

Comparison of Methods to Assess Pigment Dispersion

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Two inks made with different red pigments were evaluated by common methods to assess the degree of pigment dispersion. One pigment is more difficult to disperse than the other in the vehicle used. The five methods that could detect changes in dispersion with each pass over a three-roll mill were a light scattering particle size distribution analyzer, a NPRI fineness of grind gauge, gloss, contrast ratio measurements, and rheology. The gloss and contrast ratio measurements could detect changes with each pass over a three-roll mill only with a significant reduction in pigment particle size.

INTRODUCTION

The dispersion of a pigment plays a major role in the properties of the final film formed by an ink, paint, or any other pigmented coating. The pigment particle size distribution has an effect on the color strength and shade,¹ opacity and transparency,² gloss,³ and outdoor weatherability⁴ in the final film. The particle size distribution has an effect on the coating in the liquid state on its rheology⁵ and, for fluids of low viscosity, on how stable a system will be against pigment settling.

This study takes a look at some common methods to assess the pigment dispersion within a system. Those methods are fineness of grind, contrast ratio measurements⁶ for opacity and transparency, color strength and shade development, gloss, particle size measurement by light scattering, rheology, and optical microscopy. We limited our investigations to these methods as these are the most commonly used in the industry. We did not investigate less commonly used methods such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of a dried paint film section,⁷ quasi-elastic light scattering (photon correlation spectroscopy),⁸ image analysis,⁹ hydrodynamic chromatography,¹⁰ back-scattering studies,¹¹ ultrasonic attenuation spec-

troscopy (UAS),¹² centrifugal sedimentation measurements,¹³ or "ink fingerprinting"¹⁴ although they are all available to us. We applied the noted methods to two red pigments in a model vehicle for screen printing inks that contained no dispersion agents. One pigment is considered by us to be more difficult than the other to disperse in this vehicle. We were curious as to why this is so and if the common methods noted previously would give us some insight.

There are numerous types of fineness of grind gauges used in the industry.¹⁵ We prefer a National Printing Ink Research Institute (NPRI) one-mil grindometer for a fineness of grind gauge as opposed to a Hegman or PC gauge. The NPRI grindometer is used routinely in the printing ink industry and is more able to detect particle sizes near the lower limit of detection than the Hegman or PC gauge. The printing industry needs finer particle sizes because of the thinner films in printing as opposed to painting. A grind gauge is easy to use, reproducible, and gives an indication of large particles in a pigmented system but gives no indication of the distribution of the majority of smaller particles in the dispersed system.^{16,17} It is generally assumed that the decrease in size of the largest particles corresponds to an improvement of the overall dispersion of pigments in the system. This has been noted in the literature for some time.¹⁸ The smallest particle size that can be detected by a fineness of grind gauge is around 10 microns according to Lawrence¹⁹ and Hall et al.²⁰ but Patton¹⁵ would suggest that the lower limit is two to five microns.

The particle sizes of pigments that give the best performance are much smaller than this. Further, there are those who feel that the action of drawing the pigmented liquid down the gauge can disperse the pigment more than it is in the undisturbed state. Still, the fineness of grind gauge, or grind gauge, is used extensively in the industry.

A relationship between the degree of pigment dispersion and the color development properties of a pigment, including the opacity and transparency, has been noted for some time by Mie.²¹ Later, Brookes²² and Chromey²³ applied specifically to pigments of all shapes Mie's theory of spheres. The Mie theory states that for a given pigment, maximum color development is achieved once that pigment is dispersed below a minimum size. This minimum size is around 0.10 micron for a moderately absorbing pigment and 0.05 micron for a strongly absorbing pigment. Further, the maximum opacity of a pigment is reached at a diameter of around half the wavelength of visible light or at around 0.25 micron.² As the particle size is decreased further, a decrease in opacity with a subsequent increase in transparency and color strength is obtained²⁴ as shown in Figure 1. For many, but not all pigments, there is a change in shade^{1,3,24-29} with a change in the particle size distribution. Therefore, the opacity/transparency and the color strength and shade of a pigment can give an indication of its degree of dispersion.

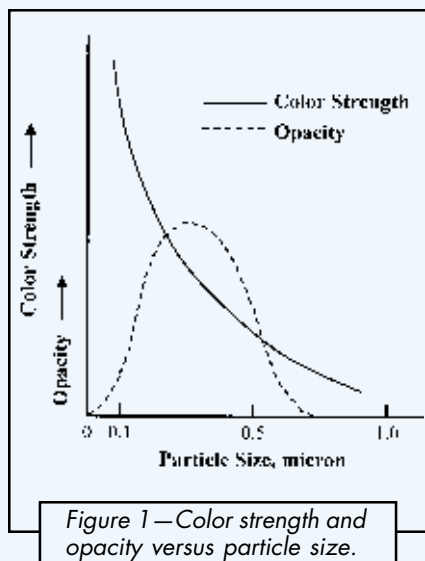
It should be noted from Figure 1 that there is a decrease in opacity with an increase in particle size above 0.25 micron. This indicates that any change in particle size from flocculation can lead to

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a significant decrease in opacity. It should be stressed that this change of opacity/transparency with particle size can occur in the liquid dispersion or with the drying or curing of the liquid after application. Figure 1 indicates also that color strength can be a practical method for assessing particle size distribution for the finest of pigment dispersions. The change in color with dispersion will be dependent on the particle shape. The theory developed by Mie was for spheres. Felder³⁰ has noted that it is the *minimum* dimension of a nonspherical particle that has the greatest effect on determining color strength.

Gloss has been known to be an indicator of the degree of pigment dispersion.^{15, 31-34} Normally, the gloss will increase with a decrease in the pigment particle size. Guenther et al.⁴ and Carr^{1,34} have noted that the specular gloss of a film can increase until the mean particle size is around 0.30 micron. There is no apparent change in specular gloss with mean particle sizes smaller than 0.30 micron, but Carr¹ did note in his study that there was a decrease in haze as the mean particle size was decreased to about 0.12 micron. This was the smallest size that could be detected in his study. Guenther et al. noted that a small fraction of particles with sizes exceeding 0.50 micron can cause a significant reduction in gloss. Therefore, gloss can be a sensitive method to give an indication of the dispersed state of a system.

The measurement of particle size by light scattering is based on the Mie theory. A particle will scatter light according to the particle diameter, its refractive index, and the wavelength of the light source(s). A schematic of a light scattering instrument is presented in Figure 2. The angle of the light that is scattered off a dilute dispersion is detected.

From this, a particle size distribution can be calculated. This method assumes for the calculations that the particles are spherical. In order for the method to be of value, one must be sure that what is being measured is a representative sample of the dispersion and that there is no change in the dispersion of the system upon dilution for measurement. The values one obtains will depend upon the algorithm used in the calculations and instrument factors such as the number and type of light source(s) and the number of detectors.^{35,36} Further, the particle sizes calculated are from all possible orientations of the particles. The particle size information that one obtains might or might not correspond to what is actually present in the dispersed state.

A discussion of the rheology of dispersions is beyond the scope of this introduction. The rheology of a dispersed system, though, will change with a change in the particle size distribution.³⁷⁻³⁹ In general, as the average particle size becomes smaller, the total surface area of the pigment increases, which results in more vehicle being adsorbed. This adsorption normally causes the yield value, viscosity, and the dynamic elasticity of a dispersion to increase and the compliance (creep)^{40,41} to decrease.

Optical microscopy is a valuable instrument that is often ignored by coating scientists. The microscope can be used to obtain a particle size distribution according to several established test procedures.⁴²⁻⁴⁴ The practical resolving power of an optical microscope is dependent on the numerical aperture of the objective and the wavelength of the light source. For oil immersion lens with a numerical aperture of 1.30 and using white light, the lowest possible limit of resolution is 0.20 micron.⁴⁵ The practical lower limit without the use of oil immersion of the objectives would be around 0.50 micron. The microscope could be used to determine the absolute sizes or dimensions of particles greater than this. Another use would be to confirm that all particle size dimensions are less than 0.50 micron which can be concluded if no individual particle can be resolved. If so,

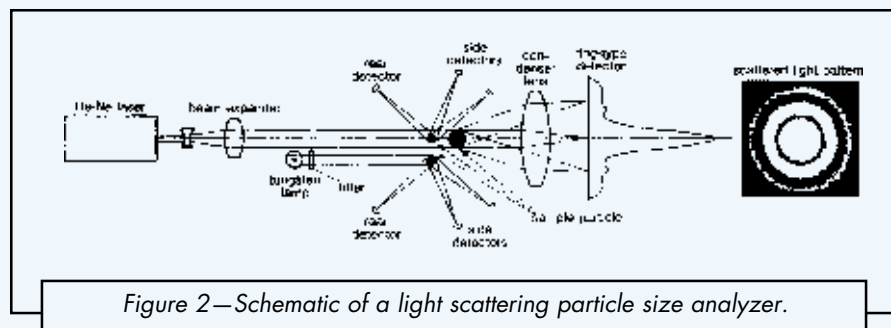
this particle size distribution would be adequate for most applications. Again, as with the dynamic light scattering instrument, the application of the optical microscope requires that the sample being investigated be representative of the pigment dispersion and that there be no change in particle size distribution with dilution. It should be noted that references 43 and 45 refer to ASTM test method E20. This test method was discontinued as of 1994.

EXPERIMENTAL

Two red pigments were studied in a conventional solvent-based acrylic vehicle for a screen printing ink. One pigment studied was a perylene red (PR 224) and the other was the IrgazinTM DPP red BO (PR 254) by Ciba Specialty Chemicals Corp., Newport, DE. The perylene pigment is considered by us to be more difficult to disperse in the vehicle used in this study.

The vehicle in this study consisted of a blend of a poly(methyl methacrylate) (PMMA) resin and a PMMA copolymer resin at a 3:5 solids ratio at 42.40 wt% total solids in EB acetate solvent. The EB acetate solvent was chosen to minimize the solvent loss on a three-roll mill while still resulting in a vehicle of acceptable solids loading and acceptable Newtonian viscosity (71.2 poises at 25.0°C).

The millbases were prepared with 20 wt% pigment in the vehicle by power mixing with a Cowles[®] blade at high shear at 3000 rpm for 40 min and then passing over a three-roll mill at pressures (feed roller/apron roller) once at 100/150 psi and the remaining times at 200/250 psi. Samples of the millbases were taken to make inks after each pass over the three-roll mill. The percent solids of each millbase were measured after every pass to determine if any solvent loss had occurred during milling. If so, the solvent loss was compensated for when making inks. The inks were made by mixing 55.20 wt% of the millbase with 44.17 wt% of the vehicle and the rest (0.63 wt%) was a silicone flow agent. The final inks had 11.04 wt% of pigment.



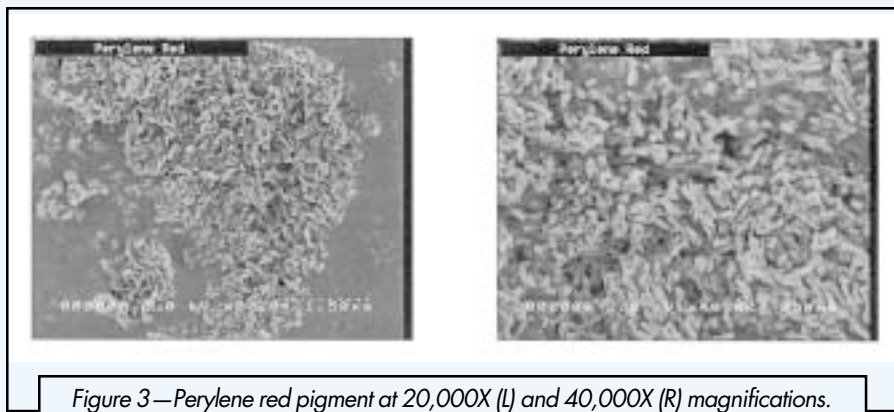


Figure 3—Perylene red pigment at 20,000X (L) and 40,000X (R) magnifications.

These inks are referred to as masstone inks. The masstone inks are labeled according to the millbases from which they were made. For example, the three-pass ink was made from the millbase that had been passed three times over the three-roll mill. The perylene millbase was passed over the mill five times but the DPP red BO millbase was passed nine times. The perylene pigment millbase was becoming dry on the three-roll mill after the fifth pass that prevented doing more passes. By comparison, the DPP red BO pigment millbase remained creamy for the entire nine passes. Prints were made by thinning the masstone inks with EB acetate solvent to a Newtonian viscosity of 18.0 poises at 25.0°C. The screen printing was done through a 230-mesh monofilament PET fabric screen onto white plasticized PVC film, clear PET film for studies by transmitted light, and onto a Morest chart (Form 03 black and white by the Leneta Co., Mahwah, NJ). The dried film thickness of the prints was two to three microns.

Fineness of Grind

The ink grind was read on a NPIRI G-1 one-mil fineness of grind gauge (Precision Gage and Tool Co., Dayton, OH). The grind reading was based on ASTM method D 1316-93⁴⁶ although there is also ASTM method D1210-96.⁴⁷ The values presented are when the preponderance of speckles disappears. The precision of this method is considered to be good. The values of repeated measurements of the same ink were within a one-unit range (average ± 0.5 unit).

Opacity

The inks screen printed on a Morest chart were checked for their opacity/transparency on a Spectraflash 500 (Datacolor International, Charlotte, NC) by measuring the contrast ratio (CR). Each value presented is calculated from five numerical readings on the Morest chart. The precision of this method is considered to be

good also. The coefficient of variation of five separate readings of the same print did not exceed $\pm 0.60\%$.

Gloss

The gloss of the prints was measured with a HunterLab D-48 gloss sensor (Hunter Associates Laboratory, Inc., Reston, VA) at 60° of the incident light according to ASTM method D523-89.⁴⁸ The data presented are the averages of five readings. This is another method of good precision that is equal to the precision of the CR method noted above.

Color Strength

Prints of the masstone inks were measured for color differences on the Spectraflash 500 using both reflected and transmitted light. Color strengths were measured by reflected light also on inks that had been mixed with a standard white. The masstone inks mixed with a standard white are referred to as "bleaches."³⁴ The inks were mixed at a ratio of 5 wt% of ink to 95 wt% of white. A Bird film applicator was used to pull two-mil films onto plain white charts (Form WA, Leneta Company). The draw-downs were oven-dried at 200°F for 20 min before reading. The masstone ink and bleach of the one-pass ink were used as the standards. Differences in color strengths between the first-pass stan-

dard of the masstone ink and of the bleached ink and the other inks were read in CIELAB. The values presented are the averages from five different readings on each print. Five separate readings of the same print would result in a standard deviation from ± 0.02 to ± 0.05 .

Particle Size Measurements

Particle size measurements were made of the masstone inks on a Horiba LA-910 laser scattering particle size distribution analyzer (Horiba Instruments, Inc., Irvine, CA). A fraction cell was used. Methyl ethyl ketone (MEK) solvent was used to dilute the masstone inks and to run a blank. About 10 mg of each masstone ink were placed in a 25 ml beaker and diluted to 20 ml with the MEK solvent. The particles were deagglomerated with ultrasonication for three minutes prior to measurements. A relative refractive index of 1.50-0.40i was chosen for the calculations of both pigments. The results will vary with a change in the relative refractive index. The results were compared based on volume and number distributions. Four diluted samples were made from each masstone ink. Eight readings were read from each of these four samples. The coefficient of variation of the eight readings of a sample never exceeded $\pm 5.00\%$ and the averages of the four samples were within ± 0.003 micron.

Rheological Measurements

Rheological measurements were done on a TA CSL² 100 rheometer (TA Instruments, Inc., New Castle, DE). The procedure for the TA instrument used a truncated 6 cm 4° cone with a gap setting of 111 microns. The procedure was to allow the sample to equilibrate on the rheometer with a solvent trap for 36 hr and then run in series a dynamic oscillation test, a creep test, and an equilibrium flow test. The 36-hr equilibration was to allow the system to attain maximum structure.^{37,38,49,50} Studies had shown that when sheared these inks take 24 hours

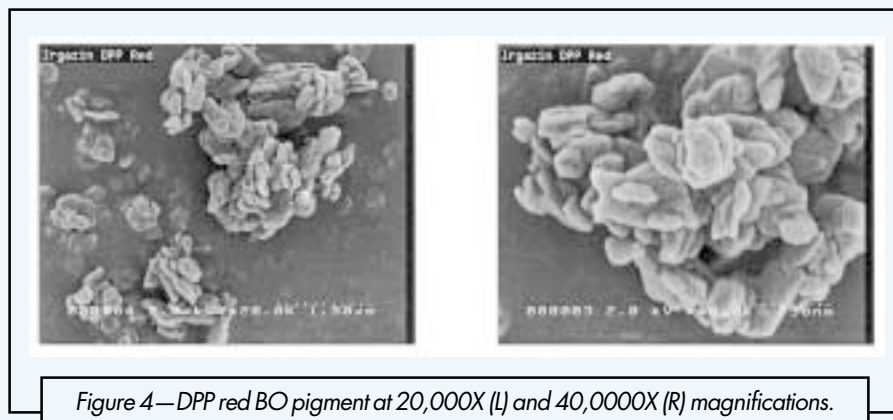


Figure 4—DPP red BO pigment at 20,000X (L) and 40,000X (R) magnifications.

Table 1—Grind Gauge, Contrast Ratio (CR), and Gloss Results versus Milling Pass

Pass	Grind		CR (%)		Gloss	
	Perylene	DPP Red BO	Perylene	DPP Red BO	Perylene	DPP Red BO
One-Pass	10.0+	9.5	35.22	44.95	53.8	68.8
Two-Pass	9.5	8.0	37.61	46.46	61.6	69.2
Three-Pass	7.0	5.5	41.46	46.51	68.5	71.8
Four-Pass	(none)	5.0	(none)	46.64	(none)	71.9
Five-Pass	5.5	4.0	49.77	46.73	74.8	72.7
Six-Pass	—	3.5	—	46.69	—	73.3
Seven-Pass	—	3.0	—	46.71	—	72.8
Eight-Pass	—	2.5	—	46.83	—	73.8
Nine-Pass	—	2.0	—	46.87	—	74.0

to reach maximum structure. The reason for this long time was attributed to a lack of dispersants in our model system. Studies have shown that when linear viscoelastic measurements are made on four different samples that have been allowed to attain maximum structure, a coefficient of variation (CV) of no greater than $\pm 15\%$ at any frequency would be obtained. The CV was smaller as the frequency was increased. The dynamic oscillatory test method was run at a 1% strain at 25.0°C from 40 to 0.003 Hz. Immediately following the dynamic oscillatory study, the rheometer measured the samples by creep. A stress of 50 dynes/cm² was applied for 15 min. The creep results were analyzed automatically. The equilibrium flow curve was done going from a stress of 1750 dynes/cm² to 10 dynes/cm² over 20 steps. An equilibrium flow curve applies a stress or shear rate at each step until there is an equilibrium value. The values for each step are then plotted. This technique takes into account the shear thinning that occurs in dispersions. The samples were run at each stress for no more than 10 min or until we reached a tolerance of 1.00%. Studies of the above were done with 4 cm and 2 cm diameter cones of various angles to make sure that the same results were being obtained and,

as such, slippage⁵¹ as any source of error in the measurements could be eliminated.

Strain sweeps^{37,52} were performed on the inks with the rheometer by allowing them to equilibrate also for 36 hr. The frequency was set at 1.0 Hz and the temperature at 25°C. A truncated cone of 2-cm diameter with a 2° angle was used with a gap setting of 55 microns. The start value and the end value of the stresses were set at 23.88 and 2846 dynes/cm², respectively. The strain sweep method is used by some to assess the stability of a pigment dispersion. The more stable a dispersion, the longer it should result in a constant G^* with an increase in strain, whereas an unstable pigment dispersion is noted by a decrease of the G^* at a lower strain.

Optical Microscopy

The dispersions were examined on a Jena Vert microscope using a 50X GF planachromatic objective with a numerical aperture of 0.90 and a reticulated 10X eyepiece for a total magnification of 500. The samples were examined by diluting in MEK, applying a drop to a microscope slide, and allowing to dry. The slide was then examined for large pigment particles with the reticulated eye-

piece. A particle size of 0.50 micron was considered the smallest practical dimension to be resolved.^{43,45}

Field Emission Scanning Electron Microscopy (FESEM)

The FESEM photographs of the dry pigment powders were characterized on a Hitachi S4500 scanning electron microscope. The dry pigment samples were mounted for analysis using double-sided adhesive tape. The photographs give some insight into the morphological information (size and shape of crystallites and agglomerates). The two magnifications chosen were 20,000X (X20.0K) and 40,000X (X40.0K).

RESULTS AND DISCUSSION

Figures 3 and 4 show the FESEM photographs of the two dry pigments at two different magnifications. These pigments are different not only in agglomerate sizes but also in shape and size of primary particles. The photographs of the perylene pigment in Figure 3 show that this pigment is highly agglomerated with acicular primary particles. The typical width and length of these acicular primary particles are 0.05 and 0.15 micron,

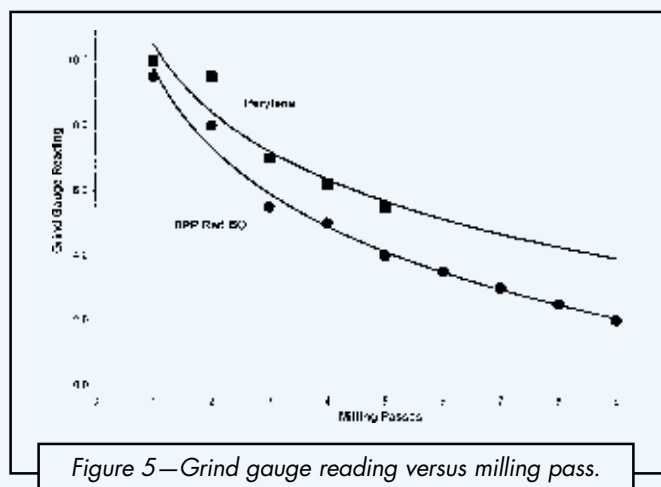


Figure 5—Grind gauge reading versus milling pass.

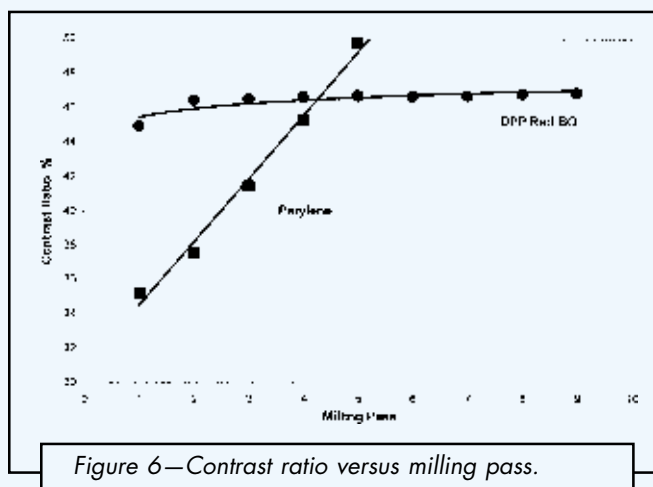


Figure 6—Contrast ratio versus milling pass.

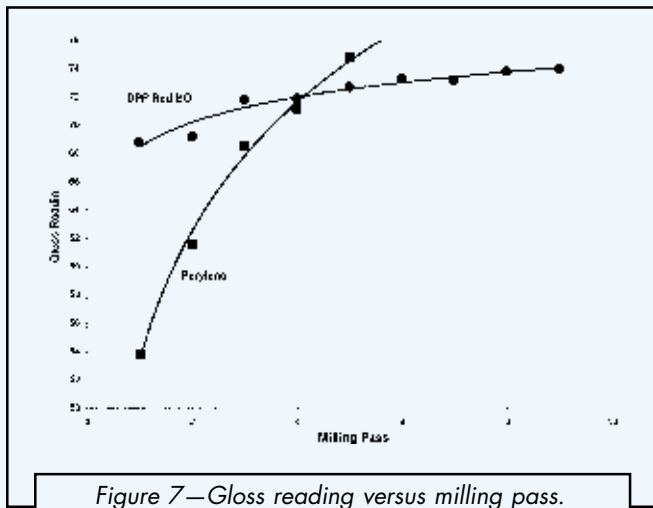


Figure 7—Gloss reading versus milling pass.

respectively. The photographs of the DPP red BO pigment in Figure 4 show a pigment that is less agglomerated with platelet-shaped primary particles. The approximate thickness and width of these platelets are 0.05-0.07 and 0.15-0.60 micron, respectively. Because of the diversified differences in shape and size of the agglomerates as well as the primary particles, accurate assessment of the degree of pigment dispersion with processing would be a challenge.

The fineness of grind results are presented in Table 1 and shown in Figure 5. A value of 10.0 on the NPRI one-mil fineness of grind gauge corresponds to 1.0 mil whereas a value of 1.0 corresponds to 0.1 mil. The values represent when the largest agglomerates can no longer be drawn down the gauge. The values in Table 1 and Figure 5 show that the greatest change for both pigments was going from the two-pass to the three-pass inks. By the grind gauge, there is a small rate of change in the degree of pigment dispersion after the third pass, but the changes in values after each mill pass are significant. Figure 5 would indicate that both pigments are being dispersed at an

equal rate, but that there are more larger agglomerates with the perylene pigment than with the DPP red BO pigment. The conclusions of the grind gauge readings are interesting in that the same conclusions will be drawn below with the other methods.

A CR value gives an indication of opacity or hiding. A value of 100% would be complete hiding whereas a value of 0% would be no hiding. Figure 6 shows the CR results of the inks with milling passes and Table 1 lists the data. The sudden increase in the CR of the perylene ink with each pass would be attributed to a significant increase with processing in the concentration of pigment particles with diameters near 0.25 micron that would increase the opacity. The CR curve for the DPP red BO pigment would indicate that there is a small increase in particles with a diameter of around 0.25 micron to affect the opacity. This would support the claim that the DPP red BO pigment contains fewer larger agglomerates to be broken down. Simpson⁵³ noted with the dispersion of TiO₂ pigments in an alkyd vehicle that there was not much increase in opacity going from paints made by hand-mixing the pigment to paints made with the pigment that had been dispersed in a ball mill up to 70 hr. He attributed this to the titanium dioxide pigment being easily dispersed such that there was more of a decrease in a few larger particles than an increase in smaller particles that govern

Table 2—Differences in Color Strengths of the Perylene Masstone and Bleached Inks

Pass	Masstone Ink		Bleached Ink
	Color Strength by Reflectance (units)	Color Strength by Transmission (units)	Color Strength by Reflectance (units)
One-Pass	Standard	Standard	Standard
Two-Pass	1.23 Darker 0.12 Bluer 2.75 Less Saturated 3.01 Delta E	3.71 Darker 2.18 Yellower 8.37 More Saturated 9.41 Delta E	2.53 Darker 0.40 Yellower 4.10 More Saturated 4.84 Delta E
Three-Pass	2.62 Darker 0.53 Bluer 7.73 Less Saturated 8.18 Delta E	8.78 Darker 6.97 Yellower 17.49 More Saturated 20.78 Delta E	5.88 Darker 0.48 Yellower 8.14 More Saturated 10.05 Delta E
Five-Pass	2.98 Darker 1.49 Bluer 6.84 Less Saturated 7.16 Delta E	9.42 Darker 6.45 Yellower 16.76 More Saturated 20.78 Delta E	5.48 Bluer 0.01 Bluer 6.55 More Saturated 8.54 Delta E

Table 3—Differences in Color Strengths of the DPP Red BO Masstone and Bleached Inks

Pass	Masstone Ink		Bleached Ink
	Color Strength by Reflectance (units)	Color Strength by Transmission (units)	Color Strength by Reflectance (units)
One-Pass	Standard	Standard	Standard
Two-Pass	0.44 Darker 0.63 Yellower 0.11 More Saturated 0.77 Delta E	1.20 Darker 1.07 Redder 1.91 More Saturated 2.50 Delta E	0.36 Darker 0.11 Redder 0.64 More Saturated 0.74 Delta E
Three-Pass	0.21 Darker 0.43 Yellower 0.17 More Saturated 0.49 Delta E	0.74 Darker 0.44 Redder 1.21 More Saturated 1.40 Delta E	0.41 Darker 0.08 Yellower 0.43 More Saturated 0.78 Delta E
Five-Pass	0.13 Darker 0.44 Yellower 0.20 More Saturated 0.49 Delta E	0.62 Darker 0.18 Redder 1.36 More Saturated 1.50 Delta E	0.45 Darker 0.11 Redder 0.86 More Saturated 0.98 Delta E
Nine-Pass	0.32 Darker 1.49 Yellower 0.21 More Saturated 0.56 Delta E	1.13 Darker 0.38 Redder 3.01 More Saturated 2.15 Delta E	0.70 Darker 0.13 Redder 1.34 More Saturated 1.31 Delta E

Table 4—Perylene and DPP Red BO Particle Sizes from Particle Size Analyzer

	Mean Volume Diameter (micron)		Mean Number Diameter (micron)	
	Perylene	DPP Red BO	Perylene	DPP Red BO
Ink	Perylene	DPP Red BO	Perylene	DPP Red BO
One-Pass	5.603	0.632	0.440	0.483
Two-Pass	0.981	0.606	0.420	0.469
Three-Pass	0.750	0.597	0.398	0.466
Five-Pass	0.743	0.588	0.394	0.459
Nine-Pass	—	0.572	—	0.452

opacity. He needed to ball mill the system for four hours to have acceptable grind gauge readings to insure that large particles would not affect the decorative appearance of the dried paint film.

Gloss has been accepted for some time as an indicator of the degree of pigment dispersion. Gloss will increase in most systems until the pigment particles are not large enough to penetrate the surface of the dried film. As noted above, our dried films are around two to three microns thick. Table 1 and Figure

7 show that there was just a slight increase in gloss with the DPP red BO pigment going from the first to the ninth pass (5.2 units) as opposed to the perylene pigment ink in which after five passes the gloss had increased 21.0 units. Again, this would support the conclusion that there are more larger agglomerates initially in the inks with the perylene pigment than in the ink with the DPP red BO pigment and, thus, each milling pass of the ink with the perylene pigment will result in more of an in-

crease in gloss. Of the results for the ink with the DPP red BO pigment listed in Table 1, the fineness of grind and the gloss would suggest that there is a change in the degree of dispersion going on over the nine passes whereas the CR results would indicate that no change in dispersion has occurred after the second pass. This would indicate that the CR method is not as sensitive to a small increase of fine particles as the fineness of grind and gloss measurements are to a decrease in a small number of larger particles. Of the fineness of grind and gloss measurement techniques for the DPP red BO pigment, the fineness of grind method was more sensitive to changes than the gloss measurement method.

Color strength is an indicator of the degree of pigment dispersion. As noted in Figure 1, this method is very applicable when the minimum particle sizes are to be dispersed below 0.3 micron. The color data are presented in Tables 2

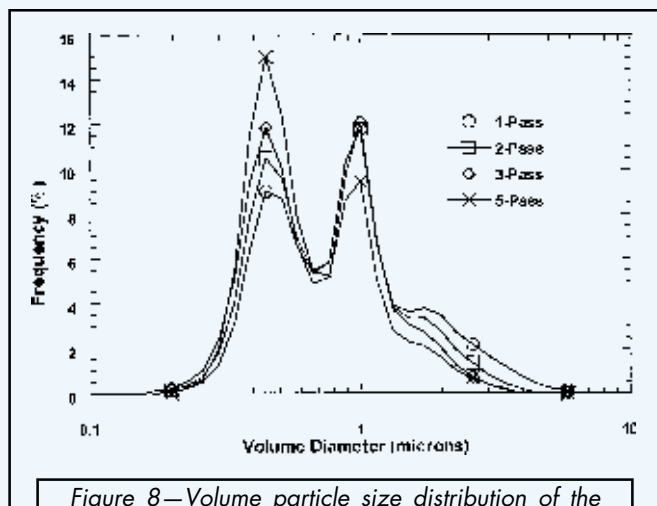


Figure 8—Volume particle size distribution of the perylene inks.

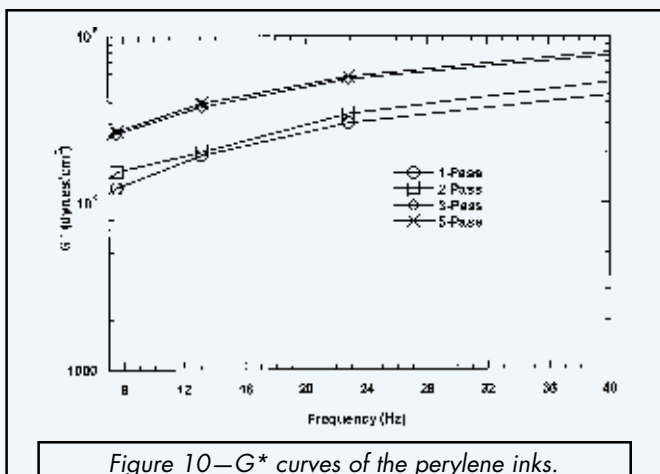


Figure 10— G^* curves of the perylene inks.

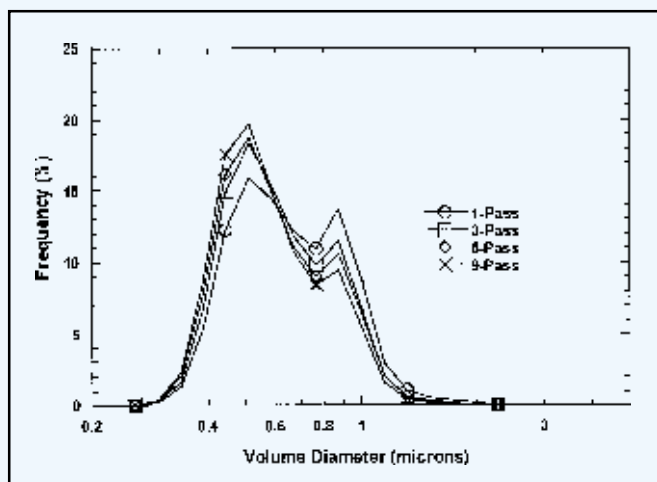


Figure 9—Volume particle size distribution of the DPP red BO inks.

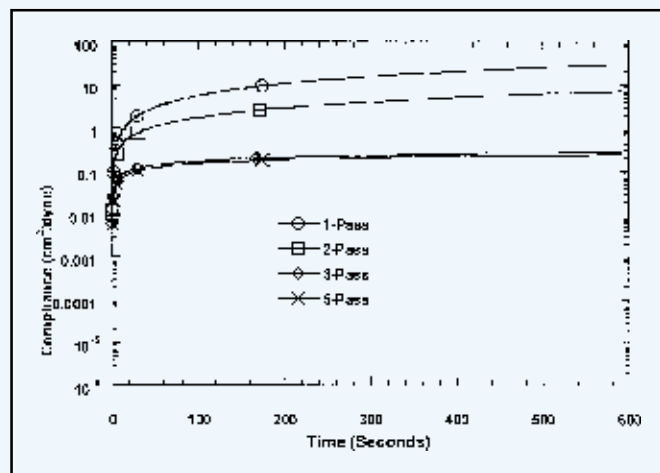


Figure 11—Creep (compliance) curves of the perylene inks.

and 3. The values presented are by (1) reflectance of prints screen-printed onto white vinyl film, (2) transmission readings of inks screen-printed onto PET film, and (3) reflectance readings of two-mil drawdowns of bleaches. The results in Table 2 show a significant change in DE for the first three passes of the perylene ink. The color strength results show no appreciable change going from the third to the fifth passes (no more than a 1.02 unit change). The results by transmission and the reflected readings of the bleaches are what one might expect. The prints are becoming stronger (darker) and cleaner (more saturated) with each pass, although significantly more yellow by transmission. The reflectance readings of the masstone ink are not what one would expect. The results would indicate that the inks are becoming stronger, slightly bluer, but dirtier (less saturated). The corresponding results for the inks made with the DPP red BO pigment are shown in Table 3. The results show no appreciable change af-

ter the second pass. The results by transmission and by reflectance of the bleaches, again, are what one would expect as the prints are becoming cleaner, stronger, and redder although the change after nine passes is no more than 2.15 ΔE units. The measurements of the color strength of the masstone inks by reflectance were not sensitive to any changes in pigment dispersion. After nine passes over a three-roll mill, this method detected less than 1.0 ΔE unit. The above color analysis results would support again the conclusion that the perylene pigment has more larger agglomerates than the DPP red BO pigment that are being broken down into smaller ones. This is resulting in more color change with each pass with the perylene pigment.

The particle size analysis results by light scattering are presented in Table 4. The mean diameters (in microns) based on volume and number distributions are presented. There is less change in the mean as determined by number than by

volume. By volume, the perylene pigment shows little change after the third mill pass (as do the color strength measurements) whereas the DPP red BO pigment shows little change per pass after the second pass (also as do the color strength measurements). The particle sizes based on the volume distribution show that the first few passes for the perylene pigment are used to break down large agglomerates. The particle size results would indicate that the agglomerates are much fewer in the BO red pigment. It should be noted that these particle size results are not consistent with the grind gauge readings. As noted, the lower size limit of a pigment detectable on a grind gauge is two to 10 microns depending on the reference.^{15,19,20} According to Table 4, the only ink that should have had a fineness of grind gauge reading greater than zero would have been the one-pass perylene ink measured by a volume distribution. Some of the perylene inks were observed under the microscope and values of

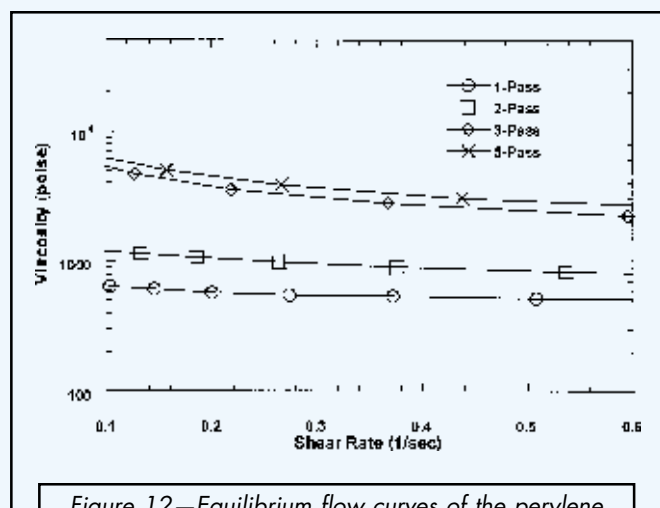


Figure 12—Equilibrium flow curves of the perylene inks.

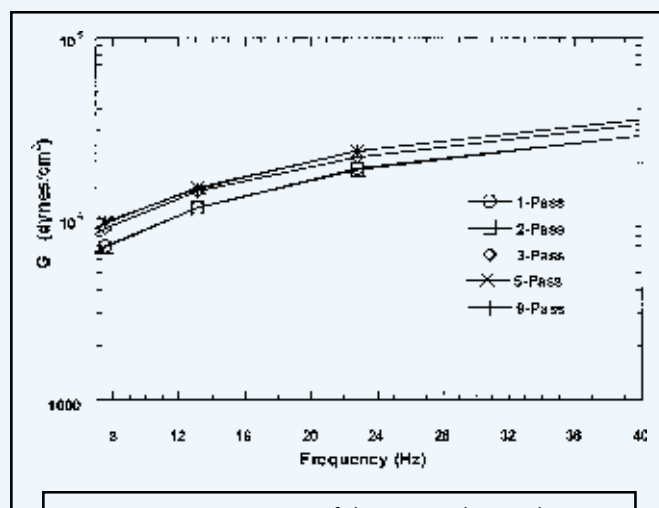


Figure 14— G^* curves of the DPP red BO inks.

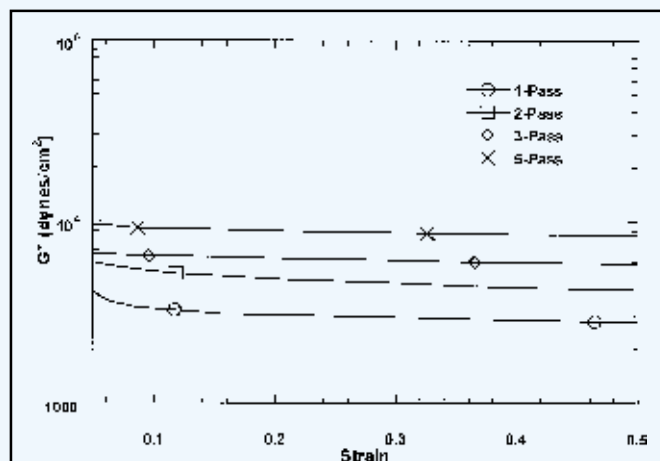


Figure 13—Strain sweep curves of the perylene inks.

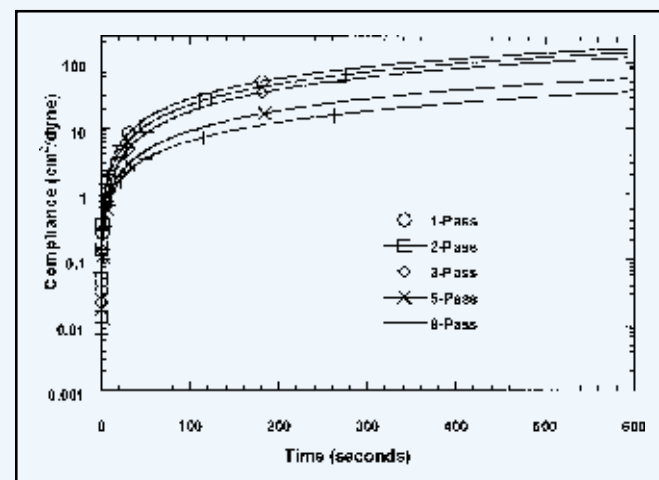


Figure 15—Creep (compliance) curves of the DPP red BO inks.

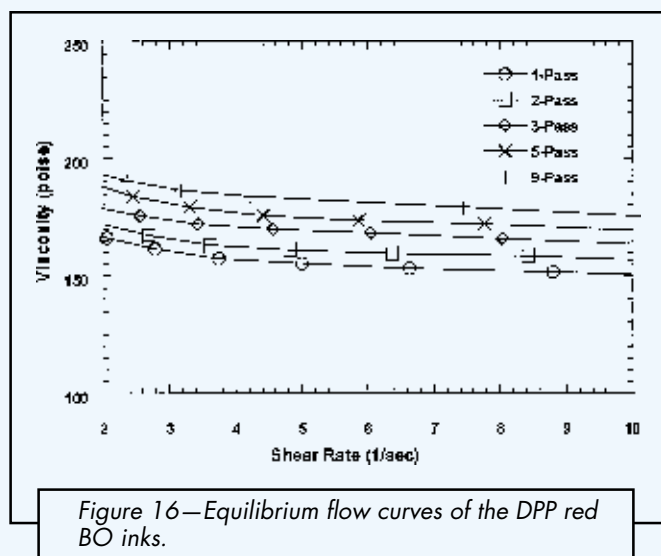


Figure 16—Equilibrium flow curves of the DPP red BO inks.

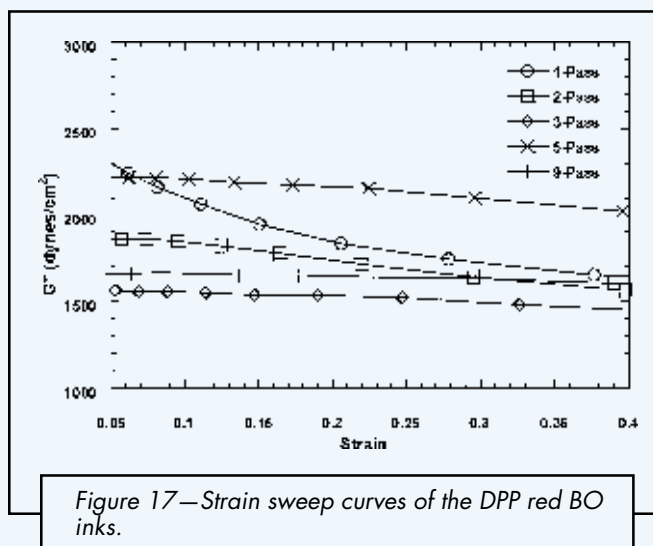


Figure 17—Strain sweep curves of the DPP red BO inks.

around 0.80 micron for the larger dimension for the largest particles were being observed. The microscope would confirm the readings by the particle size analyzer. The discrepancy between the grind gauge readings and the particle size results is believed to be that the ultrasonication of the samples before reading broke up any large agglomerates that would have been read on the grind gauge. Further, the grind gauge could detect a few large particles that would not necessarily be detected by the light scattering instrument upon dilution. The diluted samples are now read on the particle size analyzer in a flow cell by the procedure of measuring without ultrasonication, ultrasonication on the particle size analyzer for three minutes, and then reading again. This procedure gives an indication of the number of larger particles being broken down. It is interesting to note in Table 4 that by a volume distribution, the perylene dispersion has a larger mean particle size whereas by the number distribution, the DPP red BO pigment dispersion has a larger mean particle size.

Figures 8 and 9 show the changes in pigment dispersion better than the mean values in Table 4. The curves are from the volume distributions. The figures show that the lower limits for the pigment particle sizes do not change much for either pigment. There is some change in the upper limit of particle sizes. This could explain why there are small changes in the means after as much as nine passes over a three-roll mill. There are significant changes in the distributions between the two peaks for both pigments with a decrease in the peaks of the larger particle size distribution and an increase in the smaller particle size peak with each pass. The distribution curve can change with change in the choice of relative refractive index but

these bimodal distributions appear to correspond to the actual dispersions. Others in the literature with other light scattering instruments have noted bimodal distributions with the dispersions of organic pigments.⁵⁴

The G^* curves of the four perylene inks are presented in Figure 10. The curves are plotted between the frequencies of 7 and 40 Hz. The inks were read to 0.003 Hz but the curves below 7 Hz were becoming indiscernible. There is the expected trend in Figure 10 with an increase in G^* with each pass over the mill. These results suggest that the greatest change was between the 2nd and the 3rd passes as did the results for the fineness of grind, contrast ratio, gloss, and the color measurements. The creep (compliance) curves of the four perylene inks are shown in Figure 11. The trend is expected in that there is a decrease in compliance with each milling pass. These results show also that the greatest change was between the 2nd and 3rd passes. Figure 12 presents the equilibrium flow curves results for the perylene inks. The viscosity results in this figure are presented as a function of the shear rate although the study was done over a shear stress range. The trend in results going from the 1st pass to the 5th pass is expected. Further, these results indicate again that the greatest change was from the 2nd to the 3rd passes. The equilibrium flow curves, creep flow curves, and the G^* oscillation curves all gave the same relative information among the four inks. The advantage to an equilibrium flow curve is that one does not need to allow the sample to attain maximum structure before reading in the linear region in order to get good precision as one does with elasticity measurements. The strain sweep study results are presented in Figure 13. The results are expected in that there is an increase

in G^* with each milling pass. However, the results do not show much difference among the inks with regard to maintaining a linear displacement. All curves are linear up to the strain of 50%.

Figure 14 shows the G^* curves for the one-, two-, three-, five-, and the nine-pass DPP red BO inks. The results are consistent but this method cannot distinguish the one- and two-pass inks or the five- and nine-pass inks. These results here also indicate that the greatest change was going from the two-pass to the three-pass inks. The other test method that would indicate this for the DPP red BO pigment would be the fineness of grind measurement (Figure 5). The results in Figure 14 would indicate also that the differences in the inks are small. This has been indicated above by the CR, gloss, color strength, and particle size measurements. The creep flow results are presented in Figure 15. The trend of the results is expected (lower compliance with each milling pass). The one-pass ink had the highest compliance, then the two-pass ink, and then the three-pass ink. The nine-pass ink had the lowest compliance as expected. A comparison of Figure 15 to Figure 11 shows that there was more change in the dispersion of the perylene ink with each pass over the mill than with the DPP red BO ink. This has been noted previously by the other methods. The equilibrium flow curves for the DPP red BO inks are presented in Figure 16. The shear rate range in this figure is higher than that in Figure 12. Since the same shear stress range was used for both studies, this would indicate that the inks in Figure 16 are of lower viscosity than those in Figure 12. The results of Figure 16 show that the one-pass ink has the lowest equilibrium values, then the two-pass ink, and then

the three-pass ink. The nine-pass ink has the highest values, again, as expected. The differences among the nine inks are significant but not as pronounced as the differences in the perylene ink as shown in Figure 12. The results in Figures 14-16 are consistent as were the results for the perylene inks. Further, the rheological results for the DPP red BO inks show little overall differences from the one-pass to the nine-pass inks as did the contrast ratio, gloss, and color strength measurements. Figure 17 is of the strain sweeps of the DPP red BO inks. Here, there is no direct correlation between the G^* and the number of passes over the mill. The G^* range of Figure 17 is significantly smaller than that of Figure 13. The incorrect order of the increase of G^* with each mill pass in Figure 17 could be from the rheometer not being sensitive enough to the small changes with each pass as was the case with the G^* curves below a frequency of 7 Hz as noted above. The curves do follow the expected trend in that they become more linear for a longer strain with each mill pass. The curves of the one-pass and two-pass inks show nonlinear behavior over the strain range up to 40%. However, the loss of linearity of the curves in Figure 17 would indicate that the dispersion does not become stable until the 3rd pass. Experience with this pigment in this vehicle would not support this conclusion.

CONCLUSIONS

The quality of pigment dispersions as a function of processing was characterized by particle size distribution by static light scattering, NPRI fineness of grind gauge, gloss, contrast ratio, color strength measurements, and rheology. Of these, particle size distribution, fineness of grind gauge, and rheology are sensitive enough to pick up subtle differences in the pigment dispersions with each pass over the three-roll mill. Because pigment dispersions are complex fluids, it is necessary to rely on more than one characterization tool for accurate assessment of dispersion quality. The use of these methods would be applicable to all pigmented systems.

The differences in the milling of the two pigments can be explained in terms of the morphology of the dry pigments. The perylene pigment has larger agglomerates but smaller primary particles than the DPP red BO pigment. When these larger agglomerates are broken down, the total surface area of the pigment increases dramatically requiring more vehicle. This is why the ink with the perylene pigment became "dry" on the mill after five passes. The reduction

of the larger agglomerates into smaller particles is reflected in the gloss and contrast ratio measurements that were able to detect differences with each mill pass of the ink. By contrast, the smaller agglomerates of the DPP red BO pigment with larger primary particles resulted in a minor increase in surface area upon milling and, thus, the ink could be passed over the three-roll mill at least nine passes with no indication of more vehicle being needed. The reduction of fewer, smaller agglomerates with the DPP red BO pigment resulted in no or little significant changes as measured by gloss and contrast ratio.

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