Optimization of Ink-Jet Inks Using Nonlinear Programming

Walter J. Wnek and Brian R. Johnson
American Ink Jet Corp.

Abstract

The physical properties of an ink-jet ink such as its absorbance, surface tension and viscosity vary with the concentrations of its components. If each property were only a function of one of the components, formulating an ink to meet a given specification would be straightforward. Unfortunately, just the opposite is usually the case, and the problem becomes a multivariable one in which each property depends on the concentration of more than one of the components. Thus, any one property can be brought into specification by adjusting the concentration of one of the components, but then some of the others can possibly be driven out of specification with the process repeating itself. This can be particularly frustrating when multiple adjustments are being made on a manufacturing batch of ink and time is of the essence.

One approach to handling this type of situation is to treat it as a nonlinear programming problem. Each physical property is expressed as an equation in terms of the concentrations of the components that control its value. The data may be regressed using either theoretical relationships or simply empirical ones. The objective function to be minimized is the sum of the deviations that the physical properties are away from their specified centerline values. Alternately, it could be the cost of the ink. The constraints are defined by the upper and lower limits set on the physical properties and that the fractional concentrations must add up to one.

Solver, which is an Excel Add-in, was used to solve this set of equations. An example is given that demonstrates how multiple adjustments of a manufacturing batch can be reduced to just a single one via this technique.

Introduction

As a result of the tight specifications required for the functionality of ink-jet inks, small variations in their component materials can drive a manufacturing batch of ink out of specification, and this then involves adjusting the concentration of certain components. This may be done in an empirical fashion where each property is brought into specification one at a time by varying the concentration of the component that controls it the most. The difficulty with this approach is that a previously adjusted property can be driven out of specification by a later adjustment. This can result in an iterative process and many adjustments. What is needed is a procedure that takes into account these interactions where a property depends on more than just one component.

Such a procedure is described in this paper. We will first present the mathematical equations that were used to quantify the relationships between the ink's properties and the concentrations of its components. Then we will set up the problem as a nonlinear programming one to calculate the appropriate concentration changes and conclude with a real life example of its application.

Estimation of Physical Properties

Optical

The absorption spectra of the ink as a diluted solution is measured with a spectrophotometer, and the fraction of transmitted light (T) at one or more wavelengths (λ) commonly serves to specify its strength and color. The Lambert-Bear equation may be used to quantify this optical property for a mixture of dyes (Volz, 1995):

$$log[1/T(\lambda)] = A = \sum \varepsilon_i(\lambda)\, l\, C_i \qquad (1)$$

where

A = absorbance
ε_i = extinction coefficient of the i^{th} dye
l = sample thickness
C_i = concentration of the i^{th} dye (mass/total liquids)

Viscosity

The viscosity of the ink's vehicle μ_V may be calculated from (Patton, 1979)

$$log\ \mu_v = \sum [w\ log\ \mu]_i \qquad (2)$$

where w_i and μ_i are the weight fraction and neat viscosity of the i^{th} component. However, inkjet vehicles are aqueous mixtures of oxygenated organic solvents such as alcohols and glycols and undergo nonideal interactions such as hydrogen bonding. This behavior may be compensated for by using an effective viscosity for these components, and values for selected solvents have been tabulated. This approach is valid up to weight fractions of 0.3 after which certain nonlinear terms may be included. For example, w_i can be divided by $(1 - bw_i)$ to give a stronger upward trend to its viscosity curve where b is a constant. This modification is particularly useful for polymers.

The effect of dye or pigment concentration $C_{colorant}$ is then expressed in the form

$$\mu_{ink} = \mu_v\, [1 + f(C_{colorant})] \qquad (3)$$

where the function f may be taken as a power series. For the low concentrations typically involved, just a linear term usually suffices. It should be noted that pH and ionic strength could also be factors since they affect the degree of ionization of the dye's ionic groups.

Surface Tension

Surface tension is typically plotted against the logarithm of the concentration of surface active agent, and the curve is initially flat at the lower concentrations and then decreases linearly until it levels out at the critical micelle concentration (Rosen, 1979). The Gibbs adsorption equation suggests that this linear portion may be represented by

$$\gamma - \gamma_{Ref} = \Sigma \beta_i \log (C_i/C_i^{Ref}) \quad (4)$$

where Ref denotes a reference point and the β_i's are constants. It should be noted that the slopes and CMC's could be different for mixtures in comparison to their values in the single state.

Solution

The problem may be stated in the form of a nonlinear programming problem:

Objective Function

Minimize the sum of the absolute deviations from the centerline specification values for the properties in question or the amount of components added.

Constraints

The upper and lower bounds on each property.
Sum of the weight fractions equals one.

Solver, which is an Excel Add-in, was used to solve this set of equations.

Example

Table 1 gives the formulation and specifications for a certain ink-jet ink along with the measured physical properties for a particular manufacturing batch. It is seen that the transmittance, viscosity and surface tension are not in specification.

Table 2 shows the series of adjustments that were made to bring this batch of ink into specification. Since viscosity was the property most out of specification, it was adjusted first by adding water to decrease its value. Once it was in specification, it was found that the transmittance was too high, and dye was then added. Finally, the surfactant was added to bring the surface tension into specification.

Before we can use the proposed mathematical technique to solve simultaneously for all the concentration changes and component additions, we must verify that the model equations are representative of the data. The logarithm of transmittance is plotted against dye concentration in Figure 1, and a good linear correlation is obtained in accordance with Equation 1. Similarly, the logarithm of viscosity is plotted against the weight fraction of the co-solvent in Figure 2, and again a good linear correlation is obtained in accordance with Equation 2. Finally, surface tension is plotted against the logarithm of surfactant concentration in Figure 3, and a good linear correlation is obtained in accordance with Equation 4. Thus, we are justified in using these model equations.

Table 1. Formulation, Specifications and Measured Properties of an Ink-Jet Ink

Original Formulation

COMPONENT	Original Wt. Fraction	Original Wt (KG)
SOLVENT - Water	0.7355	102.970
CO-SOLVENT - Glycerine	0.1800	25.200
SURFACTANT	0.0550	7.700
DYE	0.0275	3.850
BIOCIDE	0.0020	0.280
TOTAL	1.000	140.000

Specifications

Physical Property	Minimum	Maximum	Target
Viscosity (cp)	2.10	2.30	2.20
Surface Tension (dynes/cm)	34.50	35.50	35.00
%Transmittance (at 430 nm)	27.30	28.00	27.65
pH	7	9	8
Filtraion Rating		10	

Measured Physical Properties

Physical Property	Initial
Viscosity (cp)	2.71
Surface Tension (dynes/cm)	36.50
%Transmittance (at 430 nm)	25.90
pH	7.58
Filtration Rating	2.7

Table 2. Adjustments of Manufacturing Ink Batch

Adjustment Step	Added Water (Kg)	Added Dye (Kg)	Added Surfactant (Kg)	%T	Viscosity (cp)	Surface Tension (dynes/cm)
Initial				25.90	2.71	36.50
#1	5			26.83	2.55	
#2	2.5			28.39	2.34	
#3	1.5			28.82	2.32	
#4	2			29.17	2.30	
#5	2.5			29.69	2.30	
#6	3.5			30.40	2.17	
#7		0.27		28.03	2.18	
#8		0.04		27.84	2.24	36.50
#9			0.3	27.62	2.20	35.90
#10			0.3	28.12		35.80
#11			0.5	27.54	2.21	35.20

The objective function selected was to minimize the total amount of components that needed to be added. Table 3 shows the results of the calculation along with the actual manufacturing ones. The adjusted concentrations are in good agreement, including the fact that no co-solvent should be added. It should be noted that while the added amounts are in agreement, they need not be because many such sets can result in the same adjusted concentrations.

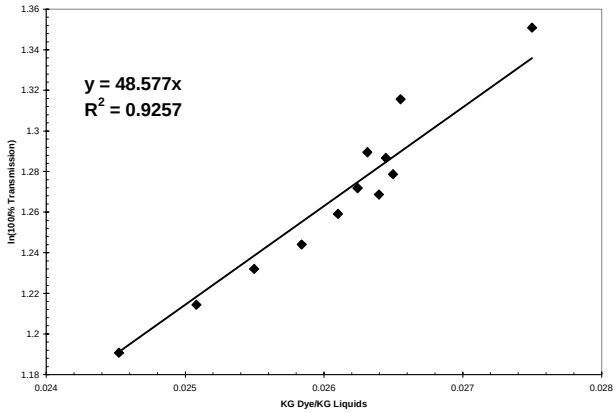

Figure 1. Logarithm of transmittance vs. dye concentration.

Solver has been quite robust in its ability to converge using the initial concentrations as its starting point. When it reaches the boundary of the operating space, it may terminate its search. If one prefers a solution within the constraints, the search can be continued by minimizing the difference from a desired value.

When there is insufficient past data to develop correlations, it has been found that measuring a given property before and after the addition of a component usually provides the necessary information. In the event that a second adjustment is needed, then one can use the last three data points to improve on the estimation of the constants.

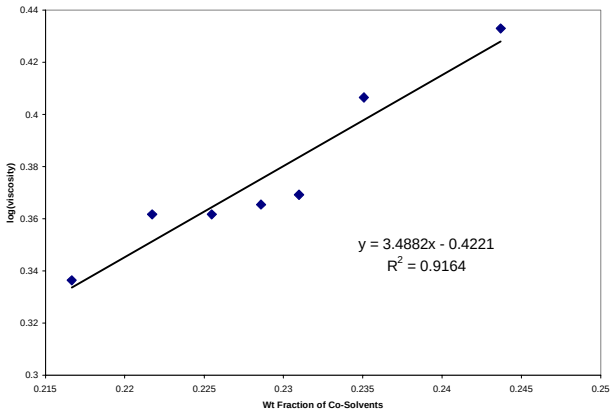

Figure 2. Logarithm of viscosity vs. weight fraction of co-solvent.

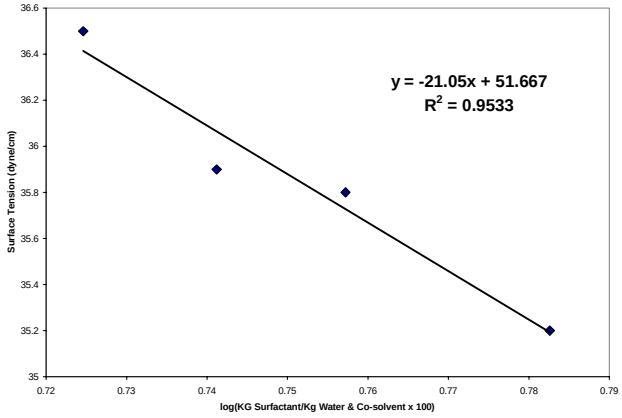

Figure 3. Surface tension vs. logarithm of surfactant concentration.

Table 3. Comparison of Calculated and Actual Ink Adjustments

	PREDICTED			ACTUAL		
COMPONENT	**Wt. Fraction**	**KG to be Added**	**New Wt (KG)**	**Wt. Fraction**	**KG Added**	**New Wt (KG)**
SOLVENT - Water	0.7566	20.732	123.702	0.7573	17.00	119.97
CO-SOLVENT - Glycerine	0.1541	0.000	25.200	0.1591	0.00	25.20
SURFACTANT	0.0616	2.368	10.068	0.0556	1.10	8.80
DYE	0.0260	0.393	4.243	0.0263	0.31	4.16
BIOCIDE.	0.0017	0.000	0.280	0.0018	0.00	0.28
TOTAL	1.0000	23.493	163.493	1.0000	18.41	158.41

Physical Property	**Specification**	**Predicted**	**Actual**
%Transmittance (at 430 nm)	27.30 - 28.00	28.00	27.54
Viscosity (cp)	2.10 - 2.30	2.30	2.21
Surface Tension (dynes/cm)	34.5 - 35.5	35.50	35.20

Conclusions

This program has been an effective tool in guiding the manufacturing engineer in his selection of the adjustments to bring an ink back into specification and has assisted in reducing the number of iterations. It is particularly helpful in the case of liquid dyes where their addition not only adds dyes but also water which in turn changes the other physical properties. Another difficult situation occurs when there are two or more dyes. Other applications have included developing formulations for new inks and color matching.

References

1. H. G. Völz, Industrial Color Testing, VCH, Weinheim, 1992.
2. T. C. Patton, Paint Flow and Pigment Dispersion, Wiley-Interscience, New York, 1979.
3. M. J. Rosen, Surfactants and Interfacial Phenomena, Wiley, New York, 1979.

Biography

Dr. Walter J. Wnek is Chief Technical Officer for American Ink Jet Corp. and is responsible for the technical activities of the company leading to the development and manufacturing of ink-jet inks. He has 20 years of experience in the electronic imaging industry with both toners and ink-jet inks. Walter holds a Ph.D. degree in Chemical Engineering from the Illinois Institute of Technology and specializes in Colloid Science and the dispersion of colorants in polymers and liquids. He has published over 30 papers and given numerous presentations at various conferences on electronic imaging and related topics.