Rheology: An Important Tool In Ink Development

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Rheology is the branch of science that deals with the flow and deformation of materials. Rheological instrumentation and rheological measurements have become essential tools in the analytical laboratory for characterizing component materials and final products, monitoring process conditions, and predicting product performance and consumer acceptance.

Rheological instruments and rheological measurements find applications in any industry in which the flow characteristic of a material determines either its processibility, performance, and/or consumer acceptance. At the same time, rheological studies help to drive the technology for better quality, consistency, acceptance, and growth.

In this article, rheology is presented as a vehicle for the growth of the ink industry. The study and growth of inks dates back to 2500 B.C. Ink was invented by the Egyptians and Chinese in the first century, when carbon residue made from burning oil, etc., mixed with water or gum was used. Since then there has been slow and steady growth in this field. Today, modern ink industries are motivated by constantly changing printing technologies and by demands from the printers and end users. Faster printing speeds, more cost-effective processes, and tougher environmental regulations are a few of the challenges currently facing the ink industry.

For all of the different types of inks, two properties—cohesion and adhesion—are very important. Cohesion describes the ink's ability to hold together; adhesion refers to its power to stick to a different material, e.g., a substrate. Printing is possible because the ink is more inclined to adhere to a different material than to itself. Ink has only two basic components: 1) pigment, which provides color, and 2) vehicle, which supplies the ink's cohesive and adhesive properties. Pigments are finely ground powders derived from various, mostly inorganic, compounds. Pigments remain in solid form both in the ink and on the substrate.

Supporting the pigments in a printable medium and making them adhere to the substrate is the job of the vehicle, the liquid portion of the ink. Sometimes referred to as the carrier or the base, the vehicle is a combination of binders and solvents. Solvents not only have to keep the ink liquid enough to be printable, but also have to control how the ink dries. Solvents must evaporate slowly so that the ink does not dry in the screen, but once the ink is printed, those solvents must dry quickly so that drying time does not slow down production. Almost all solvents used in inks that dry by evaporation are volatile substances and flammable to some degree. Water-based inks are the exception, however; they also take the longest to dry. The binder is a solid or heavy liquid that provides body to the ink. Its most important job is getting the pigment to adhere to the substrate. Binders are film-forming resins such as ethylcellulose and nitrocellulose that are used in most screen printing inks. The vehicle undergoes changes as the ink dries. Solvents evaporate, leaving only resins and pigment on the surface of the substrate.

Figure 1 STRESSTECH HR rheometer.

This paper discusses UV curable ink and heatset coated, heatset uncoated, and coldset inks.

UV curable ink

UV curable ink technology is the newest technology and is expected to develop significantly within the next few years. The benefits, such as instant drying on UV exposure, zero volatile organic compound (VOC) emission, printing on nonabsorbing substrates, and high resistance of the prints to weathering and abrasion, are the major driving forces for the growing acceptance of this technology.

Heatset coated, heatset uncoated, and coldset ink

Heatset inks dry on the substrate using heat, while coldset inks dry by air oxidation and absorption on the substrate. Heatset uncoated ink is used for retail, directory, flyer, and book printing, while heatset coated ink is utilized for catalogs, magazines, book covers, etc. Coldset ink is generally used for newspaper printing.

Experimental

The experiments were performed using the fully automated STRESSTECH HR rheometer (**ATS RheoSystems/REOLOGICA Instruments,** Lund, Sweden). For UV curable inks, a Bluepoint UV-point source (**Honle, UV America Inc.,** Marlboro, MA) was used. The complete rheometer system is shown in *Figure 1*. The rheometer and integrated light source permit user-selectable illumination and exposure time and intensity. In addition, the environment around the sample and temperature can be controlled.

The Bluepoint UV source is supplied with a 100-W short-arc lamp with cold mirror reflector and a wide range of UV intensities (200–400 mW/cm^2). Further, by employing different filters and diaphragms, the user can control the wavelength and intensity of the UV being projected onto the sample.

Results and discussion

UV curable inks

For the UV curing experiments, an 8-mm parallel plate geometry with 0.01-mm gap was used. The experiments were run at room temperature (RT). To ensure reproducibility, the measuring geometry, loading conditions, and test parameters were chosen after performing preliminary conditioning tests. Specifically, geometry was selected based on the physical properties of the samples to ensure the proper signal generation. The samples were loaded with a constant force of 5.0 N using the rheometer's patented Quantitative Differential Pressure Normal Force (DPNF) sensor. This was done to ensure that each sample had the exact same loading history. The UV source was set to provide a 200-mW/cm^2 UV intensity for both samples.

Once the loading and test conditions were selected, the curing tests were run at 5 Hz using the Fast Oscillation program (**ATS RheoSystems/REOLOGICA Instruments**), which allows for data collection rates in excess of 500 points/sec. This level of data collection is required for UV curing studies. The start stress was chosen from the linear viscoelastic (LVE) region of each material followed by a polynomial forcing function that increased the deformation on the sample coincident with the sample's cure profile.

The UV light was projected onto the sample at 5 sec after the start of the experiment, and was kept on for 10 sec. The data in terms of magnitude of complex viscosity (eta*) versus time are plotted in *Figure 2*. The analysis suggests that the initial eta* for both inks are nearly the same (~ 266 Pa sec). Upon irradiation, both inks cured within 5 sec. Ink B cured significantly faster, and the final equilibrium eta* is nearly a decade higher than ink A. After careful comparison of the curing profiles, it appears that ink B reached its final equilibrium value of eta* within 5 sec, while ink A took 15 sec. Further, as mentioned above, using the rheometer's DPNF sensor, the compressive/ten-

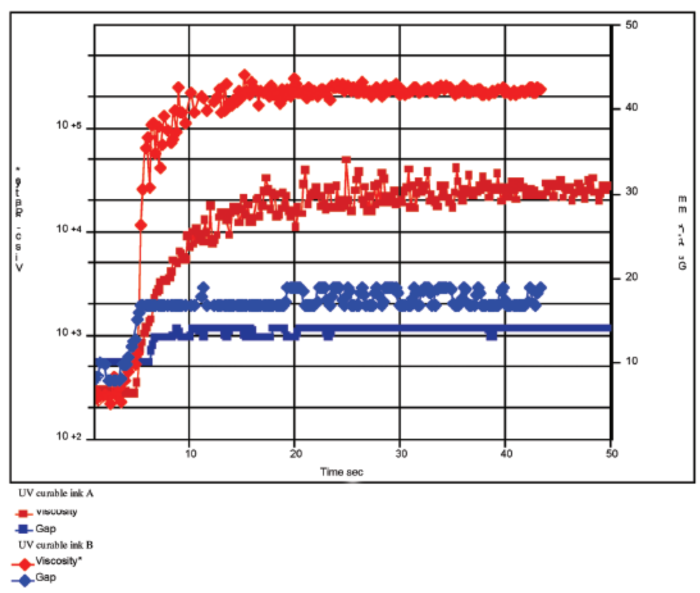

Figure 2 Plot of magnitude of complex viscosity (eta) versus time (sec).*

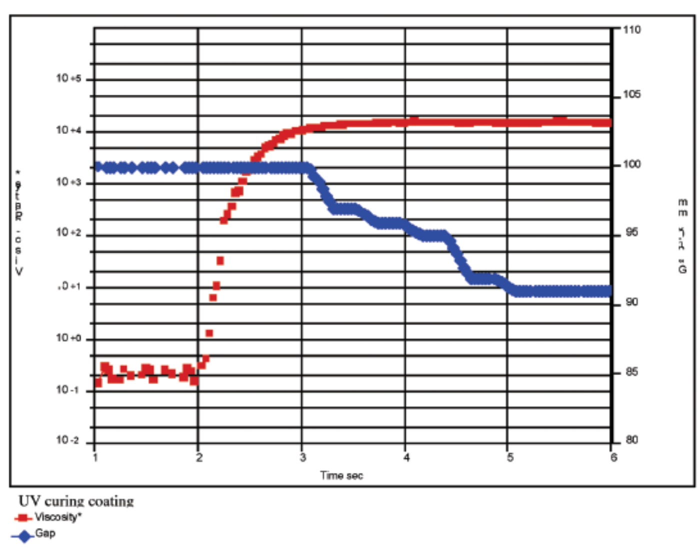

Figure 3 UV curable fiber optic coating sample.

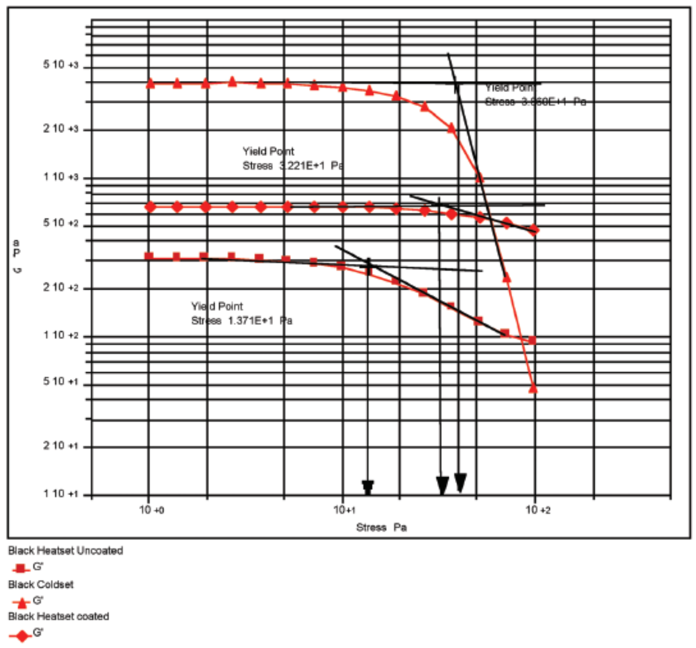

Figure 4 *Dynamic stress sweep study on three black ink samples.*

Table 1 Yield Point Analysis	
Ink sample	**Yield point (Pa)**
Heatset uncoated	10.2
Heatset coated	27.2
Coldset	38.4

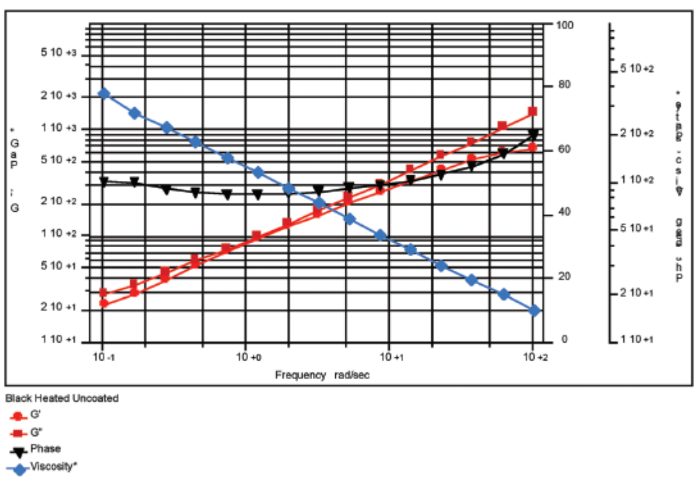

Figure 5 *Frequency sweep study: headset uncoated ink.*

sile force on the sample can be controlled while the experiment is running. This feature allows for the determination of percent shrinkage or expansion due to curing by monitoring the variation in gap. In addition, sample internal stress is kept to a minimum, and delamination from the plates is eliminated. The normal force was set to 0.5 N throughout the experiment. The data show that there was nearly a 40% expansion due to curing for ink A, while for ink B it was 70%. Similarly, if the sample densifies during curing, it can also be easily measured in a comparable fashion. *Figure 3* shows similar data for a UV curable fiber optic coating sample. Here, the sample densified by 9% upon curing under similar experimental conditions.

Since UV curable ink technology is one of the fastest technologies in the ink industry, a method to accurately monitor the UV cure profile is necessary for proper quality control and product development. The rheological measurements described here satisfy these requirements.

Heatset uncoated, heatset coated, and coldset inks

These inks are used for offset lithographic printing. Heastset uncoated ink is mainly used for retail and is available in four different colors: black, cyan, magenta, and yellow. In this study, the dynamic viscoelastic properties of black ink samples were analyzed.

For three black ink samples, a 25-mm parallel plate geometry was used. The geometry was chosen carefully after preliminary analyses to ensure the reliability of the data. All of the tests were performed at a constant 25 °C using the Elevated Temperature Cell (ETC-3) (**ATS RheoSystems/REOLOGICA Instruments**) based on the Joule-Thomson effect principle. The temperature cell can range from –180 to 550 °C with temperature stability within ±0.1 °C of the setpoint. All of the samples were loaded with a constant force of 10.0 N using the DPNF sensor. This was done to ensure that each sample had the same loading history as that used for the UV curable inks.

A dynamic stress sweep study was performed on these samples from 1.0 to 500.0 Pa. The results are shown in *Figure 4*. The yield point for these three samples is shown in *Table 1*.

The three inks have different yield points. Normally, the higher the yield point, the lower the amount of spread of ink onto the substrate. If the yield point is too small, there may be sagging of the ink on the substrate surface after application. Hence, rheological characterization is a very important tool for analyzing ink performance. Further, the breakdown of the structure above the yield point is important. For the coldset ink sample, the yield point was high, but above the yield point, the structure totally broke down and the viscosity was reduced by nearly three decades, unlike the two heatset inks, in which the viscosity dropped by less than a decade over the same stress range. This behavior indicates that the internal structure and particle–particle interaction of the ink samples is dramatically different.

To investigate the interparticle interaction, a frequency sweep study was performed from 0.1 to 100 rad/sec within the LVE region of each ink sample. *Figure 5* shows the results for headset uncoated ink, *Figure 6* for heatset coated ink, and *Figure 7* for coldset ink. The three inks have very different viscoelastic behaviors. By comparing storage modulus (G') and loss modulus (G") as a function of frequency, it is clear that heatset uncoated and coated ink particles are weakly associated, while coldset ink particles are strongly associated. The stronger interparticle interaction helps to maintain the structure of the ink, while the weakly associated particles help to better spread over the substrate.

To study the large-scale deformation and flow characteristics of the inks, steady shear experiments were run from 0.01 to 1000 1/sec. The results are plotted in *Figure 8* in the form of viscosity versus shear rate. The analysis shows that the heatset inks have very different flow properties from the coldset ink throughout the shear rate range. This is important since it clearly describes the totally different behavior of inks under shearing as related to their different applications. The coldset ink, which is mainly used for newspaper printing, has a viscosity profile showing a decreasing slope with

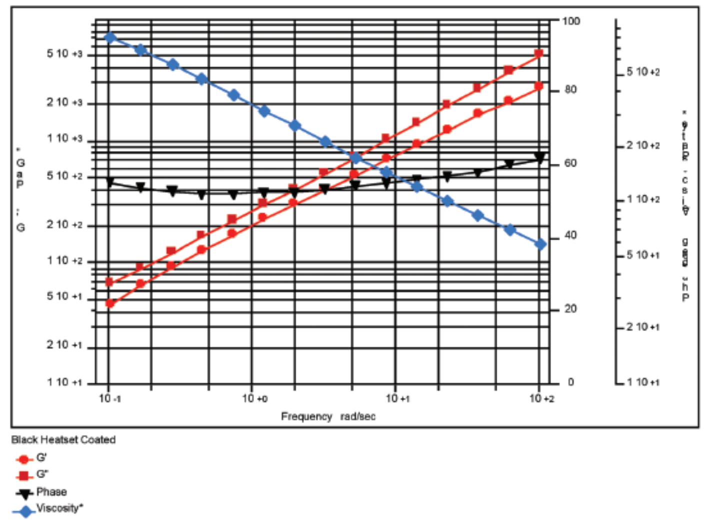

Figure 6 *Frequency sweep study: heatset coated ink.*

increasing shear rate and an indication of a yield stress at low rates, while the heatset inks show an increasing slope with increasing shear rate and an approach to a low-shear-rate Newtonian region. These data trend with the stress sweep results in Figure 4.

Rheometer system setup

The STRESSTECH HR research rheometer has a wide range of measuring systems and accessories. Measuring systems are available as concentric cylinders; cone/plate; parallel plate; double concentric cylinders; sealed/pressure cells; and dynamic mechanical thermal analysis (DMTA) of rods, bars, fibers, and films. Special measuring systems for low volume, high shear rates, and high sensitivity are also available. The measuring geometries can be made in stainless steel, titanium, polycarbonate, or any user-defined material. The instrument is supplied standard with a DPNF sensor for reproducible sample loading history, thermal expansion measurements, and quantitative normal stress measurements. The diffusion sintered air bearing has low inertia with high axial and radial mechanical stiffness.

Temperature control cells are available using circulating fluid, Joule-Thomson effect, and cryogenic covering the range –180 to 550 °C. All measuring geometries are supported, i.e., cone/plate/parallel plate, concentric cylinder, and solids in torsion and tension. Several high-pressure cells with an upper range of 15,000 psig and 400 °C are offered.

Electronic unit

The instrument electronics are contained within the mechanical unit, and the instrument is built around a dedicated, high-speed central processing unit (CPU).

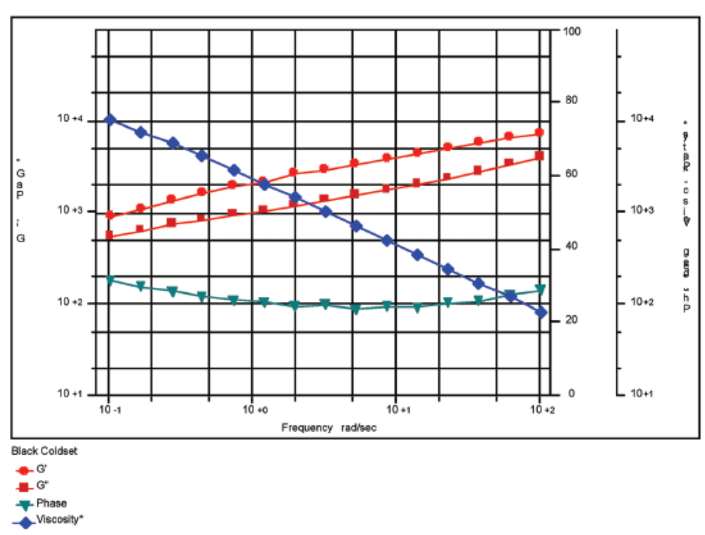

Figure 7 *Frequency sweep study: coldset ink.*

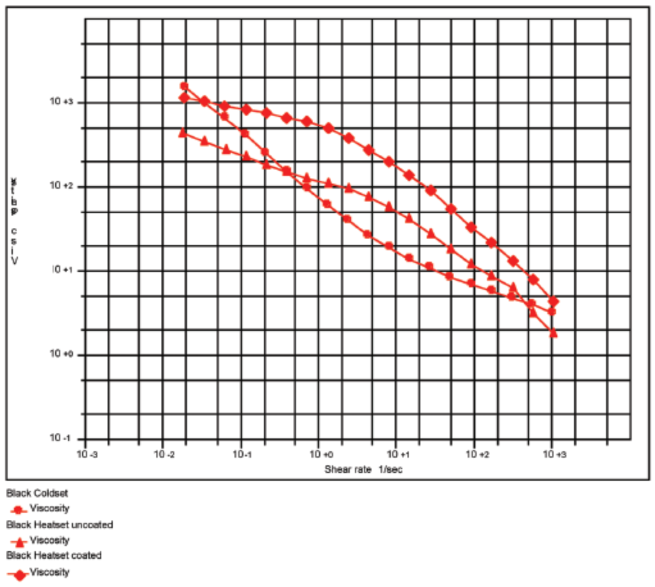

Figure 8 *Steady shear experiment: viscosity versus shear rate.*

This consolidation enhances performance and versatility due to electrical connections on the motherboard bus, rather than through cables to a separate electronics cabinet. In addition, valuable bench space is kept to a minimum. The motor control is based on digital rather than analog drive technology. The unit contains a built-in diagnostic system and quick diagnostic service port for service engineers. Also included is a port for remote control operation and fault diagnostics for service via the Internet.

Rheometer software package

RheoExplorer 5.0 software is based on the Windows operating platform and runs under Windows 2000/XP (**Microsoft Corp.,** Redmond, WA). The standard software package is a true multitasking interface with selectable user levels, offering many advantages to the scientist. It is designed to provide flexibility for configuring and using the rheology system. The computer is not dedicated to simply running the instrument, and is available for other uses when making measurements. The computer can be used for printing previous results, writing a report, or performing measurements with another instrument.

Viscometry, oscillation, creep and recovery, constant rate, yield stress, Fast Oscillation, process control, project (multiexperiment linking), time–temperature superposition, and spectrum transformation packages allow the sample to be analyzed via different rheological procedures. Powerful data analysis capabilities enable model fitting, graph and table customization, and cut/paste operation to all other Windows-based software.

The software permits automatic gap adjustments and thermal expansion compensation using the DPNF sensor. The system enhances measurement reproducibility since the sample loading history is reproduced identically each time.

Rheometers for any user level, application, and budget

The DYNALYSER research rheometer (**ATS RheoSystems/REOLOGICA Instruments**) is a research-level rheometer designed specifically to address the challenging and diverse testing needs and requirements of the dedicated rheologist (*Figure* 9). The instrument's capability and performance are the direct result of a design and development effort focused exclusively on input and recommendations from rheometer users. The accurate and versatile instrument is designed for testing any rheologically significant material, i.e., thermoplastics, thermosets, elastomers, semisolids, and/or fluid systems.

The VISCOANALYSER (**ATS RheoSystems/ REOLOGICA Instruments**) is an entry-level, modular research rheometer system that is fully upgradeable to a STRESSTECH unit as the user's needs and requirements dictate.

All of the manufacturer's rheometers are produced according to ISO 9001 and are tested to operate according to the electromagnetic compatibility rules within the European Community. The instruments are tested to be labeled with the CE mark.

Conclusion

The importance of rheology in ink processing has been demonstrated. Improved printing quality and faster processing, environmental acceptance, and cost are the factors driving ink technology. The rheometers described are applicable for a wide range of materials. A detailed interpretation of data and

Figure 9 *DYNALYSER research rheometer.*

correlation of the rheological response with the actual processing conditions is presented. The rheological characterization of materials at operational conditions provides precise information for engineers and scientists to improve and optimize their products and manufacturing processes. Most researchers and manufacturers rely on rheological measurements to develop products with a competitive edge in the marketplace. A reliable research-level rheometer and a thorough understanding of rheological measurements are necessary for success in industry.

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