

RHEOLOGY OF DISPERSIONS AS TWO PHASE SYSTEMS

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ABSTRACT

Following a brief review of past practices, an equation for the relationship between measured viscosity and volume solids is derived. The derivation of the equation is based on the concept of shear induced anisotropy, which is also presented. Using data developed on polystyrene and titanium dioxide dispersions, the equation is shown to be valid over a wide solids range. The equation allows the calculation of the degree of packing of the dispersed particles through the use of the relative shear volume. The equation and the shear induced anisotropy concept are then applied to the known properties of paper coatings. This discussion gives further insight into the hydrodynamics of blade coating and the nature of pseudoplastic and dilatant systems.

INTRODUCTION

Through the years, literally hundreds of equations have been developed to attempt to relate the viscosity of dispersions to solids level. Most of these equations have been based on the classic relationship proposed by Einstein. The basic approach of these equations is to attempt to predict the measured viscosity (N) of the dispersion as a combination of the continuous phase viscosity (N_0) and some function of the volume solids (ϕ). Simple rearrangement of Einstein's equation readily demonstrates this fact.

$$\text{Einstein} \quad N/N_0 = 1 + 2.5 \phi \quad (1)$$

$$N = N_0 + 2.5 N_0 \phi \quad (2)$$

Further confirmation of this concept comes from the fact that the initial slope of the plot of the relative viscosity (N_r or N/N_0) against ϕ in Einstein's interpretation was called the intrinsic viscosity of the dispersed phase, and it was in his doctoral dissertation on Brownian motion that he developed the equation and established the value of 2.5 for low solids levels. In these equations, the measured viscosity is viewed as being the sum of the viscosity of the continuous phase and an incremental increase in viscosity due to the addition of the solids or dispersed phase. The concept of the dispersed phase having a viscosity of its own, and thereby contributing to the total viscosity, continues to be the basis for equations still being developed. A comparative analysis of these equations shows them to retain the basic Einstein form, but to have been expanded to account for crowding factors, maximum solids volume, hydrodynamic interaction, etc.

$$\text{Robinson (1)} \quad N/N_0 = 1 + 2.5\phi/(1 - RSV\phi) \quad (3)$$

where $RSV = \text{Relative Sediment Volume}$

$$\text{Mooney (1)} \quad \ln(N/N_0) = 2.5\phi/(1 - S\phi) \quad (4)$$

where $S = \text{a crowding factor}$

$$\text{Fedors (2)} \quad N/N_0 = (1 + 1.25 \phi/(1 - \phi/\phi_m)) \quad (5)$$

where $\phi_m = \text{the maximum solids level}$

Although many of these equations have demonstrated adequate statistical correlation to the measured values in limited experiments, none have emerged as being a truly universal equation, applicable for all situations or over all solids ranges. It is the contention of this paper that the failure of these equations is due to the inherent assumption that the pigment can be treated as if it has a viscosity of its own which can be added to the viscosity of the continuous phase. Furthermore, all these equations are attempts to satisfy known data with empirical relationships rather than to develop a rigorous solution based on fundamental properties of the system.

STATEMENT OF THE NEW THEORY

A different approach to the situation can be obtained by shifting our point of view. When one considers the basic Newtonian simple shear model on which all of the preceding measurements and calculations are based, a fundamental problem can be observed. The simple shear model is based on the assumption of a uniform shear gradient throughout the liquid as shown in Figure 1. As the gap between the moving planes is

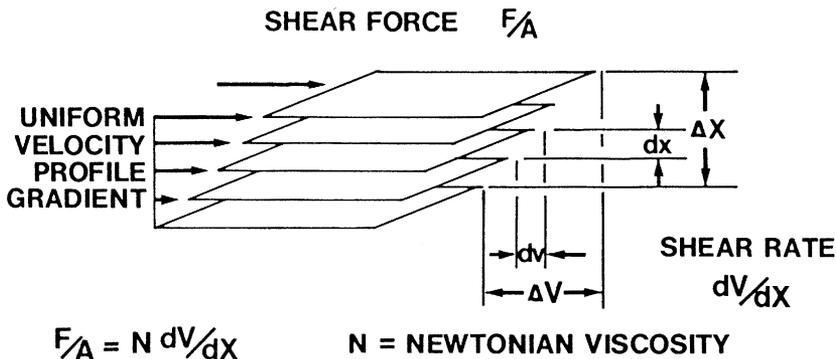


Fig 1—Definition of viscosity, simple shear model.

filled with dispersed phase, this model becomes quite difficult to accept. Accordingly, it has been proposed (3) that in a dispersion of a two phase system the dispersed phase is simply taking up space and therefore not directly contributing to the measured viscosity. The argument of this theory is that the actual measured shear force is solely due to the shear developed in the continuous phase. However, since the particles in the dispersion are occupying space in the measured gap, the shear rate on the continuous phase is increased and is not accurately calculated by using the measured gap in the instrument. In the original article presenting this theory, it was suggested that the shear plane develops in the center of the zone under shear, with the particles being forced towards the outer surfaces (4). This assumption was based on data presented at the 1980 Rheology Conference by researchers from the Los Alamos National Laboratory (5). More recent data by

Tomita and Van De Ven (6) indicate that monodisperse hard spheres orient themselves into parallel layers, both at rest and under shear. This model would lead to the formation of several shear planes between more concentrated pigment layers. The actual location of the shear plane, or shear planes, is of no consequence to the proposed theory. It does not matter where the shear plane is or if in fact there are several planes. What is important to the theory is that the dispersion behaves as if it is separated into layers and that the shear rate is different in the different layers. The simple expression of the theory would be that a fifty percent volume dispersion would be one where the gap is reduced by fifty percent. Of course it is obvious that the ratio would not be that simple or direct, but if the theory has validity, some relationship should be determinable. By any of the above interpretations, the reduced gap would increase the shear rate on the continuous phase and increase the resulting shear force proportionately.

Based on these assumptions, several other equations and calculations can be derived from the measured values. The mathematical statement of the preceding argument is as follows. The measured viscosity is the ratio of the measured shear force (F/A) to the assumed instrumental shear rate (dv/dx).

$$\text{Measured viscosity } N = (F/A)/(dv/dx) = (Fdx)/(Adv) \quad (6)$$

If, as proposed, the dispersed phase is only taking up space creating a reduced effective gap (dxe), and the viscosity of the continuous phase is what is actually being measured, it can be expressed by the following:

$$\begin{aligned} &\text{Continuous phase viscosity} \\ N_o &= (F/A)/(dv/dxe) = (Fdxe)/(Adv) \quad (7) \end{aligned}$$

It follows from this approach that we should be able to calculate either the effective gap (dxe) or the continuous phase viscosity, if the other is known, since dividing equation (7) by (6) gives the following relationship;

$$N_o/N = dxe/dx \quad (8)$$

However, the ratio dxe/dx is also the expression of the

percent of the original gap available for shear, and $1 - dx_e/dx$ would be an expression of the volume occupied by the dispersed phase, or the percent reduction of the gap. This value should be directly related to the volume solids. The nature of this relationship would intuitively be dependent on the shape, size and degree of dispersion of the dispersed phase. Hence, the insertion of the simple relationship using the relative sediment volume (RSV) shown in Equation 9. However, by referring back to Equation 8 we can see that the ratio of gaps can be replaced by the ratio of viscosities giving us a new viscosity/solids equation (Equation 10) rigorously derived rather than empirically developed.

$$1 - dx_e/dx = RSV\phi \quad (9)$$

$$N_0/N = 1 - RSV\phi \quad (10)$$

VERIFICATION OF THE NEW EQUATION

Utilizing data developed with dispersions of polystyrene spheres (4 and 7), an attempt to satisfy Equation 10 demonstrates in Figure 2 the non-linearity of the relationship. This lack of linearity has generally been viewed as a major flaw, but perhaps should be accepted as a demonstration of the true nature of the system. The problem with the non linearity of this curve can be better understood if one refers back to the basic Einstein equation and its graphical presentation. It should be recalled that plots of N/N_0 (the inverse of the ratio plotted here) is also non-linear, but that the initial linear portion of that plot has been interpreted as the intrinsic viscosity of the pigment in dispersion. It is this conceptualization of the dispersed phase acting as if it had a viscosity of its own, which is being avoided by the new approach. There is really no reason to assume that either the intrinsic viscosity or the RSV should be constant at all solids levels or shear rates. The tendency for dispersed particles to couple, cluster or even behave as though they were attached in chains has been long recognized. The paper by Graham and Steele (5) aptly demonstrated this coupling tendency and its relationship to shear rate.

It seems appropriate at this time to further clarify the concept of shear induced anisotropy. It is readily recognized that pigment dispersions such as those being considered here

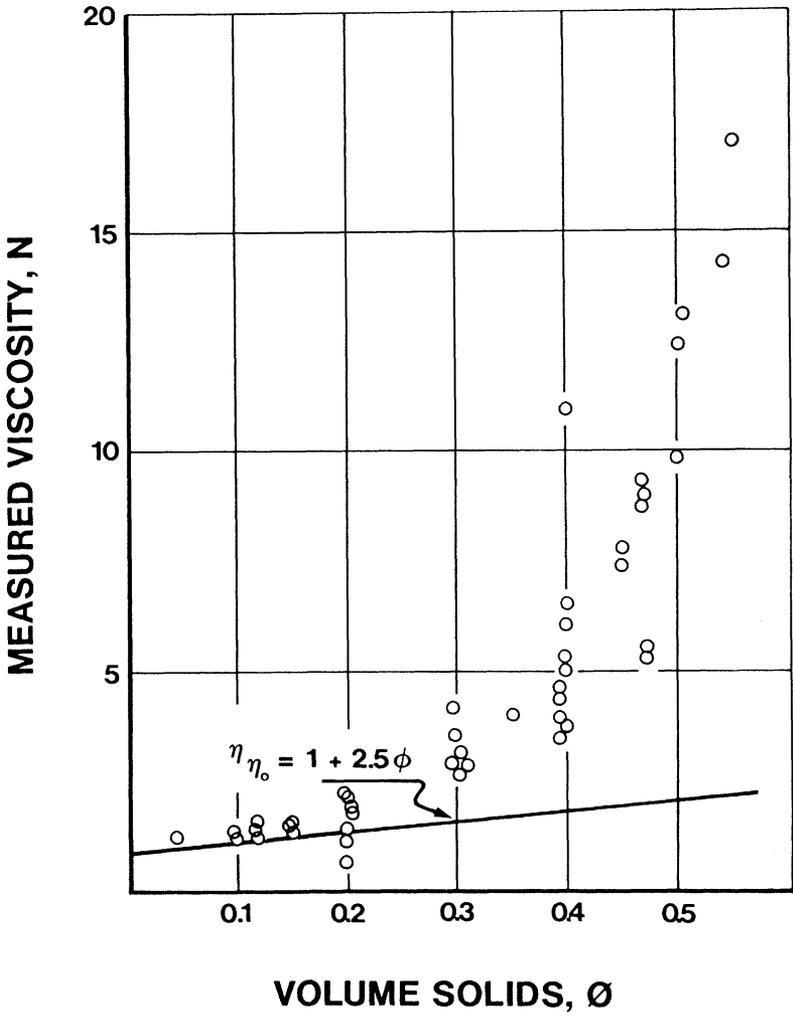


Fig 2—Relationship between measured viscosity and volume solids.

are two phase systems consisting of a dispersed and continuous phase. As such they are already anisotropic. However, there is a sort of isotropy in these systems on a macro scale, in that the dispersion should be uniformly non-isotropic throughout. What is proposed in the most rigorous interpretation of the theory is that the dispersion will separate into two new layers, one composed of pure continuous phase and the other composed of a dispersion at a higher solids level than the original. What is claimed in the present theory is that the imposition of shear will cause a redistribution of the dispersed phase, creating shear planes of reduced solids between layers of higher solids which experience little or no shear. In the original paper (4) it was proposed that a single shear layer will be created in the center of the total zone under shear. Although this approach makes it easier to develop the mathematical model, this simplistic model is not likely to develop. It is more likely that the system will respond to shear in a manner such that the shear rate will cause some coupling, increasing the effective solids level of the two phase part. This action will have the effect of reducing the solids level in the shear layer, generally referred to here as the continuous phase. A similar situation has been demonstrated by Tomita and Van De Ven (6) when they demonstrated that rigid sphere dispersions separated into layers, and that the density of the pigment layers increased as the shear rate increased. With this interpretation in mind, it is proposed that as the overall solids level is increased, the shear rate in the shear zone will increase, increasing the tendency toward coupling. If this theory were to apply, we would expect to see the RSV decrease at higher solids levels, even at constant theoretical shear rates. In order to evaluate this concept, it is necessary to use a dynamic measurement of the RSV rather than the static method utilizing pressure filtration or centrifuging. Such a method has been proposed (4) and is called the Relative Shear Volume (RS'V) to differentiate it from the relative sediment volume (RSV).

A plot of RS'V as a function of volume solids in Figure 3, using the same data source as before (4 and 7), shows the predicted decrease at higher solids levels, but not at lower solids. What is shown at lower solids is that the degree of scatter or uncertainty in calculating RS'V increases. Either interpretation is equally valid. The accuracy of the viscosity measurements on which the calculations are based decreases at

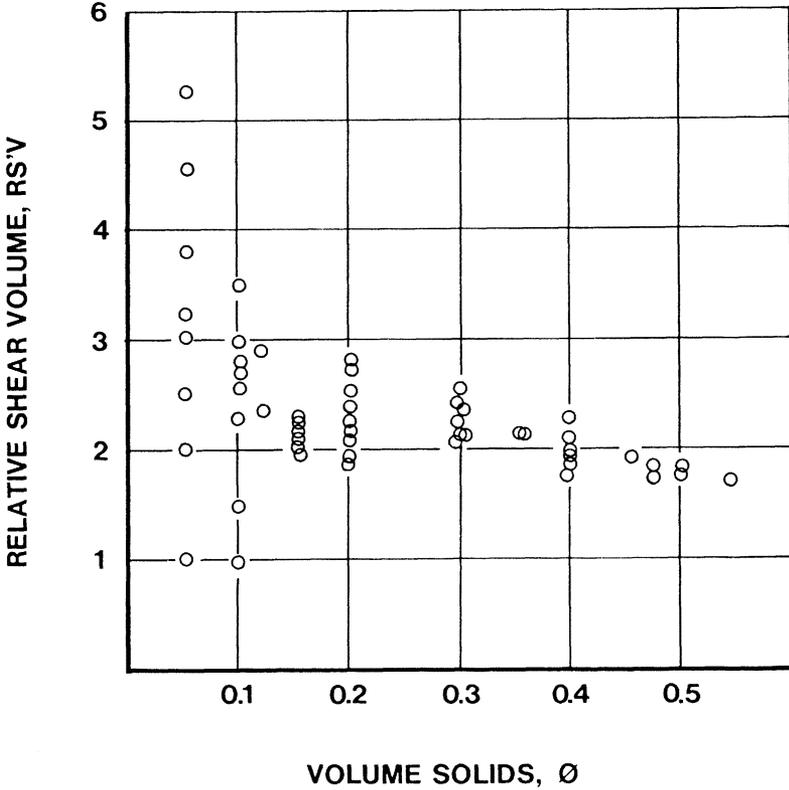


Fig 3—Relationship between relative shear volume and volume solids.

lower solids levels as does the degree of shear induced association between the particles. Furthermore, at lower solids levels and shear rates the effect of other sources of association between the particles would be expected to be relatively more important.

In his thesis project, Homes (8) evaluated the effect of degree of dispersion on the properties of titanium dioxide dispersions. As the dispersing agent is added, it is expected that the particles should flocculate less and therefore pack more tightly. The interpretation of this in terms of the RS'V is that it would be expected to decrease as the dispersant level increases. Utilizing some of the data developed by Holmes (8) displayed in Figure 4, we can see that the expected

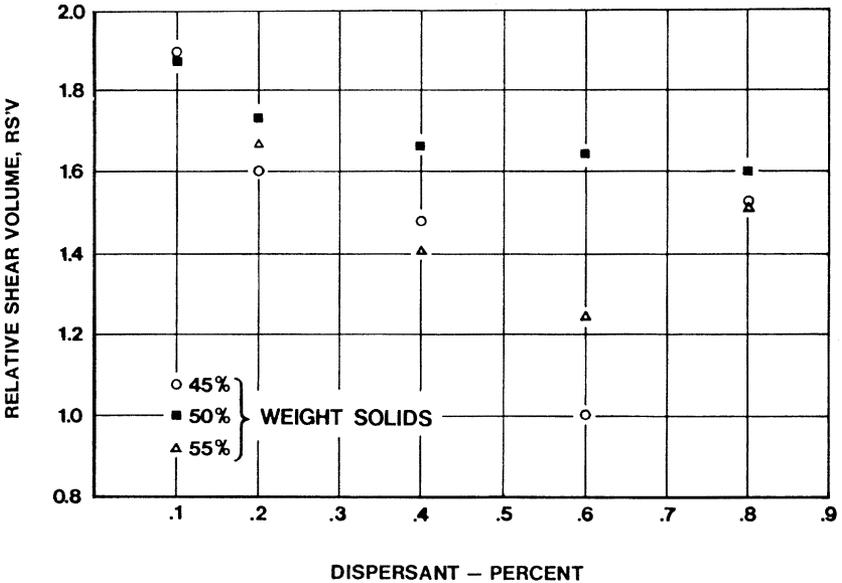


Fig 4—Relationship between relative shear volume and dispersant level.

relationships between degree of dispersion and RS'V develop. At higher levels of flocculation, the pigment system occupies more space and reduces the gap available for shear. The extension of this interpretation of the data can be shown to affect the way we interpret rheograms. When a pseudoplastic

curve is developed for a coating system, it could either be due to the presence of a truly pseudoplastic continuous phase, or it could be due to changes in the dispersed phase. If the dispersed phase is flocculated or otherwise demonstrates some degree of association between the particles at rest which is reduced at increased shear rates, a pseudoplastic curve would develop even with a Newtonian continuous phase. Accordingly, we should not expect the relationship between solids and relative viscosity (or its reciprocal) to be linear. In fact the data which has been developed and shown in earlier equations has not been linear. Using the data developed by Triantafillopoulos (7), we see in Figure 5 that a reasonably

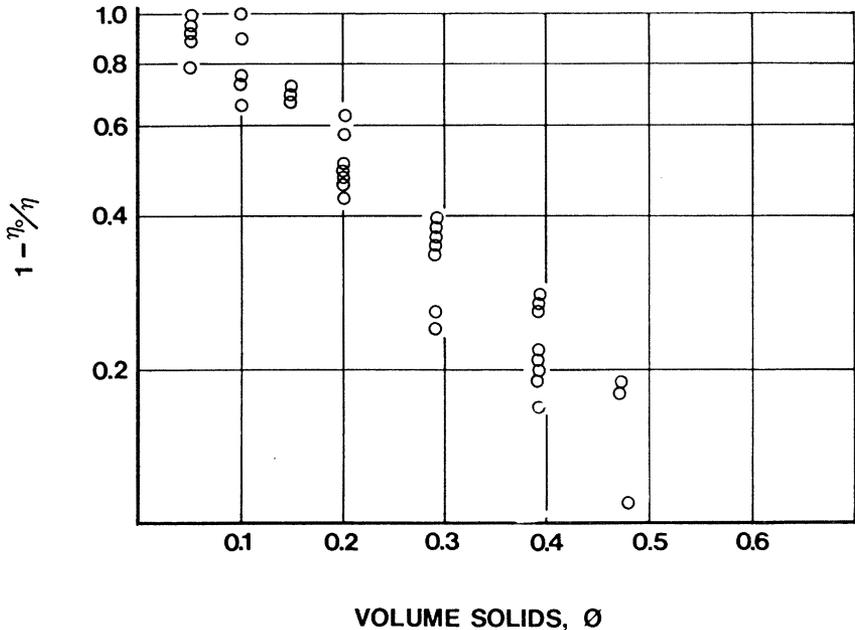


Fig 5—Semi-log relationship between viscosity function and volume solids.

good fit can be obtained if we plot the natural log of $(1 - \eta_0/N)$ as the dependent variable and volume solids as the

independent. However, the fit is not as good as would be desired. A better fit is demonstrated in Figure 6 where the viscosity ratio is plotted as a function of $1 - e^{-\phi}$. The data shown here yields a slope of about -2.2 and an intercept of 1.0, giving the following equation.

$$No/N = -1.2 + 2.2e^{-\phi} \quad (11)$$

This equation adequately satisfies the requirement that the ratio of No/N go to one when ϕ goes to zero, but fails to help with the accurate determination of the maximum solids level. Many of the earlier equations utilized the maximum or limiting solids level (that solids level at which the dispersion behaves as a solid). This value is obtained by extrapolating viscosity/solids plots to infinite viscosity. In Figure 6 it can be seen that the intersection with the abscissa would yield a limiting solids value of about 60%. This value is in relatively good agreement with other values previously determined.

As with the calculation of $RS'V$, we should not expect the limiting solids to be a constant term independent of solids level, degree of dispersion or shear rate. The preceding discussion of the relationships between $RS'V$ and dispersion, solids level and shear rate apply to the maximum solids level. Furthermore, we have seen a dramatic demonstration of the shear rate relationship in the shear blocking form of dilatant flow. In this form of flow, the material may seem to be perfectly Newtonian up until the point where shear blocking occurs and the material behaves like a solid. This system is therefore both at and below the limiting solids level at the same time, depending on the shear rate used to measure the system. It would therefore appear that if one wanted to measure this property, the best approach would be to make several measurements at high solids levels and attempt to extrapolate to find the intercept or determine the slope. If enough points can be obtained to determine a slope, the maximum solids (ϕ_m) could be determined with the following equation.

$$\phi_m = 1n (\text{slope}/[1-\text{slope}]) \quad (12)$$

Calculating ϕ_m at different points on a curve may yield different values, however, this need not be viewed as a

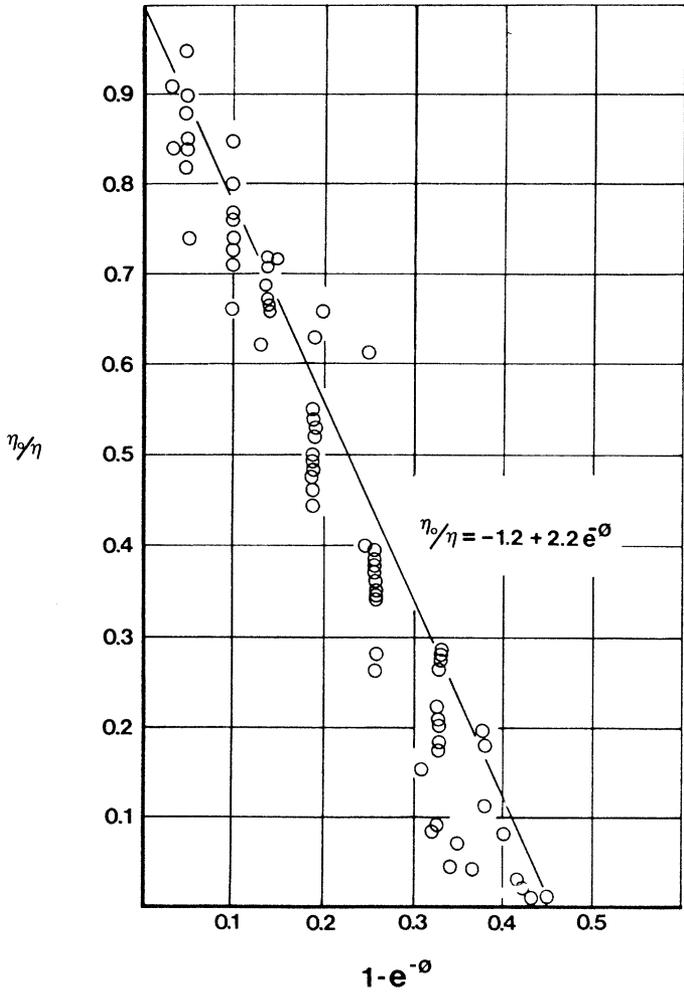


Fig 6—Demonstration of the new viscosity/solids equation.

problem. The maximum solids level is simply another indicator of the degree of packing of the dispersed phase of the system and must be expected to change just as the RS'V will as a function of shear rate, solids level and quality of dispersion.

APPLICATION OF THE NEW THEORY TO COATING SYSTEMS

It has long been recognized that the viscosity of the coating is important in its handling and application, especially at the high shear rates experienced in blade coating. If the coating does in fact experience shear induced anisotropy, it could help in the understanding of some of the observed phenomena. As the coating approaches the blade, there has always been the possibility that some of the coating or at least some of the continuous phase will penetrate into the web, a process generally referred to as dehydration. Dehydration is alleged to cause an increase in the solids level of the coating under the blade, which would lead eventually to the immobilization of this coating. Due to the roughness of the web, there will be some coating passing under the blade which will be trapped in the valleys between the fibers which could also be considered to be immobilized. In applying the present theory to blade coating, it follows that the high shear rates will cause the coating to develop a shear plane at the surface of the blade and increase the volume of immobilized coating at the web surface. An approximation of the proposed system is presented in Figure 7 where an attempt has been made to represent the relative roughness of the web, size of the blade and demonstrate the development of a shear plane at the blade surface.

The sets of parallel lines in the two models represent the relative velocities at the respective levels of the system. The isotropic model assumes that the uniform velocity gradient of Figure 1 will apply and that the velocity of the coating will increase steadily from the blade surface up until it reaches the velocity of the web. Since there is no single surface for the web, the model drawn would have to be modified to account for the reduced gap due to every high point on the web. It seems obvious that the model would end up being much shorter in the direction perpendicular to the web, having been reduced to meet the highest points of the web surface. This interpretation also is similar to the argument that there will be coating trapped in the valleys of the sheet, traveling at

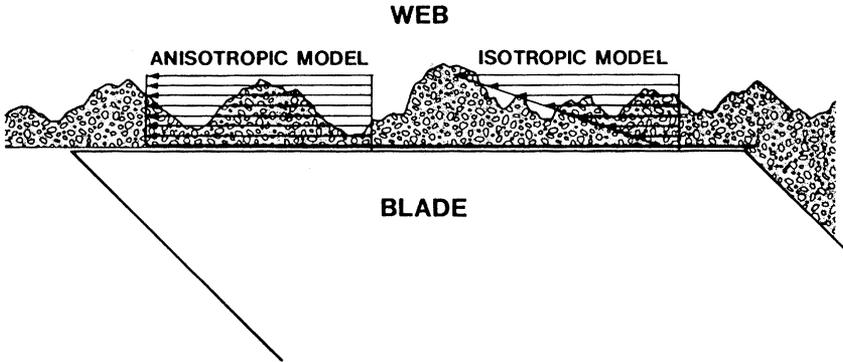


Fig 7—The application of isotropic and anisotropic models to the blade coater tip conditions.

web speed. Even above this surface the coating will still be at a high enough solids level to cast doubt on the feasibility of the isotropic model. Accordingly, the anisotropic model shows the additional shear immobilized coating above the web surface and the shear layer at the blade surface.

Many authors have attempted to describe the behavior of a coating under the blade in terms of hydrodynamics, including a paper by Guzzy and Higgins who presented a series of figures depicting the expected flow under the tip (9). A reproduction of their figures is shown in Figure 8. This drawing is typical of the ones used to develop the hydrodynamic model. As can be seen, it disregards the presence of the dispersed phase and considers the coating to behave as an isotropic fluid.

Figure 8 shows the reverse flow ahead of the nip, or actual beveled portion of the blade, and a gradual transition to a modified uniform velocity profile at the exit. Also shown in this figure is the condensing of the coating layer as the lower velocity material from under the tip accelerates to

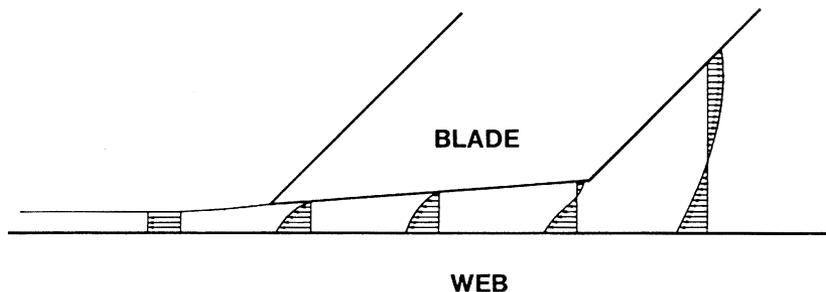


Fig 8—Hydraulic flow profiles for a blade coater tip.

catch up with the material at the web surface. The condensing phenomena would have to be observed if there truly was a large amount of reduced velocity coating coming under the tip. This theory also requires the exaggerated bevel shown in this drawing to allow it to work. If there were a nearly parallel passage, there would need to be coating at the web surface traveling faster than the web to supply low velocity coating at the blade surface. The anisotropic model of Figure 7 shows a thin layer of nearly pure continuous phase at the blade surface which could easily be supplied by dewatering of the coating layer. This theory is not incompatible with the application of hydrodynamics, to the contrary it is most compatible. The development of a shear plane comprised of primarily continuous phase would be ideal for invoking hydrodynamic theories. The system which is proposed is shown in Figure 9 to be a thin wedge of continuous phase at the blade surface where the hydrodynamic wedge would be free to develop and contribute to coat weight control.

Figure 9 also shows the condition proposed to develop before the blade. As the coating layer approaches, it is all traveling at the same speed as the web. Depending on the coat weight applied, most of this layer needs to be diverted and caused to flow down the blade. This transition could lead to the development of turbulence due to the change in direction

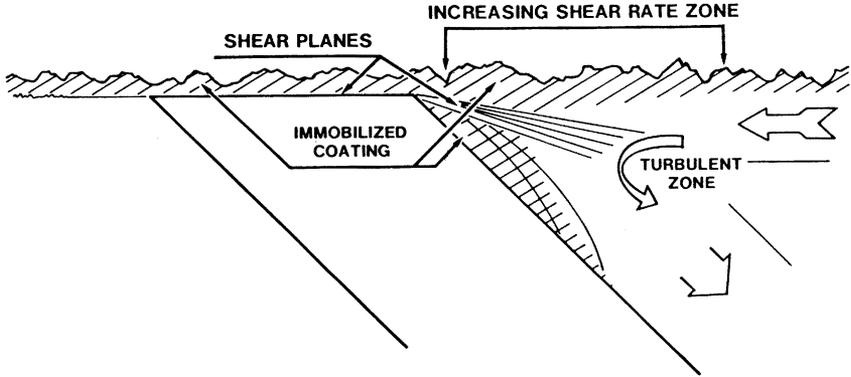


Fig 9—Proposed flow and shear diagram for a beveled blade coater tip.

as well as the sudden drop in velocity. The coating continuing on enters the increasing shear rate zone culminating in the high shear rate under the blade tip. Figure 9 shows not only the development of a shear induced immobilized layer at the web but also at the blade surface. Hydrodynamic theories would also support the formation of the immobilized zone on the heel of the blade as an obstruction in a flowing stream. The shear planes would be free to develop in the zone between these two immobilized layers, consolidating into a single layer at the blade surface.

CONCLUSIONS

Through the use of the shear induced anisotropy theory, a new equation for the relationship between viscosity of dispersions and solids level has been developed. The theory is shown to be imperfectly applied in that it is not likely that the coating system will separate into purely continuous and dispersed phases, but the use of the theory need not be avoided for that reason. The use of the theory does give a rigorously developed equation for the solids/viscosity relationship, which appears to be applicable over all solids ranges. Furthermore, the derivation of the equation assigns physical parameters to the constants, which are shown to not be constant,

so that the reasons for their deviations from constant values can be understood and utilized. Among the applications of the equation are the ability to calculate a dynamic, shear rate sensitive measure of the degree of agglomeration between the particles called the relative shear volume, and a method for calculating the maximum solids level. The use of the shear induced anisotropy concept in analyzing blade coater dynamics is also presented, demonstrating compatibility of the concept with the hydrodynamic models previously in use.

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Transcription of Discussion

Rheology of Dispersions as Two Phase Systems

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In this paper, Einstein's classical analysis of viscosity of suspensions is used as a starting point for attempts to deal with the viscosity of concentrated suspensions.

Einstein's equation is derived for creeping flow as a limiting case when the distance between suspended spherical particles is infinite, using Stoke's equation. The literature does not lack of earlier unsuccessful attempts to modify this equation in a more or less theoretical way to adapt it to concentrated suspensions (1).

A far more reasonable model for concentrated suspensions would be to start from the fact that the distance between the particles is small. The alternative limiting case to the one used by Einstein is then to assume that the fluid film separating the particles is small in relation to the diameter of the particles.

Frankel and Acrivos (2) have shown that this case can also be treated using Stoke's approach in Brenner's form. The same result can be obtained starting from Reynold's lubrication theory. This approach clearly demonstrates that the rapid rise of viscosity at high concentration is accounted for by hydrodynamic interactions of neighbouring particles, the very factor which Einstein chose to exclude.

This solution, which is rigid only for spheres of one size, is fairly sensitive to the geometry of the particle configurations. For non-spherical particles collisions, aggregations, electrokinetic and inertial effects will modify the viscous behaviour.

It is my hope that paper technologists will leave Einstein at rest when dealing with high solids content particle suspensions.

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Atalla I would like to preface my remarks by saying that I have not read your paper carefully. However, it is clear that there are two paths to dealing with the complex rheology of coating systems. You have chosen to account for all of the complexity by attempting an adjustment for the value of the viscosity whereas we all know that with the pigment and some of the binders we have coatings requiring much more complex description of their flow characteristics. Thus while in no way wishing to diminish the value of your approach I would not wish to see us ignore the other approach of say Guzzy and Higgins which attempts to deal with the properties of the fluid system as variable ones in the course of responding to the local conditions of flow.

Prof J. Kline I am not attempting to refute the hydrodynamic theories that have been proposed and that do work very well on blade applications but what I am suggesting is that in the zone being sheared the thickness of the film is much thinner than Guzzy's work would suggest.

Atalla What you are suggesting here is that whenever there is surface roughness there is a discontinuity but I do not think it is a discontinuity in the liquid. I think there is a shear plane between the particles which lie beneath the roughness peaks and the particles which are moving with the coating and that there is transfer of momentum across that plane and we both know that the transfer of momentum is continuous from the liquid deeply penetrating into the sheet to the blade itself.

Kline If it were only a liquid I would agree with you, but it is not only a liquid, it is a 60% solids dispersion which cannot behave as a liquid.

Atalla I think that is all the more reason why one would suggest that there is transfer of momentum across that plane.

Kline If you mean transfer of force, then yes I agree. But if you mean actual flow then I have a problem in agreeing with you.

Kartovaara In your Figure 3 you have plotted relative shear volume against volume solids for these polystyrene particles which must have a very narrow size distribution. Have you ever plotted this relationship for real coating pigments?

Kline Actually Figure 3 is a plot for a range of different pigment particle sizes. We have looked at coatings and other pigments. They do not all fall on the same curve of course. There will be a different packing structure for different pigments.

Kartovaara Do you have information on calcium carbonate or clay? What kind of differences do you have on these plots?

Kline I do not have specific data at present.