

Effect of Hydrophilicity and Lipophilicity Balance on Rheological Properties of Pigment Dispersions

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Keywords: Hydrophilicity Lipophilicity Balance, Rheology,
Liquid Inks, Dispersions

Abstract: Many solvent-based flexographic and gravure inks are prepared by grinding pigments in resin solutions (acrylics, polyamide, polyester, etc.). Polymer chemists and formulators have modified resins with various functional groups in order to achieve optimal ink performance. This paper demonstrates that resin hydrophilicity and lipophilicity balance has a dramatic effect on the rheological properties of liquid inks. Hydrophobic groups adsorb onto the pigment surface, while hydrophilic groups are solvated in solution and stabilize pigment particles (steric/electrostatic stabilization). Both the hydrophobic and hydrophilic groups are important for particle stabilization and an appropriate balance can result in an ink or dispersion with a Newtonian flow. Otherwise, pigment particles may flocculate and the ink becomes shear thinning. The degree of shear thinning strongly depends on the balance of resin hydrophilicity and lipophilicity and may significantly impact the ink performance.

Introduction

Solvent-based flexographic and gravure printing inks are made from resins, solvents, pigments and additives. Solvent-based ink preparation involves dispersing pigments in a grinding varnish to obtain a pigment dispersion followed by addition of a letdown varnish (a mixture of resins, additives and solvents). Resins and pigments are the backbone of the inks, though appropriate additives can be added to modify the ink performance. Letdown resins in solvent-based inks contribute mostly to ink resistance properties such as adhesion, cohesion, water/chemical resistance, and flexibility. Grinding resins

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contribute mostly to pigment dispersing, which is critical to the optical properties of ink films such as gloss, color strength, and transparency. Pigment dispersions also affect ink rheological properties, which are related to ink flow and transfer, print sharpness, ink settling and ink misting. A good dispersion is essential in formulating an ink with excellent rheological properties, optical properties and printability.

Wetting, grinding and particle stabilization are three essential steps in preparing a pigment dispersion (Patton, 1979). Some researchers have done extensive research on characterization of pigment dispersions and the effects of the dispersions on various ink properties (Tsutsui, K. and Ikeda, S., 1982; Carr, W., 1982). Effects of various additives on rheological properties of liquid inks were also studied (Smith, D., 1994). Experienced formulators may notice that resin chemistry is critical to the quality of pigment dispersions. However, no systematic study was done on this area in the literature. The purpose of this research is to examine how the resin hydrophilic and lipophilic functionality affects the dispersion rheology, ink optical properties and printability. This paper publishes Part I of this research: effects of resin hydrophilicity and lipophilicity balance on dispersion rheology. A physical mechanism for the observed phenomenon is also proposed.

Theory

Pigment Grinding

Pigment Dispersions can be prepared by a variety of mechanical agitators such as bead mills, ball mills and high-speed mixer (Leach R. H. and Pierce R. J.). The dispersed state of pigment dispersions can be quantified thermodynamically by the Gibbs-Helmholtz equation (Conley, 1996):

$$\Delta G = \Delta H - T\Delta S$$

ΔG is the energy provided by a mechanical agitator, ΔH represents the binding energy of the pigment aggregates/flocculates, and ΔS is the entropy of the pigment dispersion (the state of the particle disorder). When mechanical energy introduced into the system exceeds the binding energy of the aggregates/flocculates, individual pigment particles are dispersed, which increases disorder (positive ΔS). A change in entropy ΔS , quantitatively defines dispersion. Part of this energy, of course, is wasted and appears as heat (an increase in T).

Stabilization of Pigment Particles

After pigment aggregates/flocculates are broken into fine particles by mechanical agitator, individual particles have to be stabilized. At least three major types of interactions are involved in colloidal particle stability (Conley, 1996):

- (1). London-van der Waals force of attraction
- (2). Coulombic force of repulsion for charged particles
- (3). Steric repulsion force arising from solvated adsorbed layers

Pigment particle stability is determined by the total potential energy resulting from the above three interactions:

$$E_{\text{total}} = E_{\text{attraction}} + E_{\text{repulsion}}$$

In general, a colloidal dispersion will be stable for a reasonable period of time if the total repulsive energy exceeds the attractive energy by a magnitude several orders higher than the thermal energy of the particles. When the total attractive energy exceeds the total repulsive energy, the dispersion will flocculate quickly after the aggregates/flocculates are broken down by the agitator.

The repulsive force between pigment particles is the barrier that prevents the particles from returning to the aggregated state. Individual particles will have to remain in random suspension throughout the liquid system for a stable dispersion. To introduce an effective barrier, pigment particles must be adequately covered by resin molecules (adsorption property). A portion of the resin molecules must display similarity to the solvent (semblance property) and be solvated and direct outward to the solvent phase. Further, a barrier must be created around each particle and this barrier must be capable of preventing other particles from coming into direct contact (isolation property).

Rheological Properties of Pigment Dispersions

Viscosity is a measure of the ability of a dispersion to flow. Researchers have found that dispersion viscosity drops as amounts of dispersant added to the flocculated system increase. With zero dispersant, the highly agglomerated system disallows individual particle movement, which results in a high viscosity due to inter-particle bridging structures. As the dispersant is added into the system, agglomerates become smaller and the more discrete particles move more freely in the system, resulting in diminished viscosity.

Coarse pigment particles in the dispersions impede mechanical fluidity, tending to increase the dispersion viscosity. As the coarse particles are broken down to finer particles, viscosity tends to decrease. This occurs until the particles become

so fine that when the effect of increase in surface area and the quantity of solvent adsorbed onto the pigments becomes significant, the net effect is to reduce fluid mobility of the system, especially at low shear rates. This results most often in thixotropy.

In dispersing organic materials in polar liquids or polar solids in less polar liquids, hydrophilicity lipophilicity balance (HLB) values may provide a general guide to molecular affinities and serve a useful purpose in designing or comparing dispersant (Conley, 1996). However, this concept does not consider molecular geometry and sometimes provides misleading information. Two resins with exactly the same HLB value may perform very differently in dispersing pigment since their functionality may be distributed differently on the backbone and the identity of functional groups may be different on the molecules. Therefore the absolute HLB value may not correlate very well with the dispersion properties. However, it has been observed in this laboratory that the amount of hydrophilic group and lipophilic group present in the resin molecule has a dramatic impact on the rheological properties of the pigment dispersions.

Experimental

Proprietary resins were synthesized by the Sun Chemical General Printing Ink Division Polymer Technology laboratory for this study. The resins contain a hydrophilic monomer R_H , a lipophilic monomer R_L and a connecting monomer R_C . An experimental design (three-component Simplex Mixture, see Figure 1) was set up to examine the effect of these building blocks on the rheological properties of pigment dispersions. Ten resins were prepared in the experimental design. Table 1 summarizes the monomer compositions, HLB values, GPC weight-average molecular weights, acid values and Duran softening points of these resins. Acid values are attributed to R_H that has a carboxylated acid functionality. HLB values were calculated according to Davis's method (Davis, J.T. 1957).

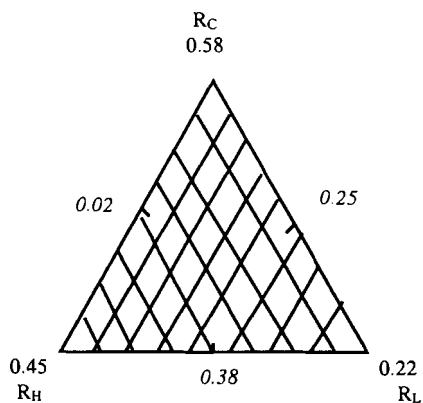


Figure 1. Monomer mole ranges in the three-component simplex mixture experimental design.

Table 1. Resin Composition and Properties

Resin ID	R_L	R_H (mol)	R_C	HLB	MW_w	Acid #	T_{soft} ($^{\circ}C$)
1	0.02	0.25	0.58	9.10	3460	45.5	107
2	0.22	0.25	0.38	6.85	4700	36.5	82
3	0.02	0.45	0.38	9.36	2830	77.0	93
4	0.12	0.35	0.38	7.96	3380	56.6	94
5	0.09	0.32	0.45	8.36	3000	52.9	100
6	0.05	0.38	0.41	8.85	2290	64.5	92
7	0.15	0.28	0.41	7.54	3290	43.3	70
8	0.02	0.35	0.48	9.23	2950	63.6	105
9	0.12	0.25	0.48	7.82	4570	41.2	100
10	0.05	0.28	0.51	8.72	3110	48.2	91

The mole range of the lipophilic group R_L in the resins is 0.02 - 0.22mol and the mole range of the hydrophilic group R_H is 0.25 - 0.45mol, as shown in Table 1. Table 1 also shows that the resins with more R_L monomers have higher molecular weights and lower softening points. The resins with more R_H monomer have higher acid values. This indicates that the resins are consistent since R_H contributes to the acid value, and R_L is a soft, higher molecular weight monomer that tends to reduce resin softening point. Prior to the setup of this experimental design, our lab had observed that a phthalocyanine blue dispersion

could not be prepared successfully without either R_L or R_H . Both the hydrophilic and lipophilic groups are essential to the dispersion.

Pigment dispersions were prepared according to the following formula with a proprietary milling technique:

Phthalocyanine blue pigment	25%
Resin	25%
n-propanol	50%

Rheological profiles of these dispersions were measured by a Rheolyst AR 1000 (TA Instrument) at a shear rate range of 1 ~ 2000 1/s with a cone and plate geometry. A cover for the cone and plate was used to prevent solvent evaporation.

Results and Discussions

Effect of Hydrophilic Group R_H

The effect of hydrophilic group R_H on rheological properties of the dispersions was studied by examining the dispersions based on the resins with equal amounts of lipophilic groups R_L and varying amounts of R_H .

Resins 1, 3 and 8 in the experimental design have equal amounts of lipophilic group R_L , 0.02mol. These resins have hydrophilic group R_H 0.25, 0.35 and 0.45mol for resin 1, 8 and 3, respectively. We could not prepare dispersions successfully from resins 1 and 8 (coagulated pigments settled immediately after the preparation). However, as R_H is increased to 0.45mol (resin 3), a dispersion was prepared successfully. This indicates that, at 0.02mol R_L , the resin needs as high as 0.45mol of R_H to stabilize pigment particles. Within the tested range, at equal amount of lipophilic group, more hydrophilic group is beneficial for making dispersions.

Resins 6 and 10 have equal amounts of lipophilic group R_L , 0.05mol, while R_H is 0.28mol for resin 10 and 0.38mol for resin 6. Their rheological profiles are shown in Figure 2. The dispersion based on Resin 6, which has higher acid functionality, exhibits a more Newtonian behavior, especially at lower shear rates. This indicates that, at the same amount of lipophilic group, a higher amount of acid functionality (hydrophilic group) results in a more Newtonian dispersion.

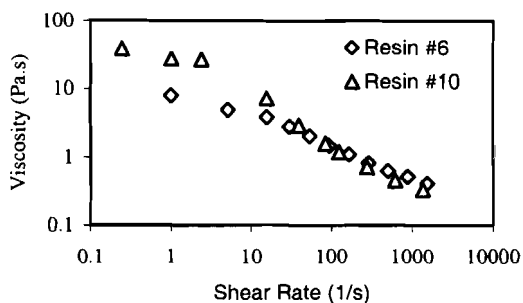


Figure 2. Viscosity vs shear rate for dispersions based on resin 6 and 10

Resins 4 and 9 have equal amounts of lipophilic group R_L 0.12mol, while R_H is 0.25mol for Resin 9 and 0.35mol for resin 4. The rheology profiles of the dispersions based on these resins are shown in Figure 3. The dispersion based on Resin 4, which has higher amount of hydrophilic group, exhibits a more Newtonian behavior. This is further evidence that, at equal amounts of lipophilic groups, higher acid functionality results in a more Newtonian dispersion.

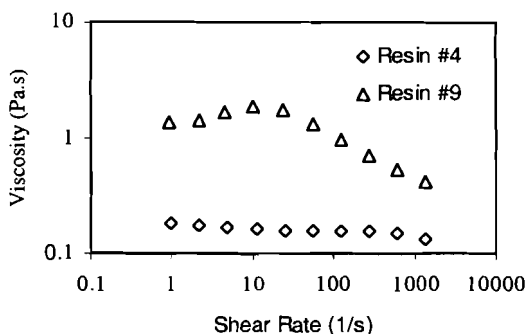


Figure 3. Viscosity vs shear rate for dispersions based on resin 4 and 9

The above results show that, at 0.02mol R_L , the resin needs as high as 0.45mol of R_H to stabilize pigment particles. When the lipophilic group R_L is increased to 0.05 – 0.12mol, dispersions can be prepared when R_H is as low as 0.25-0.28mol.

Both the adsorption property provided by R_L and barrier property provided by R_H are important for dispersion preparation. When the adsorption property becomes stronger (more R_L), less barrier property (less R_H) is required to make a dispersion.

Effect of Lipophilic Group R_L

The effect of the lipophilic group R_L on rheological properties of dispersions was studied by examining the dispersions based on the resins with equal amounts of R_H but different amounts of R_L .

Resins 1, 2 and 9 have equal amounts of hydrophilic group R_H 0.25mol, while the amount of lipophilic group is 0.02mol for resin 1, 0.12mol for resin 9 and 0.22mol for resin 2. Their rheological profiles are shown in Figure 4. We were not able to make a dispersion using resin 1 due to insufficient adsorption, as described earlier. Resin 2, which has higher R_L (0.22mol) than Resin 9 ($R_L=0.12$ mol), exhibit a more Newtonian rheology, especially at lower shear rates.

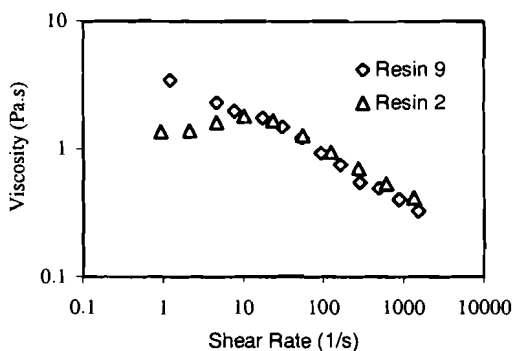


Figure 4. Viscosity vs shear rate for dispersions based on resin 2 and 9

Resins 7 and 10 have the same amount of hydrophilic group R_H 0.28mol, while the amount of lipophilic group is 0.15mol for Resin 7 and 0.05mol for Resin 10. The rheological profiles of their dispersions are shown in Figure 5. The dispersion based on Resin 7, which has a higher amount of R_L (0.15mol), showed a more Newtonian behavior than the dispersion based on Resin 10 ($R_L=0.05$ mol).

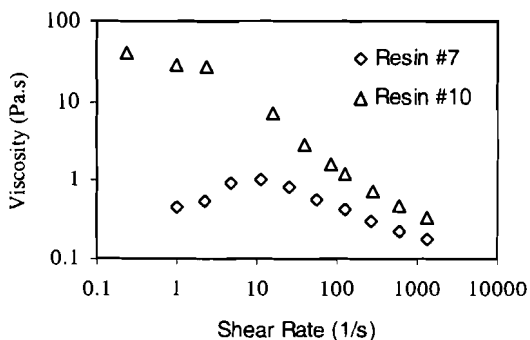


Figure 5. Viscosity vs shear rate for dispersions based on resin 7 and 10

Resins 4 and 8 have the same amount of hydrophilic group R_H 0.35mol, while the amount of lipophilic group is 0.12mol for Resin 4 and 0.02mol for Resin 8. At $R_L=0.02$ mol (Resin 8), we were not able to make a dispersion (coagulated particles settled immediately after the preparation). When R_L is increased to 0.12mol (Resin 4), a dispersion was prepared successfully.

At 0.25mol R_H , the resin needs as high as 0.12mol of R_L to make a dispersion. When the R_H is increased to 0.28mol, dispersions can be prepared when R_H is 0.05mol. This further indicates that both the adsorption property provided by R_L and barrier property provided by R_H are important for dispersion preparation. When the barrier property becomes stronger (more R_H), less adsorption property (less R_L) is required to make dispersions.

The results also indicate that, among the tested resins, as the amount of lipophilic group is the same, a higher acid value leads to more Newtonian dispersion.

The degree of shear thinning can be expressed by the Power-law model (Barnes, 1989):

$$\eta = K \dot{\gamma}^{n-1}$$

where η is the viscosity at shear rate $\dot{\gamma}$, n is called the power law index, K is called the "consistency", that is the viscosity at shear rate 1 s^{-1} .

The K and n values for the dispersions in this study are shown in Figure 6. The lower the n value, the more shear-thinning the dispersion is. The dispersions with higher K values have higher viscosity at lower shear rate.

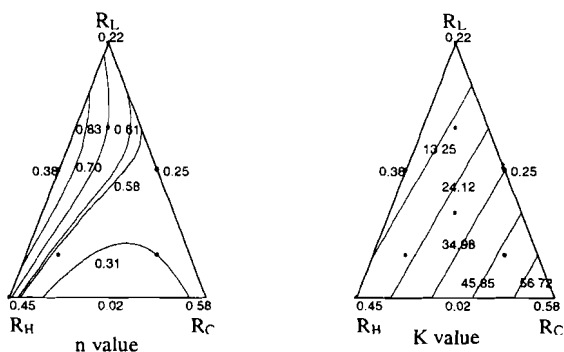


Figure 6. Power law index and consistency of the dispersions

Figure 6 indicates that at equal amount of R_L, generally the more R_H leads to more Newtonian behavior (higher n and lower K) due to stronger barrier property. At equal amount of R_H, generally more R_L leads to more Newtonian behavior due to higher adsorption property.

Mechanism

The resins must provide adequate adsorption and barrier properties to prevent the particles from returning to the aggregated state so that the particles remain in random suspension throughout the liquid system. When either the adsorption properties or the isolation properties are not strong enough, the pigment particles may become flocculated or return to the aggregated state. The result would be a more shear-thinning rheology due to the bridging between particles.

The lipophilic group R_L provides adsorption characteristics required for an effective dispersant, since the phthalocyanine blue pigment is also lipophilic in nature. The hydrophilic groups R_H, however, provides semblance property and are solvated in the solvent (n-propanol) and provide the isolation property (steric stabilization) (Figure 7).

When the amounts of R_L and R_H are both adequate, the adsorption and isolation properties are strong enough for R_L to be adsorbed onto the pigment surface and for R_H to function as a barrier. A Newtonian pigment dispersion is then achieved. If either of the adsorption properties or the barrier properties are not sufficient, pigment dispersions can not be prepared successfully. At intermediate levels of adsorption and barrier properties, the pigment particles might become flocculated and bridged, resulting in a more shear-thinning property. Figure 8 shows the physical picture of this mechanism. This is a simplified model proposed to explain the observed phenomenon. Many other factors may need to be considered when conditions change.

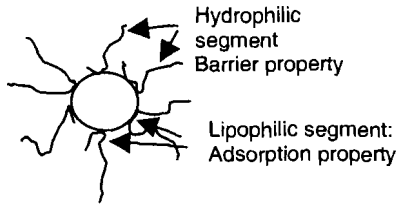
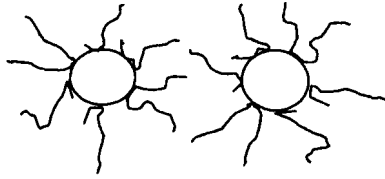
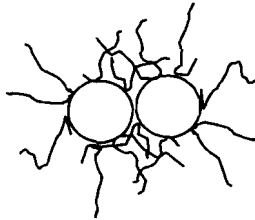


Figure 7. Roles of hydrophilic and lipophilic segments on particle stabilization



(a)



(b)

Figure 8. (a) Appropriate Hydrophilicity/Hydrophobicity Balance, Good Particle Stability and More Newtonian Flow
(b) Inappropriate Hydrophilicity/Hydrophobicity Balance, Bad Particle Stability and More Shear-thinning Flow

Conclusion

1. This paper demonstrates that resin hydrophilicity and lipophilicity have a dramatic effect on the rheological properties of solvent-based dispersions.
2. Hydrophobic groups adsorb onto the pigment surface providing adsorption characteristics, while hydrophilic groups are solvated in solution and provide barrier properties.

3. Both the lipophilic and hydrophilic groups are important for particle stabilization. An adequate balance can result in dispersions with Newtonian flow. Inadequate balance may cause pigment particles to flocculate or aggregate and the dispersions become shear thinning.
4. The degree of shear thinning strongly depends on the balance of resin hydrophilicity and hydrophobicity and may significantly impact the ink performance.

Acknowledgement

The authors would like to thank Mr. J. Fabian, Dr. W. Keaveney, Dr. A. Lou, Mr. S. Lucci, Ms. M. Mostowy, Dr. J. Parris, Dr. D. Rich, Ms. J. Truncellito of Sun Chemical Corporation for their suggestions and support for this work.

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