

Modeling the Characteristics of Pigment Cluster Formed Foams in Coatings and Polymer Formulations

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ABSTRACT: This study addressed conceptually the formation of foams in coatings and polymer formulations that are often formed from pigment clusters as a result of not having enough dispersing compound. This study introduced several new models relating to cluster sizes and cluster size distributions that resulted from combinations of existing models in the literature. Critical pigment volume concentration values were evaluated both experimentally and theoretically to try to elucidate new ways to evaluate and control the formation of foams formed from pigment clusters in both coatings and polymer formulations. The control of pigment cluster foams appears to be most easily achieved by minimizing the ultimate critical pigment volume concentration and optimizing the amount of dispersing agent added to the formulation. The ultimate critical pigment volume concentration was proposed to be

optimized by blending pigment particles with different particle shapes and different random packing fractions. Minimizing the cluster dispersion coefficient, C_{qr} , was found to be very important to keep the viscosity within controllable limits. Although experimental measurement of the parameters to isolate the clustering concepts introduced in this study may be difficult, it is expected that better quantitative measurement of clustering concepts will eventually prove to be very beneficial to providing improved suspension applications involving pigment cluster foams. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2824–2838, 2012

Key words: cluster voids; critical pigment volume concentration; pigment cluster dispersion coefficient; volume fraction pigment; zero limit volume fraction pigment

INTRODUCTION

Coating foams can sometimes be created inadvertently when pigment clusters are formed in a coating as a result of not having enough dispersing compound.¹ However, pigment cluster foams can be minimized with appropriate formulation modifications² that normally result in a reduction of the viscosity of the coating as well as making the coating more smooth and uniform. Many other physical properties of paints and coatings have also been found to be directly influenced by the concentration of pigment. Asbeck and Van Loo² then identified one specific pigment concentration designated as the critical pigment volume concentration (CPVC) that was found to be particularly important. What Asbeck and Van Loo discovered was that pigment particles that are approximately pseudospherical can only occupy so much volume in a packed configuration. As the volume fraction of pigment is increased above this maximum pigment volume packing fraction then the effective volume fraction of pigment must then remain constant but the volume of voids

in the coating must necessarily increase. This maximum pigment volume fraction above which voids are just introduced has been identified by Asbeck and Van Loo as the critical pigment volume concentration (CPVC).

After the initial identification of the CPVC by Asbeck and Loo,² at least 20 different techniques to characterize the CPVC were identified in the literature as summarized by Bierwagen and Hay.³ The characterization of the CPVC in coatings continues to remain an active area of research.^{4–7}

The sudden increase in voids above the CPVC has been found to effect different groups of physical properties quite differently. DelRio and Rudin⁸ identified three separate groups of physical properties that are influenced differently by the CPVC. These three separate groups of physical properties include:

- i. Optical properties (i.e., specular gloss, opacity, and tint acceptance).
- ii. Mechanical properties (i.e., tensile strength, block resistance, density, and scrub resistance).
- iii. Transport properties (i.e., permeability, stain removal, and electrical resistance).

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pigment volume concentration is approached. This has been explained by several authors^{1,5,6,9-12} based on fluctuations in packing density and based on different aspects of coatings being measured near the CPVC for different physical properties.

One experimental approach described by Asbeck¹ for controlling pigment clustering in coatings involves the use of a pigment dispersing agent. For the most part, the analysis addressed by Asbeck applies best to the older solvent-based coatings in which adding a surfactant or a flow agent significantly improved the ability of the pigment to disperse more uniformly. Consequently, Asbeck described the flow agent or surfactant additive in the polymer or matrix phase as having a direct influence on the dispersion of pigment clustering and the formation of pigment cluster foams in a coating formulation. In general, if a flow agent or surfactant was not added to the coating formulation, then the pigment was found to typically agglomerate in clusters in the coating at low volume concentrations of pigment and often developed pigment cluster foams. However, if just enough surfactant is added, the pigment would appear to disperse uniformly allowing the CPVC to be increased to its maximum value and the viscosity to be decreased to its minimum value.

What Asbeck found was that the volume fraction of pigment where voids first appear (CPVC) occurs at a lower volume fraction if insufficient flow agent or surfactant has been added. However, as more surfactant or flow agent is added, he found that the volume fraction of pigment where the voids first appear increases to a maximum but any further addition of surfactant or flow agent was found to be ineffective. An example of this phenomena, where the maximum CPVC was achieved at only 3% of surfactant, is illustrated in Figure 1 using the data of Asbeck.¹

The maximum flow agent or surfactant required can often be achieved at a very low level in the formulation. However, Asbeck points out that the addition of a flow agent or surfactant has often been found to be critical to achieve the maximum CPVC. Asbeck called the maximum CPVC achieved the "ultimate CPVC" (UCPVC). Thus, for the same pigment particle size distribution, very different values for CPVC, can be obtained by controlling the additives in the polymer or matrix phase of a coating formulation.

It is also possible to change the critical pigment volume concentration (CPVC) by changing the pigment particle size distribution. One property, which achieves its minimum value at the CPVC, is the viscosity of the coating. A series of articles has been published¹³⁻¹⁸ that addresses the influence of the packing fraction of pseudospherical particles on viscosity. The maximum packing, fraction, which is of-

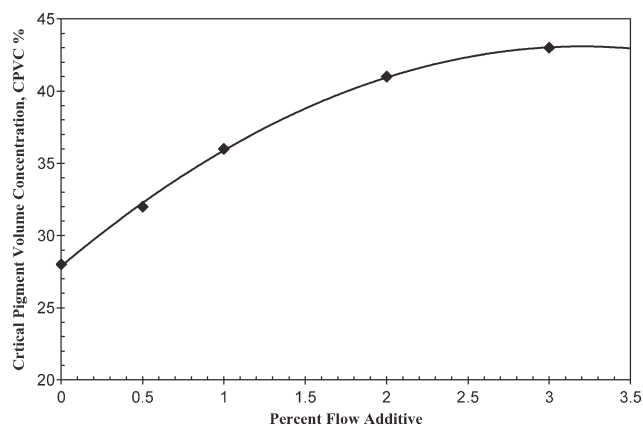


Figure 1 Critical pigment volume concentration (% CPVC) versus percent flow additive (Data of Asbeck¹).

ten directly related to the CPVC, has also been shown^{5,19} to be strongly influenced by the shape of a particle. It has been shown that the change in shape of a particle from spherical to being more fiber-like or disk-like can significantly change the concentration of the maximum packing fraction. The importance of voids on the maximum tensile strength of a composite with spherical particles was also addressed in recent publication.²⁰

Several theoretical concepts of the clustering of pigments in a coating or a polymer formulation have been addressed by several authors^{1,5,6,9-12} to explain the CPVC. Most of these concepts begin with the assumption that pigment clustering can generate a local pigment concentration in the coating that can exceed the critical pigment concentration, which in turn can generate local voids within the pigment clustered areas of the coating. However, there are no apparent discussions in the literature that attempt to identify the many variables that can be used to deliberately generate the formation of coating foams in a coating or polymer formulation.

The initial interest in the CPVC involved ways to try to minimize clustering to make a smoother coating that had nice flow properties. Contrary to this approach, this study has attempted to elucidate theoretically some new possible influences on both the size of pigment clusters as well as the distribution of clusters in a coating and/or a polymer formulation. However, although it was felt important to look for new variables to control foam formation in a coating, there has also been an attempt to optimize other associated properties like viscosity. Consequently, the primary purpose of this study was to address new approaches to control cluster size and distribution to prepare foamed materials with a range of new properties to be able to explore new applications.

CHARACTERIZATION OF THE ULTIMATE CRITICAL VOLUME FRACTION FOR 100% PIGMENT DISPERSION

If a dried paint or coating does not contain any voids then the total material volume, V_T , will be made up of the filler or pigment volume, V_F , and the matrix or polymer volume, V_M , as

$$V_T = V_F + V_M \quad (1)$$

$$1 = \left(\frac{V_F}{V_T}\right) + \left(\frac{V_M}{V_T}\right) = \Phi_F + \Phi_M \quad (2)$$

$$\Phi_F = \left(\frac{\frac{m_F}{\rho_M}}{\frac{m_F}{\rho_F} + \frac{m_M}{\rho_M}}\right) = \left(\frac{\frac{X_F}{\rho_M}}{\frac{X_F}{\rho_F} + \frac{X_M}{\rho_M}}\right) \quad (3)$$

$$\Phi_M = 1 - \Phi_F = \left(\frac{\frac{X_M}{\rho_F}}{\frac{X_F}{\rho_F} + \frac{X_M}{\rho_M}}\right) \quad (4)$$

where m_M is mass weight of matrix or polymer, m_F is mass weight of filler or pigment, X_M is weight fraction of matrix or polymer, X_F is weight fraction of filler or pigment, ρ_M is density of matrix or polymer, ρ_F is density of filler or pigment, Φ_M is global volume fraction of matrix or polymer, and Φ_F is global volume fraction of filler or pigment, respectively.

However, if a polymer coating or composite does contain some volume of voids, V_V , then the total available volume, V_{TA} , can now be written as

$$V_{TA} = V_V + V_F + V_M \quad (5)$$

Or equivalently

$$1 = \left(\frac{V_V}{V_{TA}}\right) + \left(\frac{V_F}{V_{TA}}\right) + \left(\frac{V_M}{V_{TA}}\right) = \phi_V + \phi_F + \phi_M \quad (6)$$

where ϕ_V is effective volume fraction of voids, ϕ_F is effective volume fraction of pigment, and ϕ_M is effective volume fraction of matrix polymer, respectively.

Note that the value for Φ_F can also be calculated as

$$\Phi_F = \left(\frac{\phi_F}{\phi_F + \phi_M}\right) = \left(\frac{\phi_F}{1 - \phi_V}\right) \quad (7)$$

At or above the pigment maximum critical packing fraction or the effective ultimate critical pigment volume concentration, ϕ_{FUC} , it is assumed that the dried coating yields

$$V_F = V_T \Phi_F = V_{TA} \phi_{FUC} \quad (8)$$

or

$$V_T = V_{TA} \left(\frac{\phi_{FUC}}{\Phi_F}\right) \quad (9)$$

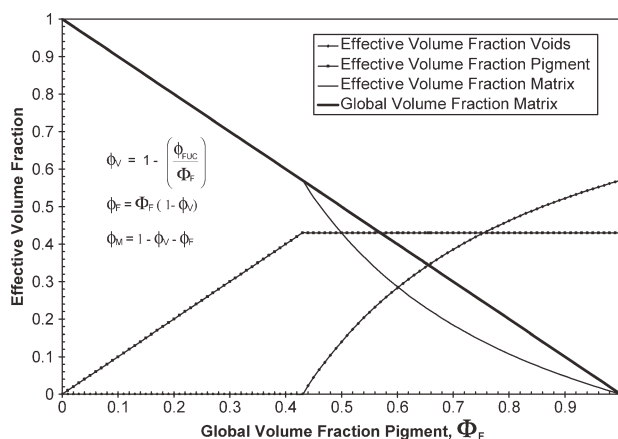


Figure 2 Effective volume fraction (voids, pigment, and matrix) versus global volume fraction pigment (100% pigment dispersion, $\phi_{FUC} = 0.43$).

and the following relationships result

$$\phi_V = \frac{V_V}{V_{TA}} = 1 - \left(\frac{\phi_{FUC}}{\Phi_F}\right) \quad (10)$$

$$\phi_F = \Phi_F(1 - \phi_V) = \phi_{FUC} \quad (11)$$

$$\phi_M = 1 - \phi_V - \phi_F = \left(\frac{\phi_{FUC}}{\Phi_F}\right)(1 - \Phi_F) \quad (12)$$

Note that the calculation of the effective volume fraction of voids, ϕ_V , filler or pigment, ϕ_F , and matrix, ϕ_M , using eqs. (10)–(12) are only valid if the calculated local volume fraction of pigment, Φ_F , is equal to or greater than the ultimate critical pigment volume concentration (UCPVC), ϕ_{FUC} , such that $\Phi_F \geq \phi_{FUC}$. When there are no voids or if $\Phi_F < \phi_{FUC}$ then

$$\phi_F = \Phi_F \quad (13)$$

and

$$\phi_M = \Phi_M \quad (14)$$

For reference, the 100% dispersed relationships indicated in eqs. (7)–(12) have been summarized in Figure 2 using the UPVC of Asbeck ($\phi_{FUC} = 0.43$) from Figure 1.

As defined in a previous article,⁵ the “lower zero limit” global volume fraction of pigment, Φ_{FLZL} , is assumed to have been achieved when the effective volume fraction of matrix, ϕ_M , is equal to the effective volume fraction of voids, ϕ_V , as indicated by the intersection of these volume fractions in Figure 2. Thus, when $\phi_V = \phi_M$, then eqs. (10) and (12) can be combined to give:

$$\Phi_{FLZL} = \frac{2\phi_{FUC}}{1 + \phi_{FUC}} \quad (15)$$

At the “lower zero limit” global volume fraction of pigment, Φ_{FLZL} , the void volume, V_V , and the matrix volume, V_M , would have the same magnitude in the total available volume, V_{TA} . This condition would be equivalent to equal probability of having either a void or matrix material between pigment particles. Such a condition would be expected to yield minimal or “zero limit” physical properties because cracks would be expected to follow along the open percolated void paths.

Similarly, the “upper zero limit” global volume fraction of pigment, Φ_{FUZL} , is assumed to have been achieved when the global volume fraction of matrix, Φ_M , is equal to the effective volume fraction of voids, ϕ_V , as indicated by the intersection of these volume fractions in Figure 2. At the “upper zero limit,” the ratio of the void volume to total effective volume and the ratio of the matrix volume to the total global volume are exactly equal. At this condition, eqs. (4) and (10) can be combined to yield the “upper zero limit” global volume fraction of pigment, Φ_{FUZL} , as

$$\Phi_{FUZL} = \sqrt{\phi_{FUC}} \tag{16}$$

and Φ_{FUZL} is equal to the square root of the critical maximum packing fraction, ϕ_{FUC} . At this condition, the ratio of the void volume, V_V , to the matrix volume, V_M , can be calculated as

$$\frac{V_V}{V_M} = \frac{V_{TA}}{V_T} = \frac{\Phi_{FUZL}}{\phi_{FUC}} = \frac{1}{\sqrt{\phi_{FUC}}} \tag{17}$$

Consequently, the “upper zero limit” condition will always require that the void volume, V_V , be slightly larger than the matrix volume, V_M . In addition, the “lower zero limit” global volume fraction of pigment, Φ_{FLZL} , will always be smaller than the “upper zero limit” global volume fraction of pigment, Φ_{FUZL} , as indicated in Figure 2. Therefore, if a mechanical property such as tensile strength does not fail at the “lower zero limit” global volume fraction of pigment, then it would certainly be expected to fail at the “upper zero limit” global volume fraction of pigment. The zero limit volume fraction relative to tensile strength was in fact addressed in a recent publication.²⁰

An example of the range of the lower and upper zero limit packing fraction can be illustrated if the ultimate critical pigment volume concentration can be assumed to be equal to that found by Asbeck ($\phi_{FUC} = 0.43$), then the values of Φ_{FLZL} and Φ_{FUZL} would yield:

$$\Phi_{FLZL} = \frac{2(0.43)}{1 + 0.43} = 0.601$$

$$\Phi_{FUZL} = \sqrt{0.43} = 0.656$$

Consequently, the failure range for mechanical properties for this example would be expected to fall between the following limits.

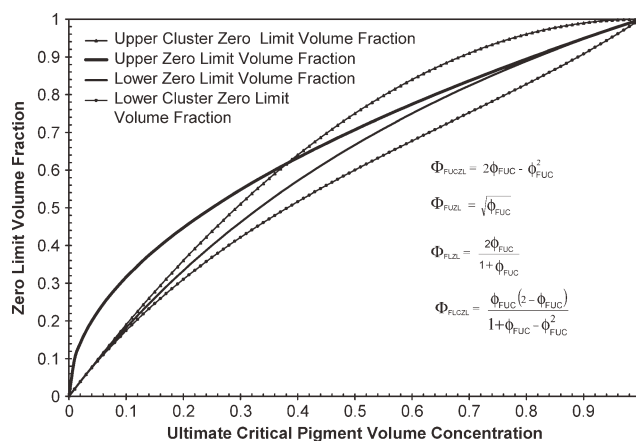


Figure 3 Zero limit volume fractions versus ultimate critical pigment volume concentration.

$$0.601 = \Phi_{FLZL} \leq \Phi_{FZL} \leq \Phi_{FUZL} = 0.656 \tag{18}$$

Formulation of a coating or composite at values higher than this range for this example would not be expected to yield useful mechanical properties.

A direct comparison between the “upper zero limit” global volume fraction of pigment and the “lower zero limit” global volume fraction of pigment is indicated in Figure 3. As expected, the “upper zero limit” will always be greater than the “lower zero limit” global volume fraction of pigment.

Review of a model addressing the relationship between pigment clustering in coating formulations and the critical pigment volume concentration

The pigment clustering model developed in a previous article⁵ addressed the introduction of voids in a coating at the critical pigment volume concentration (CPVC). As pigment particles are distributed randomly, the local value of the effective pigment volume fraction, $\phi_F(x)$, can vary from region to region. Therefore, this model defines the quantities, $\phi_F(x)$, $\phi_M(x)$, and $\phi_V(x)$ to be the local effective volume fractions of pigment, matrix, and voids, respectively, in a sphere of observation volume, V_{or} , centered around x . For any observation volume and any position x , the sum of the $\phi_i(x)$ terms equals 1:

$$\phi_F(x) + \phi_M(x) + \phi_V(x) = 1 \tag{19}$$

In terms of the local concentrations, the local value of the global volume fraction of pigment, $\Phi_F(x)$, was defined as:

$$\Phi_F(x) = \left(\frac{\phi_F(x)}{\phi_F(x) + \phi_M(x)} \right) \tag{20}$$

It was also assumed that the local effective volume fraction of voids, $\phi_V(x)$, could be described in the same form as eq. (10) developed earlier.

$$\phi_V(x) = 1 - \left(\frac{\Phi_{FUC}}{\Phi_F(x)} \right) \quad (21)$$

Now if N_o is the minimum number of particles that can define a densely packing pigment particle structure, then the probability, v , of an island with all densely packed particle sites filled existing within the coating would be

$$v = \left(\frac{\phi_F}{\phi_{FUC}} \right)^{N_o} \quad (22)$$

Because the coordination number for a spherical particle in a randomly dense-packed cluster of monodisperse particles has been described^{12,21} as being close to 8, then $N_o \cong 9$ can typically be assumed for the close-packed array in a coating. However, if the size distribution of pigment particles is broad, then N_o may be a bit larger than 9. In the absence of more detailed information, the value for N_o can also be used as a fitting parameter for CPVC data.

To parameterize the coarseness of the polymer space-filling, the total volume V_{TA} of the sample was separated into two regions: the densely packed islands occupy region d ; the rest of the coating was labeled as region c . At any point x in V_{MV} , the local volume fraction of polymer or matrix, $Q_M(x)$, can be evaluated by:

$$Q_M(x) = \left(\frac{\phi_M(x)}{\phi_V(x) + \phi_M(x)} \right) \quad (23)$$

For this analysis, it was assumed that there are only two regions. $\phi_V(x)$ vanishes in the nondensely packed areas of region c but is nonzero in region d . Because $\phi_V(x)$ vanishes in region c , then the local reduced volume fraction of matrix in region c of the coating would be

$$Q_{M_c}(x) = 1 \quad (24)$$

However, $Q_{M_d}(x) < 1$ in region d . Hence, the fluctuations in the local polymer density, $Q_M(x)$, can be considered to be a measure of the void concentration of $\phi_V(x)$. It has also been shown previously⁵ then that $Q_{V_d}(x)$ and $Q_{M_d}(x)$ can be calculated as

$$Q_{V_d}(x) = \left(\frac{\phi_V}{v(1 - \phi_{FUC})} \right) \quad (25)$$

and thus

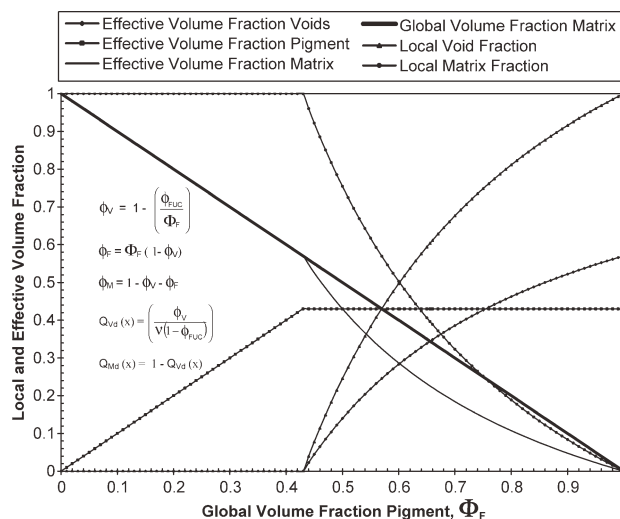


Figure 4 Local and effective volume fraction (voids, pigment, and matrix) versus global volume fraction pigment (100% pigment dispersion, $\Phi_{FUC} = 0.43$).

$$Q_{M_d}(x) = 1 - Q_{V_d}(x) = \left(\frac{v(1 - \Phi_{FUC}) - \phi_V}{v(1 - \Phi_{FUC})} \right) \quad (26)$$

For reference, a comparison of $Q_{V_d}(x)$ and $Q_{M_d}(x)$ is shown in Figure 4 using Asbeck's ultimate critical pigment volume fraction ($\Phi_{FUC} = 0.43$). Figure 4 also includes the same data that was previously included in Figure 2 for comparative purposes.

Note that when $Q_{V_d}(x) = Q_{M_d}(x)$, it can easily be shown that

$$\Phi_F = \frac{2\phi_F}{2 + v(\Phi_{FUC} - 1)} \quad (27)$$

Therefore, if $\phi_F = \Phi_{FUC}$, then $\Phi_F = \Phi_{FLZL}$, and eq. (27) reduces to the "lower zero limit" global volume fraction of pigment as described earlier.

However, if $Q_{M_d}(x) = \phi_V$, then it can easily be shown that

$$\Phi_F = (1 + v)\phi_F - v\phi_F\Phi_{FUC} \quad (28)$$

Again when $\phi_F = \Phi_{FUC}$, then eq. (28) yields the "upper cluster zero limit" global volume fraction, Φ_{FUCZL} , of pigment which can be written as

$$\Phi_{FUCZL} = 2\Phi_{FUC} - \Phi_{FUC}^2 \quad (29)$$

The "upper cluster zero limit" has also been included in Figure 3 to compare with the previously described "upper zero limit" and the "lower zero limit" global volume fractions. One interesting observation is that the "upper cluster zero limit" global volume fraction can possibly be much higher than

the “upper zero limit” volume fraction for higher values of the ultimate critical packing fraction. In addition, the “upper cluster zero limit” global volume fraction can possibly be much lower than the “upper zero limit” volume fraction for lower values of the ultimate critical packing fraction. However, the “upper cluster zero limit” global volume fraction never goes lower than the “lower zero limit” volume fraction for lower values of the ultimate critical packing fraction.

Another interesting limit occurs when $Q_{V_d}(x) = \phi_M$. For this condition, it can easily be shown that

$$\Phi_F = \frac{\phi_{FUC}[1 + v(1 - \phi_{FUC})]}{1 + \phi_{FUC} v(1 - \phi_{FUC})} \quad (30)$$

Again when $\phi_F = \phi_{FUC}$, then eq. (30) yields the “lower cluster zero limit” global volume fraction, Φ_{FLCZL} , of pigment which can be written as

$$\Phi_{FLCZL} = \frac{\phi_{FUC}(2 - \phi_{FUC})}{1 + \phi_{FUC} - \phi_{FUC}^2} \quad (31)$$

Note, in Figure 3, that the “lower cluster zero limit” global volume fraction is always at least equal to or much lower than the “lower zero limit” volume fraction for all values of the ultimate critical packing fraction.

These observations regarding the cluster zero limits could have some significant practical importance if the clusters can be controlled appropriately as will be discussed in a later section of this article.

On basis of the rudimentary observations, it was assumed that the distribution of the reduced volume fraction of matrix, $Q_M(x)$, could be described as a normal or Gaussian distribution.²² Consequently, as developed in a previous article,⁵ this distribution was characterized with its mean, $\langle Q_M(x) \rangle = \mu_q$, and standard deviation, σ_q , as:

$$\mu_q = \frac{\phi_M}{1 - \phi_F} \quad (32)$$

$$\sigma_q = \left(\frac{\phi_V}{(1 - \phi_F)} \right) \left(\frac{(1 - \phi_F) - v(1 - \phi_{FUC})}{v(1 - \phi_{FUC})} \right)^{1/2} \quad (33)$$

At this point, both the mean, μ_q , and the standard deviation, σ_q , for the local volume fraction of matrix in the coating, $Q_M(x)$, have been defined effectively for a normal or Gaussian distribution. However, an additional variable needs to be defined to characterize the coarseness of the distribution to indicate how widely separated the clustered species might be in the coating. This new variable designated as the pigment cluster dispersion coefficient, C_q , has been defined as the ratio of the standard deviation, σ_q , to

the mean, μ_q , for the local volume fraction of matrix in the coating, $Q_M(x)$, as

$$C_q = \frac{\sigma_q}{\mu_q} = \left(\frac{\phi_V}{(1 - \phi_F - \phi_V)} \right) \left(\frac{(1 - \phi_F) - v(1 - \phi_{FUC})}{v(1 - \phi_{FUC})} \right)^{1/2} \quad (34)$$

On the basis of this definition, the pigment cluster dispersion coefficient would be expected to be approximately equal to zero ($C_q \cong 0$) when the pigment is ~100% dispersed in the coating and no pigment clusters are apparent in the coating.

Note that eq. (34) can easily be solved for ϕ_V to give

$$\phi_V = \frac{C_q (1 - \phi_F) v^{1/2} (1 - \phi_{FUC})^{1/2}}{C_q v^{1/2} (1 - \phi_{FUC})^{1/2} + [1 - \phi_F - v(1 - \phi_{FUC})]^{1/2}} \quad (35)$$

Also recall that

$$v = \left(\frac{\phi_F}{\phi_{FUC}} \right)^{N_o} \quad (22)$$

and

$$\Phi_F = \left(\frac{\phi_F}{1 - \phi_V} \right) \quad (7)$$

Thus, if the values for C_q , ϕ_{FUC} , and N_o can be specified, then eqs. (22) and (35) can be used to calculate the effective volume fraction of voids, ϕ_V , directly as a function of the effective volume fraction of filler or pigment, ϕ_F . Thus, once the values for ϕ_V and ϕ_F have been obtained, then the value for the global volume fraction of pigment, Φ_F , can be calculated directly using eq. (7).

Several important limits can then be obtained from eqs. (7), (22), and (35) independent of the value of C_q . For example, the following limits can be obtained when

$$\phi_F = 0 \text{ to yield } \phi_V = 0 \text{ and } \Phi_F = 0$$

Also, when

$$\phi_F = \phi_{FUC} \text{ then } \phi_V = 1 - \phi_{FUC} \text{ and } \Phi_F = 1$$

Thus, the effective volume fraction of filler or pigment, ϕ_F , can only range from 0 to ϕ_{FUC} using eqs. (7), (22), and (34), whereas the range for the global volume fraction of filler or pigment, Φ_F , ranges from 0 to 1.

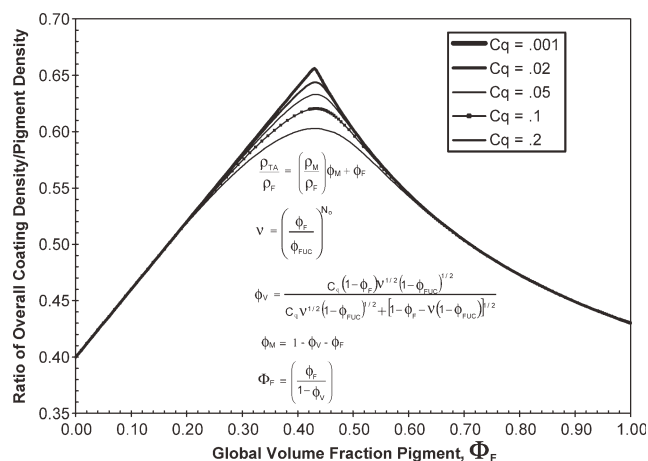


Figure 5 Ratio of overall coating density/pigment density versus global volume fraction of pigment ($\phi_{FUC} = 0.43$, $N_o = 10$).

Application of the cluster model to a physical property—Density

The density will be used to illustrate the influence of cluster voids and the CPVC on a physical property of a coating or formulation. The overall density of a coating or formulation, ρ_{TA} , can normally be described as

$$\rho_{TA} = \rho_M \phi_M + \rho_F \phi_F + \rho_V \phi_V \quad (36)$$

where ρ_M is density of the polymer or matrix phase, ρ_F is density of the filler or pigment phase, and ρ_V is density of the void phase, respectively.

Because the void volume normally has negligible mass or $\rho_V \cong 0$, then eq. (36) can be rewritten as

$$\frac{\rho_{TA}}{\rho_F} = \left(\frac{\rho_M}{\rho_F} \right) \phi_M + \phi_F \quad (37)$$

To illustrate this density model, we will assume that the pigment density, ρ_F , is ~ 2.5 times larger than the density of the matrix, ρ_M , to give the ratio of these densities as $\left(\frac{\rho_M}{\rho_F} \right) = 0.4$. In addition, we will again use $N_o = 10$ at a UCPVC of $\phi_{FUC} = 0.43$ as indicated for the Asbeck's results in Figure 1. With these illustrative values, then eqs. (7), (12), (22), (35), and (37) can be used to calculate the ratio of the overall coating density to the density of the matrix, $\frac{\rho_{TA}}{\rho_F}$, at five different pigment dispersion coefficients ($C_q = 0.001, 0.02, 0.05, 0.1$, and 0.2) as summarized in Figure 5.

As indicated in Figure 5, the maximum coating density ratio is achieved at or near the point at which the UCPVC is achieved. However, the location of this maximum is dependent on the magnitude of the pigment dispersion coefficient. Nevertheless, these results do indicate that if pigment clusters

are present in the coating then the maximum coating density would typically be expected to occur at a global volume fraction of pigment that is identical with or slightly higher than the UCPVC.

Application of the cluster model to the data of Asbeck

As discussed earlier, Asbeck¹ found that the volume fraction of pigment where voids first appear occurs at a lower volume fraction if insufficient flow agent or surfactant has been added. As more surfactant or flow agent is added, he found that the volume fraction of pigment where the voids first appear increases to a maximum and any further addition of surfactant or flow agent over 3% surfactant was found to be ineffective. As Asbeck¹ indicated that the critical pigment volume concentration (CPVC) was dependent on the introduction of voids into a coating, then some threshold value of voids would need to be established to relate this model back to the results found by Asbeck. In this particular instance, an effective volume fraction of voids of $\phi_V = 0.003$ was arbitrarily chosen to characterize the CPVC using the model developed in this study. The same "ultimate CPVC" (UCPVC) used by Asbeck of $\phi_{FUC} = 0.43$ with $N_o = 10$ at $\phi_V = 0.003$ were then used in eq. (34) to calculate C_q as a function of the effective volume fraction of pigment, ϕ_F , which was considered to be the CPVC. Asbeck's results are indicated in Figure 6 where the CPVC values or ϕ_F values cover the same range as developed by Asbeck¹ for the data generated at different levels of the % surfactant additive needed to modify the CPVC.

As previously indicated, a coordination of $N_o = 8$ is possibly more consistent with a monodisperse particle size distribution. However, it is probably more appropriate to use a coordination number of $N_o = 10$ for particle size distributions that may not

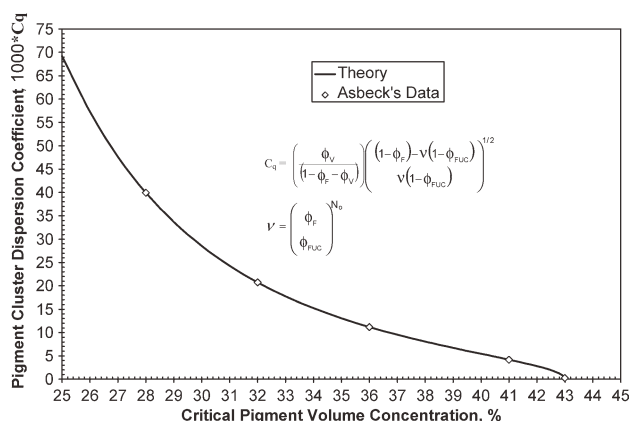


Figure 6 Pigment cluster dispersion coefficient, $1000 \times C_q$ versus critical pigment volume concentration, % ($\phi_V = 0.003$, $\phi_{FUC} = 0.43$, $N_o = 10$).

TABLE I
Calculated Cluster Model Values at Different Critical Pigment Volume Concentrations

Critical pigment volume concentration, %	Pigment cluster dispersion coefficient (C_q)	Mean (μ_q)	Standard deviation (σ_q)
20	0.204828072	0.996250	0.20405997
28	0.039949751	0.995833	0.03978329
32	0.020737000	0.995588	0.02064551
36	0.011181540	0.995313	0.01112913
41	0.004172588	0.994915	0.00415137
42.99	0.000264737	0.994738	0.00026334

$N_o = 10, \phi_{FUC} = 0.43, \phi_V = 0.003.$

be strictly monodisperse. This is especially true because the calculated results in Figure 6 did not show a particularly significant difference between the coordination numbers of $N_o = 8$ and $N_o = 10$.

For reference, several pigment cluster dispersion coefficients, C_q , at specific CPVC values included in Figure 6 have been summarized in Table I along with their calculated means, μ_q , and standard deviations, σ_q .

Three of the pigment cluster dispersion coefficients, C_q , included in Table I have been used in Figure 6 to show influence of the critical pigment volume concentration (CPVC) and consequently the introduction of voids on the effective volume fraction of filler. The results in Figure 7 have been calculated using eqs. (7), (22), and (35). In this instance, a pigment cluster dispersion coefficient of $C_q = 0.000264737$ was found to be most characteristic of the 100% dispersed pigment as indicated in Figure 2 and characterized by Asbeck at an "ultimate CPVC" (UCPVC of $\phi_{FUC} = 0.43$).

CHARACTERIZATION OF THE CLUSTER MODEL IN TERMS OF A GAUSSIAN DISTRIBUTION

The cluster model described in this study has been proposed to describe a normal distribution of the matrix material within the clusters of a coating. A normal or Gaussian distribution²² can be described by the following equations:

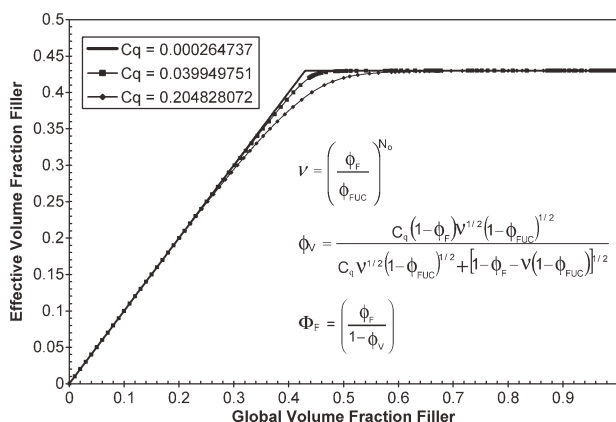


Figure 7 Effective volume fraction filler versus global volume fraction filler ($\phi_{FUC} = 0.43, N_o = 10$).

$$D(z) = \left(\frac{1}{\sigma\sqrt{2\pi}} \right) e^{-\left(\frac{1}{2}\right)\left(\frac{z-\mu}{\sigma}\right)^2} \tag{38}$$

$$G(z) = \sigma\sqrt{2\pi}D(z) = e^{-\left(\frac{1}{2}\right)\left(\frac{z-\mu}{\sigma}\right)^2} \tag{39}$$

In this instance, the z in these equations is actually the local volume fraction of polymer or matrix, $z = Q_M(x)$, as described in the previous section.

The results for three of the pigment cluster dispersion coefficients, C_q , included in Table I have been extended further in Table II. Table II summarizes the mean, μ_q , and the standard deviations, σ_q , calculated at an effective volume fraction of $\phi_F = 0.41$ for three pigment cluster dispersion coefficients, C_q , included in Table I where the ultimate pigment volume fraction was $\phi_{FUC} = 0.43$. The equations used to make the calculations in Table II included:

$$v = \left(\frac{\phi_F}{\phi_{FUC}} \right)^{N_o} \tag{22}$$

$$\phi_V = \frac{C_q(1 - \phi_F)v^{1/2}(1 - \phi_{FUC})^{1/2}}{C_qv^{1/2}(1 - \phi_{FUC})^{1/2} + [1 - \phi_F - v(1 - \phi_{FUC})]^{1/2}} \tag{43}$$

$$\mu_q = \frac{\phi_M}{1 - \phi_F} = \frac{1 - \phi_F - \phi_V}{1 - \phi_F} \tag{32}$$

TABLE II
Calculated Cluster Model Values for Three Different Pigment Cluster Dispersion Coefficients, C_q at an Effective Pigment Volume Fraction of $\phi_F=0.41$

Critical pigment volume concentration (%)	Pigment cluster dispersion coefficient (C_q)	Effective volume fraction pigment	Global volume fraction pigment	Effective volume fraction voids	Mean (μ_q)	Standard deviation (σ_q)
20	0.204828072	0.41	0.465027804	0.118332288	0.79943680	0.163747099
28	0.039949751	0.41	0.421603820	0.027523043	0.95335077	0.038086126
42.99	0.000264737	0.41	0.410078428	0.000191251	0.9996758	0.000264651

$N_o = 10, \phi_{FUC} = 0.43.$

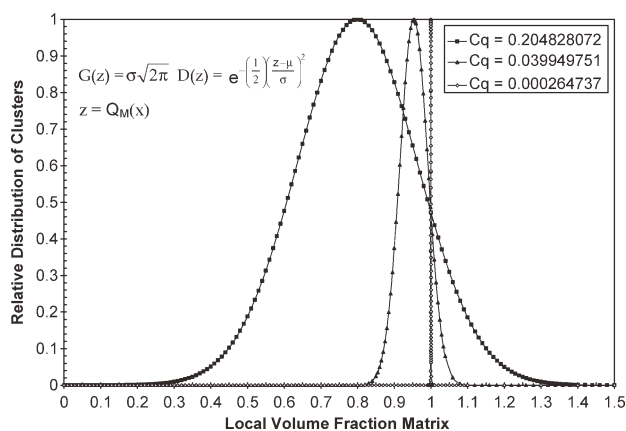


Figure 8 Relative distribution of clusters versus local volume fraction matrix in clusters at an effective volume fraction of $\phi_F = 0.41$ for three pigment cluster dispersion coefficients.

$$\sigma_q = \mu_q C_q \quad (40)$$

The mean, μ_q , and the standard deviations, σ_q , from Table II were then used to calculate the relative Gaussian distributions, $G(z)$, described by eq. (39) as shown in Figure 8. Note that the maximum possible value of the relative Gaussian distribution $G(z)$ is $G(z) = 1$ when the local volume fraction of polymer or matrix, $z = Q_M(x)$, is equal to the mean or when $z = \mu_q$. In addition, the maximum value of the local volume fraction of polymer or matrix, $Q_M(x)$, is also $Q_M(x) = 1$. Therefore, values of $z = Q_M(x)$ greater than 1 are not realistic and have been calculated simply to show the symmetry of the graphs.

At this point, it is important to note that the local volume fraction of voids, $Q_V(x)$, can be calculated as $Q_V(x) = 1 - Q_M(x)$. In addition, it can easily be shown that when $G(z)$ goes through a maximum relative to $z = Q_M(x)$, then a maximum is also obtained for $G(z)$ versus $Q_V(x) = 1 - Q_M(x)$. This is easier to visualize as indicated in Figure 9 for $G(z)$ versus $Q_V(x) = 1 - Q_M(x)$.

Some significant observations from Figures 8 and 9 would include:

- When the value of the pigment cluster dispersion coefficient, C_q , is essentially zero ($C_q = 0.000264737$), then the Gaussian distributions of $G(z)$ versus $Q_M(x)$ and $G(z)$ versus $Q_V(x)$ are very narrow because there are essentially no voids.
- However, when the value of the pigment cluster dispersion coefficient, C_q , is quite large ($C_q = 0.2048$), then the Gaussian distributions of both $G(z)$ versus $Q_M(x)$ and $G(z)$ versus $Q_V(x)$ can be very broad with lots of different potential void cluster sizes.

As the pigment cluster dispersion coefficient, C_q , increases in magnitude, then isolated clusters form a collection of particles that tend to increase in size. However, the number of these larger particle cluster sizes would tend to be fewer in number compared with the number of well dispersed individual particles. This observation can be further exemplified by noting that the maximum value the Gaussian distribution described by equation $D(z)$ is achieved when the local volume fraction of polymer or matrix, $z = Q_M(x)$, is equal to the mean or when $z = \mu_q$. At this maximum, $D(z)$ reduces to

$$D_{\max}(z) = \left(\frac{1}{\sigma\sqrt{2\pi}} \right) \quad (41)$$

Note that this is the same maximum value for both $D_{\max}(z)$ versus $Q_M(x)$ and $D_{\max}(z)$ versus $Q_V(x)$. Thus, the maximum number of clusters of any size in terms of a Gaussian distribution is indicated by the reciprocal of the standard deviation as indicated in eq. (41). Therefore, the larger is the standard deviation, the fewer would be the number of clusters characteristic of that size of a cluster. The maximum number of each cluster size has been evaluated in Figure 10 using eqs. (22) and (33) at a void volume fraction of $\phi_V = 0.003$ to yield the standard deviation, σ_q , at several different critical pigment volume concentrations, ϕ_F , where the ultimate pigment volume concentration is $\phi_{FUC} = 0.43$. Note that the results in Figure 10 have been calculated at two different coordination numbers for a densely packed cluster ($N_o = 8$ and $N_o = 10$).

$$v = \left(\frac{\phi_F}{\phi_{FUC}} \right)^{N_o} \quad (22)$$

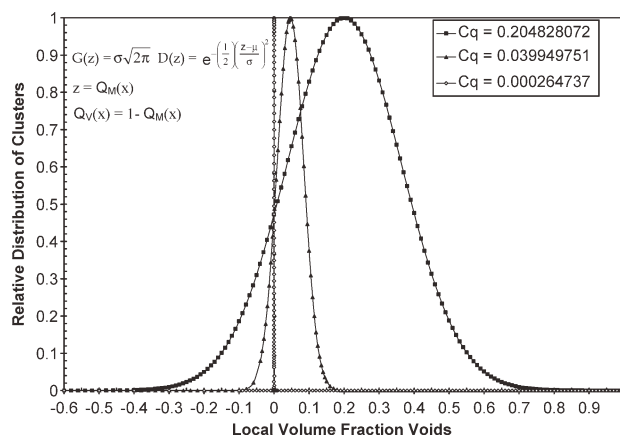


Figure 9 Relative distribution of clusters versus local volume fraction voids in clusters at an effective volume fraction of $\phi_F = 0.41$ for three pigment cluster dispersion coefficients.

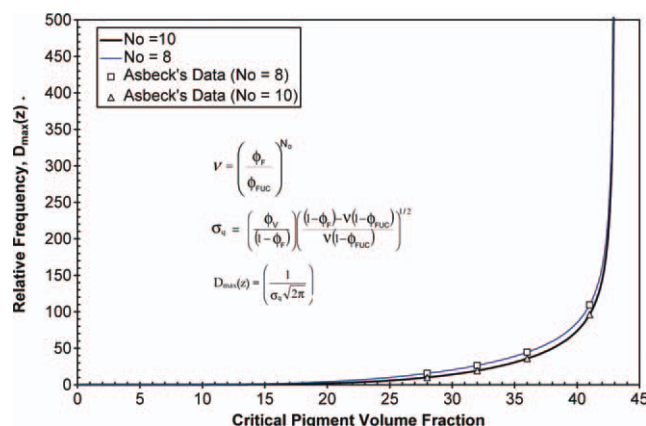


Figure 10 Relative frequency versus critical pigment volume fraction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\sigma_q = \left(\frac{\phi_V}{(1 - \phi_F)} \right) \left(\frac{(1 - \phi_F) - v(1 - \phi_{FUC})}{v(1 - \phi_{FUC})} \right)^{1/2} \quad (33)$$

For reference, Figure 10 also includes several of the critical pigment volume concentrations identified by Asbeck. It is apparent in Figure 10 that at critical pigment volume concentrations less than the ultimate pigment volume concentration ($\phi_{FUC} = 0.43$) that the clusters will be larger in size but fewer in number. However, there appears to be a negligible difference between the two different coordination numbers for a densely packed cluster ($N_o = 8$ and $N_o = 10$) as indicated in Figure 10. Consequently, a coordination number of $N_o = 10$ was retained for the additional evaluations in this study.

Model for a pseudomonodisperse distribution of the average cluster size after through mixing

In many instances, the distribution of clusters can be influenced by the concentration of dispersing molecules, i.e., a surfactant, that can act as an intermediary between the pigments in a mixture and the carrier or solvent in a solution or suspension. To be

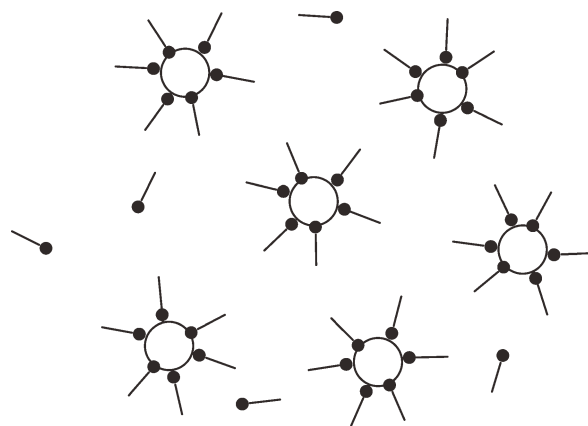


Figure 11 Pigment particles and dispersing molecules.

effective such a dispersing molecule, it would need to have one end that is attracted to the pigment and the other end would need to be attracted to the solvent or carrier fluid. The influence of such a dispersing molecule in both separating individual pigment particles as well as in forming clusters has been illustrated in Figures 11 and 12.

In Figure 11, the dispersing molecules are in excess so that each of the pigment particles can be isolated in a 100% dispersion of the pigment particles. Such a 100% dispersion often requires a significant amount of grinding in the case of a coating or a device such as a twin screw extruder for thoroughly blending a polymer compound.

In Figure 12, the dispersing molecules are not in sufficient amounts to isolate individual pigment particles. As indicated in Figure 12, low concentrations of dispersing molecules can allow the formation of particle clusters that can themselves be isolated but would not necessarily be uniform. It is only with a significant amount of mixing with either grinding and or by thorough mixing such as in a twin screw extruder that clusters in a coating or in a polymer blends can become approximately uniform.

If it can be assumed that a cluster can become an approximately uniform size by thorough mixing, then the description of a cluster in Figure 13 can be

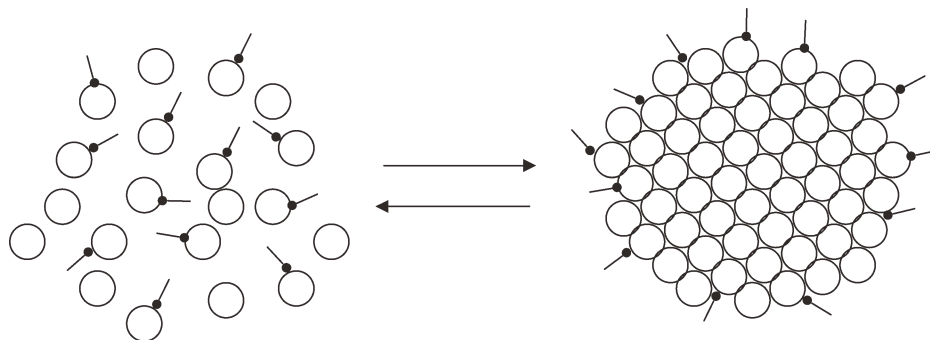


Figure 12 Pigment particles with insufficient number of dispersing molecules.

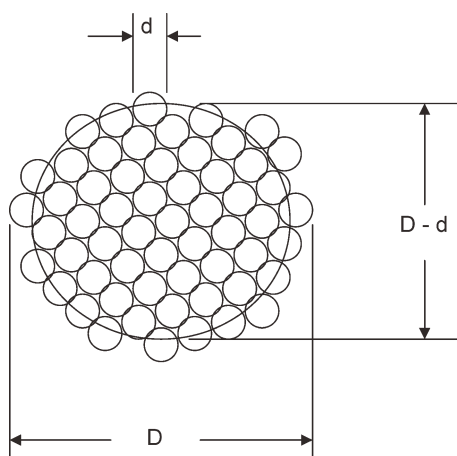


Figure 13 Cluster diameter and relative hydraulic volume.

used to generate an analysis of such a cluster configuration. The cluster diagram in Figure 13 assumes that dispersant molecules attach only to the particles on the out side of the cluster.

Asbeck¹ developed a simple model to elucidate how the relationship between agglomerate size and the CPVC can be reconciled. It is based on the concept of the relative expanded volume occupied by the well dispersed particles alone. Figure 13 shows a more or less spherical agglomerate of a number of individual particles that have dispersing molecules attached to the particle cluster. The hydraulic volume occupied by the agglomerate is not that of the spheroid D , but it is that shown by the circle drawn through the approximate center of the outside layer of particles, $D - d$. Asbeck¹ then proposed the following relationships:

$$\left(\frac{\phi_{\text{FUC}} - \phi_{\text{FC}}}{\phi_{\text{FUC}}}\right) = K \left(\frac{D-d}{d}\right)^3 \bigg/ \left(\frac{D}{d}\right)^3 = K \left(\frac{D-d}{D}\right)^3 = K V_{\text{REL}} \quad (42)$$

where D is diameter of the cluster, d is diameter of a pigment particle, and V_{REL} is relative hydraulic volume of a monodisperse particle cluster.

$$V_{\text{REL}} = \left(\frac{D-d}{D}\right)^3 = \left(1 - \left(\frac{d}{D}\right)\right)^3 \quad (43)$$

In this instance, Asbeck assumed that the ratio of relative increase in volume fraction from a critical pigment volume concentration, ϕ_{FC} , to the ultimate critical pigment volume concentration, ϕ_{FUC} , would be proportional to relative hydraulic volume, V_{REL} , which was described as the ratio of the change in volume of the average pigment particle diameter to the true diameter of the cluster. The space taken up by the dis-

persing molecules would then be expected to influence the effective size of the cluster. However, based on eq. (43), it is apparent that the resulting relative hydraulic volume of a monodisperse particle cluster, V_{REL} , can also be described as the approximate hydraulic volume of the cluster relative to the true volume of the cluster.

Asbeck further assumed that the packing of the particles in each of the agglomerates should be nearly equal to or equal to the value of the ultimate critical pigment volume concentration, which in most instances would be expected to be approximately equal to the maximum packing fraction for the pigment particles. With this assumption, then the proportionality constant, K , in eq. (42), would approach the ultimate critical pigment volume concentration or that $K \cong \phi_{\text{FUC}}$. Consequently, eq. (42) can be rearranged to show that the critical PVC, ϕ_{FC} , can be linearly related to the relative hydraulic cluster volume, V_{REL} , approximately as:

$$\begin{aligned} \phi_{\text{FC}} &= a V_{\text{REL}} + b = -K \phi_{\text{FUC}} \left(1 - \left(\frac{d}{D}\right)\right)^3 + \phi_{\text{FUC}} \\ &= -\phi_{\text{FUC}}^2 V_{\text{REL}} + \phi_{\text{FUC}} \end{aligned} \quad (44)$$

As 100% dispersion is approached, the cluster diameter, D , would approach the pigment particle diameter, d , (or $D \rightarrow d$) and the relative hydraulic volume, V_{REL} , would approach 0 (or $V_{\text{REL}} \rightarrow 0$). Likewise, as the cluster diameter ratio $\frac{D}{d}$ increases in magnitude and approaches an infinite value (or as $\frac{D}{d} \rightarrow \infty$), then the relative hydraulic volume approaches 1 (or $V_{\text{REL}} \rightarrow 1$). The range of magnitude for the relative hydraulic volume, V_{REL} , should then be $0 \leq V_{\text{REL}} \leq 1$.

Therefore, when $V_{\text{REL}} = 0$, eq. (44) characterizes a 100% dispersion and

$$\phi_{\text{FC}} = b = \phi_{\text{FUC}} \quad (45)$$

Likewise, when $V_{\text{REL}} = 1$, then

$$\phi_{\text{FC}} = a + b = \phi_{\text{FUC}} - K \phi_{\text{FUC}} = \phi_{\text{FUC}} - \phi_{\text{FUC}}^2 \quad (46)$$

Equation (46) then would be expected to define the minimum critical PVC, ϕ_{FC} , at the maximum cluster size that should be possible with any given dispersion system.

If eq. (44) could be considered to be the equation of a simple straight line, then the intercept at $\phi_{\text{FC}} = 0$ would yield

$$V_{\text{REL}} = -\left(\frac{b}{a}\right) = \frac{1}{K} = \frac{1}{\phi_{\text{FUC}}} \quad (47)$$

Although eq. (47) may be mathematically true for a linear equation, it is not strictly viable in this instance because the value of the relative hydraulic

TABLE III
Values of the Relative Hydraulic Volume, V_{REL} ,
Calculated from Asbeck's Data¹

Relative agglomerate diameter $\frac{D}{d}$	Reduced agglomerate volume $(1(\frac{d}{D}))^3$	Additive (%)	CPVC
13	0.786527082	0	0.28
5.8	0.566812907	0.5	0.32
3.4	0.351719927	1	0.36
1.3	0.012289486	2	0.41
1	0	3	0.43

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volume, V_{REL} , cannot exceed a value of 1. Nevertheless, this reference intercept at $\phi_{FC} = 0$ was calculated using eq. (45) to yield a value of $V_{REL} = \frac{1}{\phi_{FUC}} = 2.3256$ for Asbeck's data as indicated in Figure 14 where $\phi_{FUC} = 0.43$.

Asbeck did measure the approximate diameters of the pseudomonodisperse clusters that were generated from each of the critical PVC results initially shown in Figure 1. Asbeck's data results for these cluster measurements with $\phi_{FUC} = 0.43$ are shown in Table III and Figure 14. Two approaches were used to fit the data summarized in Figure 14.

The least squares fit of the data in Figure 14 yielded an average error of only 1% from Asbeck's actual data. In addition, the least square approach yielded an intercept value for the ultimate critical pigment volume concentration of $\phi_{FUC} = 0.4216$ at 100% dispersion where $V_{REL} = 0$. Taking the square root of the slope for the least squares, approach also gave a value of $\phi_{FUC} = 0.4234$. Both of these values would most likely be considered to be within experimental error of the value of $\phi_{FUC} = 0.43$ that Asbeck obtained experimentally.

Conversely, the use of Asbeck's model using eq. (44) yielded an average error of 1.8% from Asbeck's actual data, which was only a slightly higher percent error than the least square fit of the data. Amazingly, both cases as illustrated in Figure 14 fit the data very well.

As Asbeck's theory fit the data so well, an evaluation of the Asbeck's model for additional values for the ultimate critical PVC would appear to be appropriate. There is every reason to believe that the maximum range for the ultimate critical pigment volume concentration would be essentially identical to the range for the maximum random packing fraction. By using particle blends of spherical particles with different sizes as well as blends with particles of different shapes, several authors^{14,23,24} have found that the maximum random packing fraction can essentially range from near zero to 1.0. Consequently, it would be expected that the ultimate critical pigment volume concentration would also have been expected to have an approximate range of $0 < \phi_{FUC} \leq 1$.

Several values of the ultimate critical PVC in the range $0.40 \leq \phi_{FUC} \leq 1$ were used to generate the straight lines in Figure 15 using Asbeck's model as described by eq. (44). The results in Figure 15 suggest that the size of a cluster might possibly be controllable under a number of different possible conditions. It is also clear that the size of a cluster at any critical pigment volume concentration, ϕ_{FC} , would also be expected to be dependant on the type of dispersing agent applied for any given suspension or pigment polymer mixture.

The minimum critical PVC for Asbeck's data can also be calculated from eq. (46) that results from Asbeck's model where $\phi_{FUC} = 0.43$ to give:

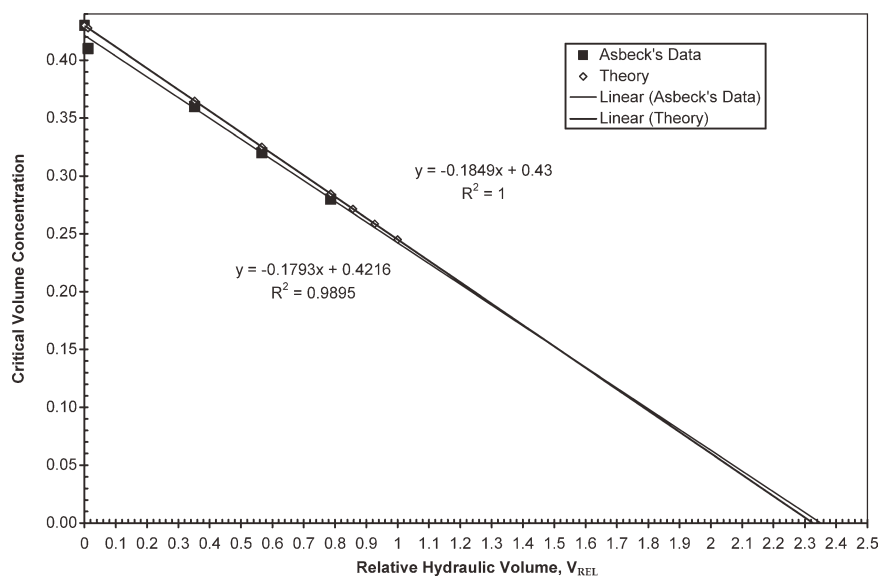


Figure 14 Critical pigment volume concentration versus relative hydraulic volume.

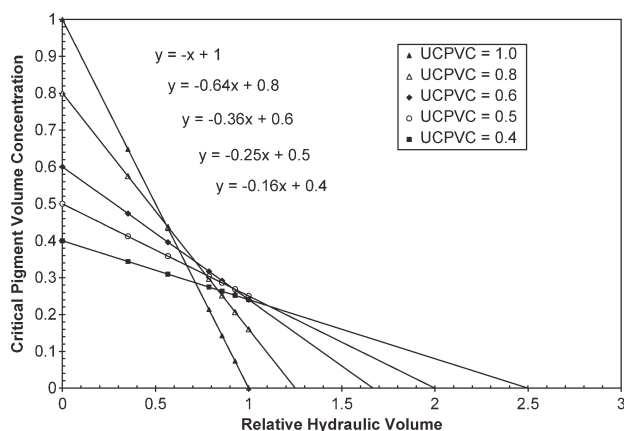


Figure 15 Critical pigment volume concentration versus relative hydraulic volume.

$$\phi_{FC} = \phi_{FUC} - \phi_{FUC}^2 = 0.2451$$

This value would be expected to occur at a value of $V_{REL} = 1$ and as expected the data in Figures 14 and 15 did in fact terminate at this value. On the basis of this result, Asbeck's critical PVC data of would then have been expected to have ranged from $0.2451 \leq \phi_{FC} \leq 0.43$.

If the ultimate critical pigment volume concentration can be considered to have an approximate range of $0 < \phi_{FUC} \leq 1$, then eq. (46) can also be used to generate the full range of minimum possible critical PVCs as shown in Figure 16. The results calculated in Figure 16 then indicate that values for the minimum possible CPVCs, $(\phi_{FC})_{min}$, would be expected to range from $0 < (\phi_{FC})_{min} \leq 0.25$. It is also clear in Figure 16 that the maximum probable minimum CPVC would be obtained when the ultimate critical pigment volume concentration achieves a value of $\phi_{FUC} = 0.50$. However, from a practical point of view, the most useful values for the ultimate critical PVC as indicated in Figure 16 would most probably

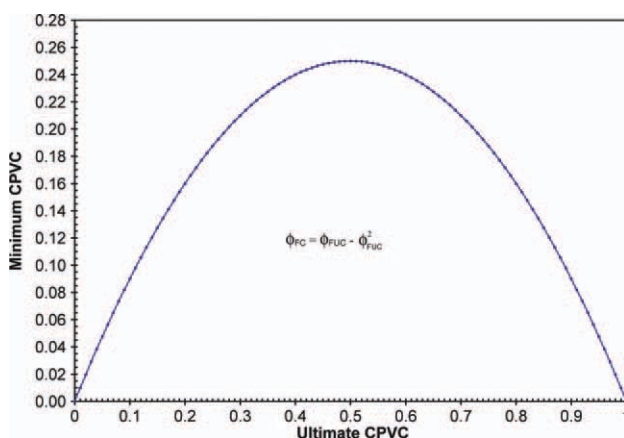


Figure 16 Minimum CPVC versus the ultimate CPVC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

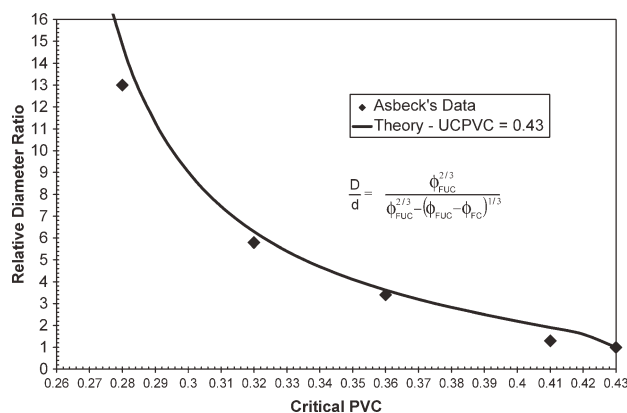


Figure 17 Relative diameter ratio versus critical PVC for Asbeck's data.

have a range of $\sim 0.20 \leq \phi_{FUC} \leq 1$. For the most part, formulations and/or coatings with low particulate concentrations do not typically exemplify superior physical properties.

The relative size of a cluster, $\frac{D}{d}$, can also be obtained by rearranging eq. (44) to give:

$$\frac{D}{d} = \frac{\phi_{FUC}^{2/3}}{\phi_{FUC}^{2/3} - (\phi_{FUC} - \phi_{FC})^{1/3}} \quad (48)$$

Asbeck's data have been replotted in Figure 17 using eq. (48) to show another form of the relationship between the cluster diameter ratio, $\frac{D}{d}$, and Asbeck's critical pigment volume concentrations, ϕ_{FC} . As expected, the correlation shown in Figure 17 between Asbeck's data and the theoretical curve is again a very satisfactory.

Equation (48) can also be applied to generate the expected cluster diameter ratios, $\frac{D}{d}$, for critical pigment volume concentration, ϕ_{FC} , curves for several different ultimate critical pigment volume as indicated in Figure 18. It is also very clear in Figure 18 that it is easier to form large clusters for lower values of the ultimate critical pigment volume concentration. It would then be expected that those particles that can be characterized by a lower maximum random packing fraction (i.e., fibers and disks)²⁴ would tend to form clusters easier than those that form a larger maximum random packing fraction. It would also be expected that the amount and type of molecule to be used as the dispersing agent or surfactant would also play a major role in the generation of the most desirable ultimate critical pigment volume concentration. Consequently, the curves in Figure 18 could very well be characterized by several different dispersion systems. The results in Figure 18 again suggest that the cluster size in the form of different cluster diameter ratios, $\frac{D}{d}$, very probably could be controllable under a number of different possible conditions.

Equation (48) can also be used to relate the cluster diameter ratio, $\frac{D}{d}$, to the pigment cluster dispersion coefficient, C_q , as will be described in the next section.

Relationship between the relative cluster diameter ratio and pigment cluster dispersion coefficient

It is possible to show a direct relationship between the relative cluster diameter ratio, $\frac{D}{d}$, and the pigment cluster diameter coefficient, C_q , as indicated in Figure 19. The relationship in Figure 18 was generated using eqs. (22), (34), and (48) modified as follows:

$$\frac{D}{d} = \frac{\phi_{FUC}^{2/3}}{\phi_{FUC}^{2/3} - (\phi_{FUC} - \phi_{FC})^{1/3}} \quad (48)$$

$$v = \left(\frac{\phi_{FC}}{\phi_{FUC}}\right)^{N_0} \quad (49)$$

$$C_q = \left(\frac{\phi_V}{(1 - \phi_{FC} - \phi_V)}\right) \left(\frac{(1 - \phi_{FC}) - v(1 - \phi_{FUC})}{v(1 - \phi_{FUC})}\right)^{1/2} \quad (50)$$

Because all of the critical pigment volume fractions, ϕ_{FC} , in this study, have been evaluated at a volume fraction of voids of $\phi_V = 0.003$, then eqs. (22) and (34) have been modified to address only the pigment volume fractions that were actually critical pigment volume fractions, ϕ_{FC} , as indicated in eqs. (49) and (50).

The results in Figure 19 suggest that the size of a cluster as indicated by the cluster diameter ratio, $\frac{D}{d}$, should be strongly influenced by the pigment cluster dispersion coefficient, C_q . However, it is again apparent in Figure 19 that it would appear to be much easier to form large clusters for lower values of the ultimate critical pigment volume concentration.

Elsewhere in the literature,⁶ it has been found that an increase in the viscosity is often associated with an increase in the pigment cluster diameter coefficient, C_q . It should also be recalled that the pigment

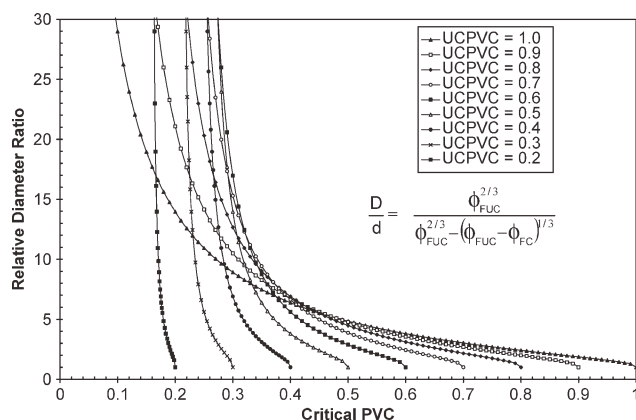


Figure 18 Relative diameter ratio versus critical PVC.

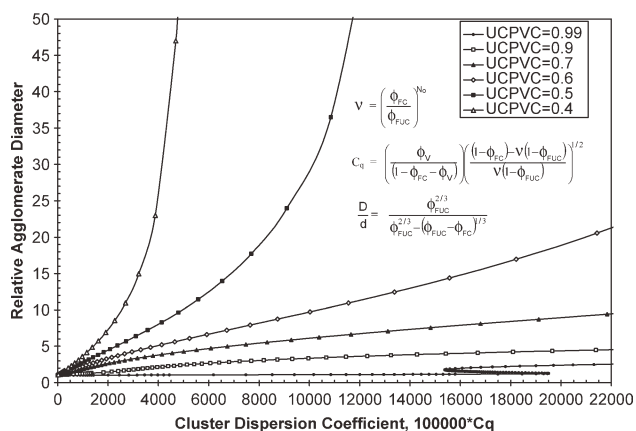


Figure 19 Relative agglomerate diameter versus cluster dispersion coefficient at several UCPVCs.

cluster dispersion coefficient approaches a minimum value of 0 ($C_q \rightarrow 0$) as the critical pigment volume concentration approaches the ultimate pigment volume concentration ($\phi_{FC} \rightarrow \phi_{FUC}$). In addition, Asbeck¹ also found in his study that the viscosity decreased with an increase in the critical pigment volume concentration until a minimum viscosity was achieved at the ultimate critical pigment volume concentration ($\phi_{FC} \rightarrow \phi_{FUC}$).

The results in Figure 19 then suggest that it should be much easier to form large cluster diameter ratios in suspensions with a lower viscosity if the ultimate critical pigment volume concentration is kept low. It would also appear that one major disadvantage of trying to create a large cluster diameter ratio, $\frac{D}{d}$, using a very high ultimate critical pigment volume concentration would be that the viscosity could easily get so high as to make most applications impractical.

Although the role of viscosity would be expected to play a major role in trying to control the cluster diameter ratio, $\frac{D}{d}$, as described in Figure 19, it is also clear that viscosity would only be one of several variables that could be used to control the types of systems that could characterize the different curves in Figure 19.

CONCLUSIONS

This study first reviewed the character and nature of a coating with a 100% dispersion of pigments with a minimum amount of clusters including a review of the identification of the “lower zero limit” global volume fraction of pigment, Φ_{FLZL} , and the “upper zero limit” global volume fraction of pigment, Φ_{FUZL} . These “zero limits” relative to physical properties result when there is at least an equal probability of a crack hitting a void phase or a matrix phase within the coating.

To address the character of clusters in coatings with less than 100% pigment dispersion, the total volume of the sample was separated into two regions: a region d with densely packed pigment

islands and the rest of the coating was region *c*. The pigment cluster dispersion coefficient, C_{qr} , was defined as the ratio of the standard deviation, (σ_q), to the mean, μ_q , for the local volume fraction of matrix in the coating, $Q_M(x)$. On the basis of this cluster analysis, three additional “zero limit” global volume fractions were identified. The first of these additional zero limits yielded the previously identified “lower zero limit” global volume fraction of pigment when $Q_{V_d}(x) = Q_{M_d}(x)$ and $\phi_F = \phi_{FUC}$.

However, a new “upper cluster zero limit” global volume fraction of pigments, Φ_{FUCZL} , was found to result when $Q_{M_d}(x) = \phi_V$ and $\phi_F = \phi_{FUC}$. One interesting observation is that the “upper cluster zero limit” global volume fraction can possibly be much higher than the previously identified “upper zero limit” volume fraction for higher values of the ultimate critical packing fraction.

In addition, a new “lower cluster zero limit” global volume fraction, Φ_{FLCZL} , was found to result when $Q_{V_d}(x) = \phi_M$ and $\phi_F = \phi_{FUC}$. It was also found that this new “lower cluster zero limit” global volume fraction should always be at least equal to or much lower than the previously identified “lower zero limit” global volume fraction for all values of the ultimate critical packing fraction.

In this study, the distribution of the local volume fraction of matrix, $Q_M(x)$, was described as a normal or Gaussian distribution that was characterized with its mean, $\langle Q_M(x) \rangle = \mu_q$, and standard deviation, σ_q . In general, it was found that this Gaussian distribution becomes very narrow with a significantly smaller void content as the value of the pigment cluster dispersion coefficient, C_{qr} , approaches a very small value. However, this Gaussian distribution becomes broader with lots of different potential cluster sizes as the pigment cluster dispersion coefficient, C_{qr} , increases. In addition, as the pigment cluster dispersion coefficient, C_{qr} , increased in magnitude then the pigment clusters tended to form more isolated clusters that increased in size but were fewer in number.

For less than 100% dispersion, it was found that a cluster of approximately uniform size can be achieved with thorough mixing where it is assumed that dispersant molecules would attach only to the particles on the outside of the cluster. A rearrangement of Asbeck’s linear model allowed an excellent correlation between Asbeck’s cluster size, $\frac{D}{d}$, measurements and Asbeck’s critical pigment volume concentration, ϕ_{FC} , measurements. The calculated curves for cluster diameter ratios, $\frac{D}{d}$, for several different UCPVCs clearly indicated that it would be easier to form large clusters for lower values of the ultimate critical pigment volume concentration.

If the ultimate critical pigment volume concentration can be considered to be directly related the maximum random packing fraction, then particle distribu-

tions that can be characterized by a lower maximum random packing fraction (i.e., fibers and disks) would appear to form clusters easier than those that form a larger maximum random packing fraction.

A direct relationship was also developed between the relative cluster diameter ratio, $\frac{D}{d}$, and the pigment cluster dispersion coefficient, C_{qr} . It was again apparent that it would be much easier to form large clusters for lower values of the ultimate critical pigment volume concentration.

As Asbeck found that the viscosity decreased as the amount of dispersing agent was increased, then the type of molecule used as the dispersing agent or surfactant would also be expected to also play a major role in the generation of the most desirable ultimate critical pigment volume concentration.

These results then suggest that it should be much easier to form large cluster diameter ratios in suspensions with a lower viscosity if the ultimate critical pigment volume concentration is kept low. It would also appear that one major disadvantage of trying to create a large cluster diameter ratio, $\frac{D}{d}$, using a very high ultimate critical pigment volume concentration would be that the viscosity could easily get so high as to make most applications impractical. Although the role of viscosity would be expected to play a major role in trying to control the cluster diameter ratio, $\frac{D}{d}$, it is also clear that viscosity would only be one of several variables that could be used to control the types of systems that could characterize the cluster diameter ratio, $\frac{D}{d}$.

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