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Rheological instrumentation for the coating industry

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RHEOLOGY IS the science of understanding the flow and deformation of materials. It plays a key role in all coating processes, including film formation, curing, and aging. Because the cost of new product development is considerable, it makes sense to introduce rheological measurements as a means of reducing both development time and cost.

Early viscometers, many of which have been incorporated into standard industrial tests, gave single-point measurements. These include the Stormer viscometer, orifice cups (Ford and Zahn), and bubble tubes such as Gardner-Holt. In order to understand the complete rheology of a product, it is necessary to characterize it over a wide range of shear rates. This can be accomplished with the STRESSTECH controlled stress rheometer (ATS RheoSystems [Wrightstown, NJ] and REOLOGICA Instruments AB [Lund, Sweden]) (*Figure 1*). The rheometer can accurately measure viscosity over a wide range of shear rates.

Figure 1 *The STRESSTECHrheometer.*

Importance of rheology for coatings

Because coatings are complex structured fluids, it is necessary to be able to apply a variety of tests to examine their complex behavior. In the past, a single-point test at a single shear rate was used to determine a single value of viscosity; however, this technique is useful only if the sample is Newtonian in nature (viscosity does not change with shear rate). This methodology is entirely false if used to measure today's complex coatings, which are decidedly non-Newtonian in nature. In order to characterize structured fluids, it is necessary that the measuring instrument be able to operate over a wide shear rate range. This allows for the entire behavior of the sample to be recognized.

Value of low shear rate information

The first instinct of the paint chemist is to duplicate the high shear rates that the product will experience while in production. While this is not entirely wrong, it does ignore the value of low shear rate information. Instruments such as the STRESSTECH rheometer have helped redefine the meaning of low shear rate control, enabling reliable and reproducible data to be obtained at low shear rates that reflect true particle–particle interaction that controls the rheology of the coating. By measuring in the high shear rate range, this delicate structure is destroyed and the coating reverts back to Newtonian behavior, where the viscosity becomes independent of shear rate. The paint chemist quickly learns that the viscosity of the coating is shear thinning over only a narrow shear rate range and that the viscosity quickly arrives at its Newtonian value and remains unchanged regardless of shear rate. After realizing that the very high shear rates are of limited value, paint chemists turn their attention to the importance of the low shear rate behavior and, using this information, the flow and leveling characteristics of the coating can be predicted. The motor of the STRESSTECH rheometers, like most controlled stress rheometers, is of air bearing design; however, this has been improved by the manufacturer. By using porous carbon construction, the tendency

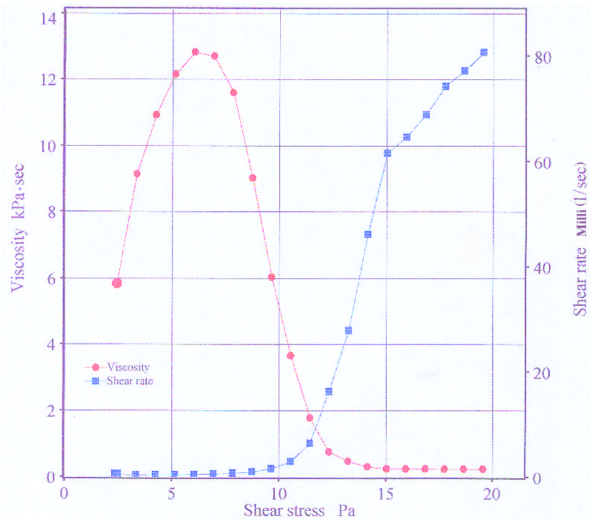

Figure 2 *Yield point determination in paint: CC 25; 2.000–20.00 Pa (up); 100.0 sec in 20 intervals; manual control; no. of measurements–1; measurement interval–50.0 sec; yield stress–6.047 Pa.*

for rotational drift that is seen in jetted air bearings is eliminated. Additional performance has been obtained by replacing the optical encoder with a patented capacitance/induction position sensor. This technology allows the rheometer to measure rotational position to better than one micro radian (1 μrad). The result of these technological improvements is improved low shear rate performance.

Long-term stability of coatings

The stability of a coating is controlled by a number of factors, including stabilization through steric and electrostatic forces. These must be large enough to overcome the forces of settling, mainly gravity and density differential between phases. With the STRESSTECH instrument, users can measure these interparticle forces by examining the yield stress of the coating. The yield stress is a critical value of stress that will cause the sample in question to flow. Values of stress less than this critical value show high values of viscosity and a sample response that is dominated by strong interparticle forces that allow the sample to behave like an elastic body (see *Figure 2*).

Another technique for examining stability of coatings is the use of oscillatory measurements. Although this is more qualitative in nature, it does allow for the prediction of storage stability by providing the storage modulus (G′) and loss modulus values (G″). The ratio of the two is called tan delta (G″/G′), the values of which indicate the degree of particle association. Generally, both high and low values of tan delta can cause settling out of suspended particles through the mechanism of too much particle association and conversely too little particle association. It is necessary to find a balance between these two extremes that will give good long-term stability. Often the storage modulus (G′) alone can be used to predict stability of a coating. Relatively high values of storage modulus at low frequency indicate superior long-term stability over time.

Thixotropy in coatings

Thixotropy is a rheological phenomenon of tremendous industrial importance. It is a time-dependent characteristic of some non-Newtonian fluids that distinguishes itself from another non-Newtonian phenomenon, pseudoplasticity, in that a thixotropic fluid has the characteristic of rebuilding its structure and consequently regaining its viscosity as a function of time. To understand the difference, several factors affecting the viscosity over the low shear rate range need to be examined, including particle–particle and particle–molecule interaction. Particle–particle interaction is heavily dependent on orientation and alignment and is generally the most easily disturbed; thus, viscosity that depends on orientation can be broken down just as fast as it came about in the first place. Orientation may be brought about by polarity of vehicle/pigment dispersions, the physical shape of the particles, adhesive or cohesive forces between phases, surface tension, and aspect ratios of the actual particles. Needlelike particles will affect the thixotropy to a greater extent than spherical shapes. However, dispersions that depend on orientation for viscosity can also be dependent on particle–molecule interaction. This gives rise to bonds that create three-dimensional networks, which are considered to be a gel. These bonds are hydrogen or ionic and are easily ruptured when subject to extensive shear. The distinguishing feature in a thixotropic fluid is its time dependency. That is, in a thixotropic fluid, the viscosity is not only dependent on the shear rate but also the time period through which the fluid is being sheared. It should be noted that an important phenomenon called antithixotropy or rheopexy also exists. This property is similar to

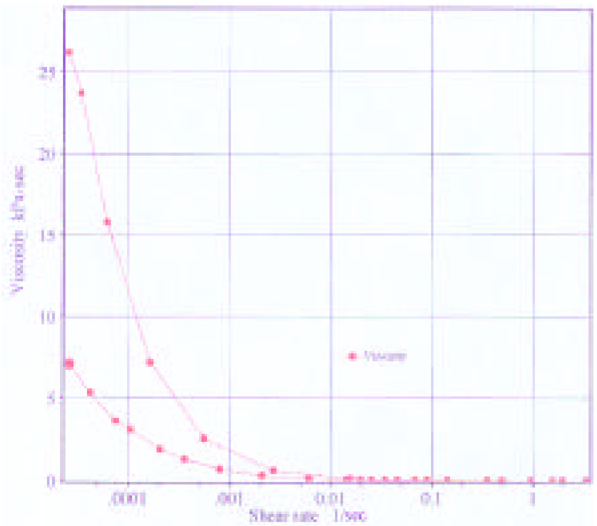

Figure 3 *Rheopectic paint sample; CC 25; 22 stresses, 0.1084–5.100 Pa; up/down continuous on estimated time–417.9 sec; manual control; no. of measurements–1; measurement interval–50.0 sec.*

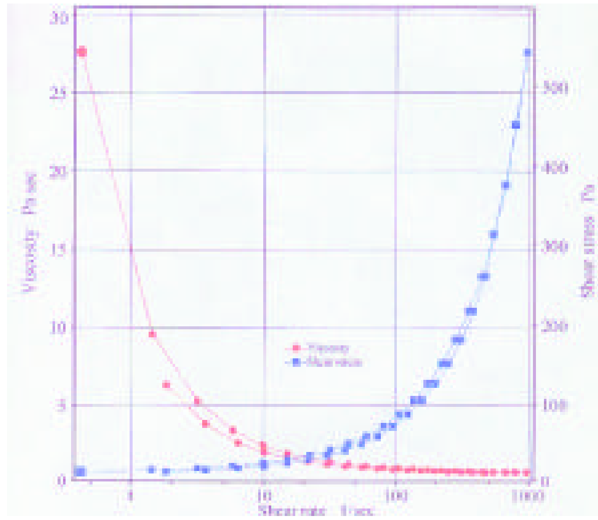

Figure 4 *Thixotropy in paint: C 30 4 ETC; 22 stresses, 11.54–542.8 Pa; up/down continuous on estimated time–241.9 sec; manual control; no. of measurements 1; measurement interval–50.0 sec.*

thixotropy in that a decreasing viscosity as a function of both shear rate and time is observed; however, the critical difference between the two is that, in a rheopectic sample, the viscosity builds faster than it decreased initially. Thus, for one shear rate, two values of viscosity are recorded: one value for the up curve and a different value for the down curve (see *Figure 3*).

Now that the different mechanisms that control thixotropy have been explained, how is thixotropy measured with the STRESSTECH unit and what does the measurement mean? Using the Windows™ (Microsoft® Corp., Bellevue, WA) user interface, the operator chooses the VISCOMETRY option. This program allows the operator to choose a wide range of stresses for the given geometry. The resulting viscosity indicates that with increasing shear rate the viscosity decreases as a result of the breakdown in structure. In the second part of the experiment, the shear rate decreases (as a result of the decreasing stress sweep). The viscosity then increases, but at a slower rate than it dropped initially (see *Figure 4*). Thus, for one shear the curve will produce two different values of viscosity. These two values will vary depending on the thixotropic nature of the sample being tested. Often it will take only seconds to completely rupture the structure of a thixotropic fluid, and the full recovery of the viscosity can be minutes or even hours. The practical importance of properties such as thixotropy in paints can be plainly seen in a typical application of paint to a vertical surface. At first, the viscosity is high, until the paint is actually applied to the surface, at which time the paint must decrease in viscosity quickly so as to allow it to spread quickly and evenly. It is then necessary for the viscosity to quickly increase so as to prevent the paint from running. These performance properties are all controlled through the thixotropy.

Rheological instrumentation

The STRESSTECH rheometer is capable of measuring very low viscosity liquids, semisolids, and molten polymers, as well as solids in a temperature from –150 to 500 °C. The rheometer's patented motor sensor assembly is an important factor in its versatility. In order to accommodate a wide range of samples, it offers a very complete range of measuring geometries, including parallel plate, cone and plate, bob and cup, double gap, torsion rectangular, and high shear systems, as well as a complete range of disposable geometries. Measuring geometries are available in stainless steel, titanium, and quartz or any user-specified materials. The rheometer offers a wide torque, temperature, shear rate, and frequency range, all controlled through true Windows-based software. It also incorporates automatic inertia compensation and automatic gap setting features.

Recent developments have resulted in a controlled stress quantitative normal force option, which allows the user to make measurements in first normal stress difference and thermal expansion. The normal force feature allows for reproducible and controlled loading. This is especially important for shear-sensitive samples.

Dedicated 32-bit CPU

The unit is built around a dedicated 32-bit central processing unit (CPU) in which the electrical connections are direct to the motherboard bus rather than by cables to a separate controller. This integrated approach results in faster and more accurate control for the instrument's position controller and motor response systems. Because the system is integrated, the instrument footprint is made much smaller, an important factor where laboratory space is at a premium. The system includes a built-in diagnostic system and a quick diagnostic service port for service engineers. The modem port allows for remote service diagnostics as well as uploading or downloading of instrument files.

Windows software

Because the unit's on-board computer does all computational and control functions, the computer is available for other uses when measurements are being made, such as setting up new experiments or writing reports.

The standard software offers measuring programs designed to be user friendly with few subdialogue levels in a generally recognizable layout. The software makes available the following test modes: viscometry, constant rate, yield stress, oscillation, oscillation stress sweep, oscillation strain control, creep, and recovery. The COMPARE software program is supplied as standard. This is an advanced plotting program that allows a full line of graphing options. In addition, an optional software package called ANALYSE is available that offers a complete range of modeling equations as well as overlaying capabilities.

The software offers test sequencing, which can organize and sequence several experiments in a series. Dialogue windows offer storable, editable functions for unique testing requirements that can be reset to default conditions with a push of a button. For example, in the oscillation frequency sweep measuring program, the stress, frequency, delay time, integration period, and fast Fourier transform sample size may be adjusted to suit individual requirements. Because the gap setting is completely automatic and computer controlled, measurement reproducibility is greatly enhanced. This is because the loading force can be precisely controlled by the normal force sensor; thus, the shear history can be accurately reproduced for every sample. This is decidedly a great advantage for shear-sensitive materials that are being loaded by different operators or are being checked repeatedly when even the same operator will tend to load the sample differently over an extended period of time.

Temperature control cells are available in many formats, including resistively heated and adiabatically cooled plate, which can be combined with a resistively heated clam shell oven for polymer melts and resistively heated and adiabatically cooled Couette. Also, the familiar water bath heating and cooling arrangement is available. For solids measurements, a resistively heated clam shell oven is offered that accommodates both rectangular and cylindrical samples. Low-temperature capabilities are achieved with liquid nitrogen as the cooling media. A closed cell for high-pressure measurements is also offered. The rheometer is produced according to ISO 9001 standards and meets strict new standards of electromagnetic compatibility.

VISCOTECH, an entry level system that is fully upgradable to a STRESSTECH unit as the user's needs and requirements dictate, is available. The VISCOTECH DSR (ATS RheoSystems) asphalt dynamic shear rheometer, specifically designed to conform to all of the SHRP instrument requirements, is also offered.

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