

# Measurement of Toner Cohesion in Liquid Inks Using a Visualization Cell

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## Abstract

The aim of this work is to measure the integrity of liquid toner images in both the development and transfer processes. To this end we have constructed a visualization cell in which we can observe the image deposition process due to a given applied voltage, and then measure the voltage required to break apart the image layer. Thus the cell permits the observation of both deposition and break-apart of toner images when either dc or low frequency ac fields are applied. The voltages required to compact the toner layer and to break it apart can be translated into consolidation stress and tensile strength of these materials; by this means we are able to compare inks in a quantitative manner.

Using the visualization cell, we have examined the behavior of different liquid toners. We have observed the effects of different charge directors and their concentrations, as well as of different toner resins. While the cohesion varies according to the types of resins and of charge directors, there is no significant change in the behavior of the inks when charge-director concentrations are varied from a charge-director-to-toner weight ratio of 10mg/g to 50mg/g. We analyze the results with simple physical models that give a semiquantitative picture of the plastic behavior of inks at high particle fraction, up to the typical toner percentage of an image.

## Introduction

In order to create high quality liquid toner images, the developed toner layer must remain intact as the forces from other subsystems act on it. For instance, in reverse roll development, electrophoretically deposited images must withstand the shear force generated by a roll rotating against the process direction; and in transfer, the electrical field breaks the toner layer from one surface and moves the particles to another surface. Thus it is important to measure the integrity of the toner images and to understand the controlling factors. The integrity of the image layer depends on the cohesiveness of the toner particles.

We have developed a technique to measure the image integrity. We have constructed a visualization cell in which

we can observe the image deposition process by a given voltage as well as measure the voltage needed to break apart the toner layer. The deposition simulates the electrophoretic development and the breaking apart of the image in the transfer process. With this device, we compare the behavior of different toners and examine the impact of various factors that contribute to these behaviors.

## Ink Aggregates as Plastic Materials

After development, toner particles form a layer of consolidated material on the photoreceptor. This layer has a high particle concentration and forms a paste, consisting of grains embedded in a carrier fluid. It is expected that the mechanical properties of this layer will be well described by the concepts of plastic behavior in granular material [1].

In a granular material, stresses are not related to the magnitude of the deformation, as it will be the case in elastic media, neither are stresses related to the rate of deformation, as in liquids. To first approximation, stresses are independent of both deformation and rate of deformation. Granular material can withstand stresses up to a yield value, above which they break apart. We have to distinguish between shear stresses  $\tau$  (applied along a direction parallel to a given surface) and normal stresses  $\sigma$  (applied along a direction normal to the surface). The magnitude of shear stress a material can withstand without yielding depends on the normal stress applied. The curve of shear versus normal stresses for yielding is referred to as the yield locus of the material. The material can withstand stresses that lie below the yield locus, whereas stresses that lie on the curve will yield.

For granular materials whose particles are large, the yield locus is a straight line intercepting the origin (Coulomb's law). In this case the yield locus is determined by the so-called angle of internal friction  $\phi$  or the internal friction coefficient  $\mu = \tan\phi$ . In this way the yield locus of an ideal granular material is:

$$\tau = \sigma \tan \phi \quad (1)$$

If the material is composed of fine particles, the forces between the particles become important and the material is said to be cohesive. In this case a shear stress needs to be applied for the material to yield at zero normal stress. This

value is called the cohesion  $c$  of the material. A negative normal stress, i.e. a tensile force per unit area, must be applied for breaking apart the sample at zero shear stress. This value is called the tensile strength of the sample  $\sigma_t$ . For low values of the normal stress the yield locus is a non-linear function and, usually,  $c$  and  $\sigma_t$  are of the same order of magnitude.

If a compressive normal stress is applied to a granular material at zero shear stress, there is a certain value of the stress at which the material does not yield but becomes compressed, i.e., more dense. This value of  $\sigma$  is referred to as the consolidation strength. When this value is overcome the void ratio  $\varepsilon$  of the sample (free volume divided by the total volume) decreases.

At non-zero shear stresses the value of  $\sigma$  needed for consolidation is smaller. The functional dependence of  $\sigma$  on  $\tau$  for consolidation is described by the consolidation locus.

Once the material has been consolidated, higher values of the stresses will be required for yielding. In other words, for every value of the void ratio  $\varepsilon$  there exists a different yield locus.

### Relation to Inter Particle Forces

The tensile and consolidation strengths are related to the forces between particles. This relation depends on the size and shape of the particles, the number of contacts between them and the void ratio.

A relation has been proposed for the tensile strength of an ensemble of spherical particles [1]:

$$\sigma = \frac{1 - \varepsilon}{\varepsilon^{3/2} \pi d^2} F \quad (2)$$

where  $d$  is the diameter of the particles and  $F$  the cohesive force per contact.

The force  $F$  depends on the nature of the particle surface, contact curvature and particle-particle distance. Usually, it is due to three mechanisms: electrostatic forces, van der Waals forces, and capillary forces.

In the case of van der Waals forces, the compression of the contacts causes the deformation of the surface of the particles, giving rise to a higher cohesive force. The relation between the tensile and the consolidation strengths is given by [2]:

$$\sigma_t = \alpha \sigma_c + \sigma_{t0} \quad (3)$$

where  $\sigma_{t0}$  is a constant and  $\alpha$  is a decreasing function of  $H$ , the hardness of the material. Typical values of  $\sigma_t/\sigma_c$  range from 0.1 to 0.3. For powder toners,  $\sigma_t$  is typically  $10^5$ – $50$  N/m<sup>2</sup> which gives inter particle forces of order of  $10^9$  N. These values are consistent with a van der Waals picture of the forces between particles. For inks, we will show later that this may not be the case.

### Experimental Technique

The visualization cell consists of two electrodes, 100  $\mu$ m thick, that are positioned 1 mm apart. The electrodes are mounted on a Plexiglas frame and covered with a piece of glass. We inject liquid ink into the gap between the electrodes through a capillary from a syringe.

The applied voltage is obtained by amplifying the signal from a function generator through a high voltage amplifier. An electrometer measures the electric current and an oscilloscope plots the current versus the applied voltage.

We observe the gap through a microscope and record on a VCR the aggregation and the breaking-apart of toner layers onto and from electrodes respectively.

We apply a sinusoidal wave with a DC offset,  $V(t) = V_0 + A \sin \omega t$ . The sample conductivity is of order  $5 \times 10^{-10} \Omega^{-1} \text{m}^{-1}$  so the electrical relaxation time is about 0.03 seconds. We chose the period of the signal to be greater than the electric relaxation time. This assures that the electric field in the gap is not modified by any space charge, and the field inside the gap becomes almost constant, as in a resistor. If pure liquid is used, the response of the system is that of a RC circuit. The behavior of the liquid is Ohmic, conduction current is proportional to the applied voltage and the plot of  $I(t)$  vs.  $V(t)$  on the oscilloscope is an ellipse. This corresponds to the dashed curve in figure 1. If we apply a DC offset, it has no influence on the shape of the ellipse.

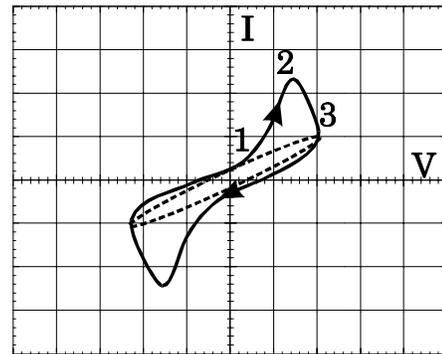


Figure 1. Typical oscilloscope record for a compaction experiment. The solid line is the measured current versus the applied potential. The dashed line is the elliptical line expected for a RC circuit.

The presence of toner particles dispersed in the liquid makes a further contribution to the electrical current, then the electric field moves charged particles towards the electrode of the opposite sign. This motion produces a non-Ohmic current that causes the  $I(t)$  vs.  $V(t)$  curves to deviate from the elliptical form. This corresponds to the part 1 of the solid line in figure 1. The current is a maximum when the layer of toner is deposited over the electrode (part 2 of the solid line in figure 1) and, finally, decays as the layer is completely built, and no more toner particles are moving (part 3).

With these ideas in mind we determine the voltage that we need to break a layer of toner in the following way. Amplitude is chosen for the sinusoidal waveform. When the DC offset is zero, the trace of  $I(t)$  vs.  $V(t)$  has no elliptical part, because particles contribute to the current in both polarities. Now if the DC offset is increased, the oscilloscope trace is no longer symmetric, because the building of the layer is done under voltage  $V_0 + A$ , while the

breaking-apart happens at the lower negative voltage  $V_0-A$ . At some DC offset half of the  $I(t)$  vs.  $V(t)$  curve appears to be elliptical; at this point we know that the layer that has been built at  $V_0+A$  is not broken at  $V_0-A$  (the elliptic part means that particles do not move). Therefore we take these values as voltages for the consolidation  $V_c$  and the break-up  $V_b$ , respectively. Direct visualization confirms the validity of this technique.

**Tensile and Consolidation Strengths for a Layer of Toner**

Figure 2 and 3 show the tensile strength (y-axis) vs. consolidation stress (x-axis) of different materials. The consolidation force is computed from the value of  $V_c$  using

$$F_c = qE_c = q \frac{V_c}{L} \tag{4}$$

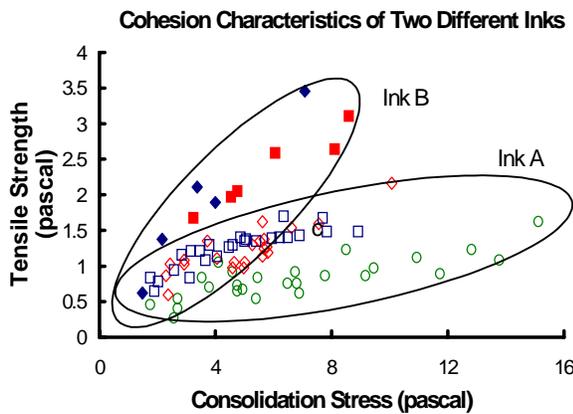


Figure 2. Tensile strength vs. consolidation stress for different inks.

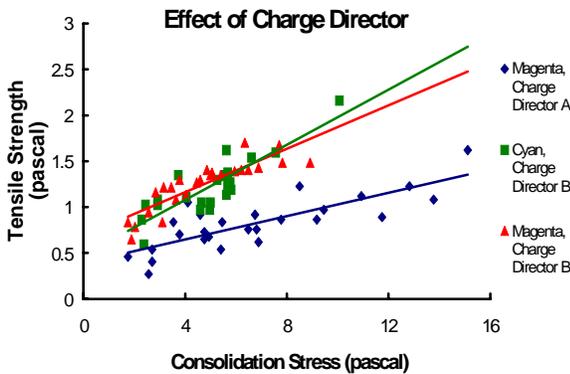


Figure 3. Tensile strength vs. consolidation stress for the same resin with different charge director

The tensile force is obtained from  $V_b$  in a similar way, using the value of  $q$  deduced from the electrophoretic mobility of toner particles,  $q \sim 30 \times 10^{-18} C$ . Tensile and consolidation stresses can be estimated from equation (2).

Typical values for  $\sigma_t$  range from 1 to 6 Pascal and for  $\sigma_c$  from 15 to 70 Pascal. The ratio  $\sigma_t/\sigma_c \sim 0.1$  is expected to be of this order of magnitude, in good agreement with equation (3). However, the interparticle forces estimated from (4) are very small, on the order of  $10^{-12} N$ . This is in contrast to the van der Waals force given by [4]:

$$F = \frac{Ar}{12h^2} \tag{5}$$

where  $A$  is the Haamaker constant,  $r$  the particle radius and  $h$  the separation between two particles. Taking  $A=10^{-20} J$ ,  $r=1 \mu m$ , and  $h=10 \text{ \AA}$ , we obtain  $F=10^{-9} N$ .

We propose that the reason for this very large difference in the inter-particle force is the double layer interaction. According to the DLVO theory of electric stabilization of colloidal suspensions [3], the inter-particle potential has two contributions: the van der Waals force and the electrostatic force. The van der Waals force, with a very deep minimum at the distance of closest approach, is attractive, and tends to flocculate the suspension. The electrostatic force is repulsive and extends along the Debye length; thus it stabilizes the dispersion by preventing the particles from becoming too close so that the van der Waals force does not become dominant. The resulting potential has a secondary minimum at a distance between particles of the order of the Debye length. At this distance the attractive van der Waals force is much smaller than at the deep primary minimum, and of the order of magnitude of the forces we have encountered. Introducing  $h \sim 0.1 \mu m$ , which is the order of magnitude of the Debye length in inks, in (5) we obtain  $F \sim 10^{-13} N$ .

Figures 2 and 3 show the usefulness of this technique for characterizing inks. Figure 2 illustrates the cohesion characteristics of two inks of different resins, and shows that increasing the consolidation stress increases the tensile strength. This is in accord with equation (3) and with common experience in liquid ink processes. The higher the voltage used for development, the higher the voltage needed for transfer. Also, figure 2 indicates that the steeper the curve the harder will be to remove a layer formed under a given voltage. For similar consolidation stress, ink B requires higher tensile strength to break the image apart.

Figure 3 shows that charge directors can influence the layer properties. For the same toner resin, the inks with charge director B (squares and triangles) are more cohesive than the ink with charge director A (diamonds). The difference caused by charge directors confirms our proposal of a second minimum due to the electric double layer. The packed layers of these inks are relative loose in structures. When the inks examined in figure 3 are compacted under higher pressures, such as in a centrifuge, these differences disappear [5]. We also show in this figure that color pigments appears to have no effect on the cohesion characteristics of the ink. This is understandable since the pigments are embedded in the toner resin and thus have little or no contributions to inter-particle forces.

In figure 3, the data representing charge director A include a number of charge-director-to-toner weight ratios, ranging from 10 mg/g to 50 mg/g. Within experimental

error, we detect no significant differences in cohesion behavior. One explanation is that the variation in Debye length in this range of ratios is small. This is consistent with other measurements; the conductivity variation for charge director A in this ratio range is much less than the difference in conductivity between charge directors A and B [6].

### Conclusion

The integrity of toner images can be understood through the concept of plastic behavior in granular materials, namely tensile strength and consolidation stress. These are well-defined concepts whose magnitudes describe the plastic behavior of toner layers.

Using a visualization cell we have estimated the tensile strengths and consolidation stresses for liquid toner layers. The process of building-up and breaking-apart the layer is achieved by applying an electric field, and the values of voltage at compaction and rupture of the layer determine the magnitudes of the respective stresses.

The values obtained for the force between particles are consistent with a distance between particles of the order of the secondary minimum in the DLVO theory.

### References

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### Biography

Shu Chang received her B.A. in physics and mathematics from Berea College, Berea, Kentucky in 1983 and Ph.D in Materials Science from University of Minnesota in 1988. She has been with Xerox Wilson Center for Research and Technology since then. Her earlier work included electronic properties at metal/semiconductor interfaces. She also worked briefly on single component development. Her main focus has been liquid toner processes, in particular, process issues related to particle cohesion and adhesion of dissimilar materials.

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