Evaluating Pigment Dispersion Quality through Dynamic Oscillation Analysis

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Introduction

The value of an ink's performance ultimately hinges on the quality of the pigment dispersion. It is well known that pigment is the costliest ingredient in any ink and is responsible for imparting the most desirable property to printed material - color. In recent years, much attention has been given to the ability of color to sell a product. Among various physical and chemical properties, pigments are selected primarily for their color. To achieve the highest degree of color intensity, the ink maker has to achieve the highest possible level of pigment dispersion or "optimal dispersion." This offers the maximum return on investment. At first glance this task seems simple, but it is not so easily accomplished. Pigment dispersions are commonly plagued by the negative affects of flocculation, instability and poor rheology. To further complicate matters, the choice of available dispersion media is nothing short of overwhelming to the formulator. Albeit, determining the best dispersion system is a necessary part of the formulating process. This often involves screening numerous raw materials or dispersion processes for their contribution to dispersion quality. This can be a very resource-intensive process. A fast, accurate, and reliable method for determining degree of dispersion is an invaluable tool for the ink formulator. This discussion seeks to provide an overview of a dynamic oscillation method that can be used for both fluid and paste inks and notes important concepts dealing with pigment dispersion.

As earlier stated, by their nature, pigments do not naturally lend themselves to good dispersion. There are forces that work against obtaining and maintaining a stable, well-dispersed system. A thorough treatise of these forces is beyond the scope of this discussion and many well-written articles and books on the subject are available. Suffice it to say that the ink formulator's primary focus is preventing these forces from dominating an ink system. This is done through chemical and mechanical energy.

The efficiency, or quality, of a pigment dispersion can be measured through color density measurements of printed inks. However, this requires preparing complete ink formulations in sufficient quantities to prepare cured printed material. An alternate test method that could test the dispersion quality of the pigment concentrate phase (prior to letback and initiation) would be beneficial in time and cost savings. Fortunately, such evaluation is possible and requires only modest investment.

Before we can look at the particulars of the test and how it can help determine the efficacy of dispersion, we should first discuss three important concepts. A thorough understanding of these concepts will enable us to understand the problems associated with pigment dispersion and how the test data depicts the extent of these problems within a given system.

Concept #1: STABILITY

Stability is the ability of an ink system to remain in a desired state without significant decay in the form of pigment particle settling or other detrimental effects. This can be a sneaky problem. To maintain stability, it is essential that pigment particles be kept separated and suspended. A formulator may have found a great dispersion system with excellent rheology and color properties, but in a short period of time these properties begin to degrade. Color becomes weaker, rheology exhibits greater thixotropy, and then the inevitable flocculation is discovered.

Concept #2: FLOCCULATION

Flocculation is the combining of two or more particles by means of attractive forces. By physical law, pigment particles resist indefinite suspension in a medium. They are constantly looking for the lowest possible energy state and that often leads to agglomeration or flocculation. However, if a sufficiently low energy state can be achieved through polymer, solvent or surfactant absorption, or through electrostatic repulsion, flocculation can be avoided. Flocculation can rob an ink of color strength and cause undesirable rheology. Factors contributing to flocculation include pigment particle size distribution, molecular weight differences between the pigment and the continuous phase, pigment concentration, and particle – particle interactions.

Concept #3: RHEOLOGY

Rheology characterizes the flow properties of an ink. It is empirically defined as the study of the flow and deformation of a material. Historically, ink formulators have focused on simple flow evaluations to characterize their inks. This often involves a viscosity measurement at one or two shear rates and for Flexo is all too commonly accomplished with an efflux cup such as a Zahn or Shell. Such a characterization offers a very narrow view of the true rheological nature of any fluid, unless of course that fluid happens to be Newtonian. Unfortunately, and despite common misconceptions, no pigmented system is truly Newtonian.

The closer a Flexo ink is to Newtonian the better it will perform on press. Nothing impacts the degree of non-Newtonian behavior in an ink more than the quality of the dispersion. Many methods exist to characterize the proximity to Newtonianism. A common and useful one is the shortness index value whereby viscosity measurements are taken with a suitable viscometer on a sample at two significantly different rates of shear. The ratio between the two values is determined by dividing the low shear viscosity value by the high shear viscosity. For a truly Newtonian fluid this value would be **1** as the viscosity of a Newtonian fluid is independent of shear rate. Logically, the closer the shortness index is to one, the more Newtonian the ink. Likewise, the greater the difference from one, the less Newtonian or “non-Newtonian” the ink. Appropriately applied, this method has merit for press performance prediction. However, this method gives limited insight into the nature of the dispersion quality. To have a good view on how well the pigment is dispersed and the stability potential, we have to leave the realm of simple steady-state flow measurement for that of microstructure analysis via dynamic oscillation.

Now that we have a basic understanding of these concepts and their potential impact, let’s look into how we can test and measure an ink for pigment dispersion quality.

DYNAMIC OSCILLATION

As previously stated, rheology is the study of the flow and deformation of a material. Deformation is the focus of dynamic oscillatory analysis. Dynamic oscillation testing requires the use of a controlled stress rheometer. This instrument has found fairly wide acceptance in the paste ink world, but relatively little has been done to explore its usefulness in lower viscosity liquid inks. Perhaps this is due to the erroneous assumption that fluid inks, being so low in viscosity, are close enough to Newtonian to consider them as such. Regardless of the reasons, the non-Newtonian nature of any pigment dispersion provides opportunity for microstructure characterization. This is especially true in the pigment concentrate or pigment-grinding phase.

In simple terms, dynamic oscillation involves the application of a controlled stress at specified amplitude on a sample across a range of frequencies. The choice of frequency range is critical in that it must lie within the linear viscoelastic region (LVR) of the storage modulus for the tested material. The LVR is easily determined by conducting a broad frequency sweep and plotting G' (storage modulus) against frequency. The oscillatory frequency range corresponding to the linear region of the G' curve is the LVR. Once established, the LVR becomes the operating basis in which all subsequent dynamic oscillatory measurements are made.

Three parameters can be plotted against oscillation frequency and used to characterize the stability and degree of dispersion:

- G' (storage modulus – a.k.a. "elastic" modulus)
- G" (loss modulus, or "viscous" modulus)
- n* (complex viscosity)

Additionally, tan δ can be calculated. This is a ratio of G' to G" (= G" / G'). This value is not plotted, but can be used to assist with evaluating dispersion stability

The relationship of these parameters to the frequency range and to each other can yield valuable insights into the microstructure of the dispersion. In general terms, and holding all other factors equal, the following axioms are held to be true.

Stable Systems – strong pigment particle-particle association

Modula relationships:

- G' dominates over G" (system exhibits more elastic response vs. viscous response)
- G' and G" exhibit no apparent dependency on oscillatory frequency
- Tan $\delta < 1$

Complex viscosity relationships:

- n* exhibits strong dependency on oscillatory frequency

Unstable Systems – no pigment particle-particle association

Modula relationships:

- G" dominates over G' (system exhibits more viscous response vs. elastic response)
- G' and G" exhibit strong dependency on oscillatory frequency
- Tan $\delta > 3$

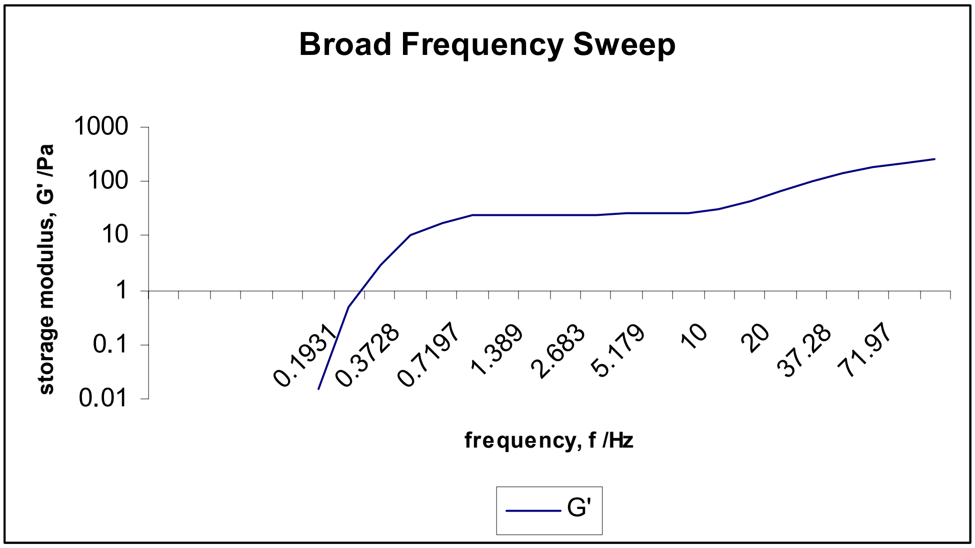
Complex viscosity relationships:

- n* exhibits no apparent dependency on oscillatory frequency

Example with Results and Discussion
In the following examples, three different pigment concentrates inks were subjected to dynamic oscillatory testing. The three parameters of interest are plotted against oscillatory frequency and conclusions are drawn based upon the relationship of the three parameters to frequency and to one another.

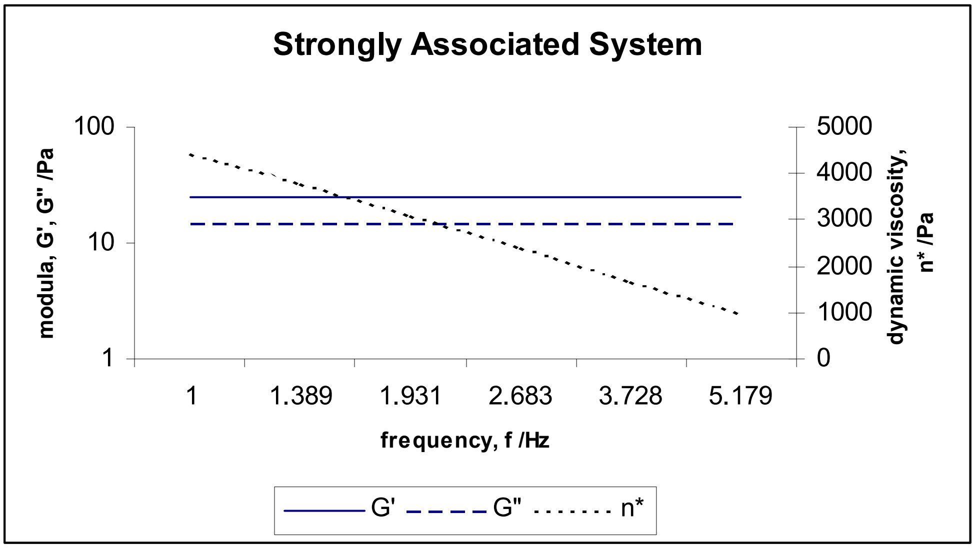
The following equipment and test conditions were employed:
Instrument: Haake RS150 rheometer
Cone: 6cm, 1°, stainless steel
Temperature: 25°C, ± 0.1
Amplitude: 5Pa
Broad Frequency Sweep: 0.1Hz to 100Hz
LVR: 0.7Hz to 10Hz (1Hz to 5Hz used)

Graph 1. **Broad Frequency Sweep to determine the LVR**



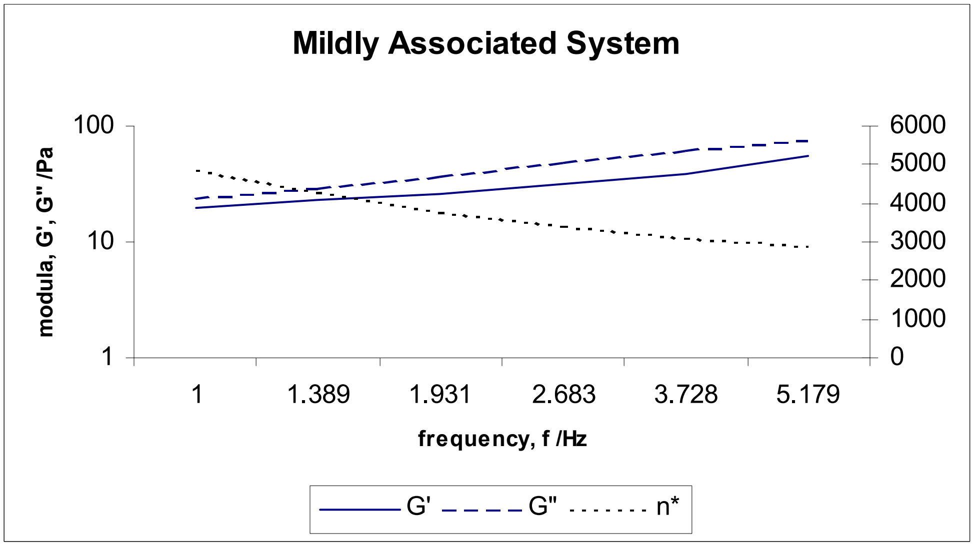
In the above graph, G' shows a linear response in the frequency range of 0.7Hz to 10Hz. Measurements made within this range are suitable for dynamic oscillatory testing.

Table 2. Strongly Associated System



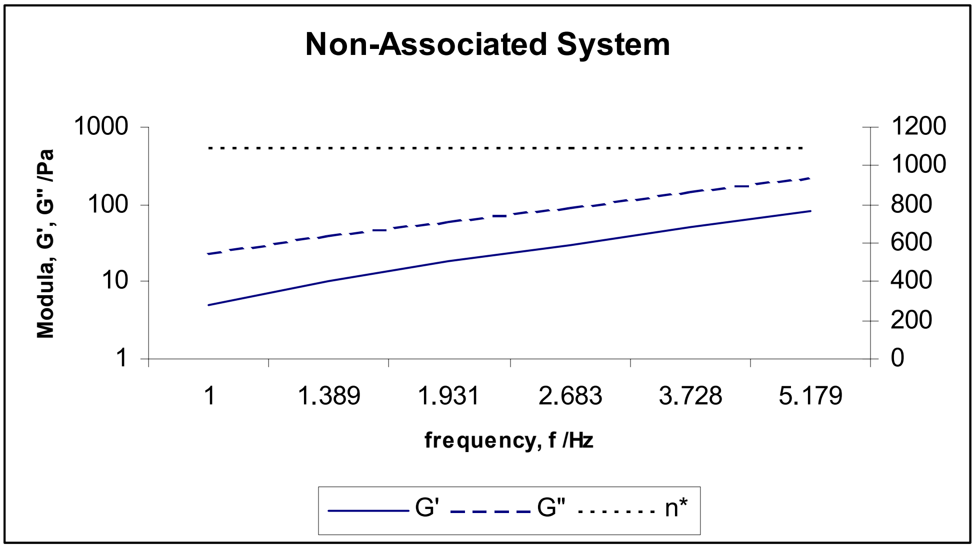
Note the relationship of each parameter to frequency. Both G' and G" show no dependency upon frequency and G' is dominant over the G" (more elastic than viscous) indicating a strong particle-particle association. The complex viscosity (n*) exhibits rapid decline with increasing frequency. Tan $\delta = 0.6$ (<1). This system is stable, not prone to flocculation or settling and is considered highly structured.

Table 3. Mildly Associated System



This example shows a mildly associated system that exhibits weaker structure than a strong associated system. G" is slightly dominant over G' indicating a potential for instability. Notice the mild dependency of the G' and G" moduli to frequency. Also, the complex viscosity exhibits a low dependency on frequency. Tan $\delta = 1.4$ (>1, <3). Flocculation and or settling may occur in this system.

Table 4. Non-Associated System



The relationships of G’, G”, and n* to frequency in this system are opposite of that found in the strongly associated system. G” greatly dominates over G’ with a high frequency dependence and the complex viscosity is totally independent of frequency. Tan $\delta = 3.5$ (>3). This system is unstable. It will likely undergo flocculation and settling. It exhibits poor structure and virtually no particle-particle association.

Closing Remarks

It should be noted that due to their low viscous nature, most fully formulated flexographic inks exhibit significant G” dominance (more viscous than elastic). However, the pigment concentrate phase, for which this method is intended, can exhibit strong G’ dominance (more elastic than viscous). The above pigment concentrates were prepared without additives that aide in wetting, stability, and curb the tendency toward flocculation. Most low viscosity fluid inks will undergo some flocculation and/or settling if given enough time and the right conditions. All applicable factors such as storage conditions, shelf life and application parameters should be considered when interpreting data from oscillatory testing. A mode of failure for one ink system may be acceptable for another.

Inks are formulated and sold with a balance of performance and economics. These two factors are not mutually exclusive and are often reciprocal in their relationship. In respect to performance alone, one property is often gained at the expense of another. In an effort to maximize the intended effect of the pigment within an ink, the ink maker benefits from having at their disposal quantitative methods that reduce the time necessary to screen raw materials and/or process variations. With dynamic oscillation, accurate characterization and reliable conclusions about an ink’s dispersion quality and stability can be quickly obtained.