Screening of Colorants for Electrophotographic Toners

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Abstract

As electrophotography has become established, the range of raw materials available has grown. This leads to the development of new colorants that are optimized for this application. For the toner manufacturer this is both a benefit and a problem. Full evaluation of new products involves dispersing the pigment (generally using an extruder) and then milling the dispersion with further ingredients to make a usable toner. This process is acceptable for a few samples of new products but few toner makers would be able to carry it out on every new colorant that comes onto the market. For the colorant maker, the problem is even greater since every new product to reach the market is the result of hundreds of research samples, all of which need to be tested.

There is a need for a screening test that will allow a quick evaluation of the likely colouristic performance of new colorants in toner type systems. This paper introduces two possible techniques. One gives the possibility to screen large numbers of samples for colouristic performance, while the second allows a rapid screening of extruded dispersions without the need to formulate a full toner capable of acceptable printing.

Introduction

Most suppliers into the electrophotographic toner industry will have their own screening tests to ensure that their products meet the needs of their customers. In general, and in colorants in particular, little has been published. This paper, which will layout some options for colorant screening based on techniques used in other areas of the printing industry

Screening Methods

In developing new colorants for any market, it is frequently necessary to make and test a large number of possible products. At laboratory scale (up to 100g), this can easily run into the hundreds. During scale up to production, the size of the sample made increases (up to 1 tonne) and the number decreases, but the quantity and quality of information needed per sample increases. Two screening methods are presented here – a first screen for large numbers of laboratory samples and a second screen for scale up samples.

First Screen

The first screen is carried out by simply dispersing the colorant sample in a solution of the toner resin in a volatile solvent. The polyester resins generally used in toners are readily soluble in a 1:1 mix of ethyl acetate and toluene. Dispersion is effected by paint shaker.

For colouristic assessment, a draw down of the final ink on standard paper (APCO II/II) is made using a wire wound bar such as a K-bar or Meyer Bar. The paper has a black strip printed on it to allow assessment of transparency. In the above example, the final dried ink film has a pigmentation level of 3%.

Table 1: Example of First Screen

Varnish	
Polyester Resin	40%
Toluene	30%
Ethyl Acetate	30%
Millbase	
Pigment	5%
Varnish	95%
Mix pigment and varnish in a 120mL glass bottle and add 150g of 2mm glass beads. Seal well and shake for 30 minutes on a paint shaker.	
Final inks	
Millbase	24.0%
Varnish	74.2%
Toluene	0.9%
Ethyl Acetate	0.9%
This gives a final ink with 1.2% pigmentation and a total solids of 40%.	

Second Screen

For scale up samples, it is necessary to use a method that is as close to the techniques that will be used in the application industry. In the case of toners, this means extrusion followed by pulverization to give a "model toner" with a particle size of 7-10μm. Although time consuming this is relatively straightforward. The problems arise when trying to assess the colouristic performance of the toner produced. In principle, the ideal method would be to make an electrophotographic print with the toner. However, to do this, each sample would need to be formulated with other additives (charge control agent, powder handling aids, waxes etc.) that may affect other properties that need to be measured. (e.g. melt flow index, charging properties). Even if the model toner is used only for colouristic assessment, it can be difficult to ensure that printing is reproducible.

The proposed second screen involves mixing the model toner with a heatset ink varnish, in which the toner resin is insoluble, and additional aliphatic distillate. A draw down on absorbent paper using a K-bar or Meyer Bar is prepared. The varnish is rapidly absorbed into the paper and leaves the toner on the surface. The resultant printed film consists almost entirely of dry toner sitting on the paper surface. The toner is then fused by heating in an oven at 120ºC.

Table 2: Example of Second Stage Screen

Dispersion	
Pigment	40%
Polyester resin	60%
Disperse by extrusion and mill to approximately 1mm	
Model toner	
Dispersion	7.5%
Polyester resin	92.5%
Mix by extrusion and mill to a mean particle size (D_{50}) of 7-10µm and a maximum size (D_{95}) of 20-25µm	
Ink	
Model toner	35.0%
Ink Varnish	58.5%
Aliphatic distillate	6.5%
The ink is blended on a rotating plate muller using the minimum of energy in order to avoid damage to the toner particles.	

For colouristic assessment, a draw down of the final ink on an absorbent substrate (commercially available photocopier paper) is made using a wire wound bar such as a K-bar or Meyer Bar. The paper has a black strip printed on it to allow assessment of transparency. In the above example, the model toner has a pigmentation level of 3%.

Colouristic Assessment

For both screening methods, the colouristic properties are assessed by instrumental measurement of print density (OD), L*, a*, b*, C and h. One disadvantage of wire wound bars is that the print film thickness can vary depending upon the condition of the bar and the technique of the user. In order to improve the repeatability, a series of tests were carried out with varying pigmentation levels in the final ink to give dried film pigmentations of 1% to 5%. The colouristic properties of each of these prints were measured. and L*, a*, b*, C plotted against OD. From these plots, the colouristics properties were estimated for a given OD.

Example of Colouristic Assessment

The example given here is for the first screen, but data from the second screen is treated in exactly the same way.

A Pigment Yellow 95 was tested as in Table 1. The final ink formulations were adjusted to give final dried film pigmentations of 1%, 2%, 3%, 4% and 5%. These were drawn down using a No. 3 K-bar (approx 24µm wet film giving 10-15µm dried film). Colouristic measurements were made, giving the following results:

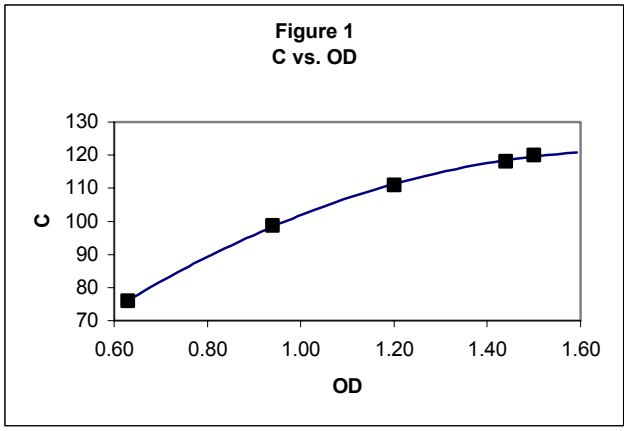
The plots of colouristic property vs. OD were fitted to a quadratic equation using least squares regression analysis[1]. The quadratic fit was then used to calculate the colouristic properties at OD = 1.0. (See Table 4 and Figures 1 and 2).

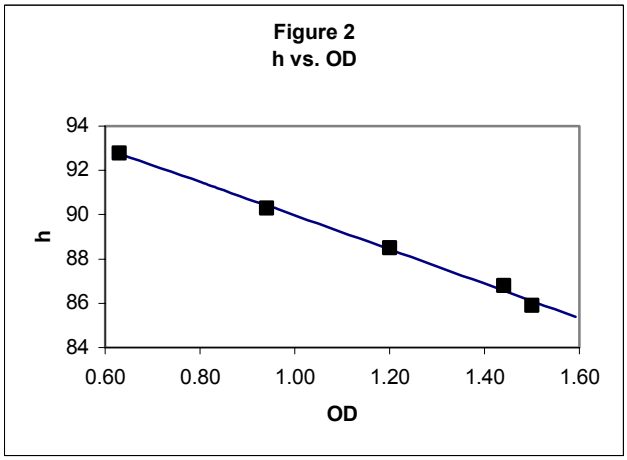
Table 3: Pigment Yellow 95 Colouristics

Pigmentation	OD	L*	a*	b*	C	h
1%	0.63	91.9	-3.7	75.9	76.0	92.8
2%	0.94	90.4	-0.4	98.8	98.8	90.3
3%	1.20	89.3	2.9	111.0	111.0	88.5
4%	1.44	88.3	6.5	117.9	118.1	86.8
5%	1.50	87.6	8.5	119.7	120.0	85.9

Table 4: Pigment Yellow 95 Colouristics at OD = 1

Pigmentation	L*	a*	b*	C	h
2.1%	90.2	0.16	102	102	90.0





Repeatability

First Screen

The testing error of the first screen was assessed using a one-way Analysis of Variance design[2]. Fourteen pigments were each tested in duplicate. The error derived from the analysis of variance was taken as an estimate of the standard deviation, s, of the test. The repeatability, r, is an estimate of the maximum difference between two values that can be reasonably considered as experimental error. In statistical terms, this is referred to as the Least Significant Difference (LSD) and is calculated from r = 2.145s (for the number of data points used here). Strictly speaking, r refers to the repeatability within one laboratory.

Figure 3

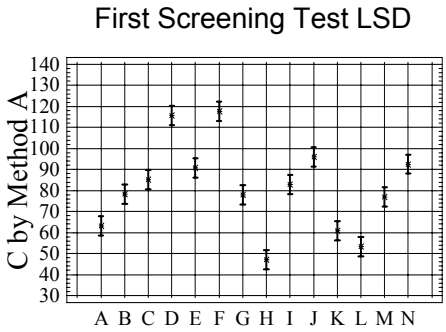
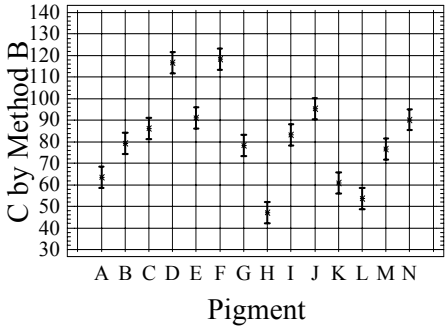


Figure 4



The values of r for the colouristic properties in the initial screen are given in Table 5, and shown graphically for C in Figures 3, 4 and 5.

Figure 5

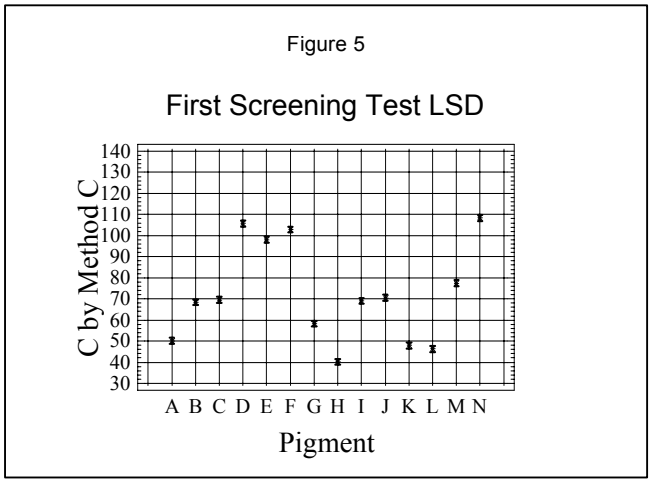


Table 5: Repeatability of Initial Screen

	Method A		Method B		Method C	
Parameter	**s**	**r**	**s**	**r**	**s**	**r**
OD	0.06	0.14	0.05	0.11	N/A	N/A
Pigmentation	N/A	N/A	N/A	N/A	0.27	0.58
L*	0.65	1.4	0.33	0.71	0.33	0.71
a*	0.70	1.5	0.53	1.1	0.47	1.0
b*	4.3	9.1	3.00	6.4	0.66	1.4
C	4.3	9.2	4.59	9.8	1.04	2.2
h	0.52	1.1	0.36	0.76	0.44	0.94

Three methods have been used to determine the colouristics. In Method A, drawdowns at 3% pigmentation were measured directly. In Method B, the five drawdowns at 1% to 5% were measured and the values for 3% calculated by quadratic least squares regression. Finally, in Method C the colouristics at OD = 1 were calculated from the regression relationship. This use of a range of concentration levels is also referred to as a "ladder technique".

Table 6: Repeatability of Second Stage Screen

	Method A		Method B		Method C	
Parameter	**s**	**r**	**s**	**r**	**s**	**r**
OD	0.05	0.11	0.04	0.08	N/A	N/A
Pigmentation	N/A	N/A	N/A	N/A	0.55	1.22
L*	1.38	3.07	1.36	3.03	0.65	1.45
a*	1.03	2.29	0.86	1.93	0.63	1.40
b*	2.36	5.26	2.78	6.20	1.81	4.03
C	1.99	4.43	1.93	4.29	1.78	3.98
h	1.46	3.25	1.22	2.72	0.85	1.88

Note that in this case, with ten data points, r = 2.228s

Figure 6

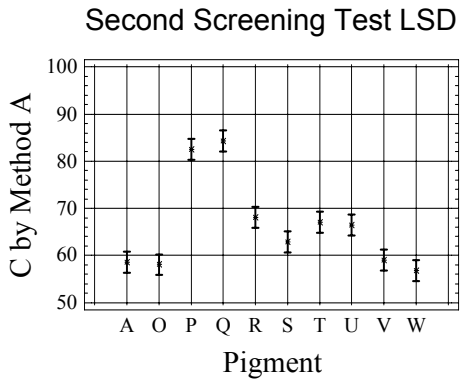
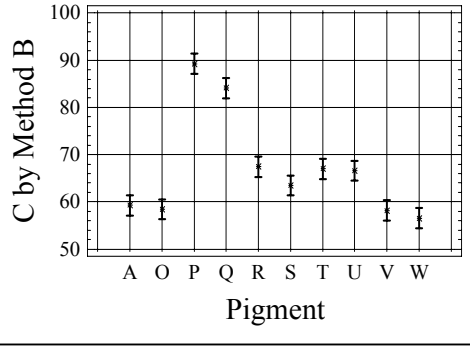


Figure 7

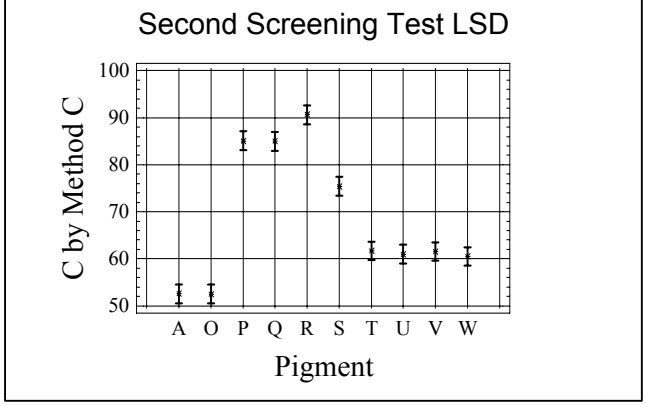


It can be seen that Method B gives a slight improvement over Method A, but that the best repeatability is achieved with Method C. This is based upon analysis of results from a range of pigments.

Second Stage Screen

A similar test protocol was used with the Second Stage Screen. In this case, ten model toners were tested in duplicate. The values for r are given in Table 6 and shown graphically in Figures 6, 7 and 8.

Figure 8



As with the First Screen, overall, Method C gives the best repeatability. It should be noted that the same K-Bar has been used throughout this work. In reality, it is likely that different K-bars will be used with different samples run on different days (or in different laboratories). Under these circumstances, Methods A and B will show significantly poorer repeatability, whereas Method C is virtually unaffected.

Conclusions

Two screening tests, one intended to give quick information on a large number of colorant samples and one to give more reliable information on a smaller number of samples, have been described.

With both of these test methods, the repeatability of measurements is greatly increased by using a ladder, or regression, technique.

Acknowledgments

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References

1. Introduction to Statistics. Ronald E Walpole, Collier-Macmillan, London, 1969. Section 11.6
2. Introduction to Statistics. Ronald E Walpole, Collier-Macmillan, London, 1969. Section 12.2

Author Biography

Dr. Grierson is a graduate of Aberdeen University. After completing a PhD in Analytical Chemistry at Kingston upon Thames, he joined Ciba-Geigy in 1980 as an analytical chemist. During his 25 years with Ciba he has been responsible for many aspects of technical service and product development with particular focus on the printing ink industry. He is currently leading a project aimed at developing colorants for electrophotographic toners.