A New Method to Predict the Maximum Packing Fraction and the Viscosity of Solutions with a Size Distribution of Suspended Particles. II

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SYNOPSIS

A new analysis technique has been developed in this paper to evaluate the upper limit of the packing fraction, φ_n, utilized in the prediction of suspension viscosities. The semiempirical equation developed for the upper limit of the packing fraction, φ_n, was generated initially from McGeary's binary particle packing fraction data. All possible D_x/D_y ratios of particles size averages were evaluated and analyzed in this formulation development. Only the D_5/D_1 and D_4/D_2 ratios of particle diameter averages were found to accurately predict the proper particle volume fraction location obtained in McGeary's data for the correct upper limit packing fraction φ_n. After developing methodology to calculate φ_n, for binary particle distributions, an extension was made to include distributions with any number n of different particle size diameters. One of the more general of the suspended particle viscosity equations, as developed in a previous paper by this author, was used to demonstrate the application of this new φ_n methodology to the evaluation of suspension viscosity properties. The blended binary suspension viscosity results of Johnson and Kelsey for near monodisperse latexes were shown to be satisfactorily predicted as a function of the binary volume composition. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Over the years many equations have been developed to predict a relationship between suspension viscosity η and the volume fraction of suspended particles, φ. The applications and needs for such equations cross many disciplines. For example, the need to understand the viscosity of spherical particle suspensions was recognized early in the development of latexes to make synthetic rubber.[1-4] Paint and coatings latex development[5,6] has also found a need for this technology. Other diverse suspensions that have utilized this technology have included the food industry to evaluate milk[7] as well as the coal industry to evaluate bitumen emulsions.[8] More recently, this technology has also been applied to filled thermoplastics.[9,10] However, the new emerging thermoplastic particulate filled thermoset resins of the type recently described by Recker et al.[11] would probably be described as one of the types of materials currently most in need of a better understanding of the relationship between particle size distribution and viscosity.

An extensive survey of the viscosity–concentration literature was made by Rutgers in 1962.[12,13] He identified 96 equations from the literature which described the behavior of these viscosity-concentration systems. Comparing the experimental data with the equations, he concluded that these 96 equations could be reduced to five useful ones. In each of these primary equations a maximum particle packing fraction φ_n is required. Several attempts have been made in the literature[14-16] to predict the correct value for φ_n based on particle size distribution. A new approach to analyze and calculate φ_n will be described and introduced in this paper.

APPLICATION OF MAXIMUM PACKING FRACTION φ_n TO A SPECIFIC GENERALIZED SUSPENSION VISCOSITY EQUATION

In an earlier paper,[17] this author showed that the primary equations identified by Rutgers[12,13] could

Journal of Applied Polymer Science, Vol. 48, 37–55 (1993)
 CCC 0021-8995/93/010037-19

be reduced to the following generalized viscosity–concentration equation.

$$\ln\left(\frac{\eta}{\eta_0}\right) = \left(\frac{[\eta]}{k}\right)\left(\frac{1}{\sigma - 1}\right)\left\{\frac{1 - (1 - k\varphi)^{\sigma-1}}{(1 - k\varphi)^{\sigma-1}}\right\} \quad \text{for } \sigma \neq 1 \quad (1)$$

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

$$\eta = \eta_0(1 - k\varphi)^{-[\eta]/k} \quad (2)$$

$$k = 1/\varphi_n \quad (3)$$

where η = suspension viscosity, η_0 = viscosity of suspending medium, $[\eta]$ = intrinsic viscosity, σ = particle interaction coefficient, k = "crowding factor," φ = suspension particle volume fraction, and φ_n = maximum particle packing fraction.

The intrinsic viscosity $[\eta]$ is obtained at low concentration levels for the following limiting slope:

$$\text{as } \varphi \to 0, \quad \text{then } \frac{d \ln \eta}{d\varphi} \to [\eta] \quad \text{for all } \sigma \geq 0 \quad (4)$$

Some optional equations that can be developed using this generalized suspension viscosity equation are summarized in Table I along with authors that first referenced some of these equations. As the particle interaction coefficient σ increases in Table I, the equations represented have been shown to have a significantly faster rate of viscosity increase as a function of particle volume fraction. More importantly, the results in Table I show that fractional values of σ are also perfectly acceptable. For example, if the data appear to fit an equation somewhere between the Krieger–Dougherty equation ($\sigma = 1$) and the Mooney equation ($\sigma = 2$), then trial and error using the generalized suspension viscosity equation (1) can most probably be used to find a value of σ between 1 and 2 that will better fit the data. Likewise, it should be noted that all of these equations, with the exception of the case for $\sigma = 0$, require the utilization of a maximum particle packing fraction φ_n.

ANALYSIS OF MCGEARY'S PARTICLE PACKING DATA

Probably the most definitive work on binary packing of particles was done by McGeary.[14] His data is plotted in Figure 1 for five sets of binary mixtures with different ratios R of the large particle diameter to the small particle diameter. Several authors[15,16] have attempted to analytically describe approaches to calculate the results described in Figure 1. Most

Table I Generalized Suspension Viscosity Equation for Selected Values of the Particle Interaction Coefficient σ

Particle Interaction Coefficient σ	Simplified Form of Generalized Equation	Previous Reference for Equation Derivation
0	$\ln(\eta/\eta_0) = [\eta]\varphi$	Arrhenius (1887, 1917)[18,19]
0.5	$\ln(\eta/\eta_0) = \left(\frac{2[\eta]}{k}\right)[1 - (1 - k\varphi)^{0.5}]$	
1	$\ln(\eta/\eta_0) = \left(\frac{-[\eta]}{k}\right)\ln(1 - k\varphi)$	Krieger and Dougherty (1959)[4]
2	$\ln(\eta/\eta_0) = [\eta]\left\{\frac{\varphi}{1 - k\varphi}\right\}$	Mooney (1951)[1]
3	$\ln(\eta/\eta_0) = \left(\frac{[\eta]}{2}\right)\left\{\frac{2\varphi - k\varphi^2}{(1 - k\varphi)^2}\right\}$	
4	$\ln(\eta/\eta_0) = \left(\frac{[\eta]}{3}\right)\left\{\frac{3\varphi - k\varphi^2 + k^2\varphi^3}{(1 - k\varphi)^3}\right\}$	

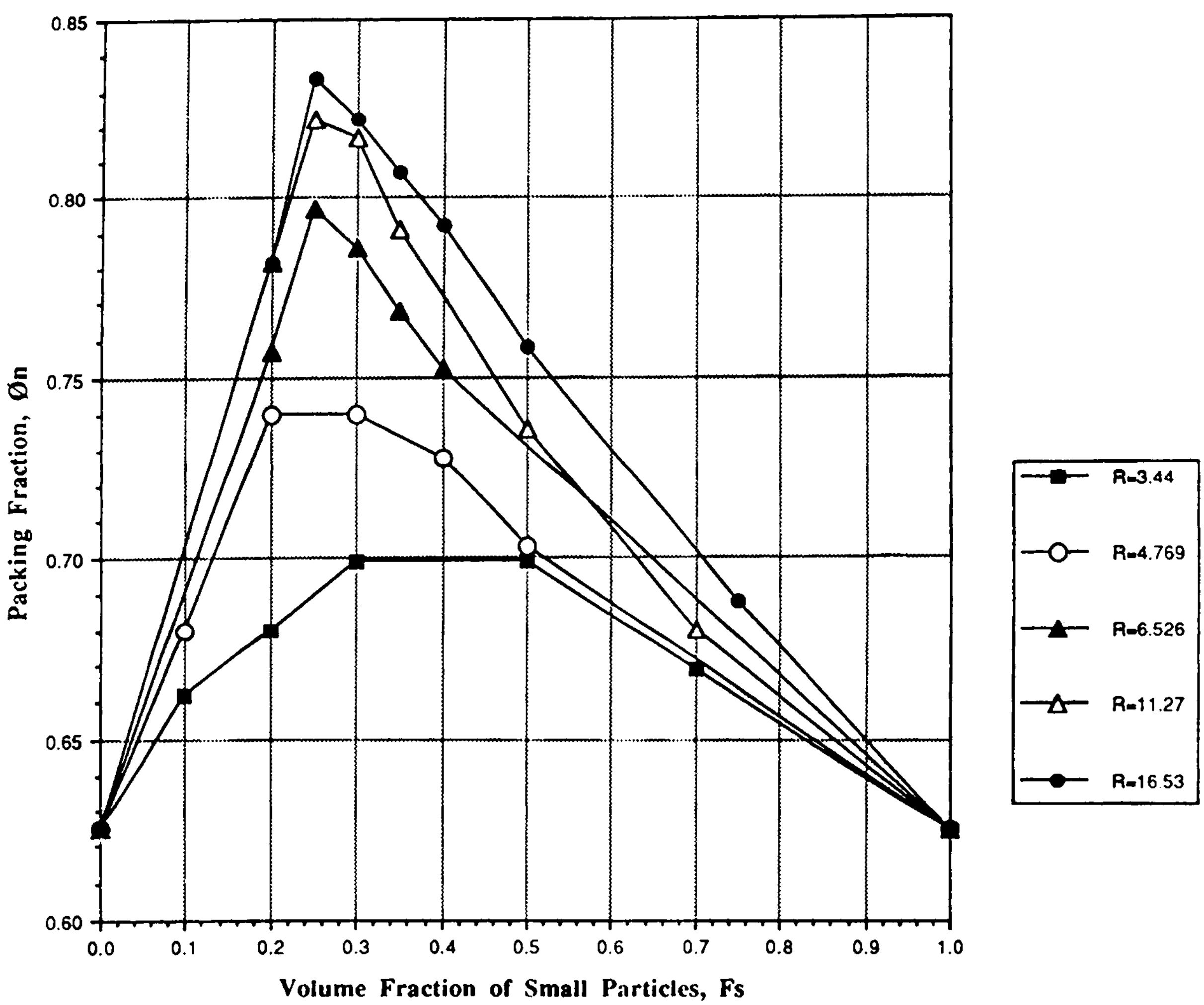

Figure 1 Selected binary particle packing fraction data sets for different ratios of large to small diameter particles (data of McGeary[14]).

of these approaches have attempted to describe the composition curve for each binary diameter ratio R, using three sets of equations for each curve. This procedure is often impractical and at the very least unnecessarily cumbersome.

After McGeary completed several binary packing evaluations similar to those shown in Figure 1, he established a maximum packing fraction $\varphi_{n\max}$ for each of these binary curves. This set of maximum packing fractions established by McGeary has been summarized in Figure 2 as a function of R the ratio of large particle diameter to small particle diameter.

Several attempts were evaluated by this author to describe McGeary's data with an empirical analytical expression. The most successful expression developed to fit McGeary's data, as illustrated in Figure 2, had the following form:

$$\varphi_{n\max} = \varphi_{n\text{ult}} - (\varphi_{n\text{ult}} - \varphi_m)e^{\alpha(1-R)} \qquad (5)$$

where R = ratio of large particle diameter to the small particle diameter, φ_m = monodisperse particle size packing fraction where $R = 1$, $\varphi_{n\max}$ = maximum particle size packing fraction for a given R ratio, $\varphi_{n\text{ult}}$ = ultimate particle packing fraction as $R \rightarrow \infty$, and α = const. The two significant limits for eq. (5) are

$$\text{when } R = 1, \quad \text{then } \varphi_{n\max} = \varphi_m \qquad (6)$$

and

$$\text{as } R \rightarrow \infty, \quad \text{then } \varphi_{n\max} = \varphi_{n\text{ult}} \qquad (7)$$

For the data generated by McGeary,[14] the maximum dense random packing fraction for a monodisperse particle size distribution where $R = 1$ was found to be $\varphi_m = 0.625$. The largest $\varphi_{n\max}$ value evaluated by

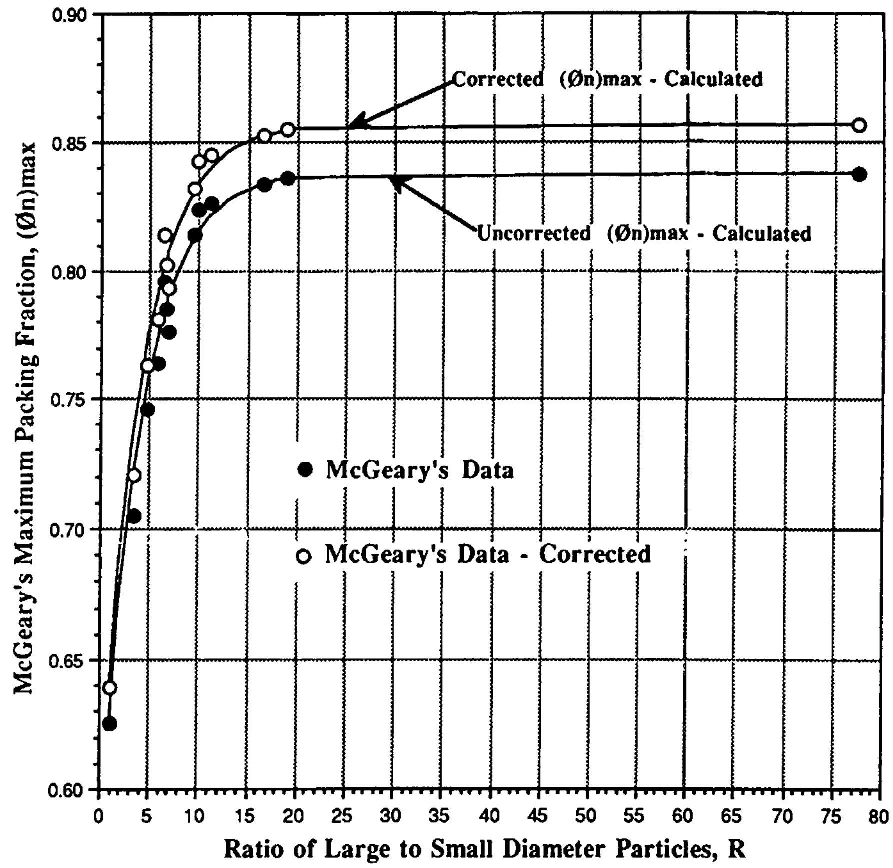

Figure 2 Comparison of McGeary's[14] corrected and uncorrected maximum packing fraction data with calculated results from empirical equation.

McGeary for $R = 78$ gave a maximum packing fraction of $\varphi_{n\max} = 0.838$. Using eq. (5), this largest R value was found to be approximately considered infinite for all practical applications from which it was established that the ultimate packing fraction could be satisfactorily estimated to be $\varphi_{n\text{ult}} = 0.838$. Using these limiting packing fractions, the minimum error in fitting all of McGeary's data resulted when $\alpha = 0.247$. The fit of McGeary's data in Figure 2 using eq. (5) with these constants was found to be more than adequate, yielding an average error of only 0.751%.

However, Lee[15] points out that monodisperse packing fractions obtained by five different sets of authors differed slightly from those obtained by McGeary.[14] These authors evaluated monodisperse packing of solid uniform spheres for both dense random packing and loose random packing. An average value of 0.639 was calculated for dense random packing by Lee for these five sets of authors. Similarly, for these same authors an average value of 0.589 was obtained by Lee for loose random packing.

Lee further points out that the McGeary's data can easily be corrected for the preferred dense random packing by multiplying each datum point by the ratio (0.639/0.625). Similarly, the values for φ_m and $\varphi_{n\text{ult}}$ in eq. (5) can easily be corrected by multiplying by this ratio. With this correction these values become $\varphi_m = 0.639$ and $\varphi_{n\text{ult}} = 0.857$. Note, however, that when fitting McGeary's data using eq. (5), α remains the same and the average % error in fitting the data also remains the same since both the data and eq. (5) were modified using the same correction factor. McGeary's corrected data and calculated values using a corrected eq. (5) have also been included in Figure 2.

THEORETICAL DEVELOPMENT OF THE ULTIMATE PACKING FRACTION $\varphi_{n\text{ult}}$

At this point it is useful to establish a general relationship for the ultimate packing fraction $\varphi_{n\text{ult}}$. For the simple case for a combination of monodisperse particles, then

$$\varphi_{1\text{ult}} = \varphi_m \qquad (8)$$

For the case of two particles of different size then the maximum packing fraction for this combination of particles would be given as:

$$\varphi_{2\text{ult}} = \varphi_{1\text{ult}} + (1 - \varphi_{1\text{ult}})\varphi_m \quad (9)$$

For this case the improvement in packing fraction for the second particle must be added from the empty space left by the first particle or $(1 - \varphi_{1\text{ult}})$. The maximum space that the second particle size can occupy of this empty space is then equal to φ_m.

It is convenient to rewrite eq. (9) in the following form:

$$\varphi_{2\text{ult}} = \varphi_{1\text{ult}}(1 - \varphi_m) + \varphi_m \quad (10)$$

Substituting eq. (8) into (10) gives

$$\varphi_{2\text{ult}} = \varphi_m(1 - \varphi_m) + \varphi_m \quad (11)$$

Similarly, for a combination of three particle sizes, then, the maximum packing fraction can be written as

$$\varphi_{3\text{ult}} = \varphi_{2\text{ult}} + (1 - \varphi_{2\text{ult}})\varphi_m \quad (12)$$

With appropriate substitutions this equation reduces to the following:

$$\varphi_{3\text{ult}} = (1 - \varphi_m)^2\varphi_m + (1 - \varphi_m)\varphi_m + \varphi_m \quad (13)$$

In general, it can be shown that for n different particle sizes the maximum packing fraction can be written as

$$\varphi_{n\text{ult}} = \varphi_m \sum_{z=1}^{z=n} (1 - \varphi_m)^{z-1} \quad (14)$$

Simplification of eq. (14) can be accomplished by noting that the sum

$$\text{Sn} = 1 + (1 - \varphi_m) + (1 - \varphi_m)^2 + (1 - \varphi_m)^3 + \cdots + (1 - \varphi_m)^{n-1} \quad (15)$$

can be multiplied by $(1 - \varphi_m)$ to give

$$\text{Sn}(1 - \varphi_m) = (1 - \varphi_m) + (1 - \varphi_m)^2 + (1 - \varphi_m)^3 + (1 - \varphi_m)^4 + \cdots + (1 - \varphi_m)^n \quad (16)$$

Subtracting eq. (16) from (15) and simplifying gives

$$\text{Sn} = \frac{1 - (1 - \varphi_m)^n}{\varphi_m} \quad (17)$$

Substituting eq. (17) into (14) yields the following simplified value for the ultimate packing fraction $\varphi_{n\text{ult}}$ for any number of particle sizes, n, in a batch combination

$$\varphi_{n\text{ult}} = 1 - (1 - \varphi_m)^n \quad (18)$$

The value of $\varphi_{n\text{ult}}$ has been calculated in the following table for two different monodisperse packing fractions identified by Lee[15] in a summary of values from the literature for dense random packing and loose random packing (see Table II).

As indicated earlier in this paper, an ultimate packing fraction of $\varphi_{n\text{ult}} = 0.857$ was required to fit McGeary's[14] data for binary combinations of particle sizes. Note that this binary ultimate packing fraction, $\varphi_{n\text{ult}}$, is between the limits for loose random packing and dense random packing as indicated in the above table. However, when fitting McGeary's data, the monodisperse dense packing fraction $\varphi_m = 0.639$ was also required. It is apparent that neither pure dense random packing nor loose random packing would give the values utilized in fitting McGeary's data.

However, if the derived expression for ultimate packing fraction, eq. (18), is rewritten in pseud ratio

Table II $\varphi_{n\text{ult}}$ **Results for Several Different Combinations of Particle Sizes**

Number of Particle Sizes in Mixture	$\varphi_{n\text{ult}}$ ($\varphi_m = 0.639$) Dense Random Packing	$\varphi_{n\text{ult}}$ ($\varphi_m = 0.589$) Loose Random Packing
1	0.639	0.589
2	0.870	0.831
3	0.953	0.931
4	0.983	0.972
5	0.994	0.988
6	0.998	0.995
100	1.000	1.000

form and if φ_m is allowed to be an adjustable parameter, then the expected results for $n = 1$ and $n = 2$ can be obtained with the arbitrary packing fraction $\varphi_m = 0.659$ using the following expression:

$$\varphi_{n\,\text{ult}} = 0.857\left\{\frac{1 - (1 - \varphi_m)^n}{1 - (1 - \varphi_m)^2}\right\} \qquad (19)$$

The expected $\varphi_{n\,\text{ult}}$ results for monodisperse, binary, and other values of n using this equation have been included in Table III.

Ultimate packing fractions calculated from eq. (19) range from monodisperse dense random packing to loose random packing fraction with as few as three particle sizes in the mixture. For more than three particle sizes the ultimate packing fractions predicted are less than either dense random packing or loose random packing. Ultimate Packing fractions with values less than loose random packing are unreasonable. It is apparent that eq. (19) is only useful to show that ultimate packing fractions should be calculated from eq. (18) with $\varphi_m = 0.589$ for mixtures of three or more particle sizes.

Another result of this simplified analysis relates to McGeary's[14] maximum values for binary ultimate packing fractions as a function of R, the ratio of large particle size diameter to small particle size diameter. Since the maximum packing fractions for binary mixtures begin with monodisperse dense packing and steadily and uniformly approach values closer to loose random packing with an increase in R, this is an indication that packing is apparently more difficult as the size difference between particle sizes increases. This may give a better understanding as to why ultimate packing fractions approach the loose random packing limit for mixtures with three or more particles.

Table III $\varphi_{n\,\text{ult}}$ Results for Several Different Combinations of Particle Sizes

Number of Particle Sizes in Mixture	$\varphi_{n\,\text{ult}}$ ($\varphi_m = 0.659$) Using Eq. (19)
1	0.639
2	0.857
3	0.931
4	0.956
5	0.965
6	0.968
100	0.970

DIFFERENT PARTICLE SIZE AVERAGES AND THEIR RATIOS IN EVALUATING PARTICLE SIZE DISTRIBUTION

It has long been suspected that a relationship existed between the large to small particle diameter ratio R in a binary mixture of particles and certain ratios of particle diameter averages. This relationship will be explored in some depth.

In general, most particle diameter averages, D_x, can be described in the following general form:

$$D_x = \sum_{i=1}^{n} N_i \mathcal{D}_i^x \Big/ \sum_{i=1}^{n} N_i \mathcal{D}_i^{x-1} \qquad (20)$$

where D_x = average particle size diameter, $\mathcal{D}_i$ = diameter of particle size i, and N_i = number of i particles. For a binary mixture of particles of two different diameters, then, the ratio of a D_x average diameter and a D_y average diameter could be written as

$$\frac{D_x}{D_y} = \left\{\frac{N_1\mathcal{D}_1^x + N_2\mathcal{D}_2^x}{N_1\mathcal{D}_1^{x-1} + N_2\mathcal{D}_2^{x-1}}\right\}\left\{\frac{N_1\mathcal{D}_1^{y-1} + N_2\mathcal{D}_2^{y-1}}{N_1\mathcal{D}_1^y + N_2\mathcal{D}_2^y}\right\} \qquad (21)$$

As described earlier, for a binary mixture the ratio R of the large diameter particle $\mathcal{D}_2$ to the small diameter particle $\mathcal{D}_1$ is defined as

$$R = \mathcal{D}_2/\mathcal{D}_1 \qquad (22)$$

The volume fraction of the small particle, f_1, in the mixture can be described as

$$f_1 = \frac{N_1\mathcal{D}_1^3}{N_1\mathcal{D}_1^3 + N_2\mathcal{D}_2^3} \qquad (23)$$

This definition also can be written as

$$f_1 = 1 - f_2 \qquad (24)$$

A ratio of f_2 to f_1 using eq. (23) can be written as

$$\frac{f_2}{f_1} = N_2\mathcal{D}_2^3/N_1\mathcal{D}_1^3 \qquad (25)$$

Substituting eqs. (22) and (24) into eq. (25) gives

$$\frac{N_2}{N_1} = \left(\frac{1}{R^3}\right)\left(\frac{f_2}{1 - f_2}\right) \qquad (26)$$

Substituting eqs. (22) and (26) into eq. (21) gives the D_x/D_y ratio as

$$\frac{D_x}{D_y} = \frac{af_2^2 + bf_2 + c}{df_2^2 + (a+b-d)f_2 + c} \qquad (27)$$

where

$$a = R^{x+y-4} + R^3 - R^{y-1} - R^x$$
$$b = R^{y-1} + R^x - 2R^3$$
$$c = R^3$$
$$d = R^{x+y-4} + R^3 - R^y - R^{x-1} \qquad (28)$$

For example, if $x = 5$ and $y = 1$, then a plot of eq. (27) for D_x/D_y or D_5/D_1 is shown in Figure 3 as a function of the small particle volume fraction f_s (where $f_s = f_1 = 1 - f_2$). Note that the position of the maximum relative to R in Figure 3 is nearly identical to that for the data of McGeary[14] in Figure 1.

The extrema illustrated in Figure 3 for eq. (27) can be obtained by taking its derivative and setting it equal to zero as

$$\frac{d(D_x/D_y)}{df_2} = 0 \qquad (29)$$

This derivative yields the following formulation to obtain roots for these extrema:

$$(a+b)f_2^2 + (2c)f_2 - c = 0 \qquad (30)$$

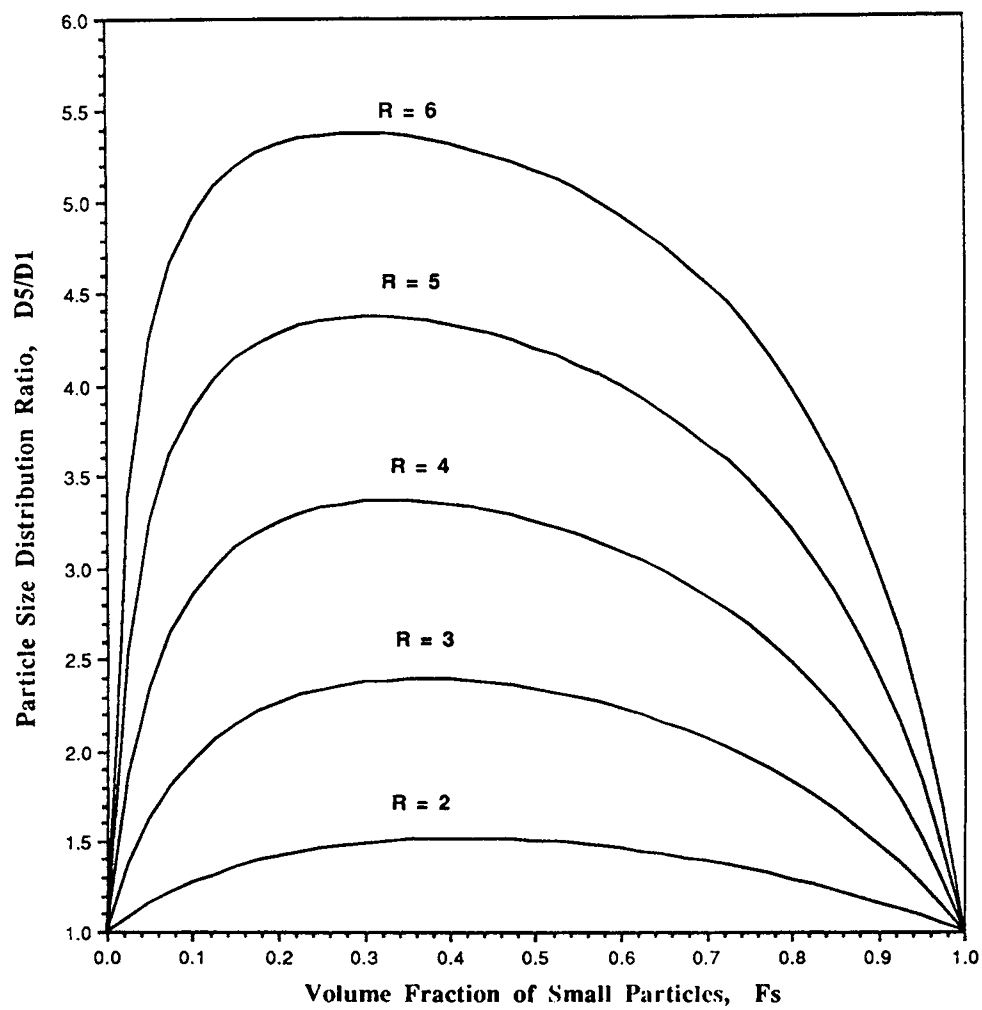

Figure 3 Binary particle size distribution ratio D_5/D_1 as a function of composition, f_s, for different ratios of large to small particles, R.

The two roots of this equation are

$$f_2 = \frac{1}{1 + \sqrt{R^{x+y-7}}} \qquad (31)$$

and

$$f_2 = \frac{1}{1 - \sqrt{R^{x+y-7}}} \qquad (32)$$

Only one of these roots, eq. (31), gives values of f_2 between 0 and 1. When this root is substituted into eq. (27), the maximum value of D_x/D_y is given as

$$\left(\frac{D_x}{D_y}\right)_{max} = R\left\{\frac{2R^{(y-x-1)/2} + R^{(y-x-1)} + 1}{2R^{(y-x+1)/2} + R^{(y-x+1)} + 1}\right\} \qquad (33)$$

This equation can also be rewritten as

$$\left(\frac{D_x}{D_y}\right)_{max} \bigg/ R = \left\{\frac{2R^{(y-x-1)/2} + R^{(y-x-1)} + 1}{2R^{(y-x+1)/2} + R^{(y-x+1)} + 1}\right\} \qquad (33')$$

Note from eq. (33) that

$$\left(\frac{D_x}{D_y}\right)_{max} \le R \quad \text{for all } x \ge 1 \text{ and } y \ge 1 \qquad (34)$$

In addition, the maximum D_x/D_y for each R value is dependent only on the difference between x and y and not the magnitude of x or y. For example, the following groups of x and y give the same maximum ratio of D_x/D_y as a function of R:

x	y	$(x - y)$
2	1	1
3	2	1
4	3	1
5	4	1
3	1	2
4	2	2
5	3	2
6	4	2
4	1	3
5	2	3
6	3	3

An example of one of these groups of x and y which define identical maxima for all values of R would include

$$\left(\frac{D_3}{D_1}\right)_{max} = \left(\frac{D_4}{D_2}\right)_{max} = \left(\frac{D_5}{D_3}\right)_{max} = \left(\frac{D_6}{D_4}\right)_{max} \qquad (35)$$

To get a better indication of how close the value of $(D_x/D_y)_{max}$ approaches R as function of x and y consider the plot of $(D_x/D_y)_{max}/R$ described by eq. (33′) as illustrated in Figures 4 and 5. It is apparent in these figures that as the difference between x and y increases that the value of $(D_x/D_y)_{max}/R$ approaches 1 much more quickly with smaller values of the diameter ratio, R, in a binary particle distribution.

Earlier it was pointed out that the position of the maximum ratio for D_x/D_y or D_5/D_1 (where $x = 5$ and $y = 1$) in Figure 3 is nearly identical to location of the maxima relative to f_s for the data of McGeary[14] in Figure 1. The question then arises as to whether another combination of x and y relative to the ratio of D_x/D_y would give a better prediction of the maxima observed by McGeary.

The large particle volume fraction f_2 associated with maximum ratio of D_x/D_y for each combination of x and y has already been shown mathematically to be defined by eq. (31). As illustrated in Figure 6, calculations with this equation have been generated at various values of x and y to establish the small particle volume fractions f_s (where $f_s = f_1 = 1 - f_2$) associated with $(D_x/D_y)_{max}$ as a function of the ratio of the large particle diameter to the small particle diameter, R. It is interesting to note in this figure that

$$\text{at } R = 1 \quad f_s = 0.5 \quad \text{for all values of } x \ge 1 \text{ and } y \ge 1 \qquad (36)$$

This result is intuitively satisfying since it predicts that the maximum ratio for D_x/D_y would occur at a condition of equal volume when both particles are the same size.

Equation (31) is also similar to eq. (33) in that groups of x and y can give the same particle volume fraction, f_s, location of $(D_x/D_y)_{max}$. Groups of x and y that have the same value of $(x + y - 7)$ also have the same maxima location. Some examples of these groups would include:

x	y	$(x + y - 7)$
2	1	−4
3	1	−3
2	2	−3
4	1	−2
3	2	−2
5	1	−1
4	2	−1
6	1	0
5	2	0
4	3	0

Based on this relationship between x and y, it is apparent in Figure 6 that values of $f_s \geq 0.5$ will be obtained for all groups of x and y that give $(x + y - 7) \geq 0$. Since all the McGeary[14] maxima were obtained for $f_s < 0.5$, it is apparent the groups of x and y that give $(x + y - 7) \geq 0$ cannot be used to give realistic predictions of the maximum packing fractions.

The results in Figure 6 also show that x and y combinations that give $(x + y - 7) \leq -2$ also predict values for $f_s < 0.2$ for $R > 4$. These combinations are also inconsistent with McGeary's data in Figure 3. This result appears to leave only two combinations ($x = 5$, $y = 1$) and ($x = 4$, $y = 2$) that accurately predict the location of McGeary's maxima.

It has already been shown that

$$(D_3/D_1)_{\max} = (D_4/D_2)_{\max} \qquad (37)$$

However, as shown in Figure 4, the relationship between $(D_3/D_1)_{\max}$ and $(D_5/D_1)_{\max}$ is significantly different. As the ratio of the large to small diameter, R, increases, it is apparent in this figure that $(D_5/D_1)_{\max}$ approaches the value of R much more quickly than $(D_3/D_1)_{\max}$. For this reason the $(D_5/D_1)_{\max}$ ratio would appear to be preferred as a measure of R to predict McGeary's binary results, even though both $(D_5/D_1)_{\max}$ and $(D_4/D_2)_{\max}$ achieve their maximum values at the same particle composition.

One average particle size diameter not included in the D_x averages described by eq. (38) is the so-called "turbidity" average D_t, defined as

$$D_t = \left\{ \sum_{i=1}^{n} N_i \mathcal{D}_i^6 \Big/ \sum_{i=1}^{n} N_i \mathcal{D}_i^3 \right\}^{1/3} \qquad (38)$$

The relationship between the turbidity average D_t and the D_5 average is indicated in Figure 7 for several widely different particle size distributions. It is apparent that these two averages can give nearly identical results in many cases.

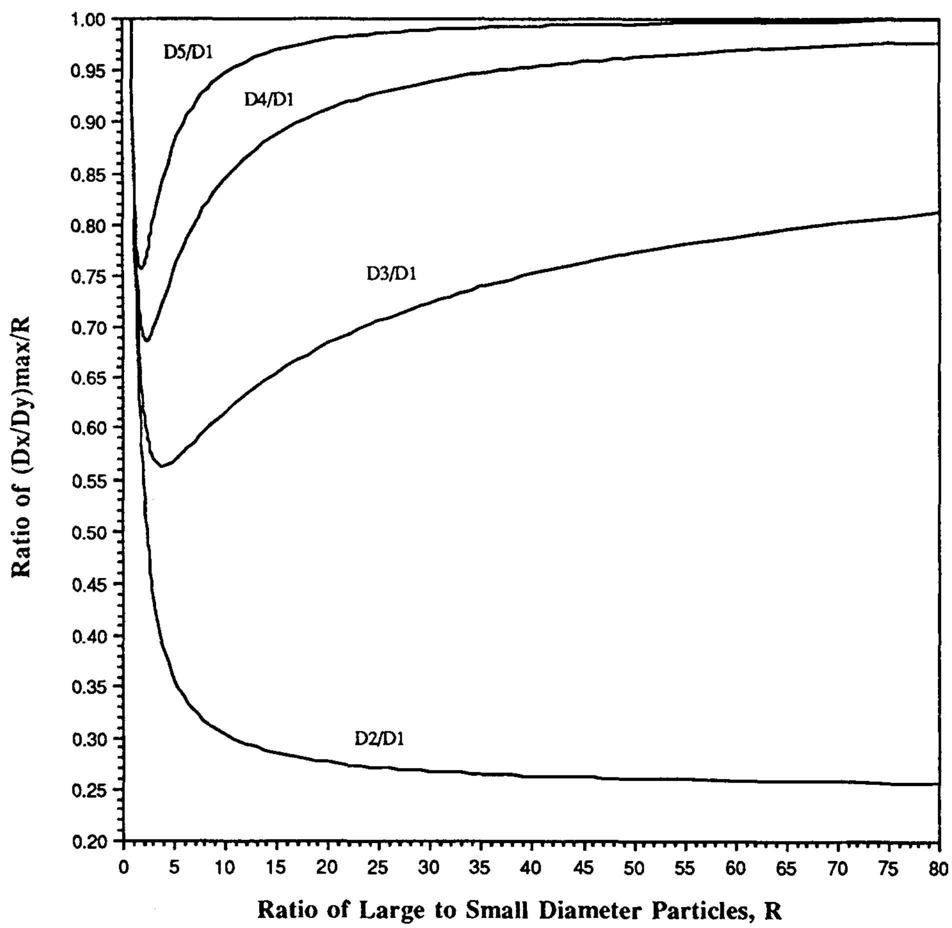

Figure 4 Ratio of $(D_x/D_y)_{\max}/R$ as a function of the ratio of large to small diameter particles, R, for selected D_x/D_y ratios.

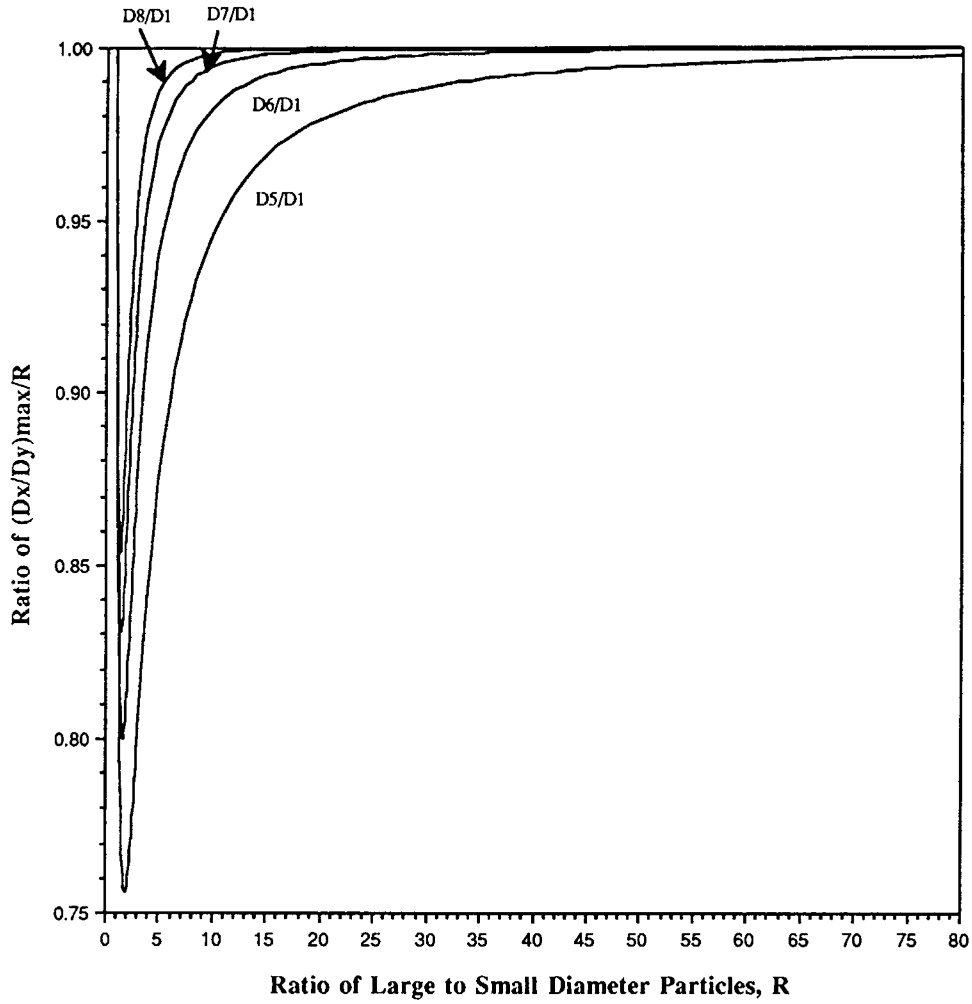

Figure 5 Ratio of $(D_x/D_y)_{max}/R$ as a function of the ratio of large to small diameter particles, R, for higher level D_x/D_y ratios.

The question then arises as to whether the ratio of D_t/D_1 is possibly better than the D_5/D_1 ratio in predicting the location of McGeary's maxima. Using eqs. (22)–(26) previously utilized to analyze D_x/D_y, the ratio of D_t/D_1 can be developed as

$$\frac{D_t}{D_1} = \{1 + f_2(R^3 - 1)\}^{1/3} \times \left[\frac{R^3 + f_2(1 - R^3)}{R^3 + f_2(R - R^3)}\right] \quad (39)$$

Again the extrema of this equation can be found by taking this derivative as

$$\frac{d(D_t/D_1)}{df_2} = 0 \quad (40)$$

The resulting equation from which the roots can be determined is

$$af_2^2 + bf_2 + c = 0 \quad (41)$$

where

$$a = R^9 + R^7 - 2R^6 + 2R^4 + R^3 - R$$
$$b = -2R^9 - 2R^7 + 6R^6 + 2R^4 - 4R^3$$
$$c = R^9 - R^6 - 3R^4 + 3R^3 \quad (42)$$

leading to the following roots

$$f_2 = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (43)$$

One maximum "turbidity average" ratio, D_t/D_1, root (with values between 0 and 1) is plotted in Figure 8. It is apparent that for small particle volume fractions $f_s(=1-f_2)$, this D_t/D_1 root gives values closer to D_5/D_1 fractions when R is less than 5 but approaches D_4/D_1 fractions at larger values of R. These calculations indicate that the D_t/D_1 ratio does not predict the results obtained by McGeary as well as the D_5/D_1 ratio.

Also included in Figure 8 are results calculated for a special D_x/D_y ratio where $x = 5.5$ and $y = 1$. Of particular interest is the predicted small particle fraction f_s for the largest binary particle diameter ratio, $R = 78$, evaluated by McGeary.[14] At $R = 78$ the small particle volume fraction f_s, calculated for the $D_{5.5}/D_1$ ratio, was found to be $f_s = 0.25$. McGeary obtained an f_s value near 0.25 for a particle diameter ratio of $R = 78$. However, for R values below 30 for the $D_{5.5}/D_1$ ratio, the small particle fractions are much larger than McGeary's results. Again, the $D_{5.5}/D_1$ ratio does not predict the full range of data obtained by McGeary as well as the D_5/D_1 ratio.

In passing, it is apparent in Figure 8 that the D_5/D_1 ratio yields an f_s value near 0.10 at the largest R ratio, $R = 78$, evaluated by McGeary. Although this value is slightly lower than McGeary obtained, the predicted f_s values at lower values of R were very close to those obtained by McGeary. This is particularly important since most practical combinations of particles in latexes, etc. would seldom be expected to exceed $R = 15$. For R values in this lower range, the D_5/D_1 ratio predicts McGeary's results remarkably well. It is also possible that if McGeary's results were duplicated for the R values near 78 that the reevaluated small particle fractions f_s at these maximum packing fractions would in fact be closer to 0.10.

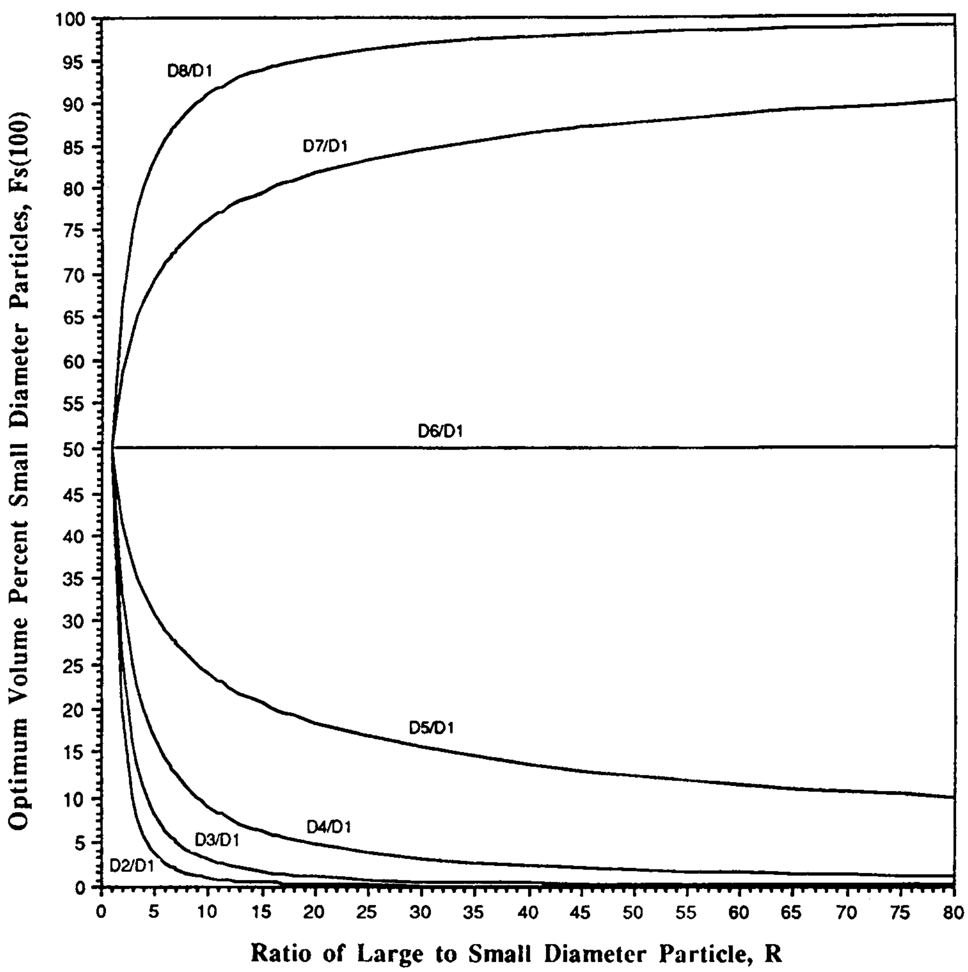

Figure 6 Derived optimum volume fraction small diameter particles, f_s, as a function of the ratio of large to small diameter particles, R, for selected D_x/D_y ratios.

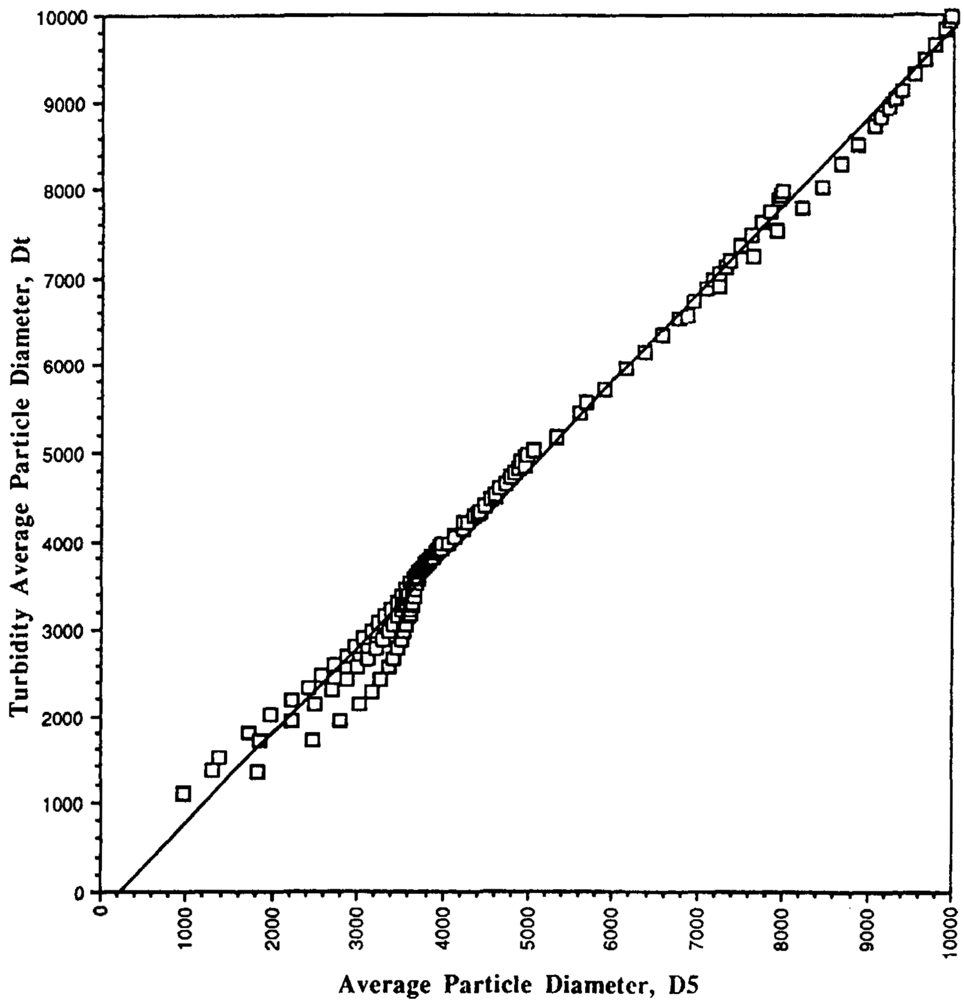

Figure 7 Calculated values for the D_t and D_5 particle diameter averages for a large number of particle size distributions.

MCGEARY'S MAXIMUM BINARY PACKING FRACTIONS CALCULATED WITH $(D_5/D_1)_{max}$ OR $(D_4/D_2)_{max}$ REPLACING R

In an earlier section it was shown that the McGeary's maximum packing fractions could be predicted very satisfactorily as

$$\varphi_{n\,max} = \varphi_{n\,ult} - (\varphi_{n\,ult} - \varphi_m)e^{\alpha(1-R)} \quad (5)$$

From D_x/D_y analysis, it has been shown that the maximum binary packing fraction is accurately predicted using the D_5/D_1 ratio. In addition, it has been shown that the maximum value that can be achieved by this ratio is equal to R. Based on this result, it would appear possible that the ratio of the large to small particle size, R, in eq. (5) could be replaced by the $(D_5/D_1)_{max}$ ratio as

$$\varphi_{n\,max} = \varphi_{n\,ult} - (\varphi_{n\,ult} - \varphi_m)e^{\alpha(1-(D_5/D_1)_{max})} \quad (44)$$

where the following limits are again applicable:

$$\text{when } \left(\frac{D_5}{D_1}\right)_{max} = 1, \quad \text{then} \quad \varphi_{n\,max} = \varphi_m \quad (45)$$

and

$$\text{as } \left(\frac{D_5}{D_1}\right)_{max} \rightarrow \infty, \quad \text{then} \quad \varphi_{n\,max} \rightarrow \varphi_{n\,ult} \quad (46)$$

The maximum value of the ratio D_5/D_1 for any R

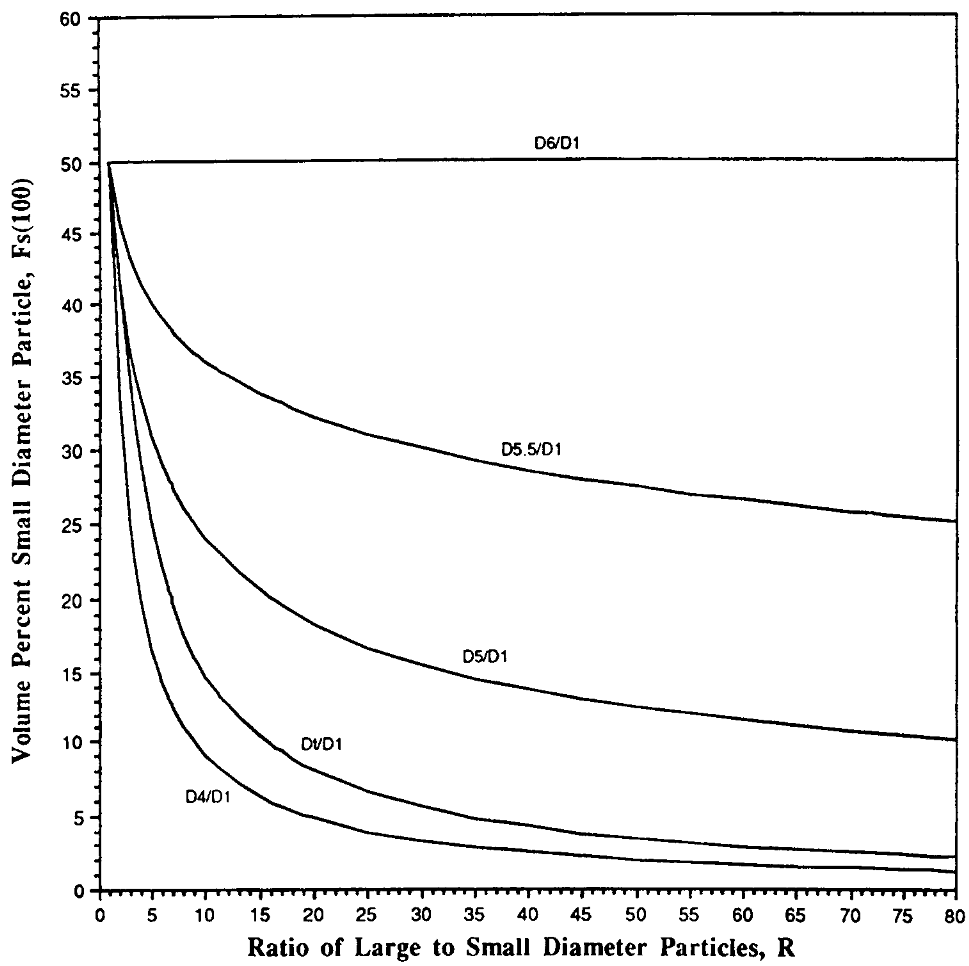

Figure 8 Comparison of the derived optimum volume fraction of small particles, f_s, for the D_6/D_1, $D_{5.5}/D_1$, D_5/D_1, D_t/D_1 and D_4/D_1 average particle diameter ratios.

value is then determined by substituting $x = 5$ and $y = 1$ into eq. (33) to yield

$$\left(\frac{D_5}{D_1}\right)_{\max} = R\left\{\frac{2R^{-5/2} + R^{-5} + 1}{2R^{-3/2} + R^{-3} + 1}\right\} \tag{47}$$

Earlier it was shown that McGeary's binary maximum packing fractions $\varphi_{n\,\max}$ could be predicted efficiently using $\varphi_m = 0.639$ and $\varphi_{n\,\text{ult}} = 0.857$. It would be expected that these same packing fractions would be satisfactory to predict values of $\varphi_{n\,\max}$ when fitting McGeary's binary data using eq. (43). McGeary's data evaluated using this expression, where

$$\alpha = 0.268 \tag{48}$$

is summarized in Figure 9. The average error in predicting McGeary's data using the ratio $(D_5/D_1)_{\max}$ in eq. (44) was only 0.467%. Similarly, when fitting McGeary's data using eq. (44) with the $(D_4/D_2)_{\max}$ ratio replacing the $(D_5/D_1)_{\max}$ ratio, then the constant α obtained was

$$\alpha = 0.488 \tag{49}$$

In addition, the average error in predicting McGeary's results for this case was 0.426%.

Note that the average error in predicting McGeary's results with either the $(D_5/D_1)_{\max}$ or $(D_4/D_2)_{\max}$ ratio that the error was nearly half the average error of 0.751% obtained using eq. (5). It is appearent that either the $(D_5/D_1)_{\max}$ or $(D_4/D_2)_{\max}$ ratio yields a significant improvement in the prediction of the absolute value of $\varphi_{n\,\max}$ over of using only R.

EXTENSION OF PARTICLE PACKING ANALYSIS TO SUSPENSIONS WITH *n* PARTICLE SIZES

If f_2 is the volume fraction of the large particle size in a mixture of two particles, then the D_5/D_1 ratio can be described by simplifying equations derived earlier in this paper as

$$\frac{D_5}{D_1} = \frac{af_2^2 + bf_2 + c}{df_2^2 + (a + b - d)f_2 + c} \quad (50)$$

where

$$a = R^2 + R^3 - 1 - R^5$$
$$b = 1 + R^5 - 2R^3$$
$$c = R^3$$
$$d = R^2 + R^3 - R^1 - R^4 \quad (51)$$

Since the binary particle expression for D_5/D_1 described by eq. (50) encompasses all compositions including the maxima values, it is suggested that the value of φ_n for all binary compositions could be adequately predicted using a modified version of eq. (44) as

$$\varphi_n = \varphi_{n\,\mathrm{ult}} - (\varphi_{n\,\mathrm{ult}} - \varphi_m)e^{\alpha(1-(D_5/D_1))} \quad (52)$$

In addition, earlier in this paper it was shown that for particle size combinations of more than binary mixtures that the general values for $\varphi_{n\,\mathrm{ult}}$ could be obtained from the following equation:

$$\varphi_{n\,\mathrm{ult}} = 1 - (1 - \varphi_m)^n \quad (18)$$

As indicated earlier in this paper, the ultimate packing fraction $\varphi_{n\,\mathrm{ult}}$ is best predicted above $n = 2$ using the monodisperse limit for loose random packing or

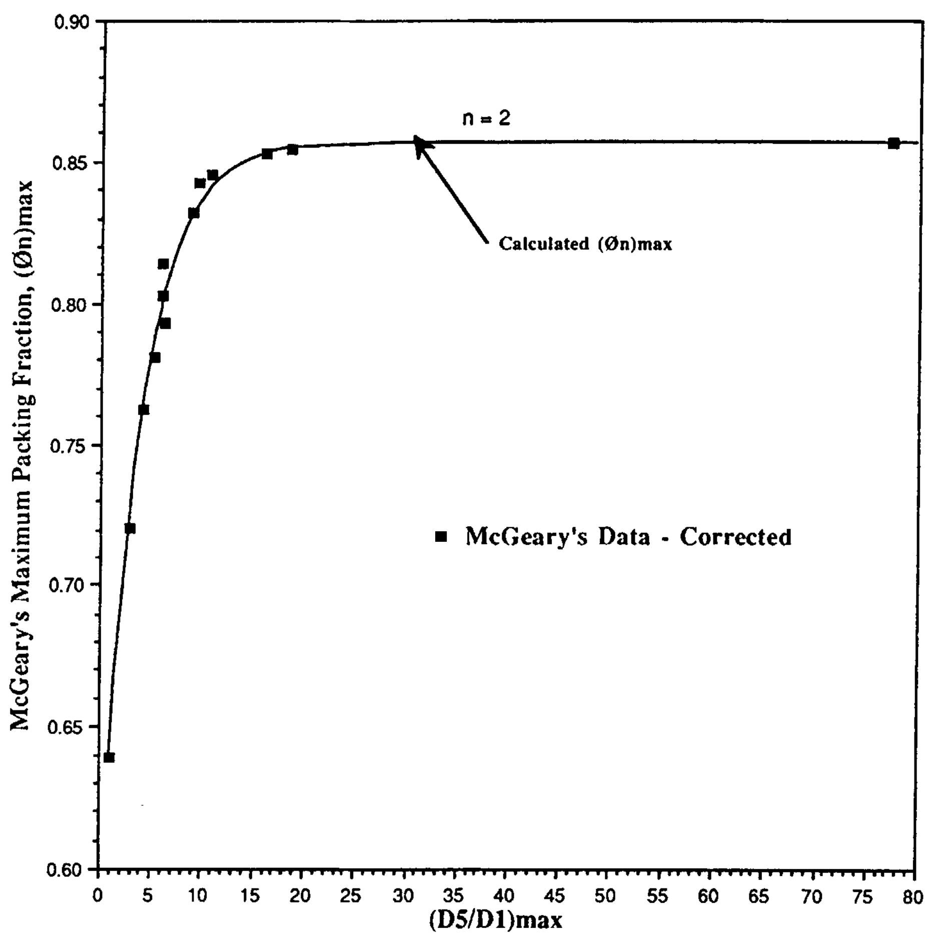

Figure 9 Comparison of McGeary's[14] corrected maximum packing fraction data with calculated results from an empirical equation using $(D_5/D_1)_{\max}$ instead of R.

$\varphi_m = 0.589$. The maximum value of D_5/D_1 for any suspension with particles involving n different size diameters can be estimated using the maximum value of D_5/D_1 for binary mixtures. As derived earlier in this paper, the calculated maximum value for both the D_5/D_1 and D_4/D_2 ratios for binary mixtures is determined at the following composition:

$$f_2 = \sqrt{R}/(\sqrt{R} + 1) \qquad (53)$$

The predicted results for φ_n calculated from eq. (52) for several different combinations of particle size diameters, n, up to $n = 100$ have been plotted in Figure 10 as a function of $(D_5/D_1)_{max}$. These results would indicate that values of $(D_5/D_1)_{max} \geq 15$ would appear to offer only minimal improvement in the maximum packing fraction for any combination of particles. It is also apparent that combinations of greater than six particles appear to offer only minimal improvement in the theoretical maximum packing fraction.

The general expressions for D_5 and D_1 in calculating the ratio D_5/D_1 for n different particle sizes can be evaluated from the following formulations:

$$D_5 = \sum_{i=1}^{n} N_i \mathcal{D}_i^5 \Big/ \sum_{i=1}^{n} N_i \mathcal{D}_i^4 \qquad (54)$$

$$D_1 = \sum_{i=1}^{n} N_i \mathcal{D}_i \Big/ \sum_{i=1}^{n} N_i \qquad (55)$$

Utilizing this calculation procedure, the value of φ_n can be evaluated for any ratio D_5/D_1. Evaluation of these averages requires knowledge of the number each kind of particle, N_i, and the diameter of each particle, $\mathcal{D}_i$, or another measure of the composition of n particle size diameters in a suspension.

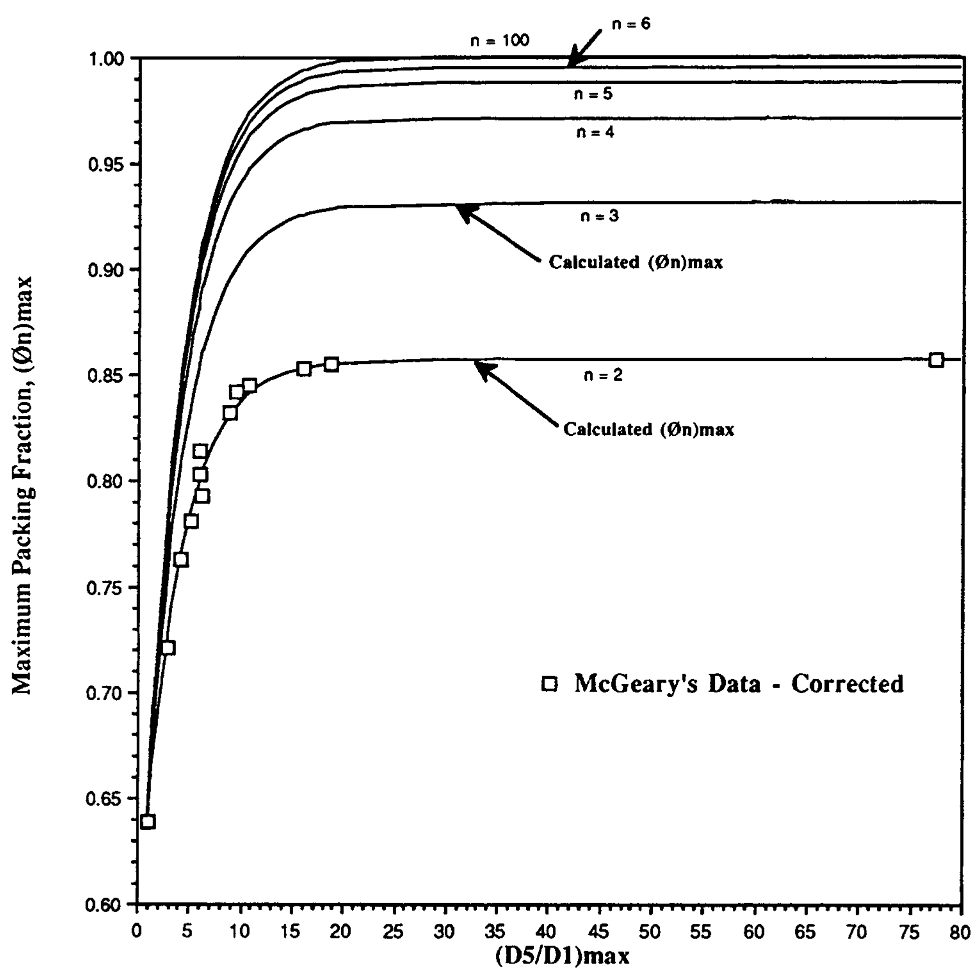

Figure 10 Theoretical calculated maximum packing fraction $(\phi_n)_{max}$ for blends of several different particle sizes, n, compared with McGeary's[14] binary maximum packing fractions.

PREDICTION OF SUSPENSION VISCOSITY PROPERTIES UTILIZING φ_n

The influence of particle size and polydispersity on the viscosity of synthetic latexes has been studied by Johnson and Kelsey.[3] By comparing loading levels of several combinations of two relatively monodisperse latexes at the same viscosity, they found that a maximum in percent solids was achieved. The effect of blending two latexes of different particle sizes to give percent solids at essentially the same 1000 cps viscosity level is shown in Figure 11. This figure illustrates that a minimum viscosity–maximum solids latex system can be obtained by suitable adjustment in both particle size and distribution.

The results shown in Figure 11 can be predicted with equations developed in this paper. This process will be illustrated by rewriting eq. (1) in the form

$$\ln(\eta/\eta_0) = \left(\frac{[\eta]\varphi_n}{\sigma - 1}\right)\left\{\left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{1-\sigma} - 1\right\} \quad \text{for } \sigma \neq 1 \quad (56)$$

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

$$\ln(\eta/\eta_0) = -[\eta]\varphi_n \ln\left(\frac{\varphi_n - \varphi}{\varphi_n}\right) \quad (57)$$

In the absence of intrinsic viscosity information for the data of Johnson and Kelsey,[3] the Einstein value[20,21] can be assumed such that

$$[\eta] = 5/2 \quad (58)$$

The viscosity of the solution can then be determined once φ_n is estimated from particle size distribution.

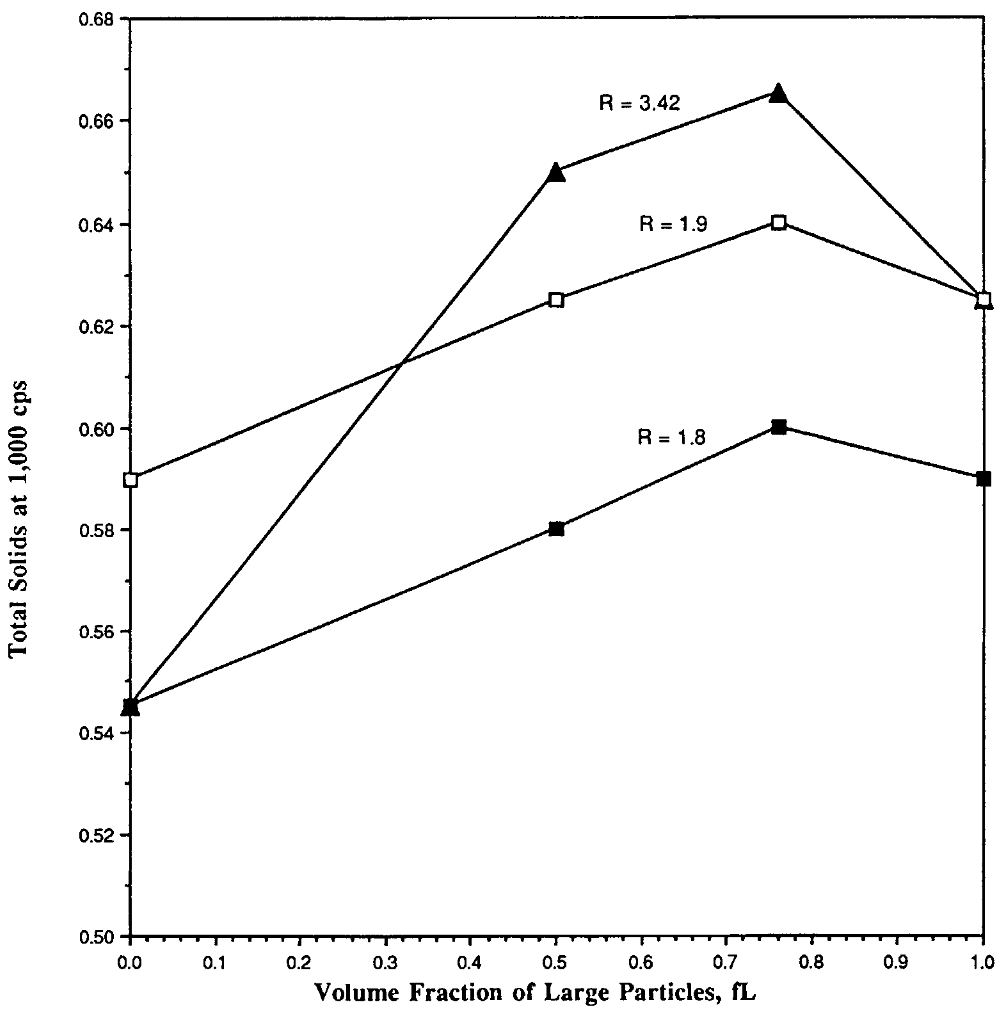

Figure 11 Total solids at 1000 cps as a function of the volume fraction of large particles, f_L, for three different sets of blends of large and small diameter particle latexes (data of Johnson and Kelsey[3]).

Utilizing constants developed earlier in this paper for binary mixture of particles, the value for φ_n can be obtained from eq. (52) as

$$\varphi_n = 0.857 - (0.857 - 0.639)e^{0.268(1-(D_5/D_1))} \quad (59)$$

For purposes of this discussion, the density of both particles and solvents in this analysis will all be assumed to be identical to minimize calculations in converting from weight to volume. If f_2 is the volume fraction of the large particle size in a mixture of two particles, then the D_5/D_1 ratio can be described by simplifying eqs. (50) and (51) derived earlier.

If two suspensions are compared at the same viscosity but at different volume fractions, f_2, they will have a constant viscosity ratio (η/η_0). Equation (56) can then be solved for the general solution for the volume concentration φ in terms of this constant viscosity ratio (η/η_0) as

$$\varphi = \varphi_n\left\{1 - \left(\frac{[\eta]\varphi_n}{(\sigma-1)\ln(\eta/\eta_0) + [\eta]\varphi_n}\right)^{1/(\sigma-1)}\right\} \quad \text{for } \sigma \neq 1 \quad (60)$$

When σ is an odd integer, a second possible solution is

$$\varphi = \varphi_n\left\{1 + \left(\frac{[\eta]\varphi_n}{(\sigma-1)\ln(\eta/\eta_0) + [\eta]\varphi_n}\right)^{1/(\sigma-1)}\right\} \quad \text{for } \sigma \neq 1 \quad (61)$$

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

$$\varphi = \varphi_n\left\{1 - \left(\frac{\eta_0}{\eta}\right)^{1/[\eta]\varphi_n}\right\} \quad (62)$$

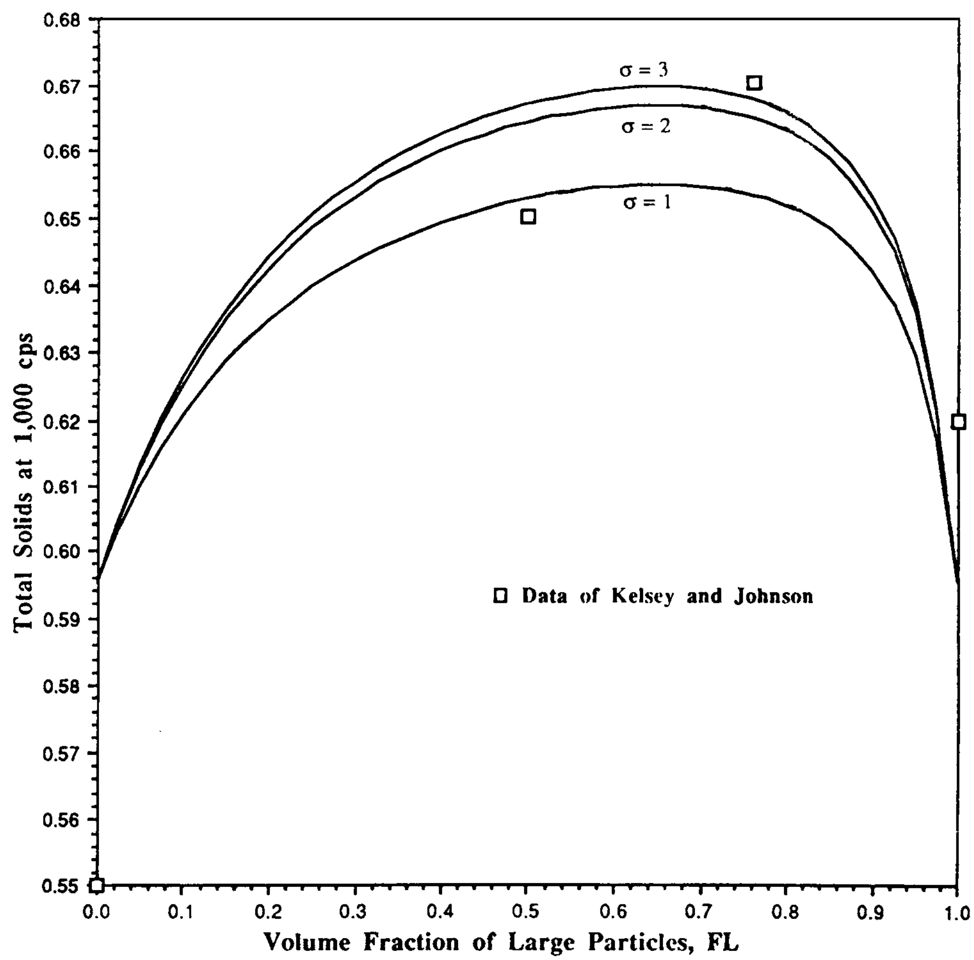

Figure 12 Johnson and Kelsey's[3] data set where $R = 3.42$ compared with theoretically calculated constant viscosity results at three levels of the particle interaction coefficient.

For comparison, Figure 12 shows the predicted total solids volume fraction φ, calculated using values of σ from 1 to 3 for one set of binary data (R = 3.42) developed by Johnson and Kelsey. In the absence of comparative viscosity measurements, a constant viscosity ratio η/η_0 was calculated from an estimated total solids intercept condition (φ = 0.595), where the volume fraction of large particles was zero. A particle interaction coefficient of σ = 3 appeared to give the best fit of the total solids data.

Predicted total solids results, using a particle interaction coefficient of $\sigma = 3$, are compared in Figure 13 for all three binary data sets measured by Johnson and Kelsey. The initial constant viscosity ratio η/η_0 for each set of data was calculated at a volume fraction of large particles, $f_L = 0.75$. These results show that the location of the maximum is nearly identical to maximum obtained from the measurements of Johnson and Kelsey. In addition, although the predicted values of the total solids were not as accurate as had been hoped, the calculated results were in the range of actual measurements and the general shapes of the curves were very similar to the measured results. More importantly, this figure shows that viscosity results can be predicted directly from the evaluation of particle size distribution. In addition, the location of the optimum particle size distribution to give the lowest viscosity can be calculated.

In this instance, monodisperse particle size distributions were assumed for both particle size latexes in each binary blended mixture. It is apparent that this accounts for the identical end points for all three binary latex series where the volume fraction of large particles, f_L, are 0 and 1. Better results would prob-

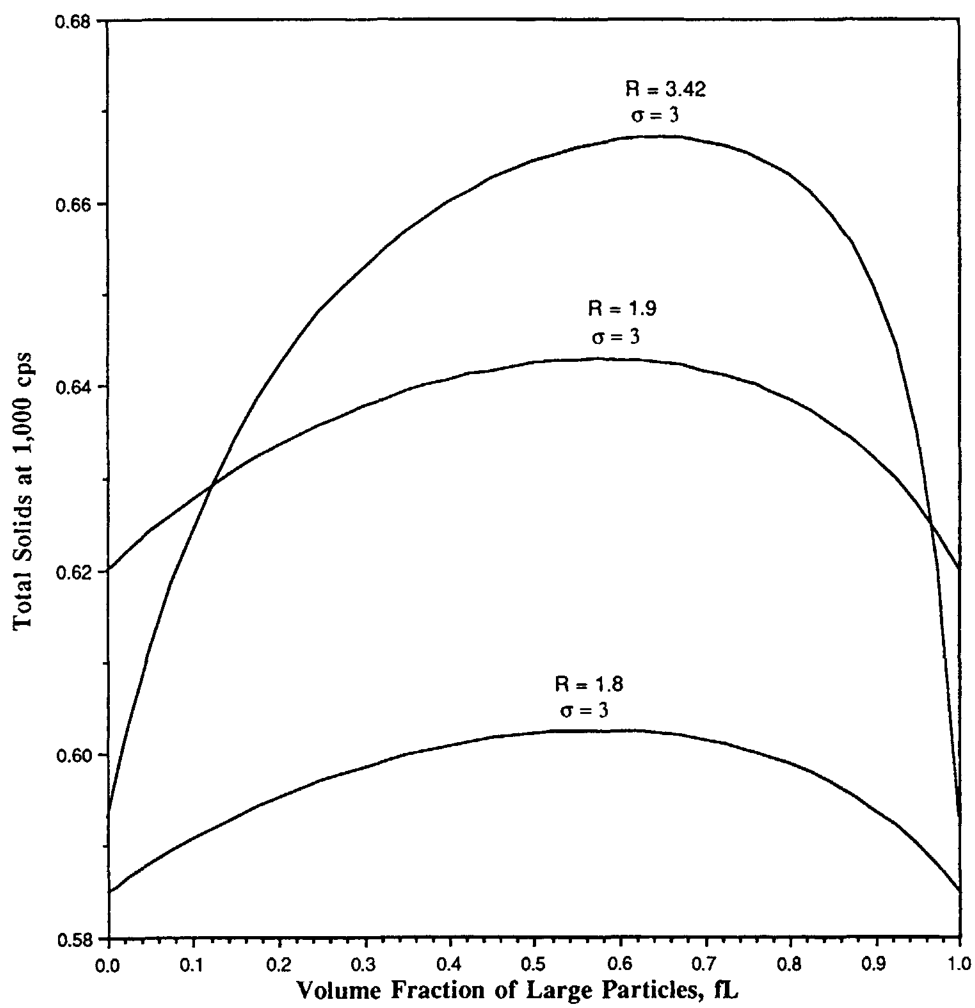

Figure 13 Theoretically calculated constant viscosity results at one level of the particle interaction coefficient for all three sets of binary blends developed by Johnson and Kelsey.

ably have been obtained if the full distribution of each latex were evaluated separately prior to blending.

CONCLUDING REMARKS

A new analysis technique has been developed in this paper to evaluate the upper limit of the packing fraction, φ_n, utilized in the prediction of suspension viscosities. A general viscosity equation for suspensions developed in a previous paper[17] by this author was used to demonstrate the viscosity methodology developed. The derivation and formulation process to evaluate the upper limit of the packing fraction, φ_n, was generated initially for binary particle size distributions utilizing McGeary's[14] packing fraction data. Specific ratios of particles size averages were also found to be very important in this formulation development. In particular, either the D_5/D_1 or the D_4/D_2 average particle size ratio was shown to be required to generate the correct value for the upper limit of the packing fraction, φ_n, at the proper particle volume fraction obtained in McGeary's data. After developing a binary particle size methodology to calculate φ_n, an extension was made to include suspensions with any number n of different particle size diameters.

The blended binary suspension viscosity data of Johnson and Kelsey[3] for near monodisperse latexes was shown to be satisfactorily predicted as a function of the binary volume composition using this new methodology. This example showed that viscosity properties of binary suspension blends, like the lowest viscosity, can be predicted directly from an evaluation of particle size distribution and composition.

In general, the foundation for the evaluation of viscosities for blended multiple particles size suspensions has been described. However, a detailed discussion of multiple particle suspension blends with more than two particle size diameters in each suspension will be left for a future paper.[22]

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Accepted January 2, 1992