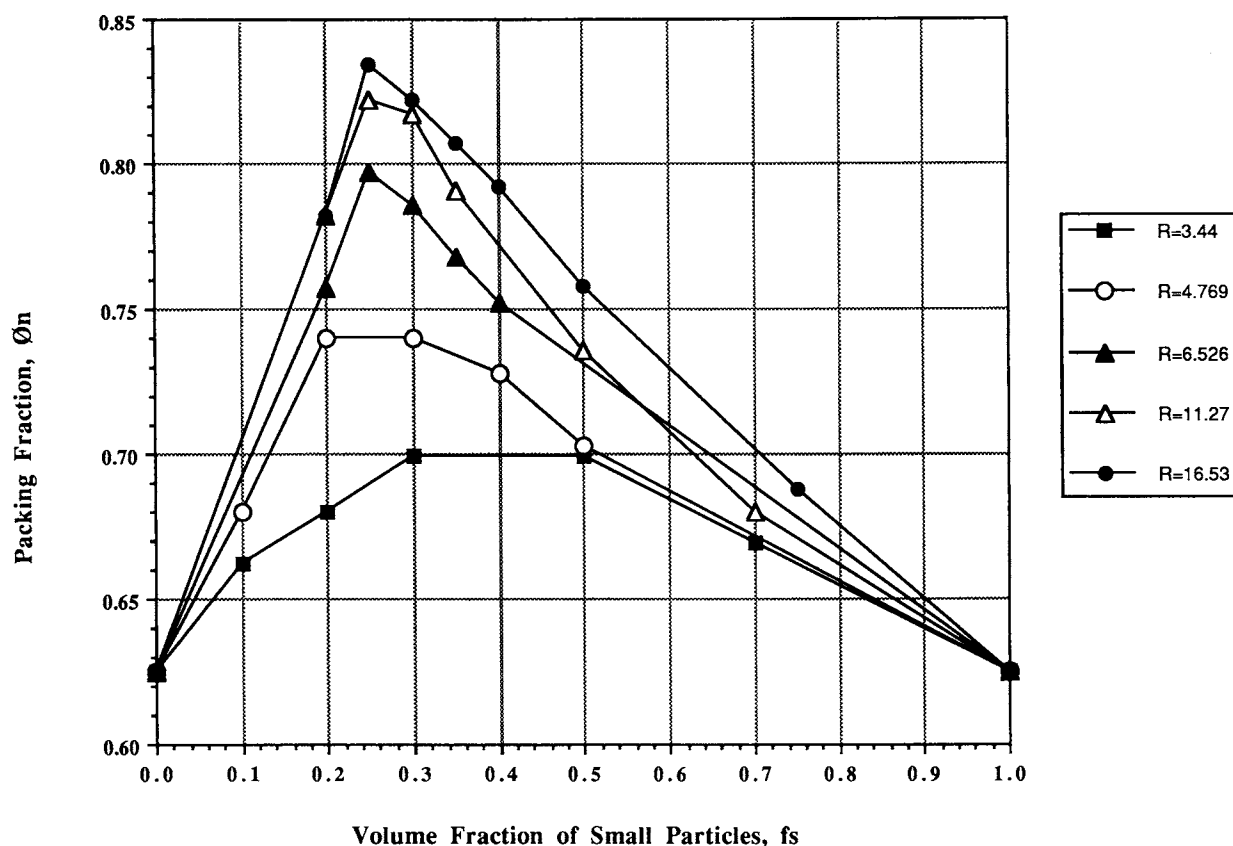
**Figure 1**  Selected binary particle packing fraction data sets for different ratios of large-to-small diameter particles (data of McGeary, Ref. 23).

large particle; and $\mathcal{D}_2$, the diameter of the small particle.

If more than two particles are in a mixture, the optimum composition to give the maximum packing fraction can be calculated by separating the mixture into a series of paired volumes. For example, the volume of a mixture of three different particle sizes can be described as

$$V_1 + V_2 + V_3 = V_T \qquad (7)$$

For the purpose of this analysis, the particle diameters in a mixture will be numbered such that

$$\mathcal{D}_1 > \mathcal{D}_2 > \mathcal{D}_3 > \mathcal{D}_4 > \cdots > \mathcal{D}_n \qquad (8)$$

With this definition, the volume fraction of the second largest particle in a tertiary mixture can be calculated as

$$f_2 = \frac{V_2}{V_T} = \frac{V_2}{V_1 + V_2 + V_3} \qquad (9)$$

These volumes can be separated into paired volumes of the type

$$V_1 + V_2 = V_{T1} \qquad (10)$$

$$V_1 + V_3 = V_{T2} \qquad (11)$$

Note that each of the above paired volume equations has one common volume of particles, $V_1$. Based on these definitions, then, the volume fraction, $f_2$, can be obtained by combining eqs. (9)–(11) to give

$$f_2 = \frac{V_2}{V_T} = \frac{V_2/V_{T1}}{V_2/V_{T1} + V_{2T}/V_{T1}} \qquad (12)$$

At this point, the following assumptions were made:

- The previously developed optimum volume fraction for binary particles described by eq. (5) was assumed to apply to any two particle volumes $V_i$ and $V_j$ in the mixture.
- The composition of the maximum packing fraction for a mixture of more than two particles

was assumed to be calculable from the optimized relationship of each separate binary pair of particle volumes $V_i$ and $V_j$ in the mixture.

Using these assumptions, the optimum volume fractions of these paired volumes can be calculated as

$$\frac{V_1}{V_{T1}} = \frac{\sqrt{R_{12}}}{\sqrt{R_{12}} + 1} \tag{13}$$

$$\frac{V_2}{V_{T1}} = 1 - \frac{V_1}{V_{T1}} = \frac{1}{\sqrt{R_{12}} + 1} \tag{14}$$

$$\frac{V_1}{V_{T2}} = \frac{\sqrt{R_{13}}}{\sqrt{R_{13}} + 1} \tag{15}$$

Taking the ratio of eqs. (13) and (15) gives

$$\frac{V_{T2}}{V_{T1}} = \left(\frac{\sqrt{R_{12}}}{\sqrt{R_{13}}}\right)\left(\frac{\sqrt{R_{13}} + 1}{\sqrt{R_{12}} + 1}\right) \tag{16}$$

Substituting eqs. (14) and (16) into eq. (12) and simplifying gives

$$f_2 = \frac{V_2}{V_T} = \frac{1}{1 + \sqrt{R_{12}} + \left(\dfrac{\sqrt{R_{12}}}{\sqrt{R_{13}}}\right)} \tag{17}$$

Further simplification is possible since

$$\frac{\sqrt{R_{12}}}{\sqrt{R_{13}}} = \frac{\sqrt{\dfrac{\mathcal{D}_1}{\mathcal{D}_2}}}{\sqrt{\dfrac{\mathcal{D}_1}{\mathcal{D}_3}}} = \frac{\sqrt{\mathcal{D}_3}}{\sqrt{\mathcal{D}_2}} \tag{18}$$

Substituting eq. (18) into (17) and simplifying gives

$$f_2 = \frac{V_2}{V_T} = \frac{\sqrt{\mathcal{D}_2}}{\sqrt{\mathcal{D}_1} + \sqrt{\mathcal{D}_2} + \sqrt{\mathcal{D}_3}} \tag{19}$$

This illustrates the simplified equation to calculate the optimum particle-by-particle composition of a particle-size distribution to achieve the maximum packing fraction. The general form of this equation can be written as

$$f_i = \frac{V_i}{V_T} = \frac{\sqrt{\mathcal{D}_i}}{\sum\limits_{i=1}^{3} \sqrt{\mathcal{D}_i}} \tag{20}$$

It can easily be shown that this result is also obtained for the other two volume fractions for the tertiary mixture described above.

This same result can be also be obtained with two other sets of paired volumes for a tertiary composition. It should be noted that each set of paired volumes equations is independent of the other sets since all required volume fraction information can be obtained from each set. For reference, the other possible paired volume sets for a tertiary composition are the following:

If $V_2$ is the common particle volume

$$V_1 + V_2 = V_{T1} \tag{21}$$

$$V_2 + V_3 = V_{T2} \tag{22}$$

Or if $V_3$ is the common particle volume

$$V_1 + V_3 = V_{T1} \tag{23}$$

$$V_2 + V_3 = V_{T2} \tag{24}$$

## THEORETICAL OPTIMUM PARTICLE-TO-PARTICLE VOLUME FRACTION FOR A MIXTURE WITH AN UNDEFINED NUMBER OF PARTICLES

In general, if there are $n$ particles in a mixture, there will be $n$ sets of paired volumes. In addition, each set of paired volumes will contain $n - 1$ paired volume equations. It can easily be shown that an equation similar to eq. (20) is obtained independent of which set of paired volume equations is used to make the volume fraction calculation.

To show that this procedure applies to $n$ particles in a mixture, a mixture of seven particles will be analyzed. For this example, there are seven sets of six paired particle volume equations. For this mixture, the set of equations where $V_2$ is the common particle volume are as follows:

$$V_1 + V_2 = V_{T1} \tag{25}$$

$$V_2 + V_3 = V_{T2} \tag{26}$$

$$V_2 + V_4 = V_{T3} \tag{27}$$

$$V_2 + V_5 = V_{T4} \tag{28}$$

$$V_2 + V_6 = V_{T5} \tag{29}$$

$$V_2 + V_7 = V_{T6} \tag{30}$$

Solving for the volume fraction of the largest particle, $f_1$, gives

$$f_1 = \frac{V_1}{V_T}$$

$$= \frac{V_1}{V_1 + V_2 + V_3 + V_4 + V_5 + V_6 + V_7} \quad (31)$$

Based on the definitions of eqs. (25)–(30), then, eq. (31) can be written as

$$f_1 = \frac{V_1/V_{T1}}{\begin{array}{c} V_1/V_{T1} + V_{T2}/V_{T1} + V_4/V_{T1} \\ + V_5/V_{T1} + V_6/V_{T1} + V_7/V_{T1} \end{array}} \quad (32)$$

Solving for the volume ratio, $V_1/V_{T1}$, using eq. (25) gives

$$\frac{V_1}{V_{T1}} = \frac{\sqrt{R_{12}}}{\sqrt{R_{12}} + 1} \quad (33)$$

Eliminating $V_2$ from eqs. (25) and (26) gives

$$\frac{V_{T2}}{V_{T1}} = \left(\frac{1}{\sqrt{R_{23}}}\right)\left(\frac{\sqrt{R_{23}} + 1}{\sqrt{R_{12}} + 1}\right) \quad (34)$$

Further development can be obtained by noting that

$$\frac{V_4}{V_{T1}} = \frac{V_4/V_{T3}}{V_{T1}/V_{T3}} \quad (35)$$

Eliminating $V_2$ from eqs. (25) and (27) gives

$$\frac{V_{T3}}{V_{T1}} = \left(\frac{1}{\sqrt{R_{24}}}\right)\left(\frac{\sqrt{R_{24}} + 1}{\sqrt{R_{12}} + 1}\right) \quad (36)$$

and from eq. (27), it can be shown that

$$\frac{V_4}{V_{T3}} = \frac{1}{\sqrt{R_{24}} + 1} \quad (37)$$

Combining eqs. (35), (36), and (37) gives

$$\frac{V_4}{V_{T1}} = \left(\frac{1}{\sqrt{R_{24}}}\right)\left(\frac{1}{\sqrt{R_{12}} + 1}\right) \quad (38)$$

Using the same approach to the other $i$th components of eq. (32) for $i \geq 4$ also yields

$$\frac{V_i}{V_{T1}} = \left(\frac{1}{\sqrt{R_{2i}}}\right)\left(\frac{1}{\sqrt{R_{12}} + 1}\right) \quad (39)$$

Combining eqs. (32), (33), (34), and (39) gives

$$f_1 = \frac{\sqrt{R_{12}}}{\begin{array}{c}\sqrt{R_{12}} + 1 + \dfrac{1}{\sqrt{R_{23}}} + \dfrac{1}{\sqrt{R_{24}}} + \dfrac{1}{\sqrt{R_{25}}} \\ + \dfrac{1}{\sqrt{R_{26}}} + \dfrac{1}{\sqrt{R_{27}}}\end{array}} \quad (40)$$

This equation easily simplifies to

$$f_1 = \frac{V_1}{V_T} = \frac{\sqrt{\mathcal{D}_1}}{\sum\limits_{i=1}^{7} \sqrt{\mathcal{D}_i}} \quad (41)$$

The extension of this proof to $n$ particles in a mixture is straightforward to obtain

$$f_i = \frac{V_i}{V_T} = \frac{\sqrt{\mathcal{D}_i}}{\sum\limits_{i=1}^{n} \sqrt{\mathcal{D}_i}} \quad (42)$$

At this point, it is only necessary to show that the optimum volume fraction described by eq. (42) allows the regeneration of the primary binary pair assumptions used as the basis for its derivation. From eq. (42), the ratio of any two optimum volume fractions $f_i$ and $f_j$ in a mixture gives

$$\frac{f_i}{f_j} = \frac{V_i}{V_j} = \frac{\sqrt{\mathcal{D}_i}}{\sqrt{\mathcal{D}_j}} \quad (43)$$

For this generalized volume pair, then

$$V_i + V_j = V_{Tx} \quad (44)$$

or

$$\frac{1}{V_i + V_j} = \frac{1}{V_{Tx}} \quad (45)$$

and

$$\frac{V_i}{V_{Tx}} = \frac{V_i}{V_i + V_j} = \frac{\dfrac{V_i}{V_j}}{\dfrac{V_i}{V_j} + 1} \quad (46)$$

Thus,

$$\frac{V_i}{V_{Tx}} = \frac{\sqrt{\dfrac{\mathcal{D}_i}{\mathcal{D}_j}}}{\sqrt{\dfrac{\mathcal{D}_i}{\mathcal{D}_j}} + 1} \quad (47)$$

Hence, it has been shown that the optimum binary assumption described by eq. (5) applies to all possible binary pairs in a mixture of $n$ particles if eq. (42) applies for all particles at the optimum composition to give the maximum packing fraction.

## COMPARISON OF THEORETICAL VOLUME FRACTION PREDICTIONS WITH MCGEARY'S EXPERIMENTAL RESULTS

McGeary[23] developed the experimental optimum composition for several binary, tertiary, and quaternary mixtures of spherical particles. Several optimum compositions generated by McGeary[23] are summarized in Table I along with the diameters making up the particles in each of these mixtures. The predicted optimum compositions calculated using eq. (42) for these diameter combinations are also included in Table I. Some observations indicated from the comparison of these theoretical and experimental results in Table I include the following:

- The volume fractions calcualted using eq. (42) agree very well with the optimum volume fractions determined experimentally by McGeary for binary, tertiary, and quaternary blends.
- The maximum difference between the calculated and measured volume fractions was no greater than 3.85%. In most instances, the % difference between the theoretical and experimental results was significantly less than 3.85%.

- Independent of the minimal difference between the theoretical and experimentally measured results for each blend, the trend of the predicted volume fractions between blends was consistent for all four compositions indicated in this table.

## EVALUATION OF THE $D_5/D_1$ RATIOS OF PARTICLE-SIZE AVERAGES AND THE COMPARISON OF PREDICTED AND EXPERIMENTALLY MEASURED PACKING FRACTIONS

The values of $D_5/D_1$ in Table I were calculated by noting that the volume fraction, $f_1$, can be described as

$$f_1 = \frac{N_1 \mathcal{D}_1^3}{\sum\limits_{i=1}^{n} N_i \mathcal{D}_i^3} \tag{48}$$

A ratio of two volume fractions gives

$$\frac{f_i}{f_1} = \frac{N_i \mathcal{D}_i^3}{N_1 \mathcal{D}_1^3} \tag{49}$$

or

$$N_i = N_1 \left(\frac{f_i}{f_1}\right) R_{1i}^3 \tag{50}$$

Substituting eq. (50) into eqs. (3) and (4) gives

$$D_5 = \frac{\sum\limits_{i=1}^{n} f_i R_{1i}^3 \mathcal{D}_i^5}{\sum\limits_{i=1}^{n} f_i R_{1i}^3 \mathcal{D}_i^4} \tag{51}$$

**Table I  Comparison of Theoretical Predictions With McGeary's Particle Composition Measurements**

| $i$ | Diameters, $D_i$ (in.) | $f_i$ (Theory) | $f_i$ (Measured) | $f_i$, % Diff | $D_5/D_1$ | $R_{max}$ | $Q_m$ | $Q_{nult}$ | $Q_n$ (Theory) | $Q_n$ (Measured) | $Q_n$, % Diff |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.5050 | 0.645 | 0.607 | 3.76 | | | | | | | |
| 2 | 0.0610 | 0.224 | 0.230 | −0.60 | | | | | | | |
| 3 | 0.0110 | 0.095 | 0.102 | −0.69 | | | | | | | |
| 4 | 0.0016 | 0.036 | 0.061 | −2.47 | 288.7 | 315.6 | 0.589 | 0.971 | 0.971 | 0.951 | 2.05 |
| 1 | 0.5050 | 0.669 | 0.647 | 2.18 | | | | | | | |
| 2 | 0.0610 | 0.232 | 0.244 | −1.15 | | | | | | | |
| 3 | 0.0110 | 0.099 | 0.109 | −1.03 | 41.5 | 45.9 | 0.589 | 0.931 | 0.931 | 0.898 | 3.26 |
| 1 | 0.1240 | 0.708 | 0.670 | 3.85 | | | | | | | |
| 2 | 0.0110 | 0.211 | 0.230 | −1.90 | | | | | | | |
| 3 | 0.0016 | 0.080 | 0.100 | −1.95 | 72.1 | 77.5 | 0.589 | 0.931 | 0.931 | 0.900 | 3.06 |
| 1 | 0.5050 | 0.742 | 0.726 | 1.61 | | | | | | | |
| 2 | 0.0610 | 0.258 | 0.274 | −1.61 | 7.70 | 8.28 | 0.589 | 0.831 | 0.791 | 0.800 | −0.91 |
| 1 | 0.5050 | 1.000 | 1.000 | 0.00 | 1.0 | 1.0 | 0.589 | 0.589 | 0.589 | 0.580 | 0.90 |

$$D_1 = \frac{\sum\limits_{i=1}^{n} f_i R_{1i}^3 \mathcal{D}_i}{\sum\limits_{i=1}^{n} f_i R_{1i}^3} \qquad (52)$$

The values of $D_5/D_1$ in Table I were then determined using eqs. (51) and (52). The ratio of the maximum and minimum diameter for each particle blend, $R_{\max}$, are also included in this table. It has previously been shown by this author[14] that the maximum value that can be obtained for $D_5/D_1$ in any binary mixture is equal to the ratio of the large-to-small particle diameters. For mixtures with greater than two particles, this analysis can easily be extended to show that the maximum possible value for $D_5/D_1$ is equal to the ratio of the maximum-diameter particle to the minimum-diameter particle, $R_{\max}$. As indicated in Table I, the values of $D_5/D_1$ ranged from 90.3 to 93% of $R_{\max}$ for the predicted compositions. Since the calculated values of $D_5/D_1$ were so close to the values of $R_{\max}$ in Table I, the calculated volume fractions for these mixtures should be close to the optimum composition for the maximum packing fraction based on previous analyses.[14]

The maximum packing fractions, $\varphi_n$, measured by McGeary[23] for several particle blends have been included in Table I along with the maximum packing fractions predicted using eq. (1). For values of $D_5/D_1$ greater than 40, it is easy to show that the maximum packing fraction calculated using eq. (1) will essentially equal the ultimate packing fraction. The ultimate packing fractions, $\varphi_{\text{nult}}$, in Table I were calculated from eq. (2) using the monodisperse packing fraction ($\varphi_m = .589$) as determined by Lee.[27] This monodisperse packing fraction was obtained for loose random packing from literature results obtained from five different sets of authors.[27] Based on these assumptions, some observations involving the packing fraction results indicated in Table I include the following:

- For three of the four calculated compositions, the calculated maximum packing fraction, $\varphi_n$, did indeed equal the ultimate packing fraction, $\varphi_{\text{nult}}$.
- All the maximum packing fractions, $\varphi_n$, determined experimentally by McGeary were successfully predicted within 3.26% using eq. (1).

## APPLICATION OF MAXIMUM PACKING FRACTION, $\varphi_n$, TO A SPECIFIC GENERALIZED SUSPENSION VISCOSITY EQUATION

In an earlier article,[13] this author showed that the primary equations identified by Rutgers[11,12] could be reduced to the following generalized viscosity-concentration equation:

$$\ln(\eta/\eta_0) = \left(\frac{[\eta]\varphi_n}{\sigma - 1}\right)\left\{\left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{1-\sigma} - 1\right\}$$

$$\text{for } \sigma \neq 1 \quad (53)$$

For the case where $\sigma = 1$, the resulting equation can be written as

$$\ln(\eta/\eta_0) = -[\eta]\varphi_n \ln\left(\frac{\varphi_n - \varphi}{\varphi_n}\right) \qquad (54)$$

or

$$\eta = \eta_0 \left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{-[\eta]\varphi_n} \qquad (55)$$

where $\eta$ is the suspension viscosity; $\eta_0$ the viscosity of the suspending medium; $[\eta]$, the intrinsic viscosity; $\sigma$, the particle interaction coefficient; $\varphi$, the suspension particle volume concentration; and $\varphi_n$, the particle packing fraction.

As previously described,[13] this generalized suspension viscosity equation predicts the form of many suspension equations that have previously appeared in the literature. For example, by varying the particle interaction coefficient, $\sigma$, the Arrhenius equation[29,30] results when $\sigma = 0$, the Kreiger–Dougherty equation[4] results when $\sigma = 1$, and when $\sigma = 2$, the Mooney equation[1] results. Fractional values for the particle interaction coefficient were also found[13] to be useful and perfectly acceptable when optimizing the empirical fit of the literature data of Vand and Eiler. Additional insight from such a data fit can also be obtained from the magnitude of both the particle interaction coefficient, $\sigma$, and the packing fraction, $\varphi_n$. As the particle interaction coefficient, $\sigma$, increases, the viscosity has been shown to have a significantly faster rate of viscosity increase as a function of the suspension particle volume concentration.

Further insight into the characteristics of the interaction parameter, $\sigma$, and the packing fraction, $\varphi_n$, can be obtained from the series expansion of the generalized suspension equation. Using a MacLaurin series expansion for eq. (53) gives

$$\eta = \eta_0 \left(1 + [\eta]\varphi + \left(\frac{[\eta]}{2}\right)\left\{[\eta] + \left(\frac{\sigma}{\varphi_n}\right)\right\}\varphi^2 \right.$$
$$+ \left(\frac{[\eta]}{6}\right)\left\{[\eta]^2 + 3\left(\frac{\sigma}{\varphi_n}\right)[\eta]\right.$$
$$\left.\left. + \left(\frac{\sigma}{\varphi_n}\right)\left(\frac{\sigma+1}{\varphi_n}\right)\right\}\varphi^3 + \cdots\right) \qquad (56)$$

It is apparent that the first two terms are the Einstein[31,32] limiting terms for all possible values for the particle interaction coefficient, $\sigma$, and the packing fraction, $\varphi_n$, when $[\eta] = 2.5$. It has also been found that $\sigma$ and $\varphi_n$ always occur as a paired ratio for second-order and higher expansion terms. Since these two parameters are paired in second-order and higher terms, if $\sigma = 0.0$, then the packing fraction does not enter into the viscosity calculation. This suggests that when the particle interaction coefficient is zero that particle packing is not important and that particles have minimum interference with each other.

However, if $\sigma \neq 0.0$ and $\sigma$ increases, it is easy to see that the viscosity, $\eta$, will increase. Likewise, if the packing fraction, $\varphi_n$, increases, then the viscosity will decrease for the same particle interaction coefficient, $\sigma$.

## OPTIMUM PARTICLE-TO-PARTICLE VOLUME FRACTIONS APPLIED TO AN AGGLOMERATED LATEX

The agglomeration of latexes is a process normally used to increase the average latex particle size from a smaller diameter to a larger diameter. Agglomeration is often preferred to the standard SBR latex emulsion process since typical emulsion processing[33,34] yields a latex viscosity that becomes prohibitive at higher total solids as the particle size of a typical emulsion latex approaches 500–600 Å. Two production techniques that have successfully agglomerated such a 500–600 Å seed latex include mechanical pressure agglomeration[33–35] and chemical agglomeration.[36–38] Each of these agglomeration processes reduces latex viscosity by generating a particle-size distribution much broader than the
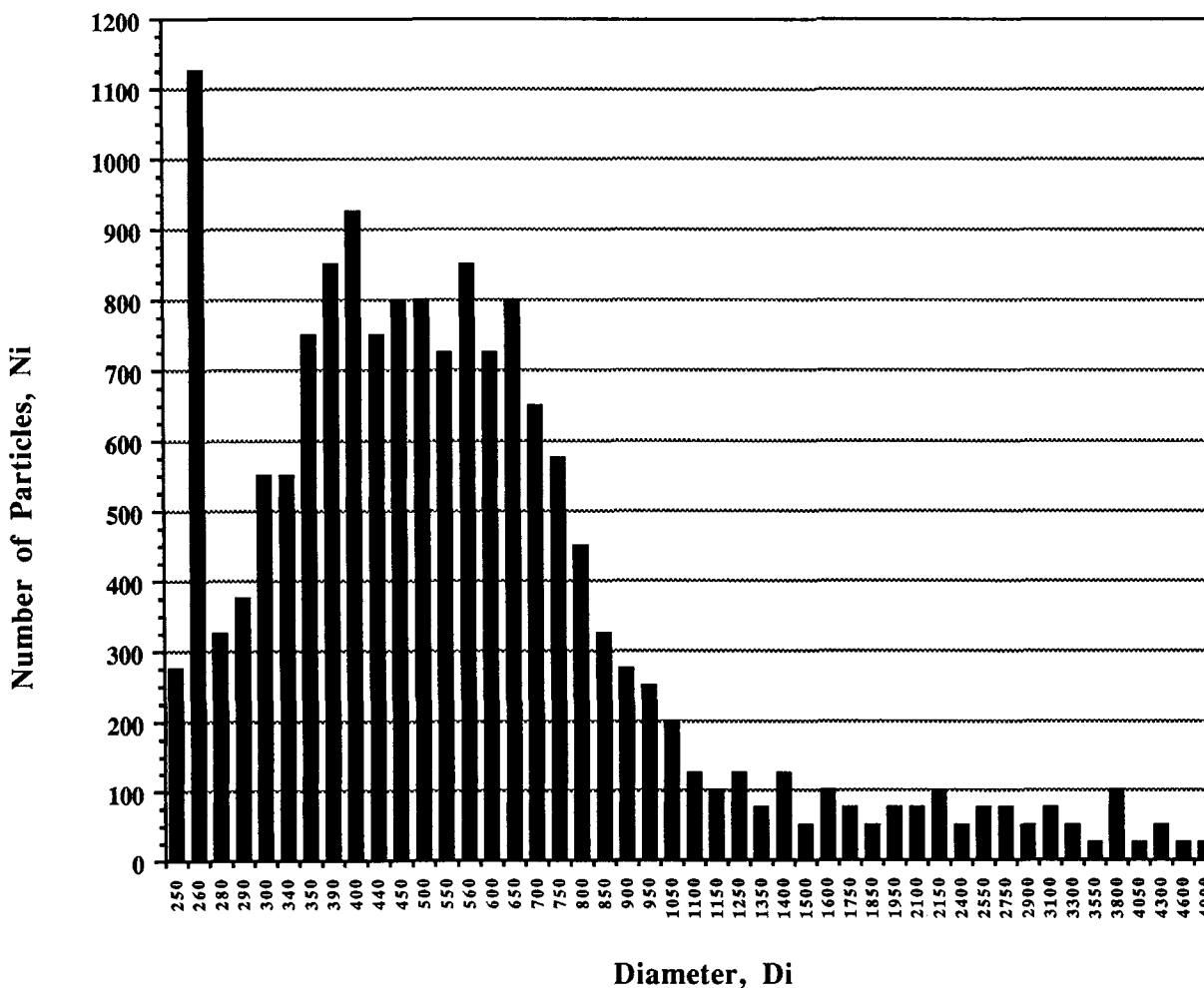


**Figure 2**   Example agglomerated latex particle-diameter distribution.

original seed latex while increasing the average particle size.[33,34,37,38]

Does the particle-size distribution for these agglomerated latexes approach the optimum volume fractions predicted using eq. (42)? An attempt was made to address this question: A particle-size distribution from an example pressure agglomerated latex of the type described by Jones[33] and Rees[34] is shown in Figure 2. This example agglomerated latex particle-size distribution was generated from micrographs and provided courtesy of General Electric Plastics. Using only the particle diameters of this latex, the optimum particle-to-particle volume fractions can be obtained using eq. (42). These theoretical volume fractions are shown in Figure 3 along with those determined experimentally. Comparison

of the experimental and theoretical results appear to agree only within a narrow range of particle sizes in this figure. However, if these results are evaluated as a function of the number of particles for each particle diameter using eq. (50), then these particle-size distributions can be compared more directly as shown in Figure 4. This figure indicates agreement is approached above 600 Å, but poor agreement is obtained below 600 Å. By replotting the data in Figure 4 at a different scale in Figure 5, the agglomerated distribution indeed appears to approach the theoretical optimum distribution above 600 Å. The new particles at diameters larger than 600 Å appear to have been generated at the expense of particles below 600 Å. Jones[33] and Schlueter[37,38] have also described additional results indicating that the
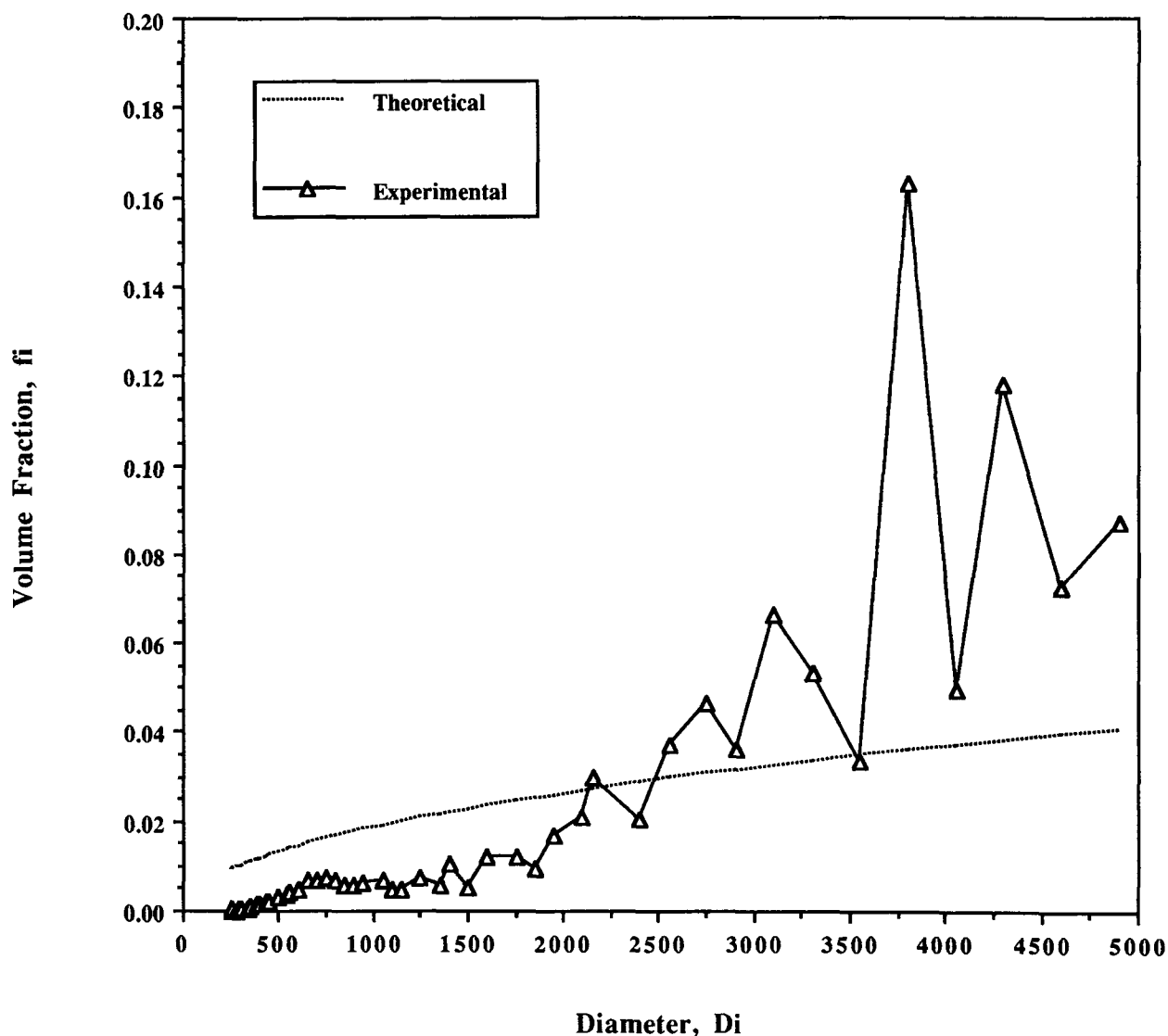


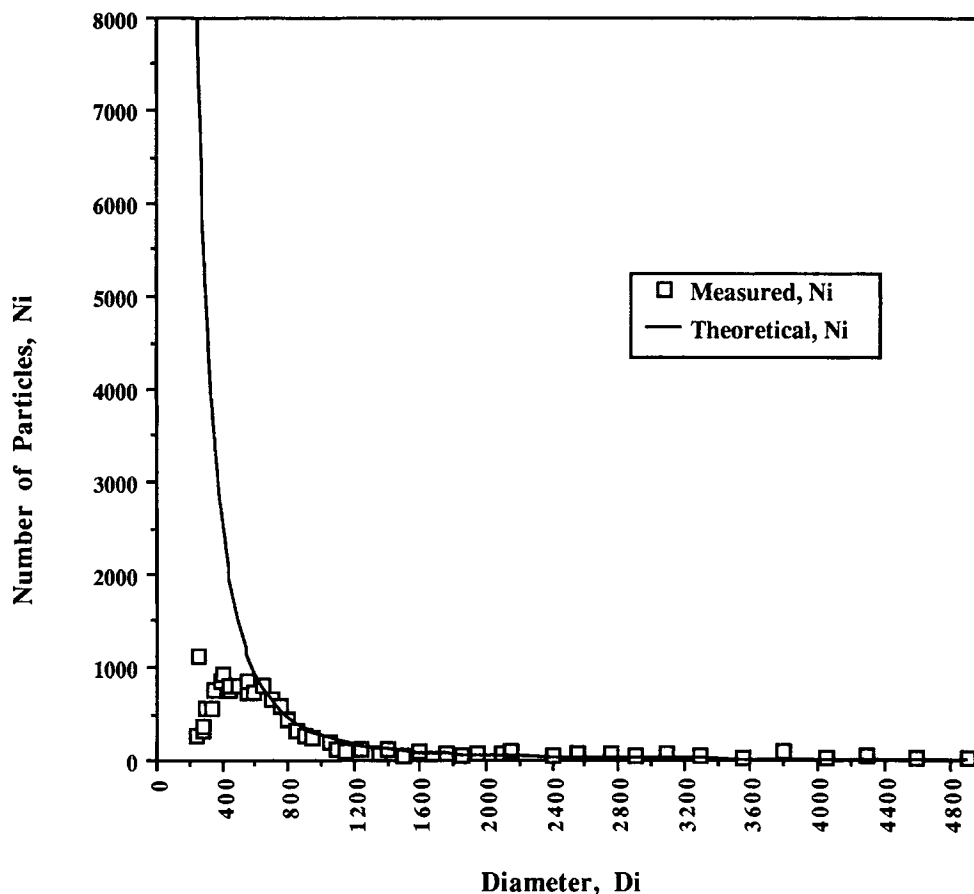**Figure 3**    Volume fraction, $f_i$, vs. Particle diameter, $D_i$.

**Figure 4**    Theoretical particle-size distribution compared to measured agglomerated latex distribution.

smaller particles do, in fact, participate in the agglomeration process to form the larger particles. The decrease in viscosity for this example of agglomerated latex appears to have been enhanced as the theoretical particle-size distribution predicated to give the optimum packing fraction was approached. This would be a satisfying result if it can be corroborated with further experimental analysis. However, it was not the intent of this article to establish this verification. The only intent was to show that agglomerated latexes do appear to approach this optimum theoretical distribution to decrease latex viscosity.

Some other interesting characteristics of the particle-size distribution of this example agglomerated latex are summarized in Table II. Since there were 47 identified different particle diameters in this latex, the calculated ultimate packing fraction, $\varphi_{nult}$, essentially reached its maximum value of 1.0. However, for this latex, there was a significant difference between the calculated particle average ratios $D_5/D_1$ and the ratio of the maximum- and minimum-

particle diameters, $R_{max}$ For this latex, the ratios of $D_5/D_1$ were less than 50% of $R_{max}$. This resulted in the calculated packing fraction for the experimentally evaluated agglomerated latex being only $\varphi_n$ = .873 and the theoretical optimum packing fraction only $\varphi_n$ = .936. This example illustrates that both the number of different particle sizes in a mixture and the relative ratio of particle diameters in the mixture are important when an improvement in the packing fraction and/or a lowering of viscosity are desired. Simply increasing the number of particles in the mixture is not necessarily a sufficient way to increase the particle-size distribution and decrease latex viscosity.

## CONCLUDING REMARKS

In a preceding article by this author, it was shown that the minimum viscosity, $\eta$, for binary particle suspension blends can be achieved when combinations of binary particles yield a maximum packing
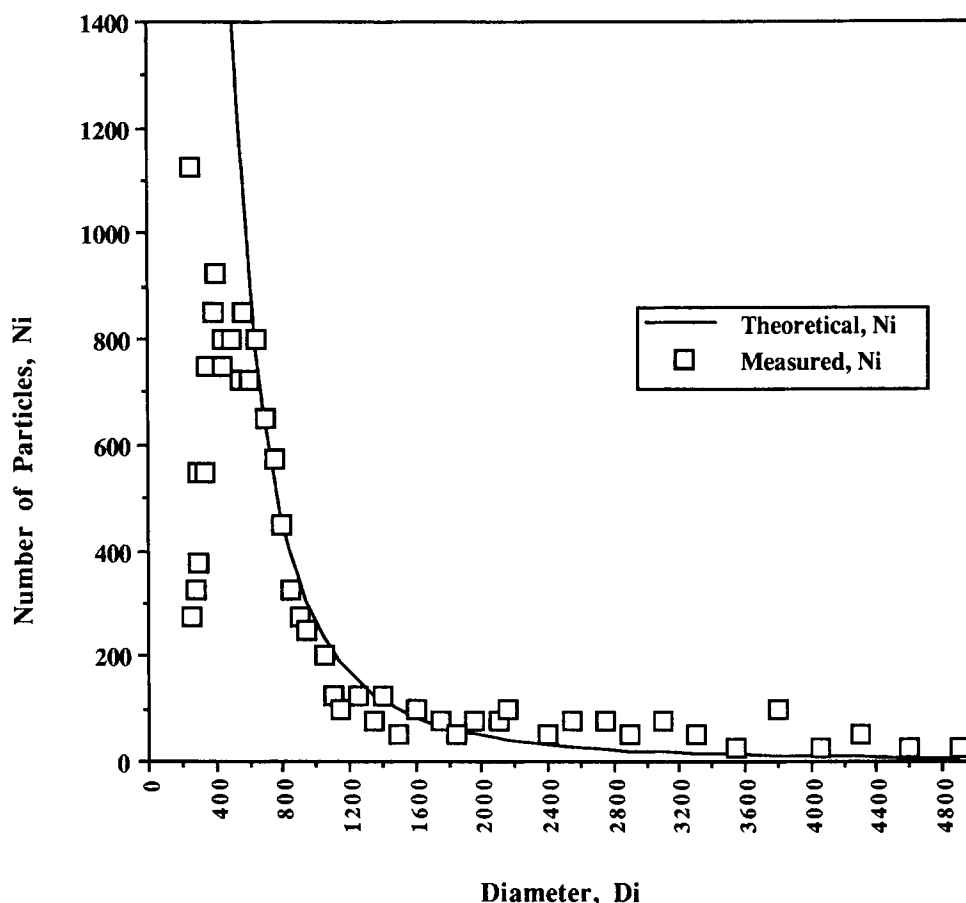
**Figure 5**   Theoretical particle-size distribution compared to measured agglomerated latex distribution.

fraction, $\varphi_n$. A subsequent article developed the methodology to achieve a maximum packing fraction and the resulting minimum viscosity for blends of two sets of particles each with a particle-size distribution. A new approach has been introduced in this article to establish the optimum composition for all particles within a mixture to achieve the optimum packing fraction.

The derivation to obtain the optimum particle volume fraction assumed that the previously developed optimum composition for binary particles applies to any two particle volumes $V_i$ and $V_j$ in a mixture. The composition of the maximum packing

fraction for a mixture of more than two particles was then assumed to be calculable from the optimized relationship of each separate binary pair of particle volumes $V_i$ and $V_j$ in the mixture. This derived equation was shown to predict the optimum particle-to-particle composition of McGeary's experimentally measured binary, tertiary, and quaternary mixtures. The difference between the calculated and measured volume fractions was no greater than 3.85% and, in most instances, was significantly less than 3.85%. The maximum packing fractions, $\varphi_n$, determined experimentally by McGeary were also predicted to better than 3.26%.

**Table II   Particle Analysis of an Example Agglomerated Latex**

| Results Evaluated | $D_1$ | $D_5$ | $D_5/D_1$ | $R_{max}$ | No. Particles | $Q_m$ | $Q_{nult}$ | $Q_n$ (Theory) |
|---|---|---|---|---|---|---|---|---|
| Experimental | 690 | 3713 | 5.38 | 19.6 | 47 | 0.589 | 1.000 | 0.873 |
| Theoretical | 388 | 3067 | 7.90 | 19.6 | 47 | 0.589 | 1.000 | 0.936 |

Theoretical particle-to-particle volume fractions evaluated for an example pressure agglomerated latex appeared to predict the particle-size distribution only within a narrow range of particle sizes. However, when the theoretical and experimental results were evaluated as a function of the number of particles for each particle diameter, it was apparent that the agglomerated distribution closely approximated the theoretical optimum distribution above 600 Å. Agreement with theory below 600 Å was unsatisfactory. Apparently, a number of new particles at diameters larger than 600 Å were generated at the expense of particles below 600 Å. The decrease in viscosity of the example agglomerated latex appeared to have been enhanced as the optimum theoretical particle-size distribution was approached. No attempt was made in this study to verify this result with further experimentation. The only intent of this analysis was to show that agglomerated latexes do appear to approach this optimum theoretical distribution to decrease latex viscosity.

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