

Rheological Prediction of the Physical Stability of Concentrated Dispersions Containing Particulates¹

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A dynamic rheological technique is presented that can be used for the prediction of physical stability of concentrated dispersions containing particulates, as well as product development and quality control. Typical physical evaluation frequently requires weeks or months before an assessment can be made. By using dynamic rheology, the prediction of physical stability can often be accomplished in less than three (3) hours. The dynamic or oscillatory rheology technique is performed in two parts. First, a strain sweep test (frequency constant, strain variable) defines the linear viscoelastic range (LVR). Second, frequency scans (from 0.01 to 5.0 Hz) are performed at various temperatures, from 5 to 49°C (40–120°F). It is critical that the frequency scans are performed in the LVR. Dynamic rheology measurements yield data on the elastic (G') and viscous (G'') moduli. Plotting the elastic to viscous moduli ratio as a function of frequency and temperature generates a 3-D surface which is a "fingerprint" of the dispersion's colloidal stability. The G'/G'' ratios correlate well with observed physical stability properties. A volume index or a simple mean/variance calculation can be used to assign a value to the graphical 3-D representations.

KEY WORDS: Concentrated dispersions, dynamic rheology, physical stability.

A common endeavor of product development scientists and technicians is the preparation of stable, concentrated suspensions or dispersions. Typically, product development involves investigating as many formulas as manageable within a potential range of concentrations, and the formula(s) with the desired product attributes, performance and aesthetics are chosen. Hopefully, one of these formulas is also physically stable, at least within the product's normal shelf-lifetime. If none are stable, then reformulation is required, now a dispersant being added, or a different thickener, viscosity modifier, etc. A more refined approach is the response-surface method (1) which uses statistically generated formulas within space constraints representing the concentrations of interest. The properties desired are the responses of that system, and the surfaces generated with this approach lead to a quick determination of an optimum formula. Again, one hopes to find a stable formulation within the chosen formulas, otherwise, reformulation is required with different additives, etc.

The determination of physical stability is a time-consuming endeavor, and it is often evaluated subjectively. The formulas are stored at various temperatures and

monitored frequently. When many formulas are being evaluated, it is common for one person to spend a large proportion of their time monitoring the physical stability. There is also the problem of defining physical stability. Is it phase separation, viscosity thickening and/or thinning with time, development of readily dispersible density (height) gradients, sedimentation, or all of the above? Frequently, only one of these attributes is ever looked at in detail, and not the various manifestations of instability. Often the formulator is forced to wait one month or longer before a final decision on the formula's stability can be made.

One of the difficulties in trying to characterize concentrated dispersions is our inability to analyze these with standard colloidal techniques such as light scattering, electrophoresis, nuclear magnetic resonance (NMR), etc. In order to use these techniques, severe dilution is necessary, which then necessitates large extrapolations. Rheology is one technique, however, that is not hampered by large ionic strengths and concentrations.

The "classical" approach to the rheology of concentrated dispersions has been the flow curve (either the stress or viscosity response) (2). With the flow curve, the viscosity at various (and, usually, very high) shear rates can be determined. From the curve profile, an assessment of the model that best describes the flow behavior is made: i.e., is the formulation dilatant, shear-thinning, plastic, Newtonian, or pseudoplastic (3)? Also, by means of extrapolating the stress curve to zero shear rate, an apparent yield value is derived (4). Unfortunately, these determinations have shortcomings. For instance, the yield value approximation is only as good as the extrapolation; obviously, the less extrapolation, the better. It is not uncommon to find errors of an order of magnitude in a yield value determination by this technique, when compared with results from a creep experiment. Furthermore, once the existence of a yield value has been established, little else can be said about that formula's colloidal stability. For instance, flow curves are shown in Figure 1 of two product formulas. Surprisingly, the product with the lower apparent yield value (and lower apparent viscosities) is the more stable dispersion with respect to phase separation. Our work with these commercial products has found no correlation between the yield value and overall physical stability, only that a yield value is necessary to prevent sedimentation.

We have attempted to streamline the procedure for evaluating product stability by looking at the dynamic (oscillatory) rheological behavior of concentrated dispersions as a function of temperature and frequency, and plotting the resultant data in a three-dimensional (3-D) response surface. Our approach has been empirical: correlation of the observed physical stability with the dynamic rheological data. The technique does not by itself point out the cause(s) of the physical instability, although it can offer rheological clues: rather, the 3-D representations

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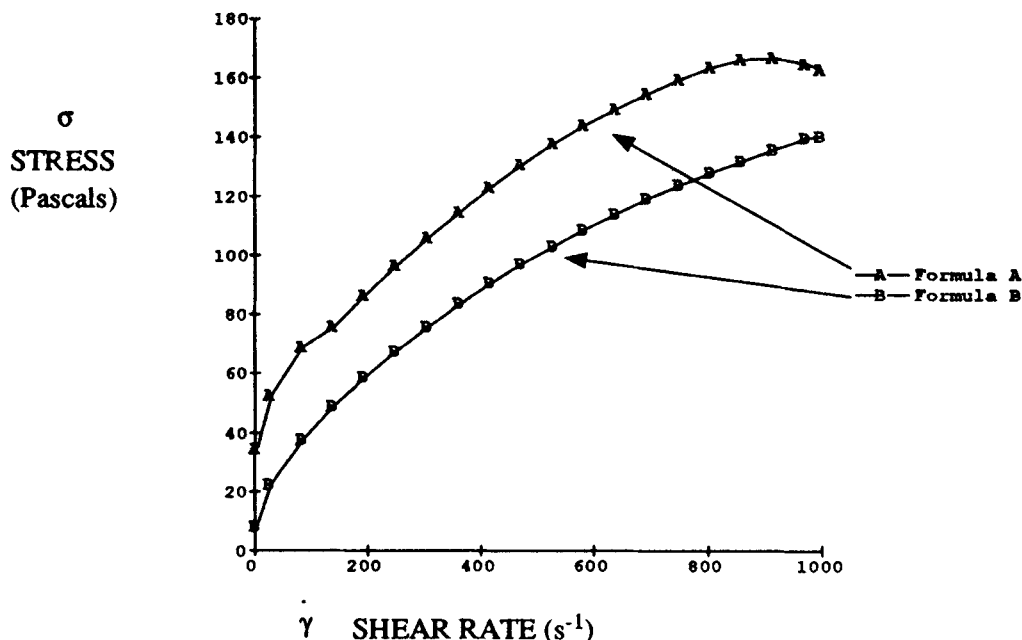


FIG. 1. Typical flow curves of two different finished product formulas, labelled A and B. Extrapolation from the straight part of the flow curves implies that formula A has a much higher yield value. However, the physical stability of B is much better than A's. Note: apparent viscosity is stress/shear rate.

allow a quick determination of the amount of structure present in the dispersion, and whether that structure is prone to large changes either as a function of temperature or frequency. The technique's main attribute is the ability to differentiate between different formulas or products, and predict which is the more stable. Further refinements are proposed to facilitate interpretation. We believe the technique can shorten the time required for product evaluation from the typical month(s) to about three hours. When used judiciously, the technique can also help in understanding the complex behavior frequently observed with multi-component systems.

EXPERIMENTAL PROCEDURES

All samples were either commercially available products or normal production lots and were used as received.

Rheological data were taken on a Bohlin VOR Rheometer (Cranbury, NJ). The measuring geometries were both concentric cylinders, either a C25 or DG24/27 (Dual Gap). The torque bars used, from 1 to 90 g-cm, were selected to optimize signal yet minimize inertia correction factors.

Samples were prepared by vigorous shaking and mixing of the products in their original containers, followed by an equilibration time of usually one day but a minimum of four hours; exceptions were made only if physical separation was observed within 24 hr, in which case the samples were run as soon as relaxation was observed with a strain sweep test (consistent results). Of course, any of a number of other rheological tests (*e.g.*, a creep experiment) could have been used to determine whether equilibrium had been achieved in the suspension, as long as the test is performed within the linear viscoelastic region. Either a splash guard in combination with a thermal

enclosure or a moisture-trap (standard Bohlin equipment) was used to minimize evaporation losses during the experiments, especially at the high temperatures.

After inserting samples in the concentric cylinders, the samples were allowed to rest for 10 min before running a strain sweep test at 25°C. The linear viscoelastic region (LVR) was determined with the strain sweep test (*vide infra*). The samples were then run in the oscillatory frequency sweep mode at an amplitude dictated by the LVR. The frequency range was 0.01 to 5 Hz, and the temperatures were 5, 21, 25, 38, and 49°C to correspond to traditional temperatures of interest for monitoring physical stability of formulas. Temperature equilibration was between 600–800 sec, depending on the sample's propensity to reach thermal and mechanical equilibrium. The temperature control, equilibration time, and frequency sweeps are completely automated in the constant temperature mode, with the typical experiment lasting approximately 2.5 hr per sample.

Once the data are collected and stored, they are translated into ASCII format with FileConvert software from Bohlin. The converted data are transferred to a VAX 8530 computer, edited with BBN's Corporation's RS/1 software (Cambridge, MA) into the format required for the 3-D graphs (axes titles, and three columns, temperature, frequency, and $\cotan \delta$). The 3-D software (K4DS) was written by Keith Mainquist of Clorox (Pleasanton, CA), and runs on an Evans & Sutherland (Salt Lake City, UT) graphics workstation. The Evans and Sutherland workstation allows real-time rotation in all three-axes; however, this feature requires normalization of the axes. Therefore, all axes start at an arbitrary zero [0] and end at one [1], meaning that the lowest value on that axis is assigned the value zero, and the highest value is assigned the value

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one. For example, the temperature axis for all the 3-D graphs in this paper covers the range from 5 to 49°C: when normalized and displayed on the graphs, the origin or zero refers to 5°C and the end or 1 refers to 49°C. The frequencies are expressed as their natural logarithms, to facilitate plotting. The K4DS software allows the plots to be graphed using the same y scale ($\cotan \delta$); we have standardized on a 0 to 20 scale. It also calculates the volume underneath the surface using IMSL'S AKIMA spline subroutine (SURF) (Houston, TX); we typically observe very good agreement between the AKIMA and other order splines, including linear interpolation over both independent variables. The statistical routine used for the median and variance numbers is from RS/1. It should be realized that there are quite a few commercially available graphing programs capable of generating similar 3-D graphs.

Background. The following discussions pertain to thickened fluid systems, specifically suspensions and dispersions: they are frequently referred to as either "sample" or "system" or "product." Our goal was to identify rheological properties that correlated with the physical stability of these commercial products, and not to determine the physical stability of these products for comparison purposes. Therefore, physical stability data are not presented, and only ranking of stability is mentioned. Because of proprietary concerns, the products are labeled only as "Product A," etc. All of these household products are aqueous compositions containing suspended particulates, and because of their high activity are concentrated dispersions (5). Therefore, particle-particle interactions dominate the rheological behavior, as well as the physical stability.

RESULTS AND DISCUSSION

A sample subjected to a force in the form of a stress will deform. When this stress is removed, the sample will respond in one of three ways. If it regains its shape and form, then its behavior is that of a Hookean solid and its response is totally elastic. On the other hand, if the sample never regains its form, that is, the sample permanently moved in the direction of the force with the movement proportional to the force, then the sample is a Newtonian liquid. Most products of interest, however, will respond with characteristics of both a Hookean solid and a Newtonian liquid. Concentrated dispersions are one such example of systems that are viscoelastic: these systems will recover some of their original form and will also move irreversibly (6). Needless to say, the rheology of these viscoelastic systems will be complex. Anyone who has taken viscosity readings will be familiar with terms such as "shear thinning," "dilatancy," "plastic" and "pseudoplastic flow," "Bingham body" (4), etc.—these are manifestations of viscoelastic systems. The rheological behavior of viscoelastic systems can be best studied using dynamic (oscillatory) and transient techniques (creep and relaxation); we have chosen to study concentrated dispersions with the dynamic techniques because of the ease of data acquisition and interpretation.

The dynamic oscillatory technique consists of inputting a sinusoidally varying strain (γ) or movement of known frequency to a sample (7). The strain causes a stress (σ) to arise in the sample, which is oscillating at the same

frequency as the strain, but out of phase with it by an angle δ (see Fig. 2): $\gamma = \gamma_0 e^{i\omega t}$ sinusoidal input strain; $\sigma = \sigma_0 e^{i(\omega t + \delta)}$ sinusoidal output stress, where $\omega = \text{radians s}^{-1} = 2\pi \times \text{frequency (in Hz)}$, $t = \text{time}$, $i = (-1)^{1/2}$. Note: expressions are valid only for small amplitude γ_0 . The dynamic modulus G is the ratio of stress to strain: $G = d\gamma = (\sigma_0/\gamma_0)e^{i\delta}$.

Switching notations to complex variables allows the separation of the modulus into a real and an imaginary part: $G^* = (\sigma_0/\gamma_0)\cos \delta + i(\sigma_0/\gamma_0)\sin \delta$. The real part, $(\sigma_0/\gamma_0)\cos \delta$, is called the storage or elastic modulus, G' , whereas the imaginary part, $(\sigma_0/\gamma_0)\sin \delta$, is called the loss or viscous modulus, G'' . The above expression is then simply: $G^* = G' + iG''$. In energy terms, G' conserves energy and, hence, absorbs it, while G'' disperses energy viscously in the form of heat.

The mechanical response of most commercial products will be viscoelastic, since the presence of suspended solids, high additive concentrations, colloidal thickeners, etc. will often induce some sort of structure upon the aqueous phase (6,8). That structure or matrix, whether static or dynamic, necessarily will confer some elasticity to the system, along with its inherent viscous character. These systems will have measurable amounts of both G' and G'' .

A more concise and precise way of expressing viscoelasticity is through the phase angle: $\delta = 0^\circ$, Hookean solid; $\delta = 90^\circ$, Newtonian liquid; $0^\circ < \delta < 90^\circ$, viscoelastic body.

The value obtained from a viscosity measurement is a function of many variables, including shear rate, time of shearing, amount and type of structure, flow behavior, temperature, etc. While there is a tremendous amount of information in a viscosity reading, the information is mostly unresolved (9). Further, the very act of rotating a sample leads to structure breakdown by forcing the particles, whose hydrodynamic, steric and electrical interactions give rise to structure in the system, to flow past each other. Finally, typical viscosity measurements (*i.e.*, by

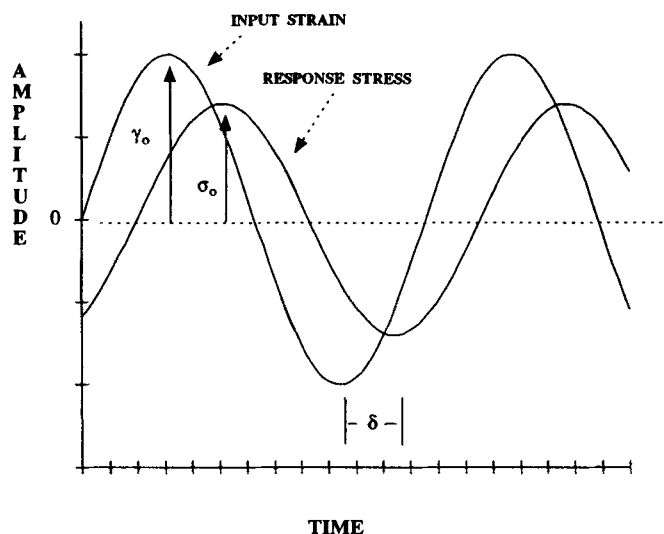


FIG. 2. An oscillating input strain generates a response stress at the same frequency. The stress is shifted by a phase angle δ , and there will be a loss in amplitude due to viscous energy dissipation.

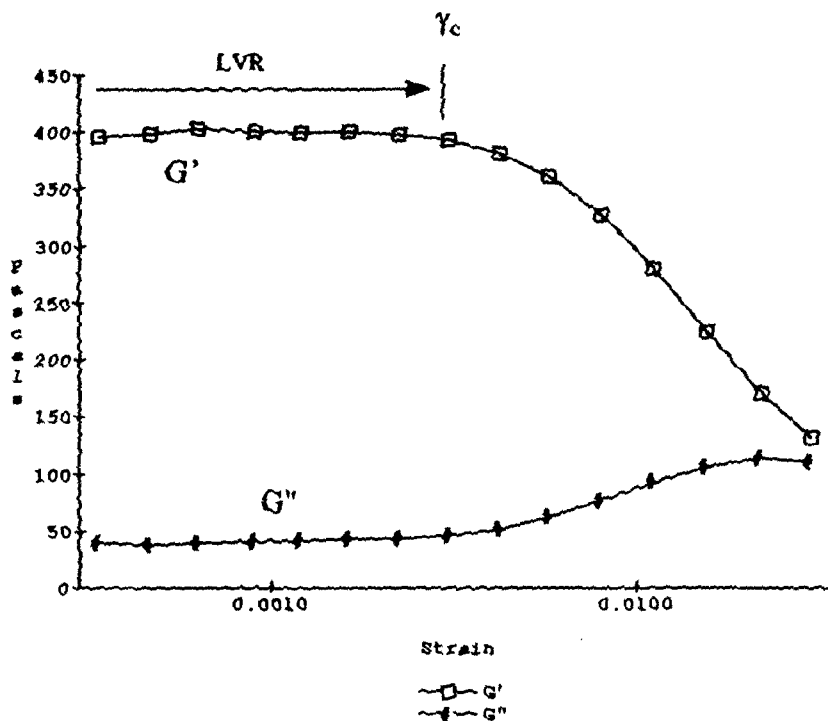


FIG. 3. Strain sweep of concentrated dispersion. The linear viscoelastic region (LVR) is all the strain that the dispersion can tolerate up to γ_c before structure breakdown and flow occurs.

rotary viscometers) do not reflect the response of a dispersion to the forces that the dispersion experiences on a shelf aging away. To investigate shelf stability, it makes sense to mimic as much as possible the conditions of storage. That is, a product on the shelf is not subjected to large shear forces but, rather, to less dramatic gravitational, thermal, and hydrodynamic forces. It is no surprise that viscosity readings, even though they are quite sensitive to colloidal changes, often have no correlation with a product's shelf stability.

In contrast, oscillatory measurements are carried out within a very specific region, the linear viscoelastic region (LVR). This region is located first with a strain sweep test whereby the limit of applied strain amplitude, γ_c , prior to flow conditions, is determined (10). See Figure 3 for an example of a strain sweep test. Within the LVR, both G' and G'' are independent of strain γ . Therefore, the moduli are only functions of temperature and frequency.

The advantages of oscillatory rheology within the LVR versus conventional viscometry are now apparent. Oscillatory rheology within the LVR probes the "at rest" structure of the colloidal matrix without breaking it as in conventional viscometry. Further, an oscillatory experiment gives two pieces of information, an elastic and a viscous parameter that can be useful in characterizing the dispersion. The ability to perturb but not disrupt is preferred in order to investigate the physical stability of concentrated dispersions under the conditions of interest, that is, at rest.

Note that viscosity can still be monitored by either calculating the complex (η^*) or dynamic (η') viscosity (see below). The viscosities thus derived are closely related to

steady-shear experiments and the frequencies (in radians s^{-1} , ω are analogous to shear rates (Cox-Merz rule (11)). One oscillatory experiment gives similar information as a steady-state measurement plus a breakdown into elastic and viscous components: $\eta^* \approx G^*/\omega$; $\eta' \approx G''/\omega$

One topic that has not been approached so far is the effect of time. Time becomes an integral part of viscoelastic systems, and, indeed, is used to define them in terms of Deborah numbers (5). It is a topic out of the realm of this paper; however, cursory definitions are still needed. Specifically, a relaxation time is defined as the time required for molecular randomization to occur after a translational excitation, such as imposing a strain on a sample, preferentially orients the molecules (or aggregates, colloidal particles, etc.) in the direction of the excitation (12). In physical terms, it is the time necessary for molecular rearrangements to absorb the energy of a perturbation and restore "equilibrium" (i.e. a system where Brownian motion is dominant). Note that a Newtonian liquid reorganizes itself practically instantaneously once a strain is imposed and, therefore, has no (within the measurable range of the rheological equipment) relaxation time. A solid never rearranges itself upon a strain and, hence, has an infinite relaxation time (i.e., $\gg 10^4$ s). It only makes sense to speak of relaxation time in terms of viscoelastic systems. However, it should also be realized that a single relaxation time is a myth for concentrated dispersions: it is better to think of relaxation time as a broad distribution around an "average" time reflecting the many types of rearrangements possible when high particle densities are present. Further, once this "average" relaxation time is exceeded by ω (i.e. when the sample does not have time

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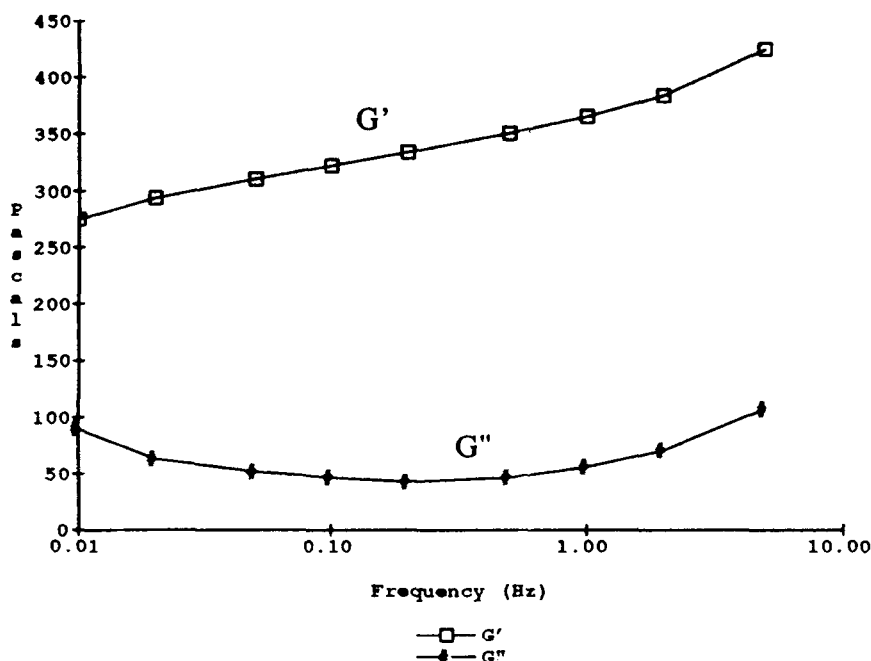


FIG. 4. Frequency sweep of a stable concentrated dispersion in the LVR at 21°C. The frequency axis is on a log scale.

to completely relax), the system has two choices: either the system rearranges itself to accommodate the strain and dissipate the excess energy (it behaves more Newtonian) or the system stores the energy elastically within its structure (the system stretches but does not break). Therefore, it is particularly important to observe the behavior of dispersions as a function of frequency because of the time dependencies involved. The frequencies used in this work cover the relaxation times of most interest, those within a fraction of a second to a hundred seconds, whereby most rearrangements will occur (8).

We began investigating the correlation between physical stability and rheology by running various rheological tests, including flow curves and oscillation experiments on commercial products. A typical oscillatory frequency sweep, from 0.01 to 5 Hz, is shown in Figure 4. Notice the small changes in G' and G'' —this is fairly typical of moderately stable concentrated dispersions. The elastic and viscous moduli are plotted as a function of frequency, with the higher frequencies responding more elastically. This response is normal and means that the frequency is higher than the system's ability to relax—the system simply cannot dissipate the input of energy viscously in the time-reference of the frequency and the energy is stored elastically. Occasionally, the response was not straightforward, especially at higher temperatures and for the more unstable systems (see Fig. 5). We soon determined that the ratio of elastic to viscous moduli, G'/G'' , appeared to be correlated to the observed physical stability. However, it also became apparent that observing the ratio at one temperature was not enough, and that the entire temperature range of interest needed to be studied. This is necessary because product stability must be maintained over a finite temperature range. In essence, this required the use of 3-D graphing whereby temperature and

frequency are the independent variables, and the ratio G'/G'' is the dependent variable.

Polymer rheologists (13) have been using this approach for some time now except that the ratio used is the inverse, *i.e.*, G''/G' . For polymers, this has an advantage since above the glass transition temperature, the ratio G''/G' is greater than 1.

By monitoring the ratio over a large frequency or temperature range, conformation changes occurring in the polymer backbone can be followed (14). However, in almost all cases, G' is greater than G'' in the case of concentrated dispersions. That is normal because in order to suspend particulates, a dispersion has to form a matrix that includes the solvent water. The matrix must be rigid enough to counter the forces of gravitation and coalescence of its particles: the amount of matrix formation is related to G' (8). In fact, whenever the ratio G'/G'' becomes less than 1, sedimentation becomes a certainty. From our point of view, we decided to look at the inverse ratio: $G''/G' = \cos \delta / \sin \delta = \cotan \delta$.

Large temperature or frequency ranges can be followed for polymers because pure polymer systems behave very linearly allowing the use of the time-temperature superposition principle (15). The principle states that frequency and temperature can be interconverted with each other; therefore, data are usually collected over a large temperature range, then converted to a frequency spectrum covering many decades of frequency. By monitoring the ratio over a large frequency or temperature range, conformation changes occurring in the polymer backbone as well as phase changes can be followed. The principle, however, cannot be applied to systems which show nonlinear behavior. The principle has been shown to fail even in a miscible blend of two pure polymers (16). Since dispersions are multi-component as well as comprising at least two

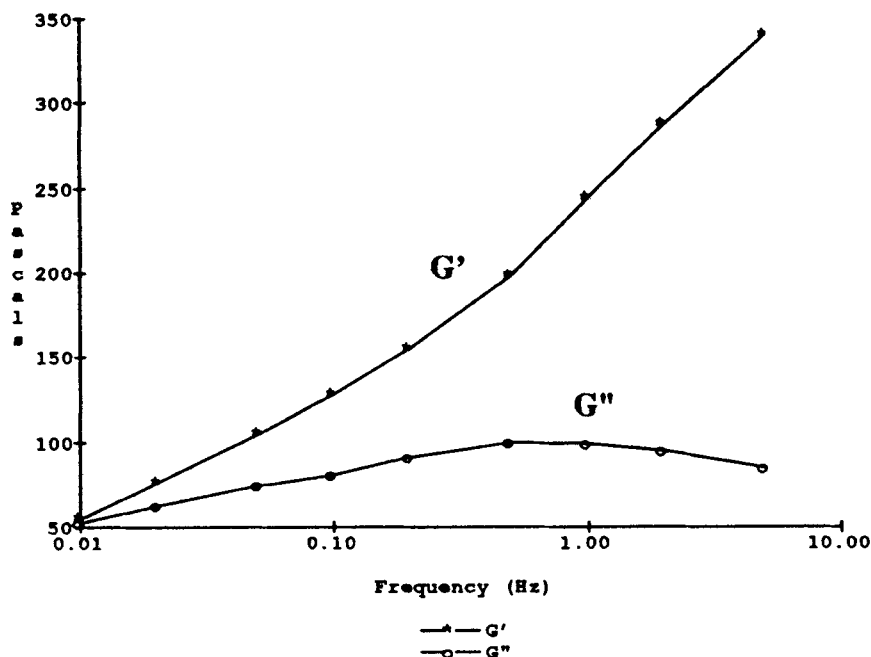


FIG. 5. Frequency sweep of an unstable concentrated dispersion in the LVR at 38°C.

phases (liquid solvent and solid particles) that show non-linear behavior outside a very small range of strain, the superposition principle was not applied to our dispersions. However, it appears that the use of 3-D graphing essentially achieves the same purpose of indicating where phase changes are occurring.

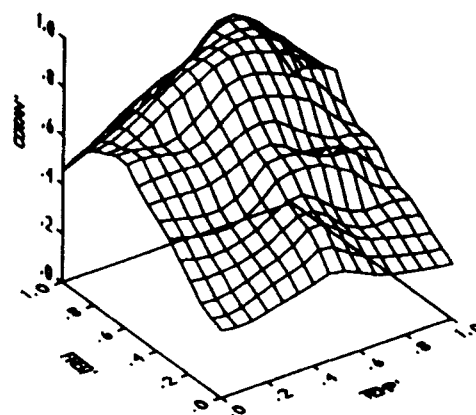
Some uses of the 3-D rheological technique in differentiating between stable and unstable products, in quality control, and for various categories of commercial products will be outlined below.

Stable vs unstable products. The correlation between the rheological 3-D graphs and a very stable (phase separation is not observed for more than one-year shelf-life and is one of the most stable systems we have encountered) and an unstable product are shown in Figures 6 and 7, respectively. Two observations are immediately apparent in these systems. The stable product C shows a substantial positive increase in the response surface as a function of frequency. However, its temperature response is almost invariant and the surface roughly forms an angle of about 45° from the xz plane ($x = \text{temperature}$, $y = \cotan \delta$, $z = \ln \text{frequency}$). Further, the response values are high, with the $\cotan \delta$ values ranging from 4.5 to over 17. When viewing the 3-D graphs, the legend on the bottom right corresponds to the axes limits, the lower number, because of normalization, is equal to zero on that axis, and the higher number is equal to 1. The first $\cotan \delta$ range indicates the actual height of the plot, whereas the second $\cotan \delta$ range is the experimental results.

In contrast, when the 3-D graphs are plotted to the same scales on all three axes, the response surface of product D (a generic brand) is basically flat and parallels the xz axis and its total response is very low, from 0.9 to 4.6. Phase separation is observed in this product within 24 hr.

Before comparing other products, it may be beneficial

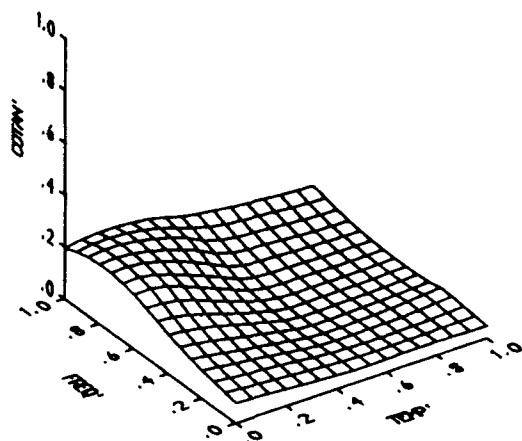
Stable Product



TEMP	5.00 - 49.0
FREQ	-4.61 - 1.61
COTAN	0.000E+0 - 20.0
COTAN	4.53 - 17.3

FIG. 6. $\cotan \delta$ response surface of product C. Note large range of $\cotan \delta$ values, relatively flat surface, and little temperature dependence. This product is the most stable so far analyzed by this technique.

Unstable Product



TEMP	5.00 - 49.0
FREQ	-4.61 - 1.61
COTAN	0.000E+0 - 20.0
COTAN	0.919 - 4.55

FIG. 7. Product D (generic brand). An unstable product has a low range of cotan δ values; this product also has values that are lower than 1 ($G' < G''$), indicating a high propensity to sediment.

to digress for a moment and consider why the cotan δ values increase as a function of frequency. Recall that the frequency is analogous to shear rate and the higher frequencies correspond to higher shear rates. All systems, including water, respond mostly elastically when the frequency exceeds its natural relaxation time; the sample simply does not have sufficient time to relax viscously at higher frequency. Likewise, as the frequencies are increased, concentrated dispersions respond more elastically, and the ratio G'/G'' increases. If the ratio remains constant or decreases at higher frequencies, then either the viscous parameter is increasing or the elastic parameter is decreasing or both (a further possibility is that the system is behaving non-linearly, in which case it is starting to flow). Either way, the structure of the system is beginning to degenerate. A stable product will have a strong matrix structure present ($G' > G''$). It is, therefore, natural to expect this structure to have large values of cotan δ and for the structure to behave predominantly elastically as a function of frequency.

Product D of Figure 7 obviously has much less inherent structure than product C of Figure 6. In fact, at the lowest frequency, the value is less than one, indicating that viscous dissipating forces are slightly larger than the elastic energy conserving forces. When these conditions exist, sedimentation or density gradients are likely to occur unless the particles' effective density is less than that of water. Viscosity also affects sedimentation, but only in a kinetic sense, that is, viscosity, if sufficiently large, can only slow down the sedimentation process. The apparent or complex viscosities, being a function of both elastic (*i.e.*, solid) and viscous (*i.e.*, Newtonian liquid) moduli, reflect both contributions. When the largest component of the viscosity measurement (within the linear region) is mostly a function of G'' only, the dispersion or suspension will not exhibit a yield value and simply will

not suspend. One needs only to try to suspend noninteracting particles with a high viscosity, mostly Newtonian system such as honey or a silicon oil to recognize this effect. The systems investigated for this report have relatively large apparent viscosities, from about 1,000 to 15,000 mPa s (cps) at approximately 10 s^{-1} shear rate. Again, it is stressed that the apparent viscosity did not show any correlation with the overall physical stability (see Fig. 1) of these products. While viscosity is important (and to physical stability the zero-shear or low-shear viscosities are the most important (17)), we believe the character of that viscosity in the linear, non-flowing region is more important (*i.e.*, its relative elastic and viscous contributions).

Finally, a cotan δ value of less than 1 implies a physical instability only with regard toward a tendency to sediment; that value says nothing about the ability to redisperse the sediment, nor does it predict other types of physical instabilities, such as flocculation, coagulation, etc. All that can be said is that stable products show large cotan δ values (greater than 1, and typically at least 3 to 4) throughout the frequency range.

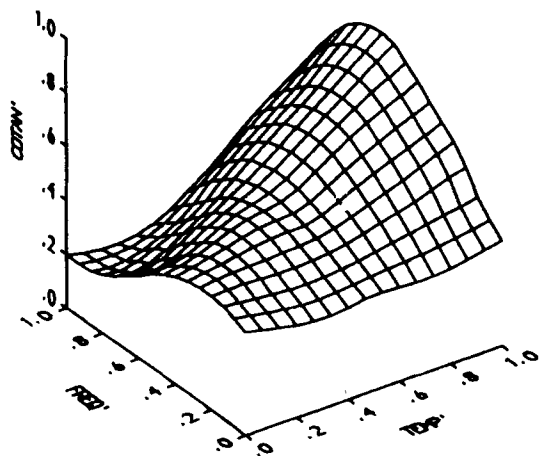
One further comment—product C does show a change in the slope of the response surface at the highest frequencies, with the response going through a maximum. We believe this is indicative of a phase transition, that is, the system is rearranging itself to accommodate the added stress of the higher frequencies. The rearrangement to high frequency response has been observed in our laboratory when surfactants are part of the suspending medium or in a system containing only an associative thickener such as a poly(acrylic acid). Regardless of the reason, the system has undergone a phase transition which is only frequency-dependent. We have previously observed that frequency-dependent phase transitions are not detrimental to physical stability.

It can be argued that in reality there is no phase transition occurring in product C at the highest frequencies but simply a structure breakdown that then allows realignment with the flow. However, it must be realized that the conditions of the experiment avoid the possibility of flow when the experiment is done within the linear viscoelastic region (LVR). Furthermore, a flowing system will have a much lower cotan δ value since it will be beyond the LVR (see Fig. 3). This is clearly not the situation here, since the cotan δ value never goes below 6 at high frequency.

It then appears that, based on the results of product C (and dozens of other formulas previously analyzed), the more physically stable products have the following criteria when tested by this technique: i) large cotan δ values greater than 1 to a maximum around 20; ii) a relatively planar cotan δ (3-D) surface with minimal temperature dependence that slopes positively as a function of frequency only; iii) the absence of large "peaks" or deep "troughs" that indicate a phase transition, usually as a function of both frequency and temperature.

Quality control. The normal cotan δ 3-D plot of product E is shown in Figure 8. This product is a dispersion of an inorganic colloid which supplies the thickening and suspending ability. Ranking this product in terms of physical stability would place it in the broad "average" category, and the 3-D plot mirrors this behavior. This product has a marked temperature dependence; most of its cotan δ increase is a function of temperature. Indeed,

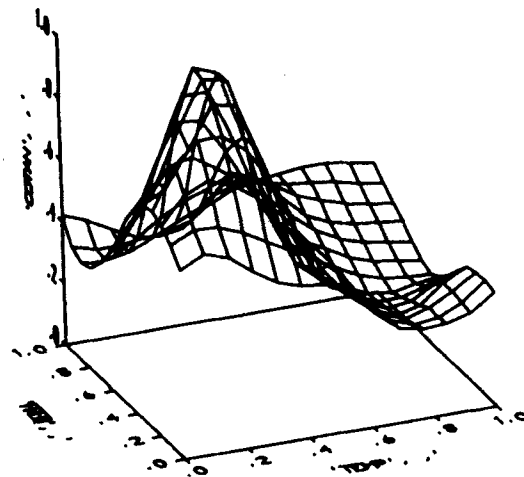
Product E



TEMP 5.00 - 49.0
 FREQ -4.61 - 1.61
 COTAN 0.000E+0 - 13.0
 COTAN 2.56 - 11.0

FIG. 8. Product E; this product is thickened with an inorganic colloid. Plotting was on a smaller cotan δ scale (0 to 13, instead of 0 to 20 of Fig. 6) to accentuate the large temperature dependence of this product.

Product E



'TEMP', , 5.00 - 49.0
 'FREQ', , -4.61 - 2.30
 'COTAN', , 0.000E+0 - 6.00
 'COTAN', , 1.37 - 5.32

FIG. 9. Different formula of product E, showing the destabilizing effect of excess addition of one of the product components. This graph is also plotted to a smaller cotan δ scale, from 0 to 6.

the product shows an increase in viscosity as the temperature increases, the opposite of expected behavior. The area that shows the most phase change is at 49°C, the highest temperature, and it is also the area where the most instability (syneresis) is observed.

Comparison of two formulas of product E in Figure 8 and Figure 9 shows that they possess very different rheological profiles. Product E of Figure 9 actually contained one of the components in excess. Routine tests, such as viscosity, pH, and appearance all indicated that this product was within expected limits, as product E of Figure 8. However, the 3-D technique immediately identified the rheological differences between these two formulas, and also suggested that product E of Figure 9 would possess lower physical stability due to its lower cotan δ values. The altered formula was indeed found to be less physically stable.

The 3-D technique can be used successfully as a QC test where other classical techniques cannot possibly help, because the response one seeks in physical stability is mechanical, not chemical. For example, if particle size is an important criteria for a product's physical stability, chemical testing may not be sensitive to this parameter, whereas rheological testing would be. Perhaps more importantly, this technique has the potential of being an exclusive QC test. In one relatively quick experiment, the whole product is analyzed, since the technique is sensitive to concentrations, composition, and even processing changes. This is far quicker and more reliable than analyzing chemically for each component, because even when compositionally two formulas are alike, they can be quite

different if the colloidal makeup is different due to processing changes. The technique is basically a colloidal "fingerprint": identical formulas produced under consistent processing parameters will have the same fingerprint. Very closely related products will show very similar surface responses, as long as the products' differences do not affect the colloidal system. An example is shown below in Figures 10 and 11 where the only difference between these products is the fragrance.

Simplifications of the 3-D technique. The 3-D graphs offer a quick visual representation of all the rheological data. With experience, assessment of physical stability can be achieved quickly by scanning the 3-D graphs. However, it is preferable to quantitate results, especially when comparing similar systems that have analogous profiles. One way of condensing all the information in the 3-D plots is to calculate the volume underneath the surfaces. The volume calculation is a corollary to the observation that a large spread of cotan δ values is preferable. Our experience indicates that the volume calculation appears to correlate well with physical stability data of different products. For QC reasons, this approach works remarkably well and simplifies interpretation greatly. Volume results are presented in Table 1, along with mean and variance results (see below).

A further simplification came when we standardized on the ranges for frequency and temperature values. This meant that both the x and z axes were the same for all the 3-D plots. Therefore, the volume determination was simply multiplying the average (mean) y-value (cotan δ) times the x and z axes. Since x times z is a constant (if

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Product F

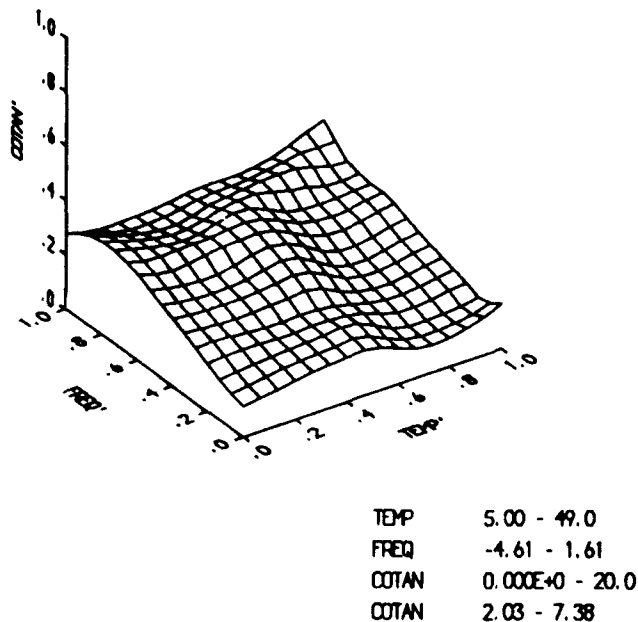


FIG. 10. Product F. The rheological "fingerprint" of this product is very characteristic and reproducible.

Product G

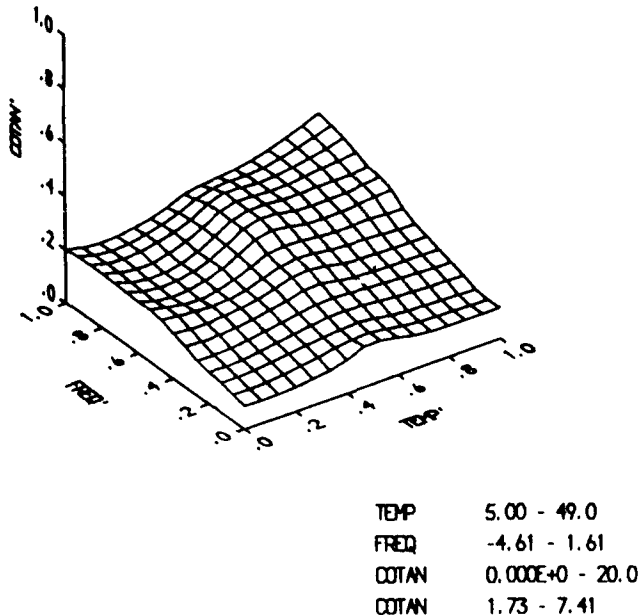


FIG. 11. Product G is almost identical to product F of Figure 10, differing only in fragrance. The rheological fingerprint is also almost identical.

the same range of values is studied), one only needs the mean y ($\cotan \delta$) value to correlate the rheological data with physical stability. The variance of the mean value (the standard deviation squared) is used as an indication of the variability. The mean value and variance can be used as quick indicators of the magnitude and amount

TABLE 1

Volume, Mean, and Variance Results

Product	Volume	Mean	Variance
C (Fig. 6)	3180	11.1	13.0
D (Fig. 7)	534	1.96	2.3
E (Fig. 8)	1030	3.9	2.3
E (Fig. 9)	570	2.79	1.1
F (Fig. 10)	1258	4.6	1.97
G (Fig. 11)	1120	4.0	1.7

of change that the surface experienced without doing a 3-D plot. However, for both the volume and mean/variance calculations, it is still difficult to fully interpret the data without the use of the 3-D graph, unless the systems are very similar. Also, one can easily miss the phase transitions, if any, without the benefit of a 3-D graph.

In summary, the 3-D plotting of the rheological property $\cotan \delta$ as a function of frequency and temperature appears to be a useful tool for predicting the overall physical stability of concentrated colloidal dispersions. The technique has proven itself useful in characterizing stable and unstable products, as well as a QC tool.

The 3-D plots are, in essence, "fingerprint" maps of the colloidal stability of the dispersions. They are, therefore, ideally suited for quality control monitoring, especially in products where physical stability is a major concern and where all components cannot be tested.

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