INK FINGERPRINTING

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Keywords: Ink, Spectrophotometry, Standardization, Pigment

Abstract: Ink is the most important element in printed materials that gives color and individuality to a design. Therefore it is essential that we avoid a Tower of Babel in referring to the various ink pigment(s) and call them according to their Colour Index name which is common language that uniquely defines any colorant. In addition, the visual spectra of an ink serves as its fingerprint so that it can be recognized and distinguished from any other pigment. Both the measured reflectance of an ink, drawn down on a substrate, and the transmission of a diluted ink dispersion can provide the spectral data. However, since transmission measurement is not influenced by the substrate spectrum, this is the preferred method of identifying ink colorants. We have developed a flow cell for measuring diluted ink dispersion which makes transmission measurements very convenient and lead to ink fingerprinting as well as determination of strength and shade for quality control purposes. Examples of pigment naming, spectral determinations, and flow cell construction will be given in the presentation.

Introduction

Inks are made from several ingredients that give properties which allow pigments to adhere to paper, plastic film, or other substrates. The principal ingredient which gives an ink its individual color is the pigment in the composition. Pigments are chemical compounds that due to their structure cause specific absorption of light in parts of the visible spectrum. Consequently, each pigment has its characteristic spectra which is like a fingerprint of that particular pigment. With this in mind, the term “ink fingerprinting” is used which implies identification of ink pigments through measurement of the spectral properties of the ink. In addition, generic names are associatated with pigments so that the identity of similar products from several manufacrers can be known.

Names

All known pigments and dyes have been listed for many years in a reference (Society of Dyers and Colourists, 1995) called the Colour Index . This document has been published jointly by the Society of Dyers and Colourists (SDC) and the

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American Association of Chemists and Colorists (AATCC). It has a listing of trade names as well as simple generic names which are given to each colorant. Other than the graphic arts major color-consuming industries, such as paint, plastics, and textiles frequently use these generic names rather than trade names. Ink pigments also can recognized by such names and an ink maker should be willing to designate his product by its generic name. That is not to say that specific trade names cannot be useful to describe specific use for a product, since many of the same pigments are found in inks for different applications.

The National Printing Ink Research Institute (NPRI, 1990) also publishes a guide to pigments used in printing ink. This guide draws on the Colour Index listing but also gives information relative to ink.

Table I gives the Colour Index generic name of some common ink pigments together with the common chemical name. In addition, a typical value is given for the maximum spectral absorption of the pigment for approximate identification. The entire spectral curve, 380 to 720 nm, is necessary for the complete identification.

Table I

Colour Index Name	Common Chemical Name	Max. Abs.
Pigment Yellow 12	Diarylide Yellow	425
Pigment Yellow 14	Diarylide Yellow	430
Pigment Blue 15:3	Phthalo Blue (Green shade)	620
Pigment Blue 15:1	Phthalo Blue (Red shade)	610
Pigment Red 57:1	Rubine Red	520
Pigment Red 57:2	Napthol Red	520
Pigment Violet 23	Carbazole Violet	580
Pigment Green 7	Phthalo Green	650
Pigment Orange 16	Dianisidine Orânge	480
Pigment Black 7	Carbon Black	400

Spectrophotometric curves are given in Fgures 1 to 4 for several typical process colors.

Figure 1. Typical Process Yellow Colors

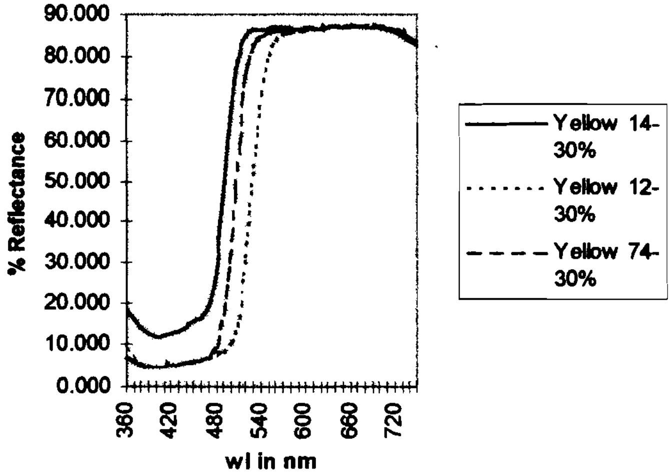


Figure 2. Typical Magenta Process Colors

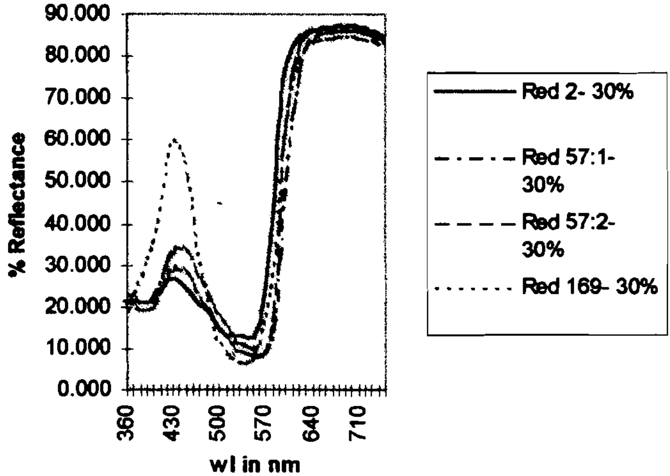


Figure 3. Typical Cyan Process Colors

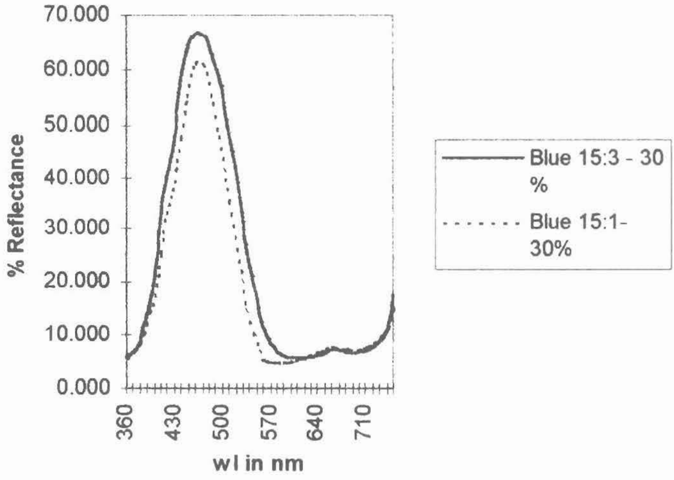
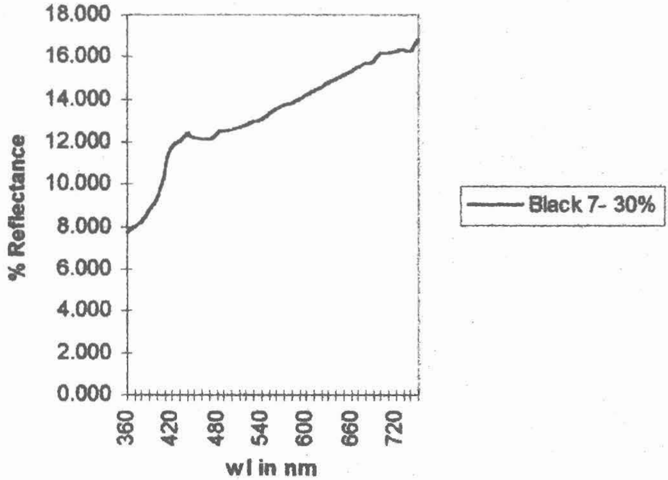
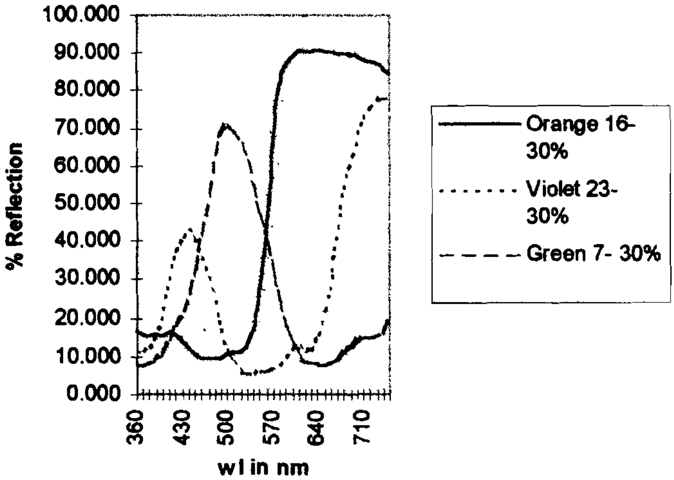


Figure 4. Typical Black Process Color



Several other pigments are useful in making inks that can be used to match spot colors. When colorants such as orange or violet or green are used in conjunction with the process color yellows, magentas, and cyan, a larger gamut of colors can be produced. The spectral curves for typical pigments is shown in Figure 5.

Figure 5. Other Pigments for Spot Colors



Process Colors versus Spot Colors

Half-tone color reproduction requires specially selected primary colors to produce the proper additive binary colors: red, green, and blue. There are a number of combinations of the available yellows and magentas (reds in Colour Index parlance) that are used with Pigment Blue 15:3 as cyan to make more or less satisfactory secondary colors. The choice is somewhat arbitrary but can only involve single pigments, not mixtures, to produce the brightest colors and maximum color gamut. On the other hand, spot colors can be made from any combination of pigments that will match the desired shade. The pigments selected for spot colors are frequently determined by fastness requirements or are necessary to match a specific logo color. Spot colors only involve subtractive color mixing with no need for additive combinations of two primaries.

Spectral Measurement

Printing inks by their very nature are fine dispersions of pigments supported by resins and other additives that promote adhesion to particular substrates. In order to evaluate inks by color measurement, it is commonplace to dilute them to bring them into range of typical spectrophotometers. The curves that are shown above in Figures 1 to 5 are measurements of drawdowns produced by dilution of the ink with an extender (a colorless resin composition). Those measuremnts are made in the reflection mode which is typical for opaque objects such as printed materials. On the other hand, inks can be diluted with certain solvents which solvate the binder resin which then can be evaluated in the more precise traansmission mode. Certain instruments are capable of making both reflection and transmission type of measurement.

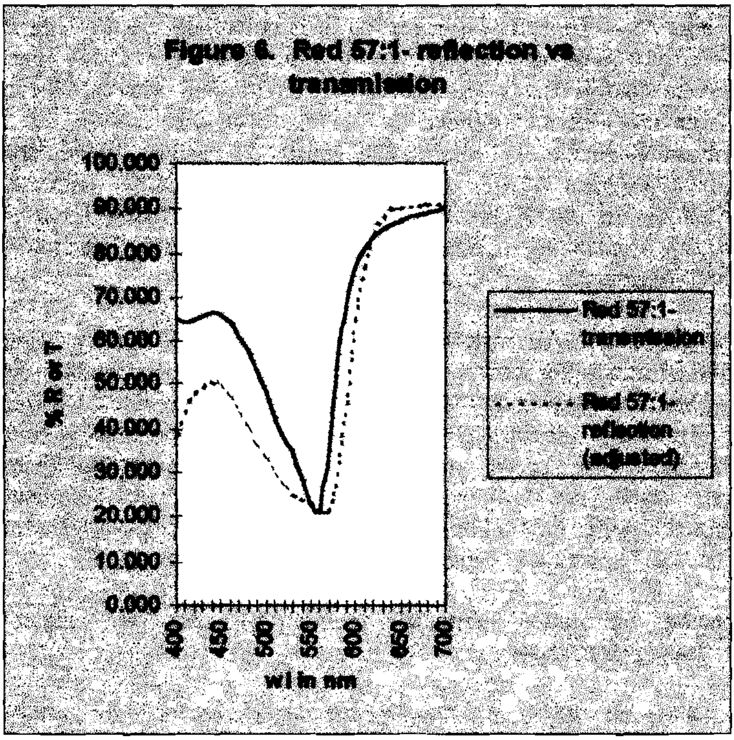
It is commonplace to make evaluations of inks by a "bleach test" in which a constant amount of a white pigment is added to an ink test specimen in order to dilute it to a level which is both visibly and instrumentally feasible. In order to reduce the influence of variables, parallel preparations are made at the same time of a standard and a test.. We have developed a much simpler test than the "bleach test" based instead on transmission measurement; this technique is introduced in this paper. In addition, we have developed special equipment, a flow cell, that makes it easy to handle the measurement of diluted inks.

Several methods are used to dilute inks in order to make them suitable for evaluation. Examples of these are: :

1. Dilute ink with about 70% of a clear extender- suitable for visual and instrumental reflection evaluation.
2. Dilute ink with white pigment- suitable for visual and instrumental reflection evaluation. With yellow pigments, a cnstsant amount of a blue pigment is added to aid in visual estimation of strength.
3. Dilute with clear solvent and evaluate by transmission with an nstrument. Water is used as the solvent with water-based inks and aromatic solvents are used for paste and screen inks

The desired level of reflection or transmission is betweenn 10 and 55% at the point of maximum absorption, lowest point of the spectral curve. The amount of dilution consequently varies according to the strength of the pigment in the ink.

It stands to reason that other factors influence either the drawdown made by dilution with an extender or with the addition of a white pigment. If dilution is achieved with a solvent in the case of transmission measurement, these influences are minimized and the effect is much more like the ink as it is printed. Furthermore, transmission data give more distinctive spectral curve shapes that aid in the identification of specific pigment types. This is illustrated in Figure 6.



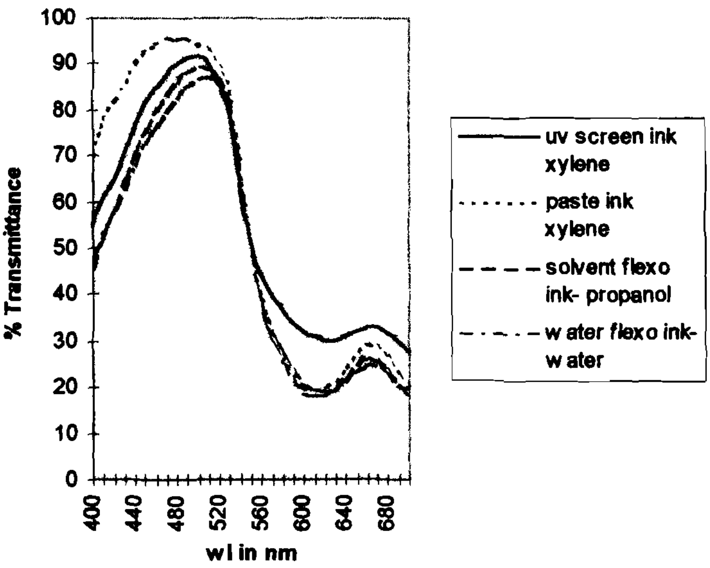
Transmission Measurements with Flow Cell

Since most printed materials are applied to mostly opaque substrates it is common to think of reflection measurements as the manner by which one obtains spectral data. Certainly, densitometer readings made on color bars on press sheets give extremely useful control information. However, we have found that the measurement of samples of diluted inks provides very useful data. In the first place, inks are very fine pigment dispersions which makes for stable dilutions that can be handled with simple techniques. We have found a flow cell to be a practical piece of equipment that enables transfer of the diluted ink sample into the beam of the spectrophotometer where the spectral measurement takes place. With different types of binders being used for various ink applications, several solvents have had to be used to effectively dilute particular inks; no universal solvent has been found for all types of inks. Typically, we have used the solvent recommended by the ink maker for clean up. The following solvents are commonly used in our work with a variety of inks:

1. Water with a small amount of surfactant for water-based inks.
2. 70% n-Propanol: . 30% n-Propyl Acetate for polyethylene inks
3. Xylene or Toluene for offset paste inks

It is interesting to note the similarity of the spectral curves of dilutions of the same pigment type in several ink systems which is shown in Figure 7. This suggests that the properties of the diluted ink are related to the pigment type and are independent of the substrate when measured in this manner.

Figure 7. Various Blue 15:3 Inks



The Flow Cell Method

The method that we have developed is based on a simple analytical technique which is described as follows:

1. A sample of ink weighing between 0.3 and 0.5 gram is accurately weighed to the nearest 0.001 gram into a plastic bottle.
2. 400 times the accurate weight of the sample is weighed into the bottle on top of the ink.
3. The bottle is capped, shaken vigorously until the ink is dispersed.
4. The dispersion is then poured into the flow cell, exchanging the contents of the cell four times.
5. The spectral measurement is made. and a report generated by software that operates the instument*

*Note that the spectro is first standardized by measuring a blank.

Construction of the Flow Cell

The configuration of the flow cell used in these experiments is based on a hollow 9 mm thick stainless steel body fitted with a pair of glass (or quartz) windows. Inlet and outlet pipes are welded to the body to conduct the liquid specimen into the beam of a spectrophotometer. A feature of the cells that were used in this work is that the windows are specially ground to allow the optical path to be reduced to about 0.2 mm. Figure 8 shows a diagram of the flow cell.

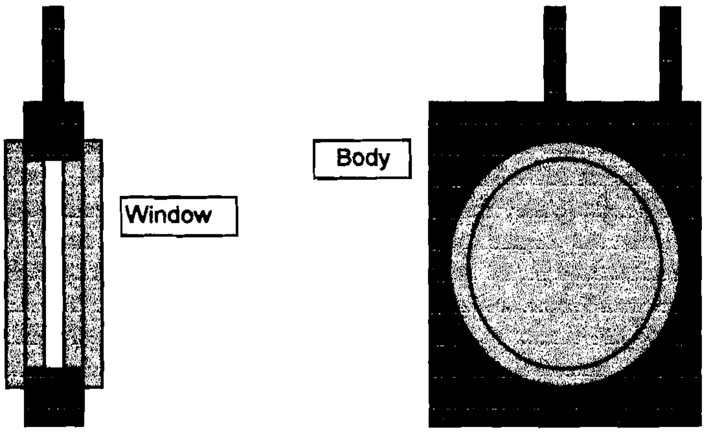
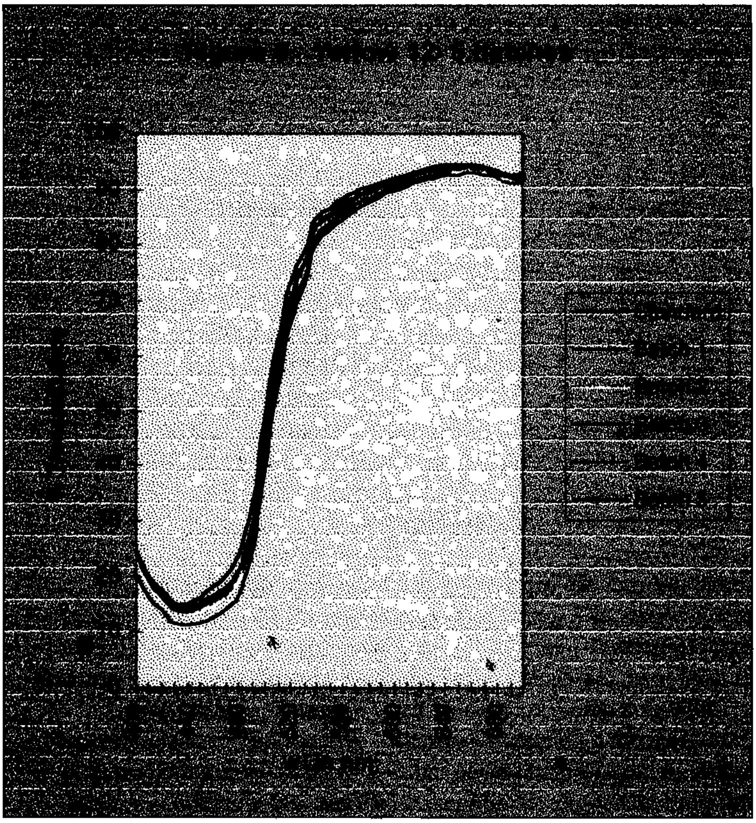


Figure 8. Diagram of Flow Cell

Flow cells have been adapted to a number of spectrophotometers which have transmission measurement capability. Ordinarily the flow cell is fed by gravity with a separatory funnel connected to the inlet and a piece of plastic tubing attached to the outlet and fed to waste. Measurements are made in a "stopped-flow" mode and after three or four flushes of the cell with a new sample. Special cleaning of the flow cell is unnecessary because a new sample automatically replaces the previous one.

Quality Control of Inks

One of the obvious uses of transmission measurements with the flow cell is for routine quality control by the printer and ink maker. The test is simple, rapid, and eliminates the many steps needed to make a drawdown on paper or other substrates. Although measurement of a diluted suspension of an ink is unlike that which is printed, good correlations have been obtained between the flow cell data and the traditional bleach tests. We did a study of repeated tests with the flow cell and found that the coefficient of variation is 1.6%.



Five samples and a standard of Yellow 12 gravure ink were obtained from an ink maker. All samples met the standard as measured by the conventional bleach test. The samples and standard were then measured with flow cell technology. The spectral curves are shown in Figure 9 and data calculated from these measurements are in Table II.

Consideration of the analysis results points to issues concerning test methodology. Bleach tests are intended to provide visual comparisons with respect to strength and shade. The color difference, ΔE, found by the flow cell method reveals much more information and a greater degree of accuracy than can be derived from traditional testing. This is especially true for yellow inks which are usually tested with a constant amount of both a white and blue pigment to facilitate visual estimation of strength. A second issue is the presence of other pigments in a strength and shade test which disguise the true properties of the ink. The transmission measurement with the flow cell dispersion is not contaminated with extraneous and confusing components and thus leads to a colorimetric comparison that is closest to that which is printed on a substrate.

Table II

Samples	% strength	Color Diff, delta E
Standard	100	0
Batch 1	111	0.67
Batch 2	102	1.17
Batch 3	95	2.48
Batch 4	101	1.64
Batch 5	98	1.20

Conclusion

It has been shown that modern technology can be used to define an ink fingerprint which consists of a generic name based on the Colour Index and a unique spectrophotometric curve. The spectra which are useful to identify a pigment that is used in an ink can be obtained either by reflection or transmission measurement. Reflection data are obtained from a printed material but transmission data are from a diluted ink sample. A flow cell has been devised to facilitate transmission measurement since this is a more definitive method than with a reflecting printed sample. In addition to simple identification, valuable quality control data can be obtained on inks through the flow cell method which is more precise than the traditional bleach test

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