Measurement of Fluid Rheology and Interpretation of Rheograms

Second Edition

by
Dr. Nick Triantafillopoulos

Measurement of Fluid Rheology and Interpretation of Rheograms

Second Edition

Dr. Nick Triantafillopoulos

Kaltec Scientific, Inc.
22425 Heslip Drive
Novi, Michigan 48375 USA
248.349.8100 fax 248.349.8909

NOTICE & DISCLAIMER

The material in this booklet was compiled by Nick G. Triantafillopoulos at The Institute of Paper Chemistry for Kaltec Scientific, Inc., in January 1988, based on information available in the literature, unpublished data, and experience with various models of the Hercules® Hi-Shear Viscometer. Special thanks are extended to Dave Bossé for his advice, and to Gary Rudemiller for helping in the composition of this document.

Kaltec Scientific, Inc., or its employees and agents, shall not have any obligation or liability for damages, including, but not limited to, consequential damages, arising out of, or in connection with, the use, or inability to use, the reported information. Kaltec Scientific, Inc., provides no warranty or guaranty of results.

TABLE OF CONTENTS

Page

Introduction 1

Measurements with a Hercules® Hi-Shear Viscometer 4
- Calculating Viscosity 4
- Estimating Thixotropy and Yield Stress 6
- Multiple Tests with the Same Fluid Sample 6
- Correlating Viscosity Data with Different Instruments 7

High-Shear Flow Phenomena of Non-Newtonian Fluids 8
- Time-Dependent Phenomena 11
  - Thixotropy 11
  - Rheopexy (or Anti-Thixotropy) 12
- Shear-Dependent Phenomena 13
  - Shear-Thinning (Pseudoplasticity) 13
  - Shear-Thickening (Dilatancy) 13
  - Structural Viscosity 14
  - Plastic Fluids 15

Implementation of Viscous Behavior 16
- General Remarks 16
- Paper Coatings 18
- Paints and Other Applications 20

Interferences in Interpretation of Rheograms 21
- Vortical Flows 21
- Temperature Effects 23
- End and Wall Effects 24
- Other Considerations 25

Epilogue 28

Appendix A
- Parameters and Mathematical Formulae for Viscosity 29

Appendix B
- Characteristic Rheograms 31

Appendix C
- Units and Useful Relationships for Hi-Shear Rheology 33

Appendix D
- Formulae for Determining Plastic Viscosities and the Leveling Index 34

INTRODUCTION

Technical information compiled in this booklet is provided for assisting users of the Hercules Hi-Shear viscometer to measure, understand, and control rheology of fluids in order to predict their performance during handling, transportation, processing, and application. Although the ultimate goal is to predict the behavior of fluids in a variety of complex flow fields, rheological properties associated with non-Newtonian viscous liquids, which include most of the common industrial fluids, are quantified only in simple flow geometries. Viscometric measurements, in general, deform a fluid sample in a simple-shear geometry under controlled conditions and measure its response in terms of torque, instrument dimensions, and geometrical constants. Thus, an attempt to "characterize" the fluid is made based on measuring a material parameter, namely the absolute viscosity, and displaying the deformation (shear) rate dependence of viscosity, namely the relationship of shear stress as a function of shear rate.

The viscosity of non-Newtonian fluids depends on the magnitude of the flow and the length of time the fluid has been flowing. Because a diverse range of shear rates prevails in most fluid processing and application operations, rheology cannot be sufficiently described by a single number. In addition, viscosity may also change with time as the fluid becomes more or less viscous upon continuous deformation. Therefore, viscosity measurements at a constant shear rate (or single-point measurements) are inadequate to describe the flow behavior of non-Newtonian fluids. Knowledge of viscous behavior over a wide range of shear rates and the response of a fluid in continuous deformations are more appropriate for revealing unique features and alleviating problems that arise from the non-Newtonian nature of fluids. Then, the shear- and time-dependent rheology of fluids can be determined and utilized to predict their behavior.

Measurement and characterization of viscous behavior of non-Newtonian fluids serve multiple purposes. They help understanding a fluid's response to deformations; knowledge essential in developing critical specifications for handling, transportation, application, and in determining the optimum conditions for the efficient operation of processing equipment. This information pertains to design and/or select appropriate equipment for mixing, dispersing, storing, pumping, and processing. Establishment of rheological criteria make it also possible to predict suitability of a certain coating composition for a given process with laboratory measurements. Consequently, viscometric tests permit taking a corrective action to optimize a formulation based on solid data. This data, in turn, can be utilized to develop

a proven strategy of application for statistical quality and process control. It also provides necessary documentation for production research and development to control rheology. Finally, understanding viscous behavior contributes to the effective end use performance and functionality.

The Hercules Hi-Shear Viscometer (HHSV)[1] utilizes concentric cylinders with a well-defined geometry to measure a fluid's resistance to flow and determine its viscous behavior in this simple-shear flow field (Figure 1). Because the gap between the rotating inner (bob) and the restrained outer (cup) cylinders is very small, the annular flow between the two cylinders approximates a velocity-driven (Couette) flow. This type of flow is similar to the one confined between two parallel plates, where the one moves relative to the other. When a fluid sample is confined between the bob and cup, rotation of the bob generates a velocity gradient across the gap. This gradient is termed shear rate and defined as the change in linear velocity (cm/sec) between two fluid elements divided by their distance in centimeters. Thus, shear rates are expressed in reciprocal seconds (sec^{-1}). While rotation of the bob causes the fluid to flow, its resistance to deformation imposes a shear stress on the inner wall of the cup, measured in dynes/cm^2.

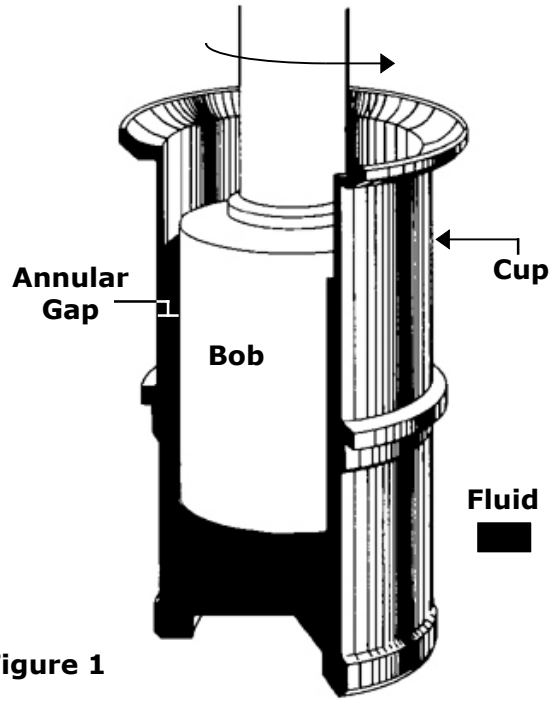


Figure 1

Absolute or apparent viscosity, for non-Newtonian fluids, can be calculated at any shear rate and up to an arbitrarily selected maximum speed of rotation. More informative, however, is the shape of the continuous flow curves (Figure 2) which are equivalent to plots of shear stress as a function of shear rate. (Although torque is the dependent variable HHSV measurements, it is traditionally displayed on the horizontal axis which incorrectly implies that it is the independent variable.) In HHSV tests, the desire is to obtain smooth curves that exclusively and uniquely describe material properties free of interference. Although viscometric flows of

[1]Developed fifty years ago by paper coating engineers in Kalamazoo, Michigan (Paper Trade J. 126(23):60-66(1948)).

Newtonian fluids are independent of the measuring geometry, both material functions and the geometry of the viscometer affect the flow of non-Newtonian fluids. This is exactly the reason for incorporating instrument dimensions and geometric constants in the equation for calculating viscosity, appearing in the next section.

MEASUREMENTS WITH A HERCULES HI-SHEAR VISCOMETER

CALCULATING VISCOSITY

Rheological measurements with a HHSV reveal the relationship between shear rate and shear stress in the form of rheograms, which displays rotational speed in revolutions per minute (rpm) versus torque in dynes-cm (see Appendix A for converting torque to shear stress and rpm to shear rate). Such measurements are achieved with tests performed in a Couette flow, where both translational and rotational deformations occur simultaneously. (Imagine a cubical unit of the fluid which undergoes extension in one direction and compression in a directions perpendicular to the first.) Recorded rheograms contain two different flow curves (Figure 2); one representing acceleration (the "up" curve) followed by another corresponding to deceleration (the "down" curve). These curves are generated during a complete testing cycle, i.e., from zero to maximum rpm and then back to zero, with the AUTO mode of the instrument. Rheograms supply sufficient information to characterize non-Newtonian fluids, that is to determine the shear- and time-dependent rheology of fluids (Appendix B). A more detailed discussion about the major types of non-Newtonian fluid flows is included in the next section.

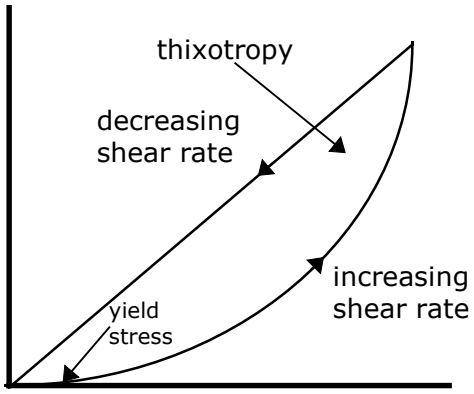


Figure 2

The shear-rate profile across the annular gap, between the rotating bob and restrained cup, is not always known or well-defined. The profile of Newtonian fluids exhibits a maximum value of shear rate next to the bob that linearly decreases at distances closer to the cup. For non-Newtonian fluids, however, the profile becomes non-linear and its shape depends on the type of non-Newtonian rheology exhibited by the fluid. The shear rate next to the bob wall can be calculated at any rotational speed by applying the mathematical

expression appearing in Appendix A. Torque, on the other hand, is always measured at the inner wall of the restrained cup, and it can be considered an accurate representation of the average value of torque exerted on the bob and cup walls, since the ratio of bob to cup radii is close to 1 (Appendix A).

An important piece of information obtained with HHSV rheograms is absolute viscosity, which can be calculated at any shear rate on a flow curve. The reported variable for non-Newtonian fluids is apparent viscosity since it is calculated using a mathematical formula appropriate only for Newtonian fluids. Most commonly, apparent viscosity (η) is reported at the maximum rotational speed at the peak of the rheogram, and calculated by:

$$\eta = \frac{9.55Ts}{rpm} \qquad \text{(Eq. 1)}$$

where T = torque in dynes-cm (equal to the product of horizontal displacement in centimeters in the recording graph and the spring constant, e.g., 400,000 dynes-cm per cm on the horizontal axis on the graph),

where rpm = the rotational speed of the bob in revolutions per minute (note: the quantity rpm/9.55 represents angular velocity (Ω) in radians/sec), and

where s = geometrical factor corresponding to the sheared volume inside the gap given by:

$$s = \frac{\frac{1}{R_1^2} - \frac{1}{R_2^2}}{4\pi H} \qquad \text{(Eq. 2)}$$

R_1 and R_2 are the radii of bob and cup, respectively, and H is the bob height, all in centimeters. Viscosity is calculated in poise (*p*), but it can also be reported in a variety of different units (Appendix C); most common is centipoise (100 *cps* = 1 *p*) which is equivalent to *mPa-sec* in SI units.

It is noteworthy that Eq. 1 has been derived under the following assumptions: (a) the flow in the gap is laminar and steady, i.e., it is characterized by curvilinear and planar streamlines that have only one velocity component with its vector tangent to the radial direction, (b) end effects are negligible, (c) the entire measuring volume remains under isothermal conditions during a test, (d) the no-slip condition is satisfied on both the bob and cup walls (i.e., no wall effects are present), and (e) the fluid remains homogeneous during the course of a test, an imported requirement when testing thick slurries.

ESTIMATING THIXOTROPY AND YIELD STRESS

The area of the loop between the up and down flow curves of a rheogram is a measure of the thixotropic breakdown, i.e., the loss of input energy during a complete testing cycle with the HHSV. For thixotropic fluids, the down curve always falls to the left of the up curve. Since precise estimation of the area in a thixotropic loop is rather tedious, thixotropy cannot be readily quantified from rheograms and some indirect methods are necessary. The least laborious procedure involves measuring the distance between the up and down flow curves at mid-point of the rotational speed from zero to maximum rpm. Accordingly, similar fluids tested with the same viscometer settings and the same maximum speed can be compared. It should be understood, however, that these quantitative comparisons are based on a gross estimate of true thixotropy. Another method appears in Appendix D, where a procedure for calculating the leveling index from the concept of plastic viscosities is also illustrated. Thixotropy, as well as leveling index, are important properties for the application of high-shear coating operations, except as thixotropy influences the back flow from a metering zone.

An approximate of yield stress of plastic fluids can also be determined from HHSV rheograms. This accomplished by measuring and reporting the torque before flow begins, i.e., before the up curve separates from the horizontal axis of the graph. This method, however, is indirect and not very accurate. It is recommended only for making relative comparisons between similar fluids. Rather than speed-controlled viscometers, such as the Hercules® Hi-Shear, torque-controlled instruments (called torque rheometers) are required for direct and accurate measurement of yield stress.

MULTIPLE TESTS WITH THE SAME FLUID SAMPLE

It has been common practice when testing paper coating suspensions to subject a sample through a second test immediately after completing the first one. Repeating the testing procedure on the same sample immediately may or may not result in the same curve. This depends on the time required by the fluid to recover its structure after cessation of flow which is a function of both particle orientation and collision effects, as well as the nature of polymeric substances into solution. Subjecting a sample to a second testing cycle before it fully recovers from its previous deformation frequently results in a smaller thixotropic loop and displacement to lower torque values. Repeated testing, generally,

represents the fluid's equilibrium shear stress-shear rate relationship, but it is meaningful only if particle shape and size effects are absent and complete reversibility of structural changes can be assumed.

CORRELATING VISCOSITY DATA WITH DIFFERENT INSTRUMENTS

When measuring viscous behavior of non-Newtonian fluids, it is often desirable to correlate data obtained with different types of instruments (e.g., bob-cup, cone-and-plate, capillary viscometers, etc.) at similar shear rates. However, viscosity measurements of dispersions having high solids content depend on both a shear-function (i.e., the apparent viscosity) and a slip-function, the later being affected by material properties and properties of the solid walls confining the viscometric flow. Thus, both viscosity and slip should be considered when comparing data from different viscometers. However, it is difficult to take slip into account because the slip function cannot readily be determined and requires multiple measurements (Proc. IX Inter. Congress on Rheology, Mexico, Vol. 2, p. 557-564 (1984)).

To compare results at different shear rates and with different instruments, viscometric data should be extrapolated only after a specific flow model (a constitutive equation) has been adopted to represent the fluid under consideration. For example, measurements with a single-point, low-shear instrument can be correlated with high-shear data from HHSV by assuming that the fluid follows a power-law model:

$$\eta = K\gamma^{N-1} \qquad \text{(Eq. 3)}$$

where the coefficients K and N need to be determined experimentally (I & EC Fund., 15(3): 215-218 (1976)).

Coaxial-cylinder viscometers have certain advantages over the cone-and plate geometry. First, the heat generated by the high rate of shear is dissipated faster in cylindrical instruments. Second, the tight V-shaped gap of the cone-and- plate geometry introduces inhomogeneity and drying-out when testing thick slurries due to a steep concentration gradient of the particles in the gap.

HIGH-SHEAR FLOW PHENOMENA OF NON-NEWTONIAN FLUIDS

The following discussion focuses on dispersions of particles which are the largest class of non-Newtonian fluids. These dispersions include both solid particles dispersed into a liquid phase and emulsions of an immiscible liquid finely suspended into another. Because it is desirable to characterize such fluids, the presence of a suspended phase necessitates understanding the origins of shear- and time-dependent rheology of suspensions.

Various flow phenomena arise when non-Newtonian fluids are being subjected to shear rates above 10 sec^{-1}. These can be classified into four main categories: (a) liquid or dispersing phase flow characteristics, (b) dispersed or suspended phase effects, (c) particle-particle interactions, and (d) polymeric effects when macromolecular substances are solubilized in the dispersing liquid phase. A thorough explanation and in depth analysis of these effects is beyond the scope of this report, but a brief discussion is included to provide some background for understanding the physical significance of flow curves obtained with the HHSV.

The dispersing liquid phase, often a Newtonian fluid like water or various solvents, demonstrates simple rheology by itself. The origin of non-Newtonian flow phenomena in most industrial fluids is attributed to various kinds of solid and liquid particles suspended in the liquid phase and/or polymeric macromolecules solubilized in it. The main effect is that, upon flow, momentum transfer through the bulk fluid changes because particles translated and rotate under the influence of the superimposed flow, in addition to the fluid motion. As a result, shear stresses may increase or decrease depending on (a) the disperse and dispersing phase interactions, (b) particle-particle interactions, which determine the degree of particle aggregation, and (c) mechanical interactions of the dispersed particles due to hydrodynamic effects. All these interactions, which can be physical, chemical, or colloidal, play important roles in suspension rheology.

Bulk rheological properties depend on a net potential energy manifested by the superposition of secondary forces (i.e., electrostatic, van der Waals, steric, and solvation) and mechanical effects due to hydrodynamic phenomena. A flow "structure" of complex nature develops within non-Newtonian fluids, as an effect of all of the above interactions. Thus, the equilibrium between association and disassociation of particles that form this structure controls rheology under shear. When the particles are also asymmetric, orientation plays an additional role.

Suspension rheology at low solids concentration is primarily dictated by the particle-liquid interfacial interactions. Under shear, there is enough liquid phase between particles to lubricate them, and the interaction between particles is mainly conducted by the liquid. With increasing solids content, however, the mean distance between particles decreases and drastic interactions such as particle-particle and hydrodynamic effects influence the flow.

Dispersed particles occupy a certain portion of the total volume available, which, consequently, is excluded from occupation by the continuous phase. This volume is directly proportional to volumetric concentration, and size and shape distributions of the dispersed phase. However, it cannot be determined precisely with either theoretical or experimental methods since the state of particle-liquid and particle-particle interactions is not know a priori. This is because particles are usually surrounded by an immobilized liquid layer (solvation layer) which is being dragged along the particles' pathlines in flow. The thickness of this layer depends on the electrokinetic potential of the particle surface, the ionic strength, polymer adsorption, and ionic interactions between the particles and the continuos phase. Thus, any functional relationship between the bulk resistance to flow and volumetric concentration depends on the closeness of the particles packed together under shear.

Hydrodynamic effects, which control the collision frequency of particles, play an additional role in determining maximum packing under shear. As volumetric concentration increases so does bulk viscosity, and these effects have a stronger impact on the characteristic streamlines of flow. Determination of packing efficiency (the ratio of volumetric concentration at a certain shear level) at various levels of shear is not a trivial exercise. This is because the rates of association and disassociation of particles under shear cannot be estimated precisely due to complex contributions of all the different interactions mentioned above.

Another critical parameter affecting bulk rheology is the state of particles' flocculation and aggregation. Association of particles due to particle-particle interactions induces formation of internal structural network in suspension generating three-dimensional lattices. Before initial shearing, the state of dispersion and its ability to start flowing depend on the potential energy barrier that keeps particles apart, which is determined by the secondary forces. At low shear rates (e.g., in the lower one third of the up curve in a 0-4,400 rpm cycle) suspension structure resists deformation and, sometimes, flow does not even occur until destruction of internal networks is completed. At higher shear rates, internal structure-breaking due to shear competes with structure-forming due to increased frequency of collisions between particles. Electroviscous effects arising from double-layer

interactions, changes in the ionic strength of the suspension, and the presence of polymeric polyelectrolytes play and additional role in bulk rheology. These effects are manifested by the existence of an electrical double-layer, surrounding all particles in suspension, since zeta potential (ζ) usually increases viscosity. For example, poor colloidal stability has an adverse effect on viscosity, while particle orientation and shape effects usually reduce high-shear viscosity.

In additional to deformation rate-dependent viscosity, shear history affects rheology due to the ability of many fluids to "remember" previous treatments. Suspensions deformed for the first time have different rheological properties from the ones occurring after cessation of flow. Structural networks break down on the accelerating shear rate portion of a rheogram and reform on the decelerating portion. The hysteresis loop between the up and down curves, therefore, is assumed to measure power loss during a testing cycle. (This loop may also appear with truly Newtonian fluids hence it is generated by viscous heating which causes viscosity to decrease). Newtonian fluids recover almost instantaneously upon removal of shear, but the recovery time of non-Newtonian fluids depends on both particle orientation and collision effects during structure rebuilding. An exception is viscoelastic fluids which have very long-lasting memory because they exhibit elasticity, in addition to viscous behavior.

Solubilized polymeric substances in dispersions, like natural or synthetic polymers, also have a profound effect on bulk rheology. Although these additives are primarily utilized to control water retention, they dramatically affect thixotropy and increase the viscosity's sensitivity to temperature. This is because solubilized macromolecules create a gel-like network in suspension, which is stronger than the network induced by particle-particle interactions, that traps a large amount of the otherwise unbound liquid phase. As a result, both the 'water holding' ability as well as low-shear (below 1,000 sec^{-1}) viscosity increase. As shear rate increases, however, gels are destructed and release entrapped water, so that high-shear viscosity decreases. Once destroyed, gels may reform upon cessation of flow.

Summarizing, both particle-liquid interface and particle-particle interactions manifest the shear- and time-dependent rheology of suspensions. These interactions control formation and/or destruction of long-range structures in suspension, so that viscous behavior depends on the rates of association and disassociation of suspended particle under shear. Since rheology of suspensions is a very complex issue, only general and sometimes vague structural concepts may be related to features of non-Newtonian fluid flows. To predict the viscous behavior of these fluids, however, precise knowledge of microscopic

states is not necessary. Macroscopic or phenomenological data, i.e., the shear stress-shear rate relationship, are sufficient to access rheology in a variety of flow fields with practical interest. This kind of information can be obtained conveniently and reliably with viscosity measurements, hence contributing to the understanding and control of rheological properties. In the next few paragraphs, non-Newtonian fluids are categorized based on their response to flow, which is expressed by graphs of torque as a function of rotational speed (rheograms). An attempt is made to explain this relationship by incorporating some structural concepts.

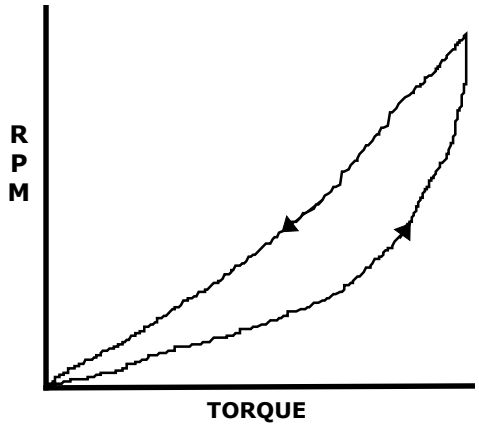


Figure 3

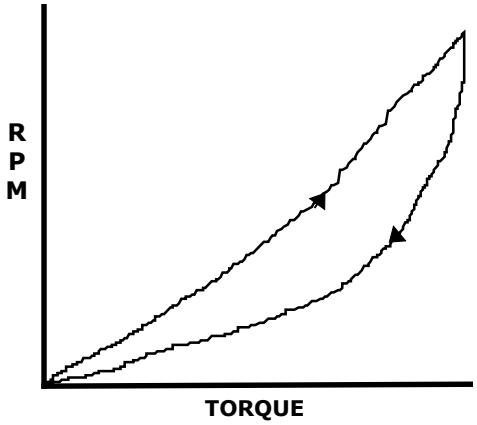


Figure 4

TIME-DEPENDENT PHENOMENA

Thixotropy

Rheograms of thixotropic fluids are characterized by a hysteresis loop between the increasing shear rate (up) and the decreasing shear rate (down) curves; the latter always falls to the left of the up curve (Figure 3). Thixotropy is manifested by catastrophic breaking of the internal structure in a suspension during the up curve and reforming on the down curve. Upon shearing, the fluid attains a state of lower potential energy due to structural changes which depends on both chemical and hydrodynamic processes. The loop quantifies power loss during continuous input of energy into the fluid sample undergoing testing and it is independent of any thermal effects. Thixotropy therefore can be defined as an isothermal, reversible reduction in viscosity with shear rate. The amount of thixotropic breakdown is sensitive to the previous shear history of the fluid, since structure reforms upon cessation of flow, but also depends on the rate of change of shear rate and its maximum value. A thixotropic loop appears in all rheograms of dispersions when the maximum shear rate exceeds approximately 10,000 sec^{-1}.

Rheopexy (or Anti-Thixotropy)

This phenomenon is the opposite of thixotropy, hence the down curve falls to the right of the up curve (Figure 4). It is defined as an isothermal, reversible viscosity increase with shear rate and it occurs when the maximum shear rate is relatively low, usually below 10,000 sec^{-1}. Rheopexy is manifested by internal structure forming due to increasing collision frequency between particles with shear.

It is important to keep in mind that both thixotropy and rheopexy are time-dependent, reversible processes; i.e., upon cessation of flow, internal structure is recovered when the fluid is left to rest for a prolonged (recovery) period time; the recovery time depends on orientation and collision effects. In thixotropic fluids, structure is being rebuilt and diminution of viscosity with shear is not permanent. Irreversible structural changes upon shearing are possible with fluids having extremely long recovery times which, from a practical viewpoint, are not attainable. An example is yogurt, where biological structure is permanently destroyed and viscosity loss over a shearing cycle is a definite occurrence.

Upon shearing a sample in viscometric flows, interchangeable time-dependent behaviors maybe evident, i.e., thixotropic to rheopectic or vice versa (Figures 5a, b). These types of rheograms are termed "scissored" as structure forming (Figure 5a) or structure-breaking (Figure 5b) occur in the up curve, while the fluid is nearly Newtonian on the down curve. Flow curves like the ones in Figure 5b are common with suspensions containing solubilized hydrocolloids (e.g., carboxymethylcellulose, alginates, etc.) where the dominant gel-like structure resists flow at low shear rates, but viscosity decreases at higher shear rates hence the structure is being destroyed.

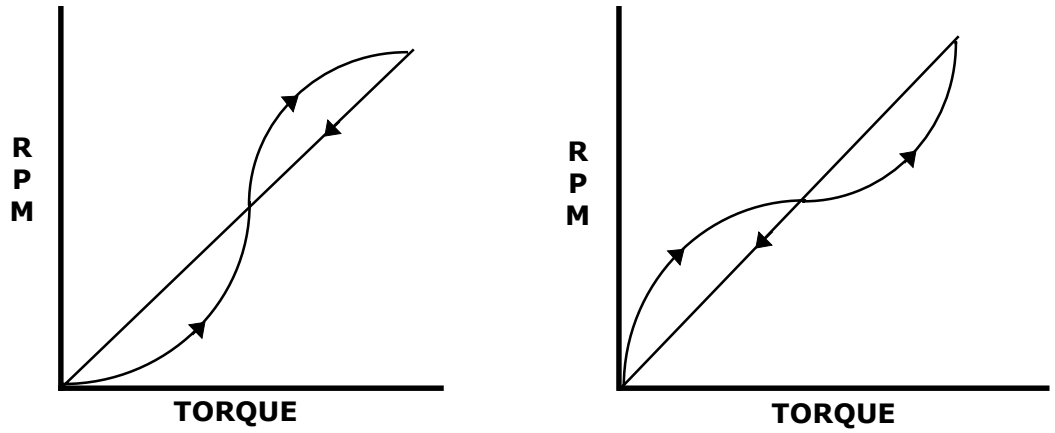


Figure 5a & 5b

SHEAR-DEPENDENT PHENOMENA

Shear-Thinning (Pseudoplasticity)

In this non-Newtonian flow phenomenon, viscosity decreases with shear rate (Figure 6) because both secondary and primary bonds are being broken isothermally and reversibly. Then, clusters and aggregates of particles originally present in suspension are destroyed by shear. Specific mechanisms responsible for this kind of rheological behavior are: (a) structure-breaking due to hydrodynamic effects where the rate of particle disassociation is greater than the rate of their association; (b) favorable orientation of macromolecules or dispersed asymmetric particles in the flow field; and (c) diminution or removal of the absorbed film (solvation layer) surrounding the particles due to hydrodynamic effects. The degree of shear-thinning depends on the structural state of the dispersion prior to shearing and on the composition of the dispersing phase. Consequently, hydrocolloids are excellent shear-thinning agents.

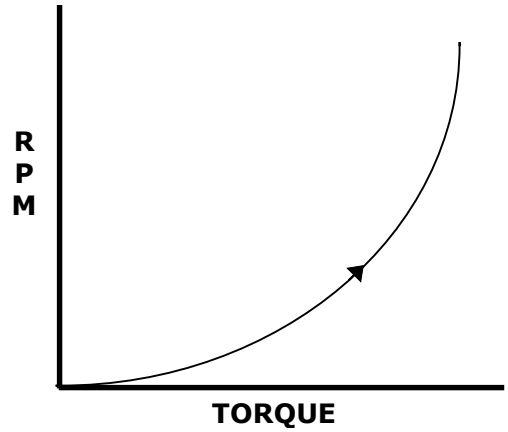


Figure 6

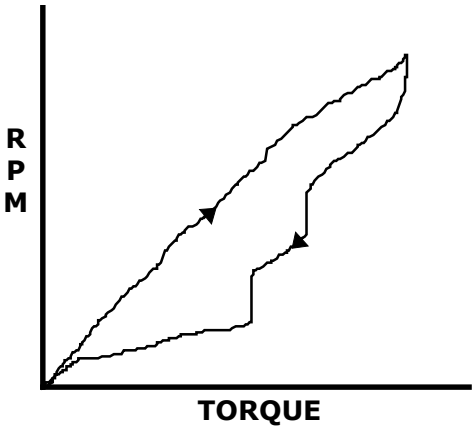


Figure 7

Shear-Thickening (Dilatancy)

This is an isothermal and reversible viscosity increase as a function of shear rate (Figure 7). Shear-thickening can be subdivided into two different categories depending on its origin. Volumetric dilatancy (or shear blocking) as appearing in Figure 8 is characteristic of highly concentrated dispersions, i.e., above 60% by weight, where the particles are closely packed together. At rest, or under slow movement, the particles fit into the voids of adjacent layers and flow is possible. At high shear rates, however, particles begin to slide over adjacent

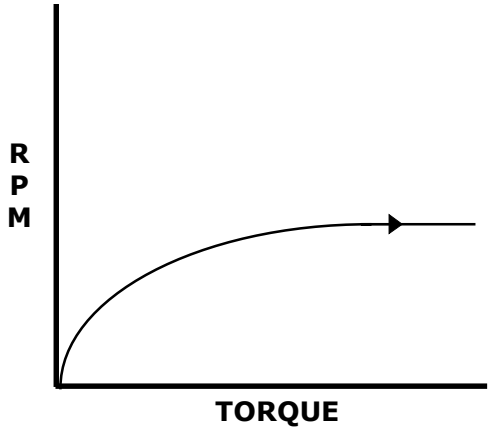


Figure 8

layers since they can no longer fall into the voids. Under these circumstances resistance to flow increases to a degree that causes the fluid to behave in a solid-like manner. Characteristics of shear-blocking are volumetric expansion (dilation) and a noticeable surface drying next to the high shear region. The specific solids concentration that induces volumetric dilatancy varies with particle size and shape distributions, as well as the stability of dispersion (i.e., the dispersion quality).

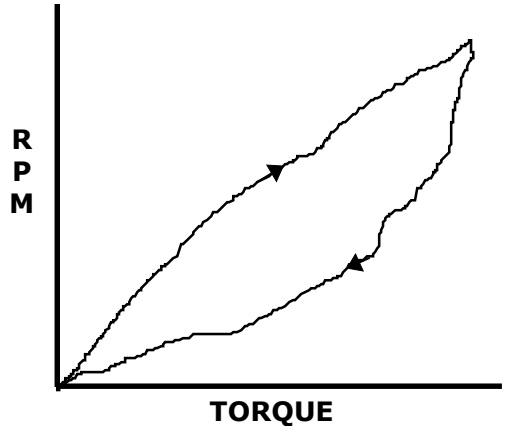


Figure 9

Another kind of shear thickening is rheological dilatancy (Figure 9). Rheograms of fluids possessing this behavior exhibit shear-thickening at the lower part of the up curve, but switch to shear-thinning at high shear rates. This behavior can be attributed to: (a) localized increase in particle concentration, such as shear-induced flocculation or aggregation, and (b) progressively increasing rates of particle alignment due to a flow velocity gradient that competes with dis-alignment due to Brownian motion. Rheological dilatancy depends on particle size and shape; it may occur at volumetric concentrations as low as 15% for large flat platelets like delaminated clays. It also depends on colloidal stability, so that poorly stabilized systems develop dilatancy at relatively lower shear rates.

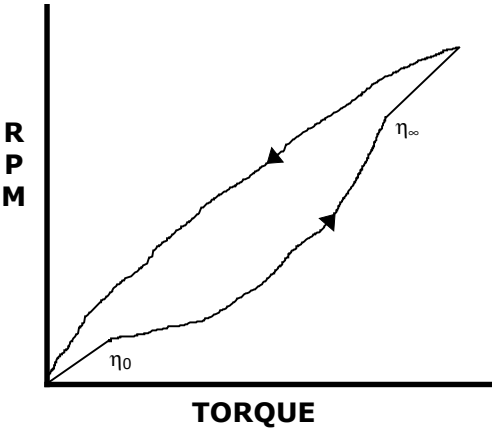


Figure 10

Structural Viscosity

This is a general type of shear-thinning behavior designated by rheograms which illustrate three distinctive regions (Figure 10): (a) Newtonian flow at low shear rates, corresponding to the zero-shear rate limiting viscosity, η_0; (b) a non-linear, usually shear-thinning, region at intermediate rates of shear; and (c) the second Newtonian regime at high shear rates where viscosity corresponds to a second limiting value,

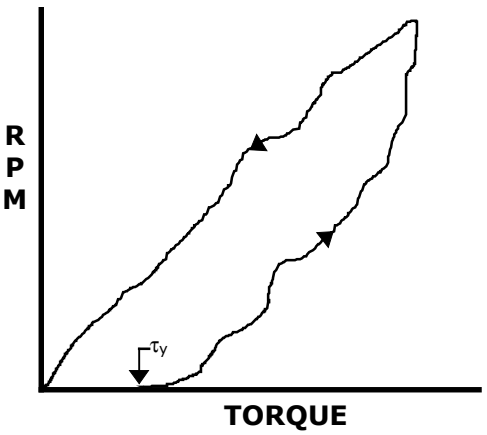


Figure 11

η_∞. Although in many cases η_0 is smaller than η_∞, this may not be always true. Structural viscosity is attributed to structure-breaking upon shearing, and fluids which appear shear-thinning or thickening over a limited range of shear rate actually exhibit this type of behavior over a wider range.

Plastic Fluids

This the phenomenon where, upon shearing, flow does not develop until a critical shear stress (or torque), termed yield stress, is exceeded. At stresses smaller than this characteristic value, the system behaves almost like a solid and deforms elastically, i.e., its viscosity approaches infinity. As shear rate increases, however, the developing stresses become greater than the yield stress and the fluid begins to flow exhibiting one or more of the flows described previously (Figure 11). Plastic flow behavior originates from strong particle-particle interaction and association due to secondary forces. The synergistic effect of these forces establishes a structure in suspension which must to be destroyed before flow can begin. Factors such as particle concentration, pH, and the type and amount of the dispersing agent determine the exact value of yield stress (τ_y).

Table 1. Characteristic shear-rate ranges (in sec^{-1}) occurring in some industrial processes.

Mixing	10 – 500
Pumping	10 – 300
Dispersion	10^2 – 10^4
Brushing	10^3 – 2 x 10^4
Rolling	10^3 – 4 x 10^4
Spraying	10^4 – 10^6
Reverse-roll coating	10^4 – 10^5
Air-knife coating	3 x 10^4 – 2 x 10^5
Blade coating	5 x 10^5 – 1.5 x 10^6

IMPLEMENTATION OF VISCOUS BEHAVIOR

GENERAL REMARKS

Viscosity, in particular non-Newtonian viscous behavior, is an important material property that contributes to a fluid's performance, and often is the main source of problems in handling, processing, and application. Viscous fluids are commonly associated with the perception of "richness," of having "body," which gives desirable appearance and texture in numerous products of everyday life. Various pseudoplastic foodstuffs like ketchup, mustard, cake frostings, etc., for instance, become thin upon spreading or chewing but, having a high yield stress, do not flow from their own weight — a feature desirable in frostings but one which makes ketchup difficult to pour out of a bottle. More complex functional features are required for specialty fluids like paints, adhesives, coatings, and emulsions, where processing requirements should also be considered in addition to end use performance.

Since a wide range of shear rates prevails when processing non-Newtonian fluids (Table 1), the deformation rate- and time-dependent rheology introduce complicated and, sometimes, unexpected problems in handling, processing, and application. Unique features of the flow field in every stage or unit operation of a process determines the relationship between rheological properties, measured in simple viscometric flows, and the hydrodynamics associated with complex flow fields. Thus, single-point or viscosity measurements in a limited range of shear rates cannot predict, or allow for extrapolation of, rheology at higher shear rates. Although many operations are characterized by high shear rates, above 10^3 sec^{-1}, a few important processes like pumping, mixing and brushing occur at relatively low rates of shear, i.e., 10^2 to 10^3 sec^{-1}.

The following discussion gives examples for implementing HHSV measurements in handling, processing, and application of suspensions or slurries of solid particles in liquid media, such as paper coatings, paints, etc.. Due to the large number and range of variables encountered for these fluids, flow behavior varies over a tremendous range. It is beyond the scope of this booklet to present details about the fluid mechanics in various hydrodynamic fields. Only quantitative discussions of some common processes like mixing, dispersion, pumping, coating, and end-product applications are presented.

In contrast to low viscosity Newtonian fluids, whose flow is usually turbulent, viscous non-Newtonian fluids flow in laminar flow streamlines. This observation significantly impacts fluid motion during mixing, dispersing, and pumping since laminar flow hinders

effective mixing; exhibits very high pressure drop in pipelines and fittings; and requires excessive power consumption for pumping. For instance, pseudoplastic fluids mixed in a Cowles disperser, where high shear rates and stresses exist close to the serrated disc rotor, exhibit low viscosity at the center which progressively increases at distances further away from the rotor. Effective mixing and dispersing, therefore, are only accomplished in the region near the rotating disc where flow is turbulent. A worst-case scenario occurs with plastic fluids, which may not even flow at all at some distance from the center. Thus, high shear is not always beneficial for mixing and dispersing solids in liquid media, whereas large diameter, slow moving impellers can be more efficient. Slightly dilatant slurries are more effectively processed in slow moving mixers with large diameter impellers like sigma mixers.

Rheological properties of fluids also influence the requirements for transport equipment. Centrifugal pumps do not work properly with viscous fluids, and piping requirements for non-Newtonian fluids are drastically different from that of Newtonian fluids. This is because the pressure drop due to frictional losses can be so high that in many cases the positive suction head reduces dramatically, and causes cavitation. With dilatant fluids, for example, pumping efficiency drops to very low levels because power consumption is unusually high. On the other hand, processing of fluids exhibiting high yield stress causes evolution of air bubbles which can not be easily removed and have deleterious effects upon fluid application processes. On transportation in pipelines, pseudoplastic fluids demonstrate pressure drops which are much less sensitive to flow rate than with Newtonian fluids, i.e., small changes in pressure cause great changes in flow rate. Consequently, pressure needs to be monitored carefully in unit operations where accurate fluid metering is required.

Viscous non-Newtonian fluids create problems in storage tanks and during movement from large reservoirs into small diameter pipes. Maintaining fluid motion throughout the whole volume of a storage container or mixing tank to prevent stagnation is difficult and, sometimes, impossible. On attempting to drain the tank, non-Newtonian fluids create stagnation pockets in the apex of the downstream walls where recirculating vortices develop. Plastic fluids, for example, will never completely drain as portions of the fluid move like an unsheared plug while a sheared mobile layer exists next to the walls of the reservoir. In confined geometries such as those occurring in molding and lubrication, however, the flow of plastic fluids has different features. No flow occurs anywhere until a minimum stress is reached, and thereafter flow develops over the entire field. In such hydrodynamic flows, no plug region exists and flow develops everywhere until the yield condition is no longer satisfied, after which flow must again stop everywhere.

PAPER COATINGS

Rheology is important in preparation and assessment of paper coating "colors," a blend of mineral pigments, binders and polymeric additives, since experience has shown that control of the color viscosity to within certain limits results in a desired coat weight and a satisfactory coating layer. Processes involved in paper coating operations are preparation, transportation, and application of color, where the ultimate goal is to continuously apply a uniform layer of liquid with a well-controlled thickness to the paper. Although similar processes are involved in coating other substrates in film form, paper is one of the most complex systems due to its compressibility and porosity.

The state of dispersion of pigments in slurries depends on the degree to which shear-induced forces separate individual particles. Optimum dispersion (having low viscosity) occurs when these forces are utilized effectively by running a mixer at high speed (i.e., high shear rates) and by making the slurry at high solids (i.e., high stresses), since the product of shear rate and stress represents energy input into the system. Thus, slightly dilatant slurries more efficiently utilize dispersing energy, but excessive dilatancy has deleterious effects as most of the fluid is carried rather than sheared around on the mixer impeller.

Upon addition of binders and polymeric substances, coating slurries usually become shear-thinning, primarily because of the decrease in volumetric concentration of solids. In addition, interactions between pigment particles, binder, and polymers form internal structures into suspension which, together with particle-particle interactions, controls rheology at low shear rates such as those occurring during screening, pumping, and transportation to the coating machine. The colors' ability to flow depends on the strength of this structure, which must be broken down in short periods of time upon shearing in screens, pumps, and pipes. Solubilized polymers, for instance, introduce rheological dilatancy at low shear rates, in the lower one third of a 0-4,400 rpm cycle with HHSV, which changes to shear-thinning as shear rate increases. Therefore, colors containing polymeric macromolecules that build protective hydrocolloids are difficult to handle and transport, but provide good flow control at high-shear regions, such as in the application zone of a coater.

Rheology of colors and the relationship of shear stress to shear rate also depend on intensity, time of initial deformation or mixing, and aging. Prolonged mixing in a high-shear device, for instance, eliminates structures formed during dispersion while it increases temperature. Such treatment reduces thixotropy and can remove rheological dilatancy appearing in scissor-like flow curves.

Coatings applications on paper can be divided into two main categories: (a) application of excess fluid to the substrate with an applicator roll, or other means, which is typically metered off with a blade, air-knife, roll, etc., and (b) a system where a flexible blade acts both as a reservoir to bring the color in contact with the substrate, and as a metering (doctor) unit, like in puddle and "short-dwell" coaters.

In systems with an applicator roll, viscosity determines the stability of color pick-up and the amount transferred to the substrate before metering. The roll picks up color through a relatively low shear rate process which requires some degree of non-Newtonian structure, since Newtonian and dilatant fluids have a tendency to splash and run off the roll. On transferring color from the roll to the moving substrate, some structuring is also desirable to avoid splashing and non-uniform film-splitting. This process quantitatively determines the color layer (filtercake) going into the doctoring device, and, therefore, controls the mass flow rate entering the metering nip. Highly viscous, mildly dilatant colors increase the thickness of the pick-up layer and, consequently, increase coat weight, all other operational variables remaining constant, because of the higher mass flow rate into the metering nip. Excessive thixotropy, in combination with high viscosity at relatively low shear rates, adversely affects the back flow of the color from the doctoring device.

In the vicinity and under the metering nip, the flow approximates a lubrication flow field where shear rates above 10^6 sec^{-1} prevail, and therein viscosity does not influence coat weight. This is exactly the reason why experience has shown that rheograms obtained with a Hercules® Hi-Shear Viscometer at shear rates ranging from sec^{-1} can be successfully utilized for coat-weight determination and quality control. Processes which actually affect coat weight occur at much lower, at least by a factor of 10, shear rates than those occurring under the nip.

Color rheology also affects the hydrodynamic stability of puddle-type or short-dwell coaters by modifying the characteristic streamlines in the pond upstream. Unsteady recirculating flows (vortices), which may develop as machine speed increases, can disturb the laminar layer in contact with substrate entering the nip and, therefore, create non-uniform coat-weight profiles. This effect will be more dramatic for colors containing highly asymmetric pigment particles (i.e., which may have a width comparable to the metering gap) at high volumetric concentrations, where proper orientation of particles in the vicinity of the nip is critical.

As solids concentration in colors increases, volumetric dilatancy generates problems which deteriorate the quality of the coating film exiting the metering zone downstream. Appearance of "lines" running along the machine direction where color is depleted are known as streaks and are associated with wiskering and formation of "stalactites" on the backside of a blade. Formulations which exhibit rheological dilatancy and/or yield stress do not always show such problems and they are advantageous in the sense that they form more stable laminar layers before metering. However, they require greater pumping power are more difficult to transport.

PAINTS AND OTHER APPLICATIONS

Rheology of paints is another example of implementing viscous behavior to application and end-product performance. Because paints are pseudoplastic or plastic, high viscosity at relatively low shear rates means that large amounts of them can be held on a brush without dripping. When applied on a surface, shear rate increases hence decreasing viscosity which results in easy spreading for good coverage. In processes like rolling, brushing, and spraying, thixotropy plays the predominant role. Shear-thinning paint formulations which also have a high degree of thixotropy, i.e., demonstrating a substantial reduction in viscosity with shear and time, have good leveling properties but develop sagging problems. Formulations, on the other hand, which have relatively high viscosity that is not significantly affected by time do not exhibit sagging, but have poor leveling capabilities.

Foodstuffs, pastes, adhesives, lubrication greases, and cement slurries require closely monitored rheology for optimizing their end use performance. Compounds with high yield stress, for instance, have low leveling capacity when applied on smooth, horizontal surfaces. Nevertheless, they demonstrate good coverage and produce a thick layer when applied on a vertical surface. Thus, sealants and adhesives require controlled yield stress to prevent dripping when applied, but yet can easily flow out of their original tube. As these compounds are made to flow, viscosity has to be high enough to hold their extruded form, yet low enough (shear-thinning) to provide good spreading; a property required for working them into areas in need of filling. After spreading, there must be sufficient thixotropy to permit structural recovery, which allows the fluid to keep its form in the filled area until curing.

INTERFERENCES IN INTERPRETATION OF RHEOGRAMS

Proper interpretation of rheograms and calculation of apparent viscosity are valid only when all approximations defining planar Couette flow are satisfied. Erratic results may be obtained from either improper operation of the instrument or an indication that some reservations should be encountered, such as lower maximum shear rate for extremely viscous fluids. Although, in general, the Couette flow assumption pertains to testing fluids with an assumption pertains to testing fluids with a Hercules® Hi-Shear Viscometer, improper sample preparation and testing procedures can generate erroneous results. In addition, certain phenomena independent of material properties, such as hydrodynamic events or air entrainment during testing, may interfere with a measurement.

The scope of the following discussion is to show how some of these interferences can be identified and, sometimes, prevented or corrected. This does not mean to suggest that all kinds of interferences will be present in every viscometric test. Some features, like slipping and the associated air entrainment, represent characteristic properties of the fluid under consideration and should be reported as such since in practice such a fluid will also be unsatisfactory. In other words, the instrument in its way is indirectly indicating that a fluid may be problematic during its application or limited to its performance.

VORTICAL FLOWS

The curvilinear movement of fluid in the annular gap of HHSV induces three-dimensional hydrodynamic instabilities when the rotational speed of the bob increases beyond a critical value depending on gap dimensions and viscosity. At first, disturbed flows (resembling a stack of automobile tires stacked on top of each other) appear, termed Taylor vortices. These flows become periodic in time with single and double frequencies of oscillation at higher speeds. Such hydrodynamic flow instabilities will eventually degrade to turbulence at even higher rotational speeds. Taylor vortices can sometimes be visualized on the air-fluid interface at the top endface of the bob during the course of a test.

Theoretically, onset of Taylor vortices depends on the following criterion for the modified Reynolds number (Re_m) in Couette flows:

$$Re_m = \left(\frac{(rpm)\rho\, R_1\, X_0}{9.55\eta}\right)\sqrt{\frac{X_0}{R_1}} \angle 41.3 \qquad \text{(Eq. 4)}$$

Where X_0 is the annular gap in cm and ρ the density of the fluid in gm/cc. The onset of vortical flows constitutes an interference as the total torque measured increases due to additional stresses introduced by hydrodynamic instabilities. However, this increase in torque does not relate to rheological properties of the fluid.

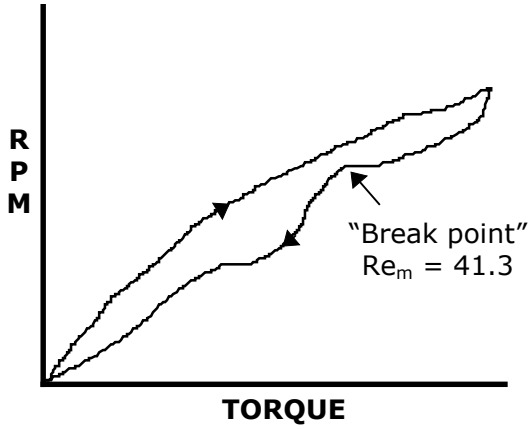


Figure 12

Development of vortical flows appears on the up curve of the rheogram as a distinctive point or sharp transition, referred to as "break point," above which the flow curve shifts to greater viscosities since the slope of the drawn curve becomes steeper (Figure 12). Although rheograms with a break point can be recorded even when testing Newtonian fluids, confusion can be created when the fluid is non-Newtonian because the shape of the flow curve due to vortical flows resembles dilatant-type behavior. Utilizing the criterion listed in Eq. 4, however, it can be clearly determined if vortical flow interferes with a measurement by calculating the (theoretical) critical speed (RPM_{cr}) for onset of vortical flow as:

$$RPM_{cr} = \frac{41.3\eta}{G\rho} \qquad \text{(Eq. 5)}$$

where viscosity is manipulated on the up curve at the break point and G is a geometrical factor pending on the size of the bob used:

$$G = \left(\frac{R_1 X_0}{9.55}\right)\sqrt{\frac{X_0}{R_1}} \qquad \text{(Eq. 6)}$$

Numerical values of factor G are 1.63×10^{-3} (bob A), 0.42×10^{-3} (bob E), and 0.15×10^{-3} (bobs F and FF) which, when substituted in Eq. 5, provide an answer in rpm. If the calculated RPM_{cr} is close to the speed corresponding to the break point rpm from the rheogram, then increased viscosity in a flow curve is a hydrodynamic effect and it does not represent dilatancy. The critical rotational speed for onset of Taylor vortices depends on gap width (smaller gaps require higher speeds for vortical flow to occur) and on the fluid properties, namely viscosity and density. The speed required for onset of unstable flow is

proportional to viscosity. For example, flow interferences appear in rheograms with the E-bob geometry during a 0-4,400 rpm testing cycle when viscosity is less than 6.2 cps.

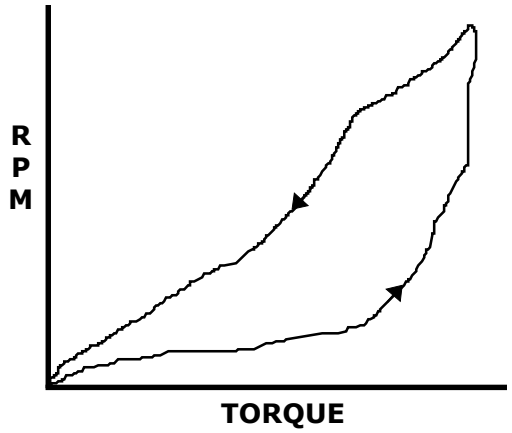


Figure 13

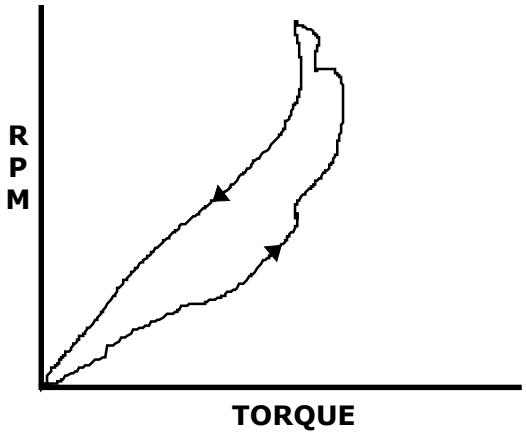


Figure 14

TEMPERATURE EFFECTS

The approximation of isothermal conditions during an HHSV test is another assumption that warrants concern, as the thermodynamic temperature rise due to viscous heating generates a temperature gradient across the gap. Because the gaps utilized with HHSV are very small and the thermal conductivity of the metallic walls is high, the relatively large surfaces of the bob and cup act as heat sinks. Therefore, the energy dissipated as viscous heat during a testing cycle quickly transfers from the fluid to the walls, and the system may be assumed isothermal. The temperature difference across the gap, under stationary conditions, has been measured to be approximately 1°F and is, therefore, considered negligible.

Thermal control at all shear rates is difficult even with installation of a constant temperature bath around the cup wall. This is because viscous heating during the small time period of a test (i.e., 20.4 sec from 0 to maximum rpm) cannot be dissipated quickly enough to keep the sample under controlled temperature. Heating effects influence viscosity measurements of thick fluids, having viscosity above 300 cps at few reciprocal seconds or as measured with a Brookfield viscometer, at shear rates above 30,000 sec^{-1} (Figures 13, 14). As an example, paper coating suspensions demonstrating such high low-shear viscosity can show a temperature rise between 2 to 40°F undergoing a 0-4,400 rpm testing cycle with the E bob.

END AND WALL EFFECTS

In the mathematical analysis of HHSV measurements, the gap width is approximated as being small in comparison to its vertical dimension, the bob height, so that radial Couette flow prevails therein. Shear forces at the top and bottom endfaces of the bob, however, can introduce deviations from ideal Couette flow. These deviations can be predominant at the bottom of the bob-cup configuration, since the entire bottom surface of the bob shears the fluid trapped between it and the bottom of the cup. As a result, an unknown but finite amount of torque is transmitted onto the cup wall, in addition to the torque exerted by the fluid inside the gap. This endface effect can be minimized when the gap width-to-height ratio is made very small, i.e., the radii ratio R_1/R_2 is as close to 1 as possible. In all the geometries provided with the Hercules® Hi-Shear Viscometer (except with bob D), the ratio is between 0.97 and 1 and, therefore, endface interferences can be considered negligible.

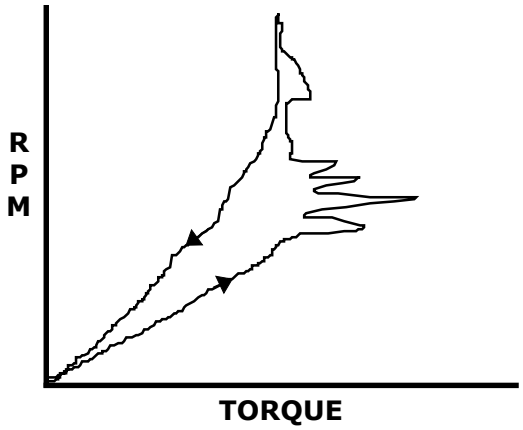


Figure 15

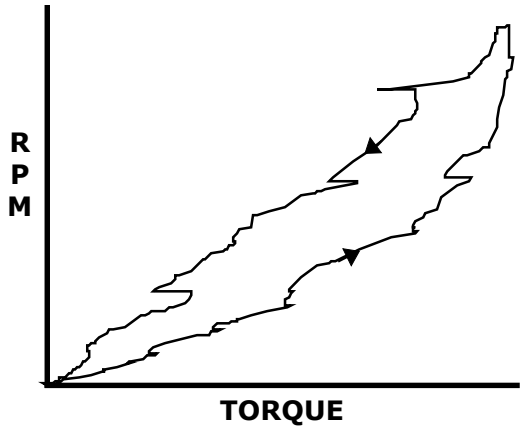


Figure 16

Interpretation of HHSV measurements becomes more complicated with suspensions containing dispersed solids, such as slurries in a low viscosity medium with solids volumetric concentrations above 40%. In such cases, the no-slip assumption that the fluid adjacent to a wall moves with the same velocity as the solid surface may be no longer valid (Rheol. Acta, 17:156-165(1976)). Upon shearing concentrated suspensions, for example, the local solids concentration may be lower at a wall than in the bulk so that large velocity gradients are being produced in the low viscosity layer next to the wall and, therefore, results in slipping. When this phenomenon occurs, torque cannot be uniformly transmitted across the gap throughout the total shearing volume. Rheograms with slipping exhibit unstable flow curves which are characterized by zig-zag patterns with large amplitudes of oscillation above a certain rotational speed (Figure 15). When the zig-zag patterns have small amplitudes and appear throughout the whole cycle of a test, they indicate existence of an excessive amount of finely dispersed air bubbles into the sample (Figure 16).

Slipping can also be visually identified as the rotating bob "cuts a hole" into the sample, which results when ambient air is sucked in the measuring zone. The assumed mechanism is that air displaces fluid in contact with the bob wall because viscosity next to this boundary is lower than in the rest of the sample, due to inhomogeneity arising from centrifugal forces or particle orientation effects.

Although slipping usually occurs with slurries having relatively high viscosity and yield stress, it should not be assumed in all of these cases. It can be detected by taking measurements with three bobs having different diameters, such as bobs A, E, and F. If mutually consistent shear stress-shear rate relationships are obtained, wall slip is not occurring. However, if inconsistent results are obtained, further analysis of the Couette flow is required to account for wall effects (J. Rheol., 2:210-216(1931); 32(1):53-67(1988)).

In general, curves representing shear stress as a function of shear rate and obtained during tests with different bobs should be the same, assuming that all bob-cup configurations are concentric. Inconsistent results, occurring in a series of HHSV measurements with the same fluid, are an indication that slipping is affecting the tests and that this is a characteristic property of the fluid. It may also be an indication that problems will be encountered when attempting to process and apply the fluid since slipping can induce ambient air entrainment in flows with moving free boundaries. Quantifying the linear speed at the bob wall corresponding to slipping, therefore, is critical for quality control.

OTHER CONSIDERATIONS

Heterogeneity of the testing sample may be experienced during viscometric flows of thick slurries. An example is the obvious settling of solid particles out of suspension when gravitational forces, which always act perpendicularly to the direction of flow, cause particles to settle to the bottom of the cup. The resultant solids concentration gradient creates a non-uniform and unknown distribution of rheological properties in the sheared volume. Inhomogeneity problems, however, are dominant only when viscosity of the liquid phase is low and solids volumetric concentration is high. Therefore, it is unlikely that such problems will occur with most paper coatings, paints, and polymeric solutions where the dispersing phase viscosity is high.

When shearing a fluid in a gap of HHSV, a radial pressure gradient develops which balances the centrifugal forces associated with the circular streamlines of Couette flow. For

ordinary Newtonian fluids, the free interface between ambient air and the fluid (on the top endface of the bob) is depressed next to the rotating bob since there is a higher pressure balancing the centrifugal force. Thus, a hydrostatic pressure gradient is established across the gap causing the free surface on the top to sink close to the rotating cylinder (bob). The opposite phenomenon is observed when normal forces are present with viscoelastic fluids as the fluid tends to climb up the bob wall. It is because of such circumferential pressure gradients that fluids, tested with a HHSV at high rotational speeds, have the tendency to roll and climb up the inner wall of the cup or the rotating bob against the force of gravity. If the circumferential pressure exceeds the vapor pressure of the fluid, vapor bubbles form which result in cavitation is determined from the force balance:

$$\left[\frac{(\text{rpm})R_1}{9.55}\right] > \sqrt{\left[\frac{2(P_{atm} - P_{vp})}{\rho}\right]} \qquad \text{(Eq. 7)}$$

where P_{vp} is the vapor pressure of the fluid.

Both circumferential pressure gradient and cavitation can introduce substantial instabilities to the smoothness of flow curves. As air displaces the fluid next to the bob or cup, stress can no longer be uniformly transmitted through the gap, and zigzag patterns appear on the graph in a manner similar to when slipping occurs (Figure 15). Two ways to avoid such disturbances are to (a) reduce the maximum rpm, or (b) overfill the gap with fluid such that the topface of the bob is covered with fluid. The second technique suppresses air entrainment because it removes the free surface, that induces instabilities in to the shearing zone of the gap, but it introduces an additional complication since the material above the gap contributes an unknown amount of torque, typically accounting for 10% of the total. Sometimes, however, it is difficult to attribute instabilities like zigzag patterns exclusively to a single cause, since they may arise from a series of different problems. A proper method would to investigate all probable causes and isolate a single one by eliminating all others.

Another problem commonly occurring in measurements with coaxial cylinders, especially when an instrument has been used for many years without preventive maintenance, is eccentricity of bob and cup, i.e., the bob rotation is not concentric with the cup (Figure 17). Eccentricity can be identified by plotting the moment coefficient C_M as a function of the modified Reynolds number Re_m in logarithmic axes (see Appendix A for calculating these dimensionless group variables). Data obtained with every concentric bob-cup system should fit a straight line having slope of negative one and intercept the x- and

y-axes in specific points (Figure 18). If vortical flow interferences are absent, data lines falling above or below the above (theoretical) line indicate eccentricity, and the bob and cup system needs to be realigned.

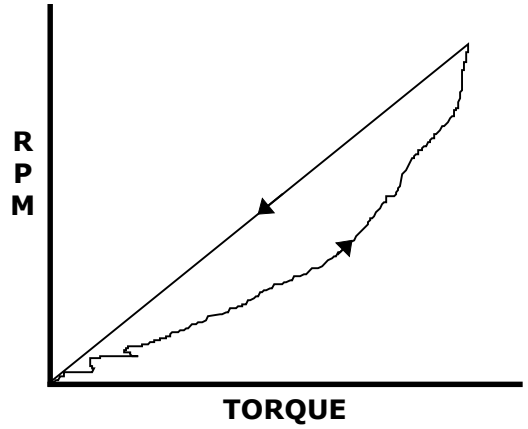


Figure 17

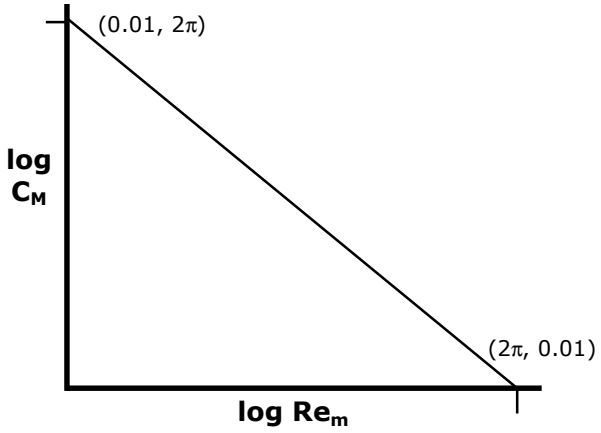


Figure 18

EPILOGUE

The Hercules® Hi-Shear Viscometer provides useful information for relating non-Newtonian viscous behavior of fluids to processing, application capabilities, and performance requirements. Although such information can be utilized to formulate multiphase fluids, like coatings and paints, and implement quality control predicting the precise respond of a fluid to the hydrodynamics of a specific process is not always obvious. This is because the flow features involved in many fluid mechanical processes are much more complicated that the one depicted in simple viscometric flows. Successful implementation of viscous behavior, therefore, relies mostly on practical experience rather than a well-substantiated scientific approach. Kaltec Scientific, Inc., maintains an extensive list of technical articles with reference to numerous applications of HHSV data, which are available upon request. It also provides technical assistance for properly interpreting rheograms.

APPENDIX A

Parameters and Mathematical Formulae for Viscosity Measurements with a Hercules® Hi-Shear Viscometer

The shear rate at a distance R from the axis of bob rotation inside the annular gap is:

$$\gamma = \frac{2\Omega R_1^2 R_2^2}{R^2 X_0 (R_1 + R_2)} \qquad \text{(Eq. A1)}$$

where Ω is the angular bob velocity (equals to rpm/9.55), R_1 and R_2 are the radii of bob and cup, respectively, and X_0 is the width of the annular gap. This expression applies only for Newtonian fluids, since for non-Newtonian fluids the shear rate profile in the gap is usually unknown. The shear rate, however, on bob's surface remains the same irrespective of the kind of fluid. By substituting R with R_1 in Equation A1:

$$\gamma(R_1) = \frac{2\text{rpm}(R_2^2)}{9.55 X_0 (R_1 + R_2)} \qquad \text{(Eq. A2)}$$

The shear stress (τ_1) in dynes/cm^2 exerted on the bob's surface from the fluid's resistance to flow is:

$$\tau = \frac{T_1}{2\pi R_1^2 H} \qquad \text{(Eq. A3)}$$

where T_1 is the torque and H the bob height. Because the ratios of bob to cup radii are very close to one, the measured torque T_2 at the inner wall of the restrained cup can be approximated by the average torque in the gap; i.e., $T \equiv T_2 \approx (T_1 + T_2)/2$.

Two useful dimensionless parameters for analyzing the hydrodynamics of Couette flow in a Hercules® Hi-Shear Viscometer are the Reynolds number (Re) and the moment coefficient (C_M). The Reynolds number is theoretically calculated as:

$$\text{Re}_m = \frac{\text{rpm}\ \rho\ R_1\ X_0}{9.55\eta} \qquad \text{(Eq. A4)}$$

where ρ and η are the density and absolute or apparent viscosity of the fluid. A modified form of this expression, to be used for estimating the critical speed for onset of vortical flows, is:

$$Re_m = \frac{rpm\ \rho\ R_1\ X_0}{9.55\eta}\ \sqrt{\frac{X_0}{R_1}} \qquad \text{(Eq. A5)}$$

The moment coefficient is equal to:

$$C_M = \frac{T}{\rho H \Omega^2 R_1^4} \qquad \text{(Eq. A6)}$$

The mechanical energy E, in erg/cm^3 per unit fluid volume, imparted to the fluid sample during its deformation in a test can be calculated from the following expression:

$$E = \eta\gamma^2 t \qquad \text{(Eq. A7)}$$

where t is the period of time during which the sample has been sheared, equal to 20.4 seconds when using the AUTO operational mode in a HHSV.

Table 2. Geometrical factors and other useful constants.

Parameter	Bobs (rotors)							
	A	**B**	**C**	**D**	**E**	**EE**	**F**	**FF**
Cup radius, R_2 (cm)	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Bob radius, R_1 (cm)	1.95	1.95	1.95	1.50	1.98	1.98	1.99	1.99
Bob height, H (cm)	5.00	2.50	1.00	2.50	5.00	1.00	5.00	1.00
Gap clearance, X_0 (cm)	0.05	0.05	0.05	0.50	0.02	0.02	0.01	0.01
R_1 / R_2	0.975	0.975	0.975	0.750	0.990	0.990	0.995	0.995
X_0 / R_1	0.0256	0.0256	0.0256	0.0333	0.0101	0.01	0.0050	0.0050
H / R_1	2.564	1.282	0.513	1.667	2.525	0.505	2.513	0.503
s-factor	0.00020	0.00041	0.00100	0.00620	0.00008	0.00040	0.00004	0.00020
G-factor	0.00163	0.00163	0.00163	0.00143	0.00042	0.00042	0.00015	0.00015
shear stress factor[a]	0.0084	0.0167	0.0419	0.0283	0.0081	0.0406	0.0080	0.0400
shear rate factor[b]	4.24	4.24	4.24	0.478	10.52	10.52	20.99	20.99

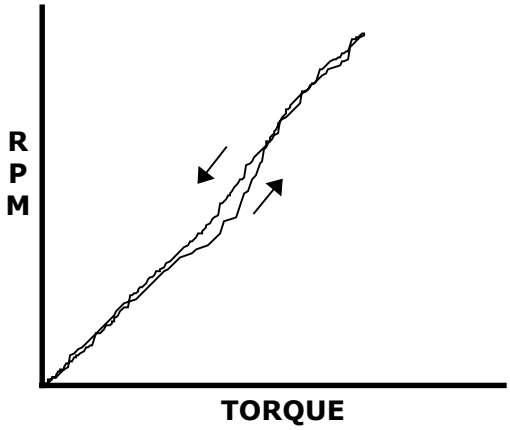
a) Factor x Torque = shear stress, as force per unit area, acting on inner cup wall. Its value has units of dynes/cm^2.

b) Factor x rpm = shear rate next to the bob surface. It represents the linear velocity gradient per centimeter of the flow field very close to the rotating cylinder. Its units: cm/sec per cm, or sec^{-1}.

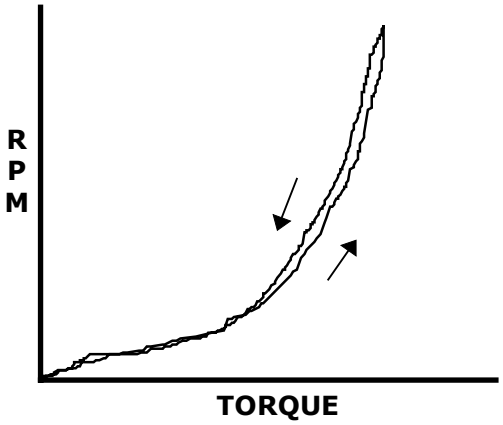
APPENDIX B

Characteristic Rheograms

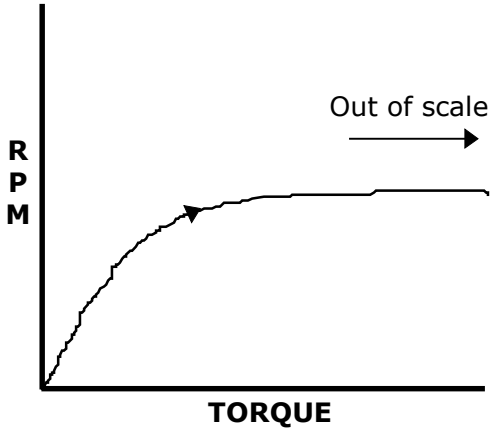
Newtonian:



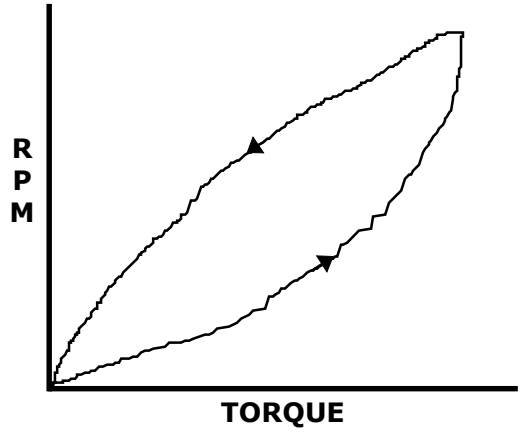
Shear Thinning (Pseudoplastic):



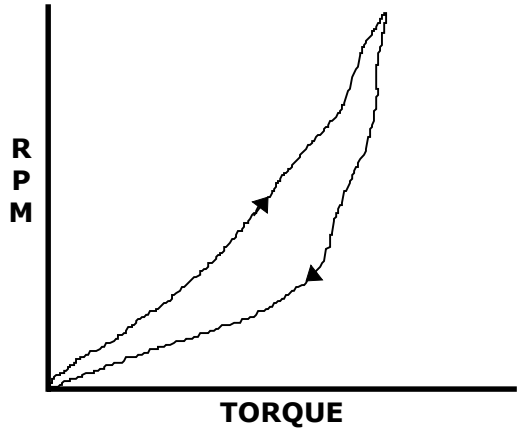
Shear Thickening (Dilatant):



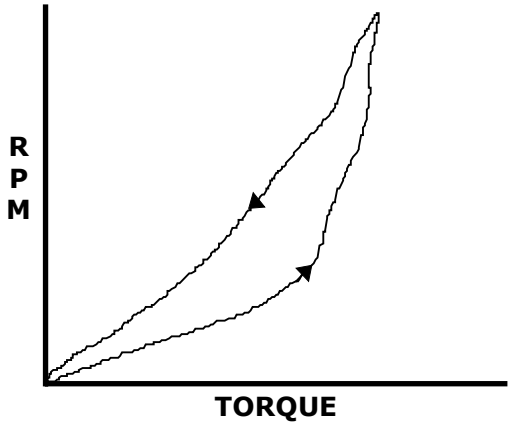
Thixotropic:



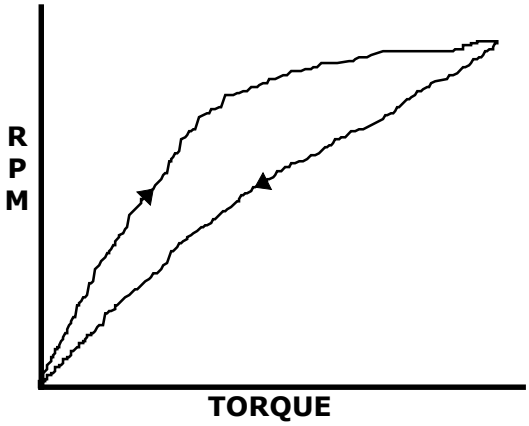
Pseudoplastic Rheopectic:



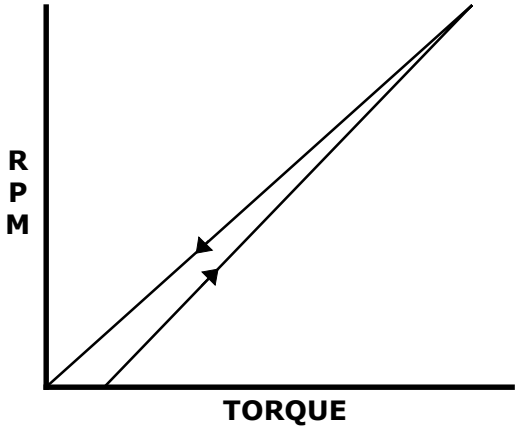
Pseudoplastic Thixotropic:



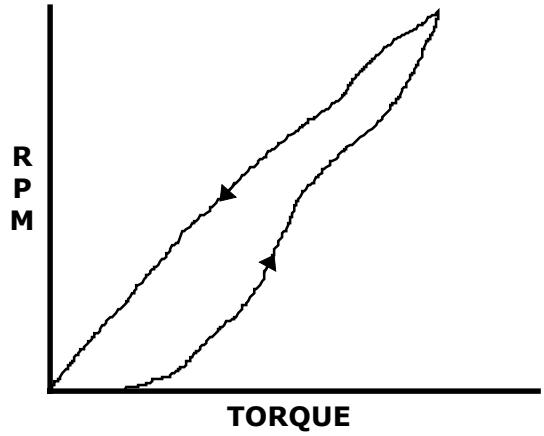
Dilatant Rheopectic:



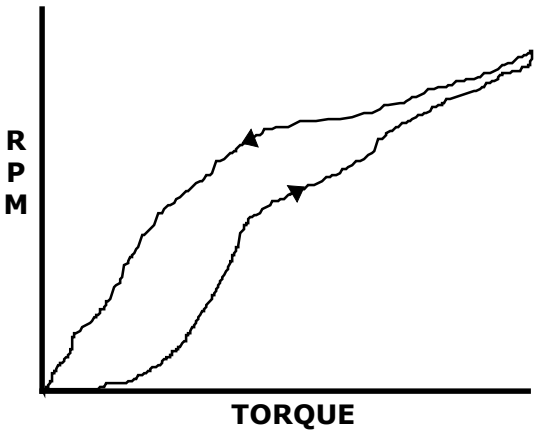
Bingham Plastic Thixotropic:



Plastic-pseudoplastic Thixotropic:



Plastic-dilatant Thixotropic:



APPENDIX C

Units and Useful Relationships for High-shear Rheology

PARAMETER	UNITS	RELATIONSHIPS
Force (F)	Newton (N)	1N = 10^5 dynes = 101.9716 gm_{force}
Torque (T)	Newton-meters (N-m)	1N-m = 10^7 dynes-cm
Shear Stress (τ)	Newton/meter^2 (N/m^2) Pascal (Pa)	1 N/m^2 = 1 Pa 1 Pa = 10 dynes/cm^2
Shear Rate (γ)	seconds^{-1}	sec^{-1} is the ratio of fluid velocity in cm/sec per cm field depth.
Viscosity (η) (absolute)	Poise (p) Centipoise (cp) Pascals-seconds (Pa-sec)	1p = dynes-sec/cm^2 = gm_{force}/cm-sec 1 cp = 0.01p 1Pa-sec = 10p, 1mPa-sec = 1cp
Kinematic Viscosity (ν)	stokes (s)	1s = p-cm^3/gm = cm^2/sec

APPENDIX D

Formulae for Determining Plastic Viscosities and the Leveling Index

The following parameters were invented to describe viscous non-Newtonian fluids (usually apply for pastes like starch solutions) from data obtained with high-shear rheograms. For purely shear-dependent rheological behavior, like with pseudoplastic and plastic fluids, these parameters are: (a) two "plastic viscosities" $\boldsymbol{U_1}$ and $\boldsymbol{U_2}$, calculated at two different rotational speeds, e.g., 2,200 and 4,400 rpm, and (b) the yield factor ***Y***.

Plastic viscosities are calculated from two points on the up flowcurve of a rheogram corresponding to a set of rotational speeds and torques, (RPM_1, T_1) and (RPM_2, T_2), respectively:

$$U_1 = \frac{9.55 T_1 s}{rpm_1 b} \qquad \text{(Eq. D1)}$$

and

$$U_2 = \frac{9.55 T_2 s}{rpm_2 b} \qquad \text{(Eq. D2)}$$

where parameter b represents the slope and it is equal to:

$$b = \frac{\ln\left(\frac{rpm_1}{rpm_2}\right)}{\ln\left(\frac{T_1}{T_2}\right)} \qquad \text{(Eq. D3)}$$

It is common practice to select the first point midway between zero and maximum speed, the second being the one corresponding to maximum speed at the peak of a rheogram.

In the case of plastic fluids, the yield factor ***Y*** can be estimated in dynes/cm^2 by measuring the horizontal displacement on the recording graph (in cm) from the origin and up to the point where flow begins, the flowcurve is not parallel to the x-axis. Then,

Y = (displacement in cm) × (spring or torque scale constant in dynes-cm per cm) × (the stress factor from Table 2, Appendix A).

For fluids which also demonstrate time-dependent (thixotropic) behavior, two more plastic viscosities can be calculated from points on the down flowcurve:

$$U_1' = \frac{9.55T_1's}{rpm_1'b'} \qquad \text{(Eq. D4)}$$

and

$$U_2' = \frac{9.55T_2's}{rpm_2'b'} \qquad \text{(Eq. D5)}$$

where

$$b' = \frac{\ln\left(\frac{rpm_1'}{rpm_2'}\right)}{\ln\left(\frac{T_1'}{T_2'}\right)} \qquad \text{(Eq. D6)}$$

The coefficient of thixotropic breakdown is then defined as:

$$M = (b - 1)\,[2(U_2 - U_1)] - (b' - 1)\,[2(U_2' - U_1')] \qquad \text{(Eq. D7)}$$

and the leveling index (***L.I.***) is:

$$L.I. = \frac{M}{U_2} \qquad \text{(Eq. D8)}$$

The leveling index parameter is used to indicate the ease with which a coating or other viscous pastes will level after leaving a metering nip. Expressed as a dimensionless ratio of the thixotropic coefficient to plastic viscosity, high L.I. is obtained when a fluid has a high degree of thixotropy and a low plastic viscosity. In general, L.I. values below 0.30 indicate poor performance in fluid application in low-speed coating process. This index, nevertheless, has limited predictability of rheological behavior in high speed operations, where immobilization of the coating layer occurs within milliseconds.