# TOOLS TO GUIDE LOW VOC INK VEHICLE SELECTION

Timothy C. Vogel*

Abstract:   As the trend continues toward very low VOC ink formulations, ink vehicle selection becomes more critical.   Basic physical characteristics of a vehicle such as viscosity and non-volatile content are not good enough.   There are other physical measurements that can give the formulator more insight into the behavior of a particular vehicle.   Dynamic surface tension, particle size, and viscosity versus shear profile are three useful measurements that can guide ink vehicle selection.   In addition, they can help explain differences in aqueous ink print quality.

With the advent of more stringent government regulations, liquid ink formulators are called upon to further reduce the VOC (volatile organic content) levels of water-based inks.  In the past, several steps have been made to bring us from hydrocarbon solvent based inks to our current aqueous ink systems. The first water inks were based on a combination of water and alcohol.  They were diluted with a mixture of 80% water and 20% alcohol.  This kept the ink surface tension low and also maintained a fast drying speed.

_____
*Sun Chemical Corporation

The second step was to minimize or eliminate
the alcohol and replace it with a small level
of surfactant. This level was typically
between one and five percent. The surfactant
was adequate at reducing the surface tension
of the ink, but the drying rate was slower
than an ink with alcohol. The next generation
of water inks will need to go one step
further. A reduced level of surfactant is
necessary since the latest goal is to reach
VOC levels of less than one percent as
determined by EPA Method 24.


What is left? We removed organic
solvents like acetates and toluene with the
first water inks. We have reduced and removed
alcohol. Now we must reduce or remove the
surfactant in the ink. The only remaining ink
ingredients are water, pigment and vehicle.
We are now challenged to select or design the
best possible water-based ink vehicle system
— a vehicle that will be able to approximate
the performance properties of previous
formulations, which had the assistance of a
solvent.


Where do we begin? Should we survey all
available suppliers and try everything in
sight? Maybe, but that would take a long time
and would we learn anything in the process?
We would probably learn how to do a very fast
resin evaluation, but that's all. Instead of
this trial and error approach, let's begin by
asking ourselves a few questions. What
performance properties do we want from a
vehicle? What physical properties can we
measure and how can we relate them to printing
performance?


In this particular presentation I will be
discussing some of the tools used to guide our
internal polymer synthesis group to create a
very low VOC water-based liquid ink emulsion
polymer. The targeted application was a
packaging gravure ink for absorbent substrates

like paper and board. These tools can also be used to guide vehicle selection of commercial resins and the same physical property/ performance considerations apply. Certainly these physical characteristics can also be helpful when selecting a vehicle for flexographic ink applications.

The first question we must ask about a particular resin sample is, what is it? Most samples are supplied with information like percent solids, viscosity and a general chemical description for example: styrenated acrylic latex or acrylic solution. We must look more closely at the physical characteristics of a resin sample. More specifically we measured physical characteristics of emulsion polymers. Since the drying rate of most solution resins is slower than the drying rate of emulsions, the bulk of our vehicle system will be an emulsion. However, solution resins may be used as additives to improve print quality.

The first tool I will discuss is the dynamic surface tension. In order to ensure that all resin samples were evaluated at equivalent conditions, each sample was first diluted to printing viscosity. Then dynamic surface tension was measured on the diluted resin samples. This procedure was necessary because the resin samples supplied represented a wide range of viscosity. Resin concentration and viscosity both affect the dynamic surface tension. We held viscosity constant since most printers run their ink at a specific viscosity, not necessarily a specific resin concentration.

If there is a lower concentration of resin solids, there will be a higher percentage of water. Water has a very high surface tension (72.1 dynes/cm at 25°C) so any additions of water to a resin sample will increase the surface tension of that sample.

Most resins when added to water will lower the surface tension of water. An important physical characteristic of a resin sample is its surface tension at printing viscosity. Since we are now formulating inks without the addition of surfactant or alcohol, the only component left to lower the surface tension of water is the vehicle. Actually, some emulsion resins are stabilized with surfactants so the process of adding resin to an ink adds surfactant as well.

Let me explain the significance of measuring dynamic surface tension and then we will look at a sample of data and corresponding prints. This will help us correlate our physical measurements with printing performance properties.

When a gravure press is running at 1500 ft/min (7.6 m/sec), and assuming a 20 inch (50 cm) cylinder diameter, then each integral of the cylinder is entering the ink pan five times per second.

(1500 ft/min)*(1 rev/20Ⅱ in)*(1 min/60 sec)* (12 in/1 ft) = 5 rev/sec

In other words we are creating a new ink film surface five times per second. With this in mind, we need to measure the surface tension of the ink under the same conditions. That is exactly what is done when we measure dynamic surface tension.

To take our measurements we used the Sensadyne 6000 by Chemdyne Research Corporation. This instrument passes an inert gas through a large orifice and small orifice immersed into a test liquid. The rate at which gas bubbles are formed can be adjusted to our desired rate of five per second. This means that we are creating a new gas/liquid interface at the same rate the press is creating an ink/air interface. The instrument

uses the maximum bubble pressure method to calculate the surface tension of a test fluid. The pressure differential between the small orifice and the large orifice is used to calculate the surface tension of a liquid. The upper limit and lower limit for surface tension readings are calibrated with standard fluids of known surface tension. In our case we used pure water and isopropanol as our upper and lower limits respectively. At 25°C and with a bubble rate of 5 bubbles/second, isopropanol has a dynamic surface tension of 20.9 dynes/cm and water has a surface tension of 72.1 dynes/cm.

As expected, the surface tension of a nitrocellulose solvent-based ink is lower than the water/alcohol diluted ink. This ink in turn has a lower surface tension than the straight water diluted ink. What this means is that we must strive to lower the surface tension of our very low VOC ink (VLVOC) knowing that we may not reduce it to the level of an alcohol/water ink.

DYNAMIC SURFACE TENSION
OF DIFFERENT INK SYSTEMS
AT THE PRESS-READY VISCOSITY OF 22" ZAHN #2
REPORTED IN UNITS OF dynes/cm

| SOLVENT DILUTED INK | WATER ALCOHOL INK | WATER DILUTED INK W/SURFACTANT | WATER DILUTED INK NO SURFACTANT |
|---|---|---|---|
| 25 | 29 | 35 | 42 |

In comparison, the following is a list of the dynamic surface tension of water diluted emulsion resins at the press ready viscosity of 22" Zahn #2.

## DYNAMIC SURFACE TENSION OF DILUTED RESINS

| | | |
|---|---|---|
| 152 | 68.0 | dynes/cm |
| 743 | 60.7 | " |
| 126 | 52.7 | " |
| Acrylic solution | 52.0 | " |
| 80 | 45.3 | " |
| 1103 | 44.2 | " |
| 133 | 36.5 | " |
| 132 | 31.1 | " |

From these readings we would expect the quality of the prints to improve as we travel down the list. In general this trend is true, however there were several samples that did not fit this pattern. The best print was actually achieved by using resin 126. Unfortunately we cannot rely on just one physical characteristic to tell us which resin is best. So now we must compare these samples in other ways.

Next we will examine the rheology of each resin sample using the Haake Rotational Viscometer. This instrument consists of a rotating cylinder, called a spindle, inside a cylindrical cup. This cup is enveloped by a fluid reservoir connected to a constant temperature bath. The liquid sample is placed into the cup. When the spindle is suspended in the cup it forces the sample between the walls of the stationary cup and the sides of the spindle. The spindle is driven at a programmable speed by a DC motor. The resistance of a sample to flow causes movement of a torsion bar mounted between the motor and the spindle drive shaft. This movement is detected by an electronic transducer. Signals proportional to the speed and torque are related to shear rate and shear stress. Viscosity is the ratio of shear stress to shear rate. The results of a measurement can be presented as a plot of shear stress versus shear rate or the data can be displayed as a plot of viscosity versus shear rate.

How does this relate to printing? When excess ink is wiped off of the cylinder with a doctor blade, the ink is subjected to high shear. After the ink is transferred to the paper it is subjected to very low shear. The question is what are the flow characteristics of each resin sample under low shear conditions? How will it flow once it is transferred to the substrate?

In general, there are three possible responses in viscosity to increasing shear rate. The viscosity of the test liquid can increase. It can stay the same. Or it can decrease. If the viscosity increases as shear rate increases the fluid is called shear thickening or dilatant. Remembering that viscosity is the slope of the shear stress versus shear rate plot, below is the rheogram of an ideal dilatant fluid:



Dilatant substance
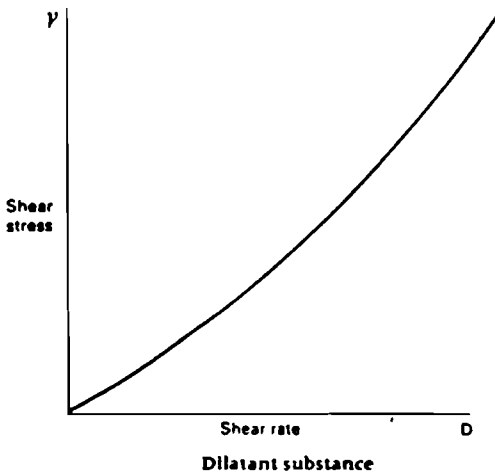
The slope of this graph increases as shear rate increases.

The rheogram of a Newtonian fluid has a constant positive slope. This means that viscosity is constant as the shear rate increases. Below is the graph of an ideal Newtonian fluid plus the graph samples of 126 and the acrylic solution sample.
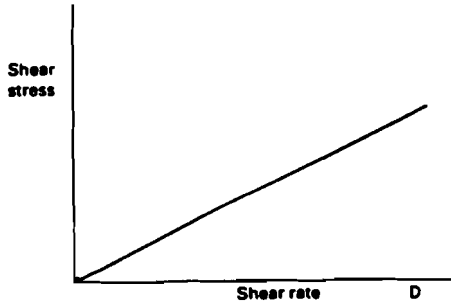
**Rheogram for Newtonian liquids**

Tau [Pa]          Tau= f (D)                    SunChemical



1 SAMPLE 126
* ACRYLIC SOLUTION
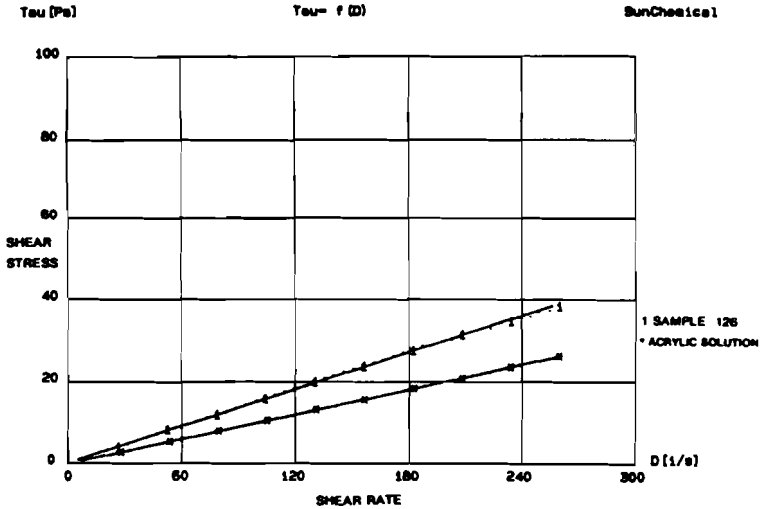
If the viscosity decreases with increasing shear, the fluid is called shear thinning or pseudoplastic. Following is the graph of an ideal pseudoplastic fluid plus the graph of samples 80, 743, and 1103. The slope of each rheogram decreases as shear rate increases.

Pseudoplastic substance
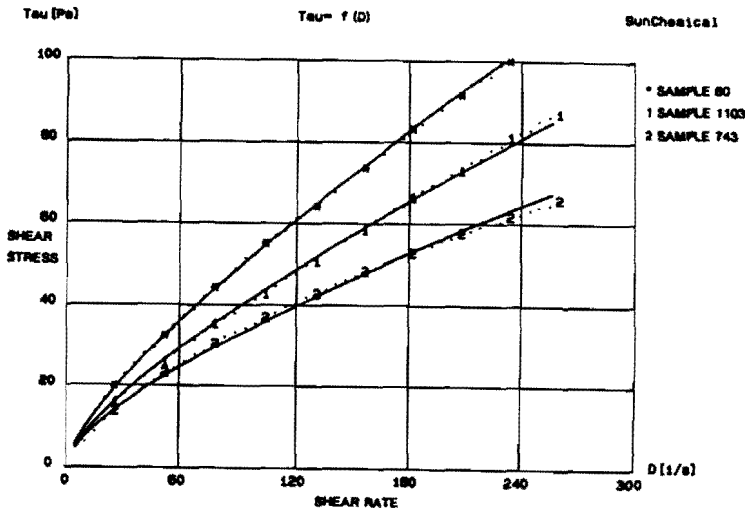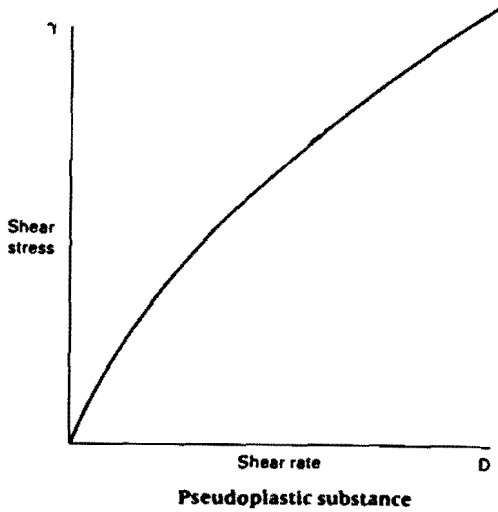


As we examine the rheological profiles of our resin samples we see that they are not the same. When we correlate the rheological plots with print results we find that the Newtonian samples print more smoothly than the pseudoplastic samples. None of the samples we examined were dilatant. If we consider the point in time when the ink first hits the paper, these results make sense. An ink that is pseudoplastic, in the absence of high

shear, will have a high viscosity and therefore will not flow. The result of this impedance to flow is an uneven coverage of the paper. The print has high and low ink spots. However, the sample with a Newtonian flow characteristic will still have a low viscosity in the absence of high shear. Therefore it will produce a print that is more smooth.

Still we have not explained all of the differences we see in the prints of experimental inks made with our VLVOC emulsion resins. Maybe dynamic surface tension and rheological profiles can't give us all the information we need. Perhaps there is another physical measurement that could help us. Certainly there are many other physical characteristics of an emulsion that we could measure. One helpful measurement is the particle size of the emulsion particle.

We measured the particle size with the aid of the MICROTRAC Ultrafine Particle Analyzer. This instrument uses the scattering of a laser light projected through a sample to compute particle size. It is designed to measure particle size in the range of 0.0054 microns to 2.75 microns.

The instrument is based on the fact that light scattered by particles will be Doppler shifted by the Brownian motion of the particles. If a particle is stationary the frequency of the reflected light equals the frequency of the incident light. If however, the particle is moving relative to the incident light source, the frequency of the reflected light will be shifted. The measured frequency and wavelength will change in such a way that their product (the speed of light) will remain constant. This principle is called the Doppler shift or the Doppler effect named after Johann Doppler (1803-1853). This shift can be measured by comparing it to an unshifted reference beam. The amplitude of

the shift will be proportional to the velocity of the particle. The velocity distribution of a large number of single sized particles averaged over time will approach a known functional form. This velocity distribution is a function of particle size.

A sample of large particles will have a low median velocity while a sample of small particles will have a higher median velocity. This velocity distribution is also affected by temperature and fluid viscosity. All samples were therefore run at the same temperature and each resin sample was diluted with water to a concentration of one percent. This was done for two reasons, first the viscosity of each sample was effectively the viscosity of water and second a large number of particles would overload the detection sensor. Since the temperature and viscosity are now known, the velocity distribution is now a function of particle size alone.

In simple terms, the smaller the particle size the closer the emulsion approximates the flow characteristics of a solution resin. In addition, small particles yield increased print gloss compared to emulsions with large particles. When we examined particle size we found an explanation to the poor print quality of resin samples 132 and 133 (particle size of 0.21 microns and 0.13 microns respectively). This may sound small, however the particle size of resin 126 was 0.05 microns. This is one third or one fourth the diameter of the other emulsion particles. As we can see by the rheogram, the flow characteristics of 126 are slightly more Newtonian than the 132.

Even a visual examination of the undiluted resin revealed a distinct difference between the samples. The 126 resin sample was translucent while the 132 and 133 samples were both an opaque white. This is a direct result of the emulsion particle size.
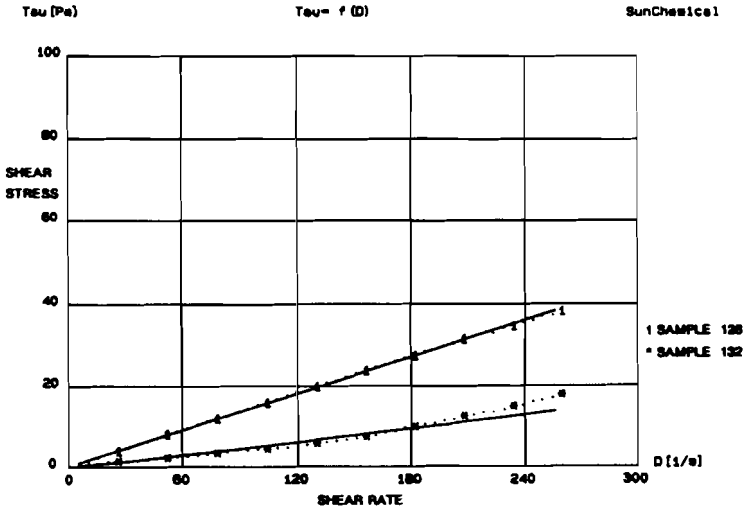
Following is a comparison of the particle size distribution for samples 126 and 132. These graphs plot the percentage of particle population at each particle size (reported in microns). From the comparison of these two graphs we see that the average particle size of 126 is smaller than for sample 132.


Our search for a very low VOC resin is not completed. We do not at this time have the perfect resin. However with the help of these tools our search has direction and we have eliminated many candidates from our search. At this time what we do have is a very low VOC resin system that does have good printability and gloss. The challenges that remain for this system are resolubility and tack. These challenges can be met by adjusting the monomer composition of the emulsion polymer. It may also be possible to improve the remaining properties with additives.


Although not every project involves the same goals as this project, the same physical

properties of dynamic surface tension, rheological profile and particle size may be useful in meeting your project goals.



PARTICLE SIZE DISTRIBUTION FOR SAMPLE 132 (IN MICRONS)

PARTICLE SIZE DISTRIBUTION FOR SAMPLE 126 (IN MICRONS)

## SELECTED BIBLIOGRAPHY

Bassemir, R.W. and R. Krishnan
July 1990    "Practical applications of
             Surface Energy Measurements in
             Flexography," FLEXO (Ronkonkoma,
             N.Y.) vol.15, no.7, pp.31-40.

Belote, S.N. and William W. Blout
1981         "Optimizing Resins for Low VOC,"
             Journal of Coatings Technology.
             (Blue Bell, P.A.)  vol.53,
             no.681, pp.33-37.
Cappuccio, A.R.
1984         "Where Do We Stand with low VOC
             Ink?,"  FLEXO. (Ronkonkoma, N.Y.)
             vol.9, no.10, pp.22-31.

Chem-Dyne Research Corp.
             Sensadyne 6000 Tensiometer
             Operator's Manual.

Haake Buchler Instruments, Inc.
             VT500 Rotoviscometer Operator's
             Manual.

Halliday, D. and Robert Resnick
1978         "Physics Parts 1&2"
             (John Wiley & Sons, New York),
             3rd ed., pp.929-932.

Klus, J.P. et al
1983         U.S. Patent 4,416,148 (November
             22, 1983).

Leach, R.H. et al editors
1988         "The Printing Ink Manual"
             (Van Nostrand Reinhold Co. Ltd.,
             London, England) 4th ed., pp.666-
             698.

Leeds & Northrop
             MICROTRAC Ultrafine Particle
             Analyzer
             Operator's Manual 179521 Rev. A.

Patton, T.C.
1979        "Paint Flow and Pigment
            Dispersion"
            (John Wiley & Sons, New York),
            2nd ed.

Winnik, M.A., et al
1992        "Latex Film formation at the
            Molecular Level:  The Effect of
            Coalescing Aids on Polymer
            Diffusion," Journal of Coatings
            Technology (Blue Bell, P.A.)
            vol.64, no.811, pp.51-60.