Basic Concepts of Stability and Instability in Water Based Inkjet Pigment Dispersions

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Abstract

We shall review the main concepts of pigment dispersion stability and apply them to derive practical rules regarding inkjet ink both for OEM and refillers useful in general , but particularly for SOHO printers.We shall also propose two conceptual sketches to understand the stabilization phenomena.

Introduction

The use of pigments in inkjet inks render them extremely sensitive to pigment stability variation. The variables involved lead to a rather complex system, which depends on the electric and entropic behavior both of the pigment and the media of dispersion.

Historically we find carbon black dispersions made by the Egyptians with Arabic gum 2000 b.C. , but the modern theory of dispersion only appeared in the middle of the 20th century, proposed by Djarguin, Verwey, Landau and Overbeek (the so called DLVO theory) and explained the stability by means of electrostatic forces. That theoretical effort basically solved the whole question for part of the dispersions, those that are electrostatic in nature,, but had to be completed more recently to account for dispersions stabilized by entropic effects. Since both are of use for inkjet ink formulation we shall understand them further on this paper.

Ink Composition

Ink jet inks composition can basically be described as:

1. Base/ Solvent : the fluid that in which the other components are mixed
2. colorants: the materials that give colors
3. Additives: many other materials that give specific properties

The solvent we shall consider is water and in the above concept materials named elsewhere as cossolvents are treated here as additives (in the way that actually the simplest ink would be a mix of water and colorant).

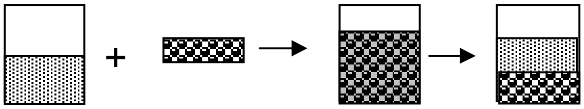
Our main subject here are colorants. They are generally materials that have color and can be of two natures, regarding to their solubility in the base,

1. dyes : which dissolve
2. pigments: which do not dissolve in the base.

The elder formulations of inkjet inks were solely dye based, in them stability issues were less important. With the advent of Du Pont pigmented inkjet dispersions in 1992 the formulators have almost all gone to pigmented base inks, at least for black inks

Dispersion and Flocculation

Dispersion is the mixture between particles that are large in respect to the size of the base that are not soluble in that base. If those particles are not stabilized the result is generally known as flocculation

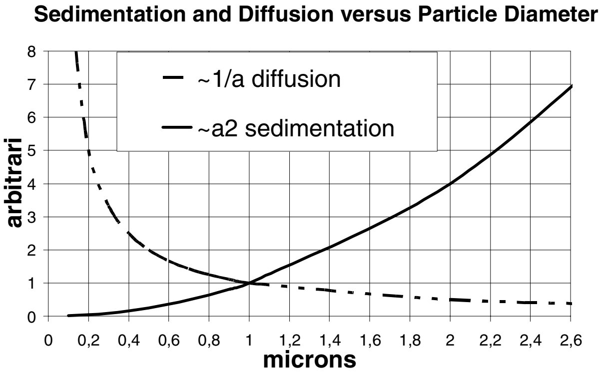


Roughly speaking, particles that don't flocculate are those that can be kept "floating" by the bumps of water molecules, in a Brownian like movement. So in practice the first step for a dispersion to be stabilized is to grind it.

Grindig and wetting

In a first approach there are two tendencies of the particles due to its thermal movement. One is to sediment, and is proportional to the square of the particle radius. The other is to diffuse to the medium which is proportional to the inverse of the radius. Those curves cross at a radius of 1 (in our case 1 micrometer) bringing the first rule for stabilization:

I. to grind the particles bellow 1 micron.



When grinding we create new surfaces against the surface tension of the materials, that energy is the one we have to provide to put the particles apart. Further on with this article we will see the importance of that. Anyway right now we can say that in this point lies the importance of wetting additives for grinding , they act to ease the access of the media to the new surfaces. So there goes rule number two:

II. wet, using additives if possible, the surface of the pigment

And those two are the easy rules, we will have to dig dipper to get more interesting information.

At this point we would rather take a look to what theory would predict to loose particles that neither attract nor repel each other. From Smuloshki we know that in this case the half life for a group of particles to flocculate (diminish its concentration by a half), in the usual conditions of an inkjet ink is given by

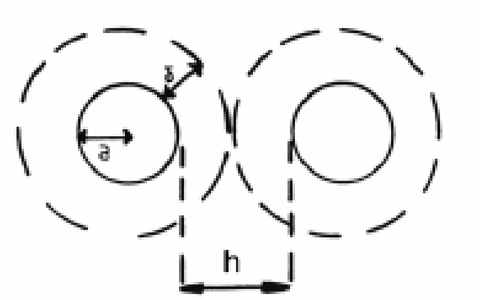
$$t_{\frac{1}{2}} = \frac{3}{4}\frac{\eta}{kTn_0} \qquad (1)$$

$$t_{\frac{1}{2}} = \frac{3}{4}\frac{0{,}01}{1{,}38.10^{-16}x298x5.10^{10}} = 365.\text{sec}$$

Meaning that, left alone a dispersion would flocculate in about six minutes

Particle Attraction

The actual picture looks even worst, because, due to interparticle electric forces, basically dipole-dipole London forces, particles tend to attract each other. London forces act up to a distance of 10 nm (nanometers), so to keep a dispersion stable we have to maintain voids (h) between particles larger than that.



We do so in two maners

- by interposing an electric double layer
- by generating a entropic barrier

Before we go any further we can understand right now one point, that of clogging of cartridges from which water evaporates.

It is clear that the higher the relative volume of the particles to that of the whole dispersion the smaller shall be the separation of the particles.

If we remember the concept of pigment volume concentration

$$PVC = \frac{V_P}{V_P + V_b} \qquad (2)$$

Where V_p is the particle volume and V_b is the volume of the medium and calculate the distances for spherical particles, considering inkjet pigments of 100 nm we get that the separation goes bellow 18 nm for PVC> 45 , in other words to flocculation.

Electrostatic stabilization

Since the nature of attraction is electrostatic, nothing is straighter than creating an electric repulsion to overcome it. That is done by the generating a double layer of opposite charge in the surface of the pigment, the thickness δ of it is given by

$$\delta = \frac{1}{\chi} = \frac{P}{z}\sqrt{\left(\frac{1}{c_{bulk}}\right)} \qquad (3)$$

P is a medium dependant constant, z is the ion valence and c_{bulk} the ion actual concentration in the bulk solution of the dispersion. The quantity $1/\chi$ is the characteristic Debye length that for small electrical potentials is coincident with the gravity center of the space charge and then called the thickness of the double layer.

The double layer DVLO theory suggests that the stability of a particle in solution is dependent upon its total electrostatic potential energy function V_{TE}. which is calculated by adding the attractive electrostatic component V_A and the repulsive V_R contributions

$$V_{TE} = V_A + V_R \qquad (4)$$

We have that

$$V_A = -A/(12\, p\, h^2) \qquad (5)$$

$$V_R = 2\, p\, \varepsilon\, a\, \zeta^2\, e^{(-\kappa h)} \qquad (6)$$

Where A is the Hamaker composite constant for the dispersion (the quadratic average of the components Hamaker constant), h is the particle separation, p is the solvent permeability, κ is a function of the ionic composition and a is the particle radius. ζ is the Zeta potential, a quite straightforward measure that can be made from elecroforetic considerations of the apparent hydraulic diameter of a particle surrounded by ions of a double layer, it is the potential in the plane were the liquid can move perceptibly with respect to the layer. As a practical rule stability of the dispersion occurs for ζ (-30; +30) mV. Zeta potential is sensitive to pH. If it changes the ionic cloud can be depressed form excess of ions either positive or negative, what will lead to flocculation.

From the equations we can see that an increase in particle radius will actually stabilize the dispersion a situation that we have to avoid in inkjet inks. That is sometimes the case in refilling where the mixing of new ink will redisperse particles that are larger than those acceptable to the cartridge system and will eventually clog.

The dipole forces are only attractive when they are in phase , the Hamaker constant is actually a function of h and of the materials in dispersion and is what leads to retardation and repulsion, if the relation of the pure Hamakers constant (that of the base and the solid alone) is close to one , retardation will lead to dispersion easier to stabilize.

Also we have to consider concentration effects For water and monovalente ions

$$\chi 2 = 3{,}78.106\ \text{cbulk}^{1/2}, \qquad (7)$$

so, if the concentration of ions in the bulk of the dispersions goes above 10^{-3} molar, the separation drops bellow 10 nm. and there is flocculation.

Steric/ Entropic Stabilization

An alternative path to maintain particles apart from each other is to generate a physical barrier, a layer of polymers on the surface of the pigments. This works due to probabilistic considerations. If we have a polymer that has a sufficiently large tail (to work as δ) that is soluble in the medium and a site, an anchor, that is compatible to the pigment, the net result is that from the stand point of the bulk dispersion we will have a large "soluble-like" particle, stable.

In analogy to the double layer theory, we consider a total potential based on steric repulsion V_S so

$$V_{TS}=V_A+ V_S \qquad (8)$$

The effect can be understood in two levels, first as an osmotic effect, then explaining that effect through entropic probabilistic. We shall use both levels.

When we increase the pressure at constant temperature we have an increase in chemical potential the osmotic pressure is the one required to overcome the variation on chemical potential of the solute that bears salvation. Osmotically we have that

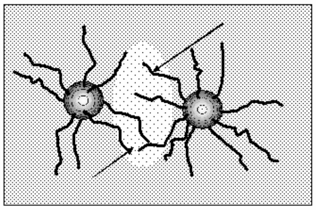
$$\Pi / c_2 = RT / M_2 + \beta RTc_2 + .. \qquad (9)$$

Π is the osmotic pressure c_2 the concentration of polymer in the layer , R the gas constant, T the absolute temperature, M_2 the molecular weight of the polymer and β the virial coefficient. The stabilization comes from the osmotic pressure generated when the polymer chains try to interpenetrate, that increases the chemical potential which leads to the flow of media that pushes apart the pigments.

If we take a closer look to the virial coefficient β we find also a way to qualify media. The coefficient is calculated by:

$$\beta = ½(N_A V_d / M_2^2). \qquad (10)$$

Where N_A is the Avogadro number and V_d the excluded volume, that volume that once occupied by polymer can no longer be used by other. The grater this volume (hence the grater β) the better is the polymer dispersed and the grater the stabilization an therefore the medium is called a "good" one for the dispersion.



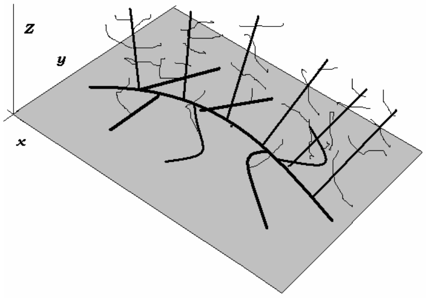
The next level of understanding steric stabilization is by considering that a chain that mixes with another losses some degree of freedom, related to the average volume occupied by the chain, that turns into entropic losses that tend to be probabilistically overcome by stabilizing the dispersion. The average volume occupied by a polymeric chain of dispersant is related to the way it is unfold in the medium. Consider the chain as composed of a sequence of vectors that goes from the head (attached to the pigment) to the end of the tail, the average distance head to tail will be the resulting vector R of a module that scales up to

$$\mathbf{R} \sim f N^n. \qquad (11)$$

Where n is a factor dependent on β, N the number of vectorial like monomers and f a numerical factor depending on the length and actual angles of the links that construct the vector like model. For a proper medium n = 3/5, for a bad medium n= 1/3, that means that if a chain goes from a "good" medium to a 'bad" it will lead to a reduction in the average distance of *cerca* one fourth power of the monomer length, potentially leading to flocculation in the eventual mixing different dispersions.

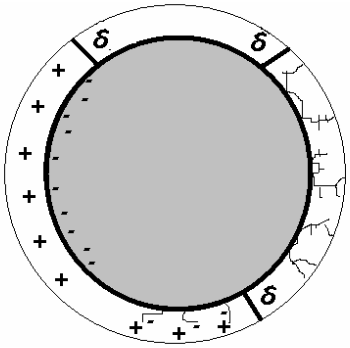
Another point to consider is the anchor head of the polymer. It is a bond either by chemical or physical of the polymer to the pigment surface. Loosing this bond will destroy the stabilization. This can happen if the media interacts too strongly to the polymer and also may happen during drop ejection, when is has been proposed that shear rates could tear apart dispersants.

Considering the dispersion needs, a prefect stabilization polymer molecule would be like the one shown left, with a large branched anchor skeleton, that has small anchor branches in the ***xy*** plane (the surface molecule) and longer reaching branches that reach into the z axis (the bulk of the dispersion). Both branches should have similar dendrites (sub-branches) that lead to dispersion. A molecule like this would be able to cover a large area of the surface, be strongly attached and spread towards the bulk without the need of long dispersion branches that could lead to inter-particle mingling and ties. Such a molecule would not be of a high molecular weigh also.



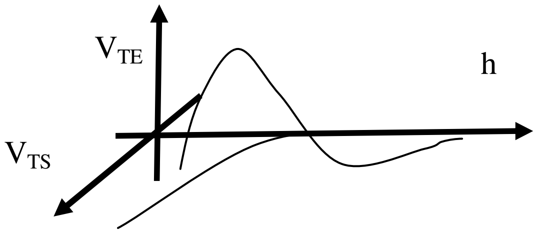
The total potential

A third way to stability would be simply using both electric and steric means. We could represent them all in a single sketch as seen to the left. In grey there is the particle, and δ is the separation due to either of the means.



A common misconception, specially when mixing different dispersions, is to simply add their total potential. The problem with that is that if a particle has an electrostatic repulsion potential it doesn't mean it has any stability against a non charged, steric stabilized particle, and vice-versa. That should be regarded as different dimensions

So the classical representation of ***V*** (potential) against ***h*** (particle separation) should be made in space rather than in plane as depicted below.



And the attraction forces should also be regarded as different, first the classical electrostatic force in the plane of V_{TE}, secondly the surface tension as the entropic opposite to separation, V_{TS} plan. The entropic attraction which would not act except in total disappearing of the interface leads to no distance attraction, and to the classical formulation, that only considers electrostatic forces, except for total contact

Information Sum

The only way we can work with a direct addition of terms is if we use an information model, in a sense ,as we said later on everything depends on the change of information between particles, so we could use Shanon equation and write

$$I_t=I_e+I_s = (-q_e\log_2 q_e)+(-q_s\log_2 q_s) \qquad (12)$$

Where ***I*** is information, ***q*** probability of the event of flocculation and the subscripts *t, e* and *s* hold for total, electrostatic and steric. The probabilities should be related to the proportion between total collisions and collisions that generates agglomeration. Bellow a certain level of information there should be agglomeration, above that, stability.

Conclusions

From the above discussion we can summarize rules useful to avoid flocculation of a dispersion:

For electrostatic dispersions:

a. avoid introducing ions, specially those of higher valences.
b. Avoid pigments with different ζ
c. Avoid changing the media pH
d. Beware of mixed effects they can create island of stability

For steric dispersions

a. Verify the media β
b. Use dispersants with sufficient tail (δ)
c. Avoid free polymer
d. Use the proper polymer surface and total concentration
e. Beware of the bonding to pigment

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Author Biography

Herán Murua Recived his BS in chemical Engeneering in the Mackenzie University 1992 since 1999 he has worked in Ink Press as Technical Director his work being in development of inkjet inks and refilling machines. He is also author of two books and numerous articles in the field of inkjet and toner recharging