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Radovan Sporka
Western Michigan University

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UV-VIS SPECTRAL ANALYSIS OF SPOT COLORS

by

Radovan Sporka

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Radovan Sporka

UV-VIS SPECTRAL ANALYSIS OF SPOT COLORS

Radovan Sporka, M.S.

Western Michigan University, 2002

Press return inks represent a continuous problem in printing industry. The best way of utilizing them is to mix them into new colors. Efficiently to do so, it is necessary to determine their composition first. The spot color inks for product gravure were analyzed using Perkin Elmer Spectrometer LAMBDA 900. UV/VIS/NIR analysis of mixtures showed rather similar course of ink spectra in ultraviolet and near infrared region. Thus, the VIS range from 400 – 700 nm was used for further analysis. The unique course of spectral curves of each pigment in visible region enabled successful qualitative analysis of two- and three- pigment dispersion mixtures. Quantitative analysis was performed using MS Excel Solver program. Linear combination model was used for retroengineering of ink mixtures. It was found to be reliable technique. Also linear, quadratic, and cubic spline functions were discussed. The cubic splines were considered to be the best fit.

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CHAPTER I

INTRODUCTION

Gravure is used to print, decorate or coat an amazing range of products, from narrow width plastic films to vinyl shower curtains and wall coverings [1]. Some of these products such as floor and wall coverings enjoy a relative immune market to ups and downs in the economy. In many of these product-printing areas, gravure is the acknowledged process of choice due to the endless repeatability of a printed image permitted by the print cylinder. This printing process is very often employed because of the ability to print on various substrates, to apply coatings, and to keep the brilliance and consistency of the reproduction.

Custom color matching using non CMYK ink system is common in product printing applications, such as used in flexography and gravure. Typical product printing application using custom color blending are wallcoverings, decorative laminates, floorcoverings, vinyl and plastic printing.

In custom color printed products the ink color palette (spot color) is generated by blending individual pigments. As in most liquid printing operations, more ink is blended than is needed for the reproduction run. This is due to ink application design constrains, which include ink sumps, pumps, and cylinder pans. The main problem with redundant ink is with its management due to environmental concerns and high inventory costs.

In the product gravure, the exact match of the spot color is very often needed, which might be a problem, due to complexity of spot color blends. The customer, however, wants to have the same hue printed again, no matter how difficult this problem is to the printer. The aim of this work was to analyze spot colors and quantitatively determine their individual components in order to be able to match such colors. The ultimate goal was to increase the efficiency of the color matching process.

CHAPTER II

LITERATURE REVIEW

Pigments

Pigments together with dyestuffs convey the visual identity of an ink and invariably contribute the major costs [2]. Properly chosen, pigments give brilliant color, gloss, transparency or opacity which are necessary to the finished ink. The key property of pigments is their insolubility in a vehicle. They also exhibit many different properties such as lightfastness, alkali resistance, dispersion, and compatibility with various ink systems. Colored pigments impart the color of the printing ink by themselves or in conjunction with other materials such as metallic, pearlescent or fluorescent components [3]. When applied to a substrate, they either remain on the surface or tend to fill the voids. There is many different types of pigments. Some are inorganic, but the majority of them has petrochemical origin, and is made via organic synthesis.

With the proper understanding and selection of pigments, ink can be formulated not only to achieve the correct hue, but also give lasting performance in the finished ink film [3].

Classification of Pigments

Pigments are identified using an international system for classification called the Color Index System developed by the Society of Dyers and Colorists (SDC) [4] and the Association of Textile Chemists and Colorists (AATCC) [5]. This system indicates a generic name and constitution number which are given to all pigments according to their chemical composition, hue, and sequence in which the color was registered.

A separate coding system names the category, color, identification and chemical class of material [6].

The first letter indicates the category:

A - acid dye
B - basic dye
P - pigment
F - food pigment
L - lake
N - natural pigment
V - vat pigment

The second letter indicates the color:

B - blue
O - orange

Bk - black
Br - brown
G - green
M - metal
V - violet
R - red
W - white
Y - yellow

The color index number identifies the color and the sequence of registration. The five-digit number designates the constitution number, which makes known the structure of the pigment. The first one or two of these digits discloses the chemical class of the pigment [7].

Pigments which are chemically similar but differ in the metal, acid or crystal form used in salt formation use the same generic name but are differentiated by a colon and a additional number.

The Color Index System identifies the pigment regardless of manufacturer [3]. Companies manufacturing a pigment under a particular Color Index Code must provide and maintain the proper chemical structure to be considered under that Color Index Code.

Pigment Composition

The classification of pigment types can be seen in Figure 1 [8].

Azo Pigments

Azo pigments contain the - N = N - azo chromophore within the molecule. The azo group is formed by the reaction of a primary aromatic amine with nitrous acid, forming a diazonium salt, which is reacted with a coupler to form the pigment or the sodium salt [3].

There are two main groups into which azo-pigments are divided: metallized and non-metallized.

Metallized ones contain one or more acid groups in the molecule, which are reacted with a metal salt to render the pigment completely insoluble. The commonly employed salts are those of barium, calcium, and strontium. Other salts can be also used.

Non-metallized azo pigments do not contain any of acid groups, thus do not require metallization to completely precipitate the pigment. Non-metallized reds are divided into two groups depending on the number of amino groups and nature of the amine used. Mono-azo pigments contain one amino group in the molecular structure; the diazotized amine is reacted with a coupler to form the pigment. Bisazo pigments are formed from aromatic primary diamines, which are diazotized and reacted with a coupler to form the pigment.

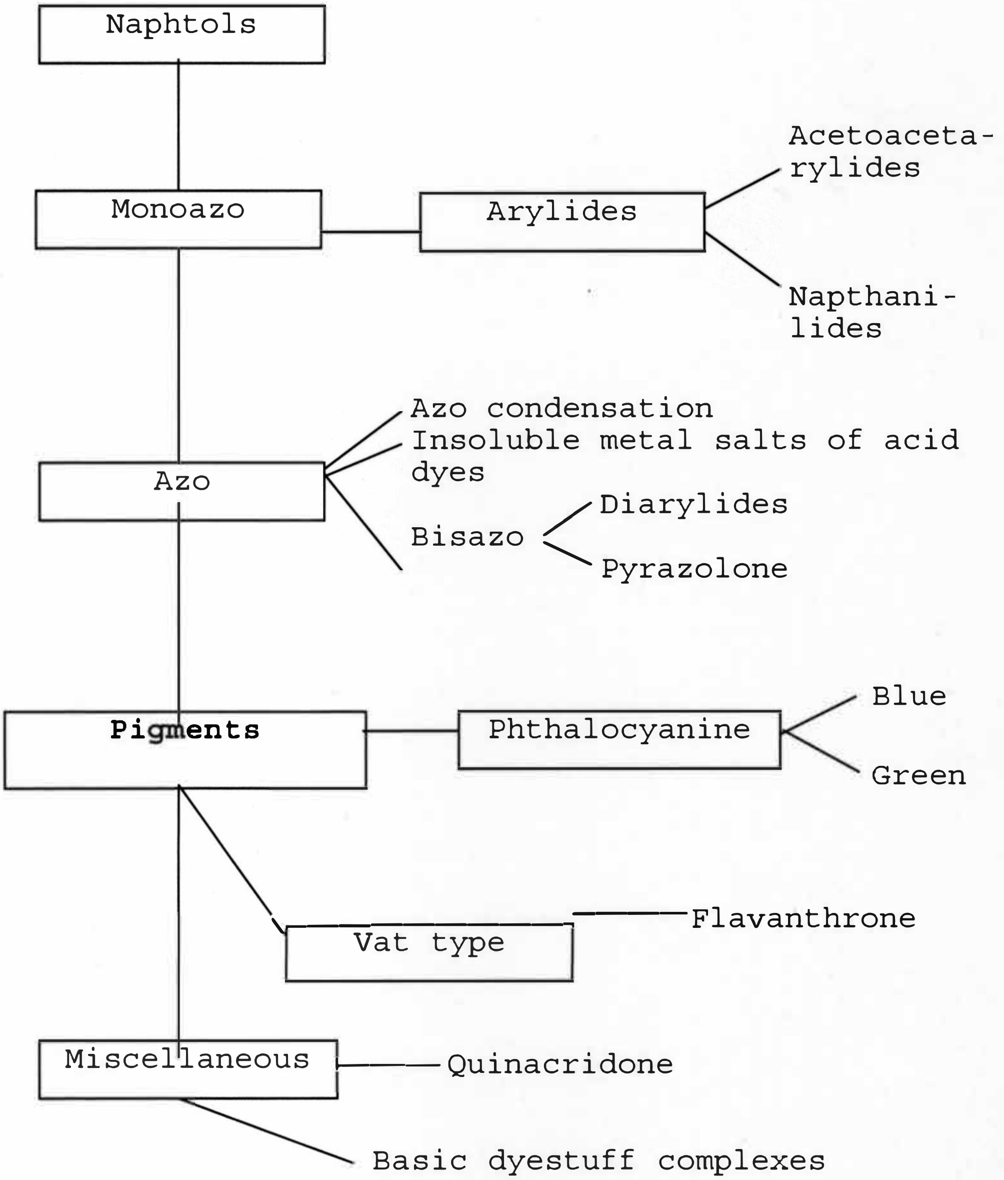


Figure 1. Classification of Organic Pigments Used in the Printing Ink Industry.

Metallized Azo Pigments

Metallized Azo Red Pigments

These pigments are based on four coupling components [3]:

- beta-naphthol
- beta-oxy-naphthoic acid (BONA)
- 2-hydroxy-3-naphthanilides (Naphthol AS)
- naphthalene sulfonic acid derivatives

Metallized reds offer a large variety of shades due to the phenomenon of crystal modification. Available color ranges from yellow shades such as C.I. Pigment Orange 46 (Figure 2) and the barium lakes of Lithol Reds and Permanent Red 2B (Figure 3) to the bluer shades of calcium lakes of Lithol Red, BONA Red and Lithol Rubine (Figure 4).

Reds based on BONA are bluer in shade, since reds based on beta-naphthol are yellower in shade.

Metallized reds possess moderate fastness properties to solvent, lightfastness, and alkali resistance. These pigments are very economical and offer competitive pricing in the ink industry.

Metallized Orange Pigments

Metallized orange, C.I.Pigment orange 46 (Figure 2), is very often used due to its strong yellow shade, and as an inorganic orange replacement.

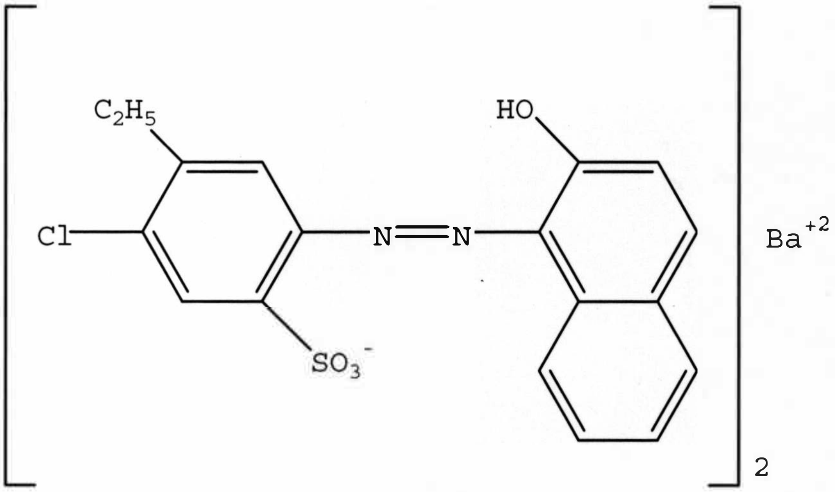


Figure 2. C.I.Pigment Orange 46, C.I.15602, Ethyl Red Lake C.

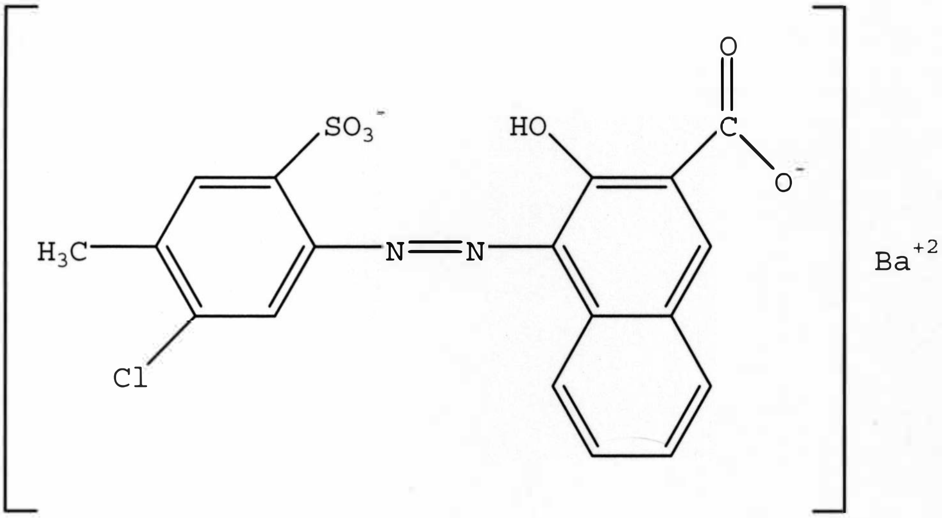


Figure 3. C.I.Pigment Red 48:1, C.I.15865:1, Permanent Red 2B (Barium).

Metallized orange is economical in price, offers good lightfastness, strong color and tinctorial strength, fairly good heat resistance, excellent resistance to acid, alkali, and water [2].

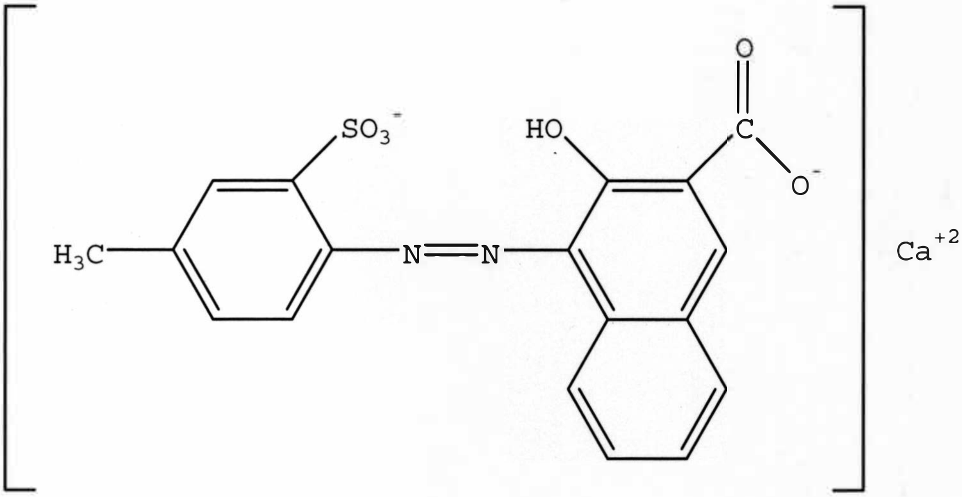


Figure 4. C.I.Pigment Red 57:1, C.I.15850:1, Lithol Rubine (Calcium).

Mono-Azo or Arylide Yellow Pigments

Many arylide yellows are currently in production. Shades range from very greenish yellow to a bright warm shade. This group of pigments has historically been used in the coatings industry. They have been implemented in many formulations for increased lightfastness and as alternative to diarylide yellow pigments. They are normally fairly opaque pigments, but there are some grades that are sufficiently transparent to be suitable for superimposition. Arylamide yellows are widely used for their fastness to light and tinctorial strength as well as resistance to alkali and soap. They are unsuitable for inks that require heating because they will sublime and bleed strongly in some non-popular organic solvents, paraffin wax, and plasticizers [2].

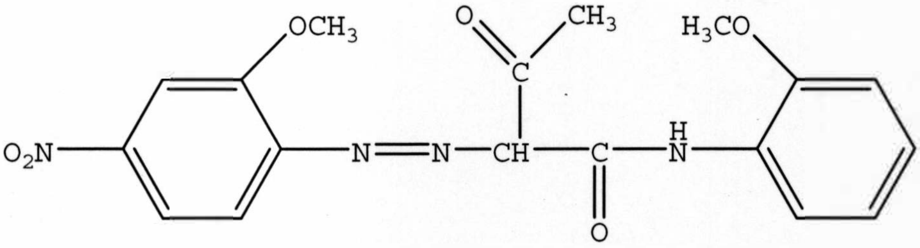


Figure 5. C.I.Pigment Yellow 74, C.I.11741, Arylide Yellow.

Mono-Azo Red Pigments

Coupling diazonium salts with Naphthol AS produces mono-azo red pigments. These pigments are widely used in the paint and ink industries due to the color strength, low price and fastness properties. Mono-azo red pigments exhibit from moderate to good alkali resistance (Figure 6).

Dinitroaniline Orange

This pigment is used in the coatings and ink industries due to its strong color and shade. It is often used as a replacement for inorganic orange or used in blending to produce barium-free colors.

C.I.Pigment orange 5 (Figure 7) exhibits moderate lightfastness, solvent resistance, as well as weather fastness [3]. However it has poor flow properties in inks and finds use mainly in inexpensive systems for printing on kraft paper and polyethylene where a bright reddish shade can be combined with good covering power [2].

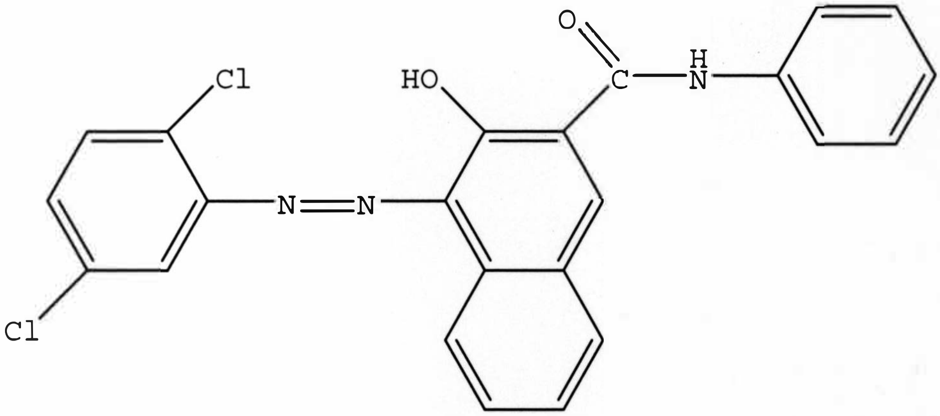


Figure 6. C.I.Pigment Red 2, C.I.12310, Naphthol Red FRR (Medium Shade).

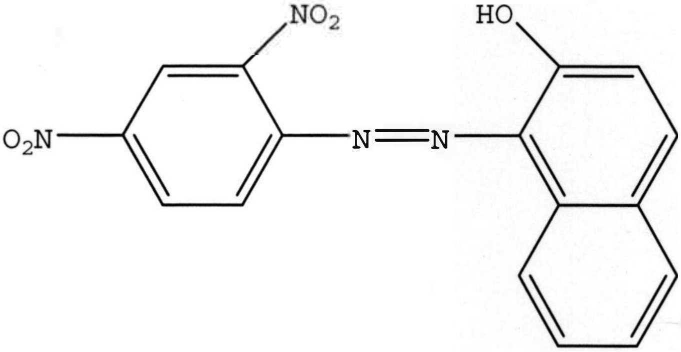


Figure 7. C.I.Pigment Orange 5, C.I.12075, Dinitroaniline Orange.

Non-Metallized Bisazo Pigments

Bisazo or Diarylide Yellows

These pigments (Figure 8) are produced both, by coupling acetoacetarylides or pyrazolones with diazonium salts, or by the diazotation of aromatic amines that are coupled to bisacetoacetarylides [3].

Diarylide pigments involve the largest group of organic yellows currently in use. The tinctorial strength of this important range of pigments is considerably greater than the mono arylide yellows. Lightfastness ranges from fair to excellent, resistance to heat and soap is excellent. The range of properties available in Diarylide yellows is sufficient to satisfy the majority of the requirements of inks for most printing processes [2].

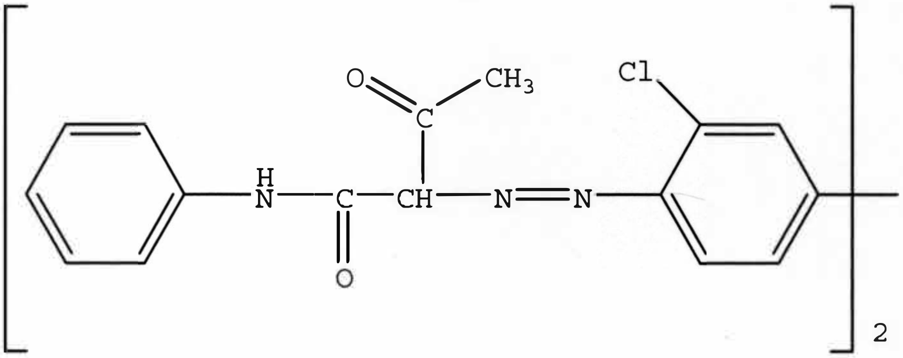


Figure 8. C.I.Pigment Yellow 12, C.I.21090, Diarylide Yellow AAA.

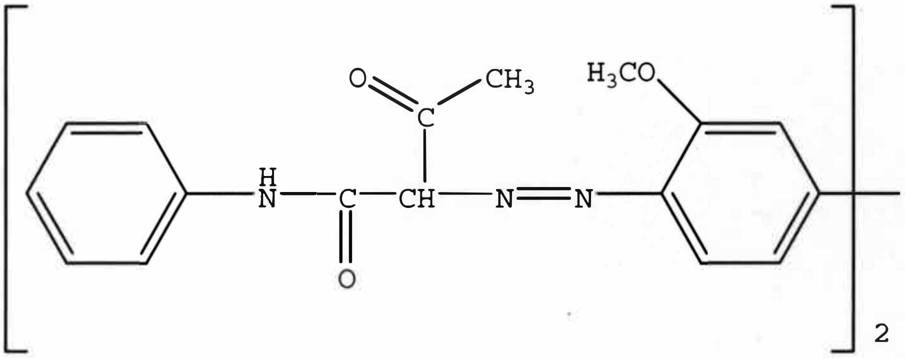


Figure 9. C.I.Pigment Orange 16, C.I.21160, Dianisidine Orange.

Bisazo Orange Pigments

The major bisazo oranges used in the printing ink industry are C.I.Pigment orange 13, 16, and 34 (Figure 9). These pigments are based on o-dianisidine and pyrazolone [3]. They offer a clean yellow shade and are used as a monopigment and in blending with other pigments to produce a variety of color shades. C.I.Pigment orange 16 is a typical of diarylide yellows having very high tinting strength. The hue is bright reddish orange, one of the few diarylides without a chloro group.

Bisazo oranges are moderate in resistance properties and priced very economically, which makes them very popular for printing ink systems.

Phthalocyanine Pigments

Phthalocyanine Blue

Copper phthalocyanine blue is the most widely used blue in the ink industry. A copper complex of tetra-azatetrabenzoporphine, this molecule exhibits a planar, completely conjugated structure with excellent stability [3].

Phthalocyanine blue is today produced in several crystalline forms. The most important are the alpha, beta, and epsilon forms. Several types of each crystalline form are produced which exhibit different properties for crystallization resistance and non-flocculation to strong solvents. The alpha crystal (Figure 10) produces a very red shade product and is used mainly in paints and plastics, with some use in the ink industry. The beta crystal produces a greener pigment, which exhibits greater stability to heat and solvents. The beta blues are used to a large extent in the ink industry and cover the major blue used.

Phthalocyanine blues exhibit a strong color and tinctorial strength and excellent resistance properties to acid, alkali, solvent, lightfastness and weatherability [3]. Their clean shade and good economics make them very popular.

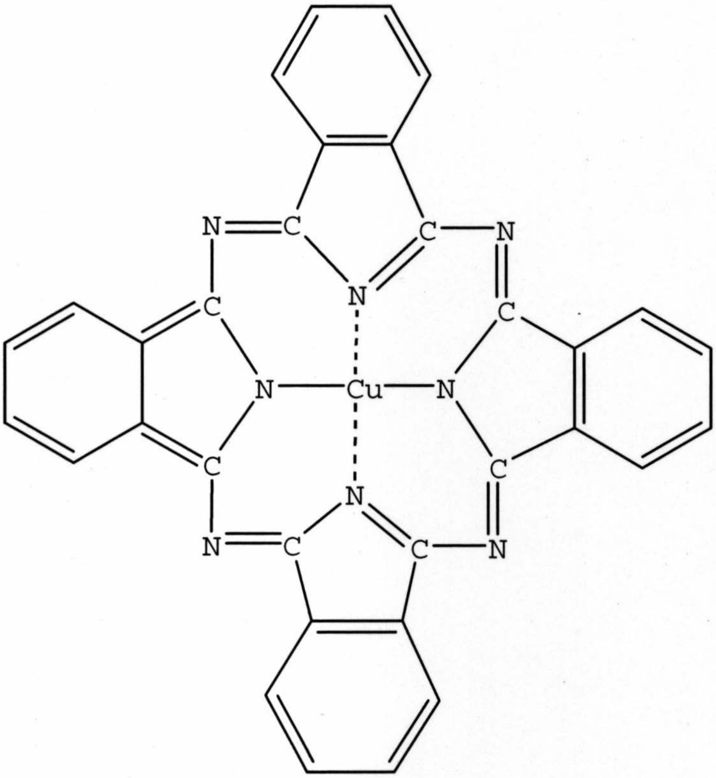


Figure 10. C.I.Pigment Blue 15, C.I.74160, Copper Phthalocyanine Blue (R.C.).

Phthalocyanine Green

Phthalocyanine green is the halogenated form of copper phthalocyanine blue. Progressive substitution of chlorine on the copper phthalocyanine molecule produces phthalocyanine green (Figure 11). The higher the degree of chlorine substitution the yellower the product.

The phthalocyanine greens are the major greens used in the ink industry because of their clean shade, strong color and tinctorial strength and excellent resistance properties to acid, alkali, strong solvents, lightfastness and weatherability.

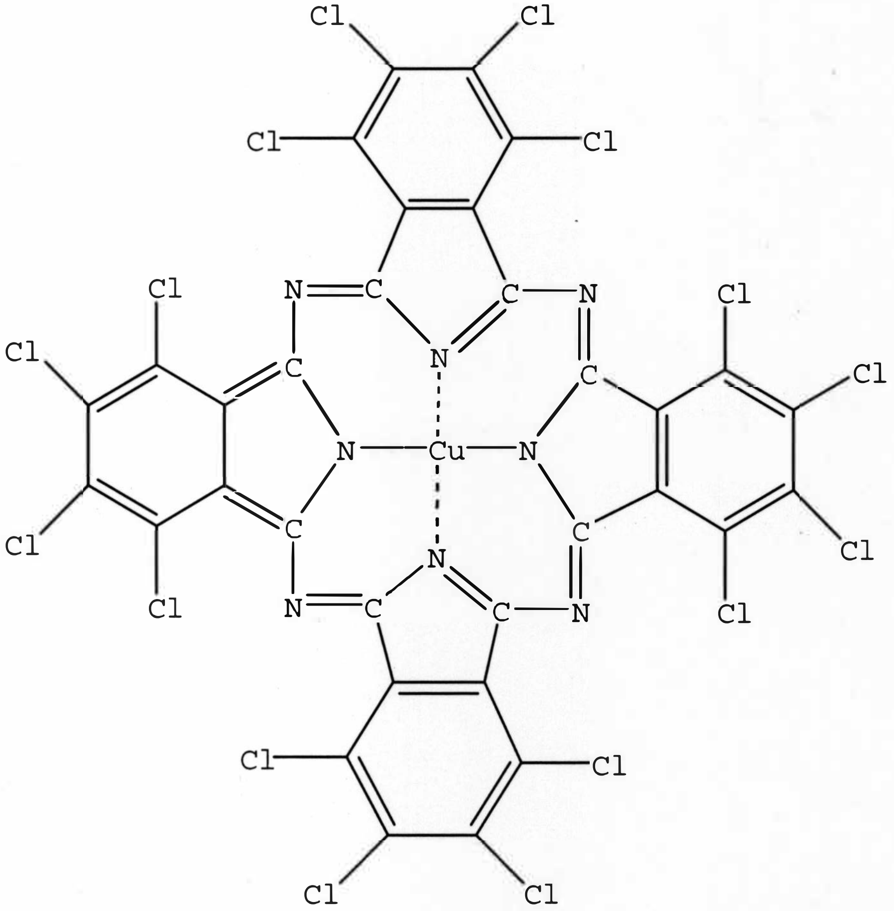


Figure 11. C.I.Pigment Green 7, C.I.74260, Copper Phthalocyanine Green.

Spot Colors

Spot color also called pre-mixed inks, are the inks used for printing a specific color. Spot color inks are cost-effective for two- or three-color printing and may also be used for colors that process printing cannot adequately produce.

In contrast to process or four-color technique, spot color does not require the overlay of different layers of ink in order to achieve the final color. Spot color is mixed according the formula before going onto the press. While there are limitations to spot color (it cannot be, for example, printed full color photos using only spot), there are still some significant payoffs for choosing this technique:

- It is usually less expensive. Each spot color uses its own plate for printing, so if the document contains only two colors, the project will require only two plates, one for each color. With process color, it is necessary to run four plates, one for each of the primary inks (cyan, magenta, yellow, and black). Hence, spot color can be the most economical way of adding color to the document.
- Spot color is often cleaner and brighter than process color. Sometimes projects done in process color will include an extra plate for a spot color, because of the accuracy and variability in intensity offered by spot.
- Use spot color inks when special inks such as metallic, fluorescent, or pearlescent are de-

sired.

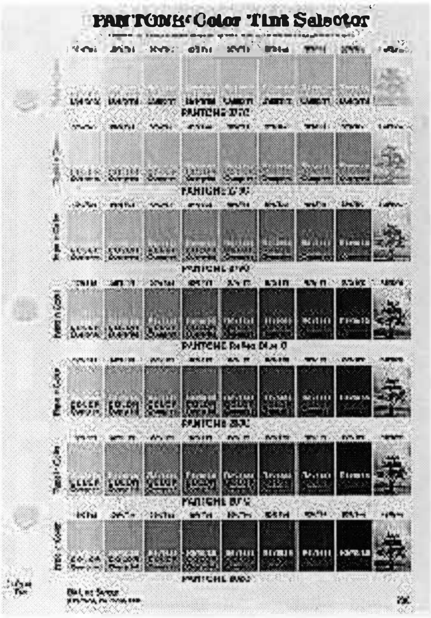
In spot color printing the inks are mixed by the manufacturer and are applied one color to a plate. If "exact" color matching is required, exact color can be specified by means of spot color system, such as the Pantone Matching System (or PMS) number codes.

The illusion of more colors in a job can be created by using shades of the PMS colors. These are known also as tints. Tints are created by using only a percentage of the full color, with 10% being very light and 90% being very dark. It can be sometimes difficult to visualize how a tint will print. For this purpose a color tint book from Pantone (Figure 12) should be used. It shows each PMS color in tints from 10 to 90%, as well as black overprinting and white reversing out of each tint.

When the process colors are picked, they are always a combination of cyan, magenta, and yellow. The method of picking a PMS color is looking up the swatch book until the desired color has been found (Figure 14). Then the number is used.

The PMS colors are chosen from a Pantone swatch book (Figure 13).

Uncoated PMS colors will have a U after the number; coated PMS colors will have a C after the number, depending on the substrate printed.



PANTONE® Color Tint Selector

Figure 12. Color Tint Book From Pantone.

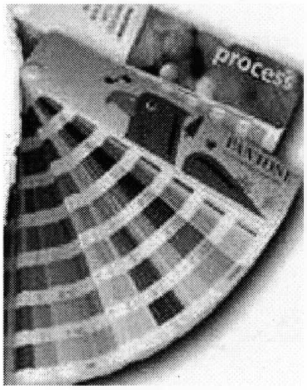


Figure 13. Pantone Swatch Book.

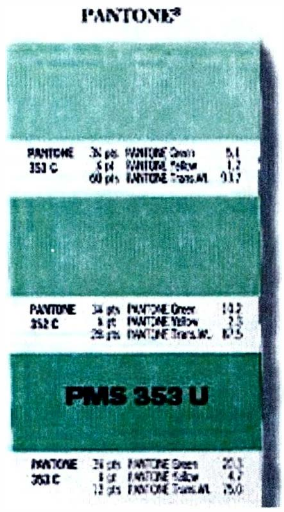


Figure 14. Picking the Green Color (PMS 353 U) From the Swatch Book.

Color Matching

Procedure used in color matching of printing inks will depend on the nature of the work and on level of experience of the color matcher. The supplied pattern usually consists of a print, not necessarily produced by the process to be employed on the required substrate.

Selection of Raw Materials

The exact requirements of the printer are very important and must be ascertained before the color matching process can start. Before handing the project to the color matcher, some information is required. These include general type of ink, the printing process, the substrate and its sample. Also the fastness of the ink has to be considered.

Another thing to deal with is the question of what is the final product going to be used for. If the ink is required for food packages, the selected inks and their pigments must meet the needed properties and required restrictions (e.g. rub resistance, suitability for deep freezing, toxicity, odor, etc.).

If there are further after printing processes involved, these have to also be taken into the consideration.

Matching Techniques

After collecting of the needed data, the process of testing the color and choosing the pigments most likely to be required can start. It will be necessary to examine full strength and reduced prints of single pigments against the pattern under standard illuminant D_{65}.

Procedures

Inks are commonly matched by blending individual pigments already dispersed in a suitable varnish. The ink factory normally produces the pastes with the commonly used pigments dispersed in a range of vehicles. To avoid needlessly increasing the range of pre-dispersed pigments in vehicles, the matching should be made with those already available. The use of dry color in the matching process should be avoided if at all possible, because differences in degree of dispersion will add a further variable to the system [2].

The selection of colorants and the tinting to shade of a printing ink is more time consuming. The holding of printing machines while corrections for color are made and the delays in printing ink manufacture are extremely costly. Thus newer and more intelligent computer-assisted methods of color matching are being developed for printing inks. Also more economical use of colorants and press return inks cannot be neglected.

Instrumental Color Match Prediction

Part of the light falling on a printed surface is absorbed (K) and the rest is scattered (S). The scattered fraction of a light could be measured as diffuse reflectance (R). The relationship between these two values was worked out by Kubelka and Munk in 1931(1).

$$K/S = (1-R)^2 / 2R \qquad (1)$$

The model used by Kubelka and Munk [9] is the basis of most programs used for color match prediction. The model works for an opaque film of even thickness, with a pigment of very small particle size and evenly dispersed in vehicle. If the film of printing ink is relatively thin and transparent, a significant role is played by its uneven thickness and distribution on the substrate and the pigment particle size in relation to the ink film thickness. Analysis of systems with different concentrating of the light-scattering centers shows that deviations from the ideal medium produce changes in the dependence of the apparent Kubelka-Munk scattering and absorption coefficients on the true absorption coefficient [10]. Thus, many correction factors for the above mentioned model have to be applied. The procedures have been proved valuable in some areas. Research is continuing into more satisfactory relationships between measured reflectance and colorant composition. It has been shown by Dunkan that the K/S function is additive [2]. Every K/S at any wavelength calculated from the reflectance is the sum of K/S values of the components (Figure 15). Also the values are linear, what means, that for example if the concentration of constituent is doubled, the K/S contribution of this constituent will be doubled, too (Figure 16).

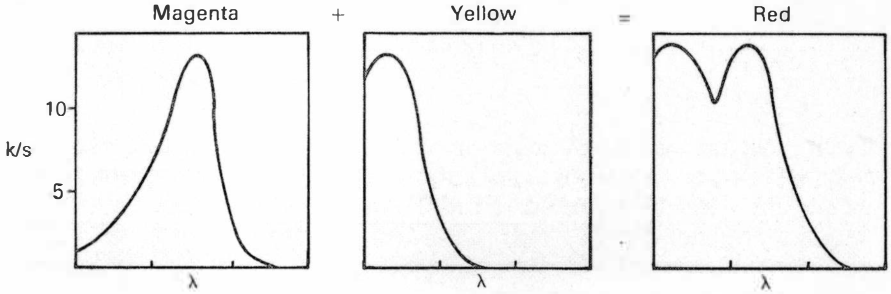


Figure 15. Addition of K/S Curves.

The linearity is illustrated by a group of K/S curves for a rubine red ink, with increasing concentration of pigment (Figure 16), where at maximum absorption ~560 nm, the K/S values are nearly linear.

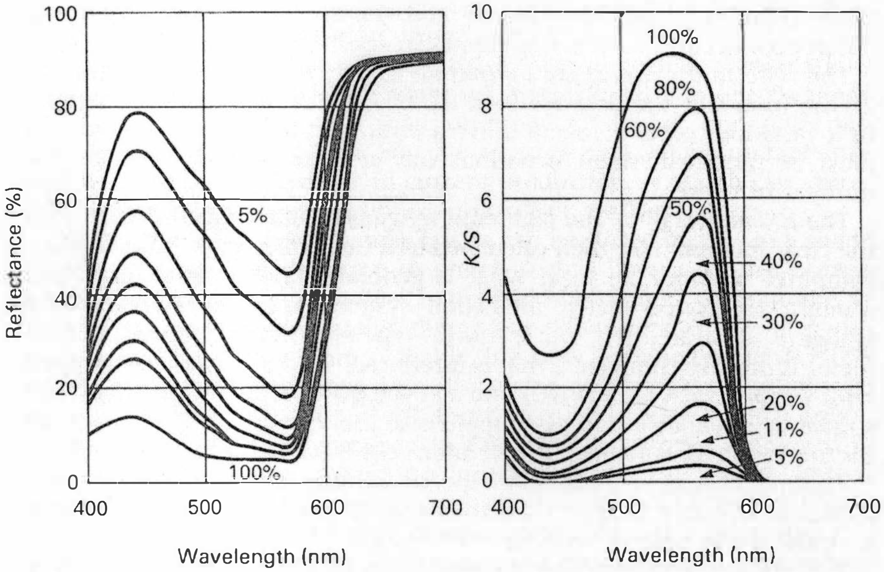


Figure 16. Reflectance and Derived K/S Curves of a Range of Concentrations of a Red Ink.

Thus it is possible to relate the reflectance at each wavelength to the concentration of the constituent pigment (2).

$$(1-R)^2/2R = K/S = a*(K)/(S)_A + b*(K)/(S)_B + c*(K)/(S)_C \quad (2)$$

Where a, b, c are concentration of pigments A, B, C. Since the printing ink is relatively transparent, the K/S value of substrate cannot be neglected.

Match Prediction Procedures

The K/S values for all the pigments at a range of concentrations must first be prepared. This is normally done by taking a base ink and reducing with clear medium to give a range of concentrations from 5 to 100%. Prints of these must be very carefully prepared, usually on a standard substrate using an accurate proofing press. In the case of liquid inks an R-K coater is used. When liquid inks are tested, special care must be taken to ensure constant viscosity through the whole process so that an accurate film thickness is applied [11].

The reflectance curves are measured, usually by taking 16 readings at 20 nm intervals. The K/S values of all the pigments, at usually nine concentrations plus the clear medium, are then calculated.

It is possible to calculate a color match from all possible combinations of pigments, but the ink technologist usually wish to select a range with special properties (e.g. light or product fastness).

Once a shade has been matched, it is wise to store the data. These data will be accessible for the nearest match to search before attempting a new matching.

One of the biggest limitations is the basic theory used. A critical review of Kubelka-Munk by Dr James Nobbs of the Department of Color Chemistry at Leeds University points out that in the case of semi-transparent layers the inherent limitations of the theory produce errors [11].

The light scatter is assumed to come mainly from the substrate. This assumption is probably the source of errors that leads to some of the poor results. Plots of K/S vs. concentration are never linear as predicted by the theory, thus there is a need for a range of concentrations. Complex calculations are necessary if the white ink is employed in the formulation, because some of the scattering comes from the ink and some from the substrate. In this case it is much better to reduce the ink with a standard base white and apply a sufficient film thickness to hide the substrate. The scattering then is almost totally provided by the white ink, and it is predictable.

Color Difference

All printing ink manufacturers keep a large library of prints and standard ink samples against which production materials are compared [12]. Prints must be carefully stored and be accompanied by data showing how the specimen was prepared, the weight of ink applied, the type of substrate employed and other details relating to special properties.

The difference in color between two specimens, can be represented by their distance apart in color space. It can be expressed mathematically by formula (3).

$$\Delta E = (\Delta H^2 + \Delta S^2 + \Delta L^2)^{1/2} \qquad (3)$$

Where Δ means "difference in", E is a total color difference, H represents hue, S saturation, and L lightness.

It is necessary to attempt to convert values obtained from color-measuring instrument, so that ΔE is the same visually for all parts of color space. The equation used are numerous, but no one system satisfies all applications. Ideally we should direct at the system where ΔE = 1 is a good commercial match. A good commercial match is difficult to define. It is dependent upon the product, customer's particular needs and is still usually the matter of personal judgment. Very often the color specialists spend a lot of time getting matches closer than they need to be. Very often there is an adequate variation in strength tolerated. On the other hand, the hue is quite critical for customers.

The CIE have produced a number of equations to calculate ΔE. The latest CIEL*a*b* equation was introduced in 1976. It is an improvement of older L, a, b type system. The system is based on the idea of color opposites (Figure 17). Therefore, L* is the measure of lightness and varies from 100 for a perfect white to 0 for absolute black. +a* indicates redness and -a* indicates greenness. +b* indicates yellowness and -b* indicates blueness. The L*, a*, b* functions are derived from X, Y, and Z as shown in formulas (4), (5), and (6), respectively [13].

$$L = 116(Y/Y_0)^{1/3} - 16 \tag{4}$$

$$a = 500[(X/X_0)^{1/3} - (Y/Y_0)^{1/3}] \tag{5}$$

$$b = 200[(Y/Y_0)^{1/3} - (Z/Z_0)^{1/3}] \tag{6}$$

Where X, Y, Z are tristimulus values, and X_0, Y_0, Z_0 are tristimulus values for perfect diffuser for illuminant used.

For total color difference, ΔE, the equation (7) is generally employed.

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \qquad (7)$$

Total color difference, ΔE, is normally calculated for illuminant D65. If the value changes with a change of illuminant, the specimens are metameric.

With the use of these color systems the magnitude and direction of color difference between a sample and standard can easily be determined and understood.

Visible and Ultraviolet Spectroscopy

An obvious difference between certain compounds is in their color. In this respect the human eye is functioning as a spectrometer analyzing the light reflected from the surface of a solid or passing through a liquid. Although the sunlight (or white light) is observed as uniform or homogeneous in color, it is actually composed of a broad range of radiation wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. As shown on Figure 17, the component colors of the visible portion can be separated by passing sunlight through a prism.

Electromagnetic radiation such as visible light is commonly treated as a wave phenomenon, characterized by either wavelength or frequency (Figure 18).

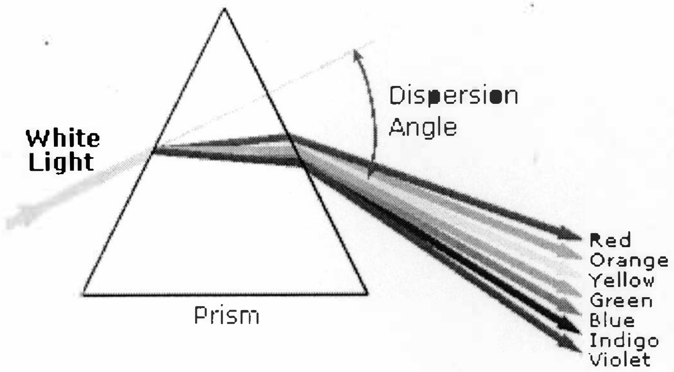


Figure 17. Dispersion of Sunlight on a Prism.

Wavelength is defined as the spatial distance between adjacent peaks of the wave, and may be designated in meters, centimeters or nanometers. Frequency is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz). Visible wavelengths cover a range from approximately 400 to 800 nm (Figure 19).

When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelength is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown on Figure 20.

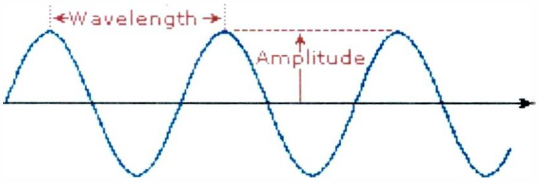


Figure 18. Example of a Wave.

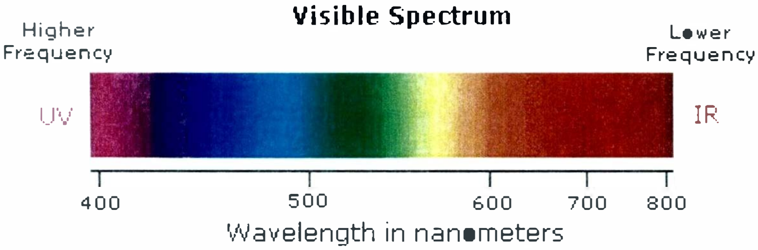


Figure 19. Visible Spectrum.

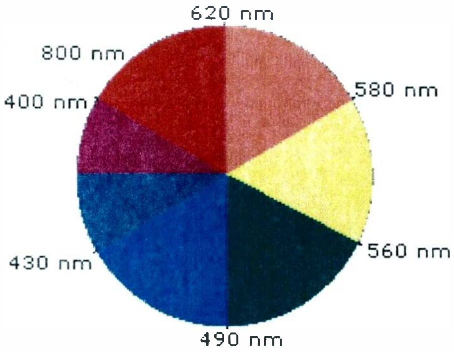


Figure 20. Color Wheel.

Here, complementary colors are diametrically opposite from each other. Thus, absorption of 420-430 nm light renders a substance yellow.

UV-Visible Absorption Spectra

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, the accurate measurements of light absorption at different wavelengths in and near the visible part of spectrum have to be taken. Commercial optical spectrometers enable such experiments to be conducted. The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy to 143 kcal/mole. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for spectral analysis. A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown on Figure 21.

Of the six transitions outlined, only the two lowest energy ones (left-most) are achieved by the energies available in the 200-800 nm spectrum. As a rule, energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), with the result being an excited state. The phenomenon of emission and absorption spectra results from electron being forced from their normal levels to higher levels; the return of the electron to its normal level could result in emission spectra, or the electron could, through following transmission levels other than those involved in the absorption, radiate the absorbed energy in the form of heat (infrared or other radiation) [14].

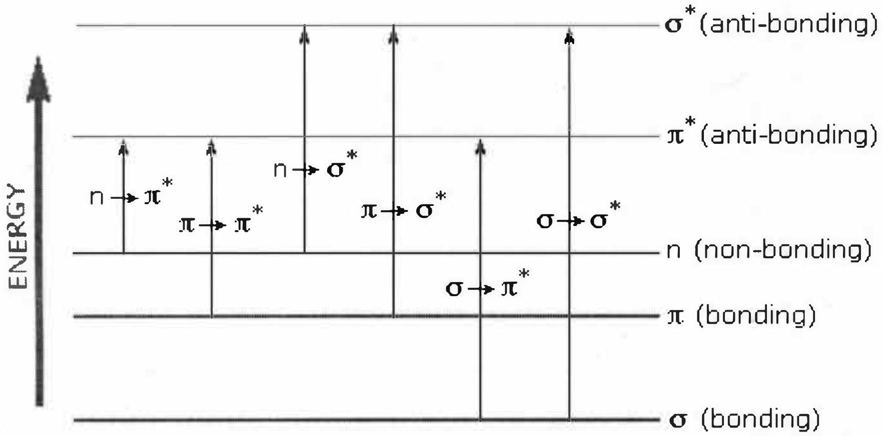


Figure 21. The Electronic Excitations That May Occur in Organic Molecules.

An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength. Absorbance usually ranges from 0 (no absorption) to 2 (99% absorption). Because the absorbance of a sample will be proportional to the number of absorbing molecules (their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way.

The corrected absorption value is called molar absorptivity (8), and is particularly useful when comparing the spectra of different compounds.

$$\varepsilon = A/\ c\ l \tag{8}$$

Where A = absorbance, c = sample concentration in moles/liter, l = length of light path through the sample (in cm).

The Importance of Conjugation

Conjugation of double and triple bonds shifts the absorption maximum to longer wavelengths. In case of polyenes (typical of these pigments are carotene, lycopene, xanthophyll, etc.) the color deepens (larger λ_{max} - wavelength of maximum absorbance) with the increasing length of the chain (i.e. increase in the number of double bonds in conjugation) [15]. To understand why conjugation should cause shifts in the absorption maxima of chromophores (light absorbing group), we need to look at the relative energy levels of the π-orbitals. When two double bonds are conjugated, the four π-atomic orbitals combine to generate four π-molecular orbitals (two are bonding and two are antibonding). In a similar manner, the three double bonds of a conjugated triene create six π-molecular orbitals, half bonding and half antibonding. The energetically most favorable π -> π* excitation occurs from the highest energy bonding π-orbital (HOMO) to the lowest energy antibonding π-orbital (LUMO). Increased conjugation brings the HOMO and LUMO orbitals closer together. The energy required to effect the electron promotion is therefore less, and the wavelength that provides this energy is increased correspondingly.

Infrared Spectroscopy

Infrared spectroscopy can be defined as the study of the interaction of material systems with electromagnetic radiation in the infrared region of the spectrum. The infrared region is valuable for the study of the structure of matter because the natural vibrational frequencies of atoms in molecules and crystals fall in the infrared range [16].

Extensive experimental study has shown that the energy changes observed in molecular spectra are, in general, of three types: rotational, vibrational, and electronic energy. The molecular energy is the sum of these components and changes in them give rise to emission or absorption spectra in the far infrared (rotational energy changes), the near infrared (vibrational) and in the visible or ultra-violet regions (electronic) [17].

Spectrophotometry

Spectrophotometry is an analytical technique used to measure the amount of light of a particular wavelength absorbed by a sample in solution. The wavelengths of light used in ultraviolet-visible spectrophotometry are from 250 nm to 750 nm.

The Beer-Lambert law relates the transmittance T of a material at a particular wavelength to its absorbance A through the equation (9).

$$A = \log_e(1/T) \tag{9}$$

The transmittance T is given by the relationship between the light incident on the material I_o and the light transmitted through it I (10).

$$T = I/I_o \tag{10}$$

For a given sample, absorbance depends on five factors: the identity of the absorbing substance, its concentration, the pathlength, the wavelength of light, and the solvent. This relationship can be expressed by Beer-Lambert law (11).

$$A = \varepsilon lc \qquad (11)$$

Where A is the absorbance (a unitless quantity), l is the pathlength or thickness of the cell (cm), c is the concentration of the absorbing species (usually in molarity), and ε is an experimentally determined constant called the molar absorptivity (if the concentration is in molarity).

From the equations (9), (10), and (11), the equations (12) and (13) result.

$$2.303\log_{10}(I_o/I) = \varepsilon lc \qquad (12)$$

$$\log_{10}(I_o/I) = 0.4343\varepsilon lc = D \qquad (13)$$

Where D is optical density of the material. Reflection density is defined in terms of the reflectance factor, which is obtained in an analogous way. In this case, a reference white (white tile) is assumed to reflect 100 % of the incident light whereas the ink film absorbs some of the light and therefore reflects less than 100 % [18].

In this work it is assumed that the reflection measurement is analogous to transmittance measurement under the condition of perfect reflection at the ink-substrate interface (Figure 22) and therefore it is justified using the Beer-Lambert law for the analysis of reflection samples.

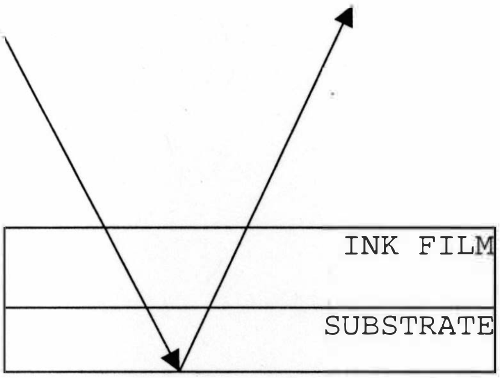


Figure 22. The Perfect Reflection at the Ink-Substrate Interface.

It is obvious that there is a linear relationship between absorbance and concentration in the Beer-Lambert law. Therefore, a plot of absorbance versus concentration, called a calibration curve, gives a straight line at a particular wavelength and temperature (Figure 23).

The slope of the line is εl. The pathlength or thickness of the spectrophotometer cell is constant and is known, so ε can be calculated from the slope of the line. To generate a calibration curve, the absorbancies of a series of solutions of known concentration are read at the particular wavelength and plotted. The slope and molar absorptivity are then calculated. The calibration curve or molar absorptivity can then be used together with the absorbance of a sample of unknown concentration to determine its concentration.

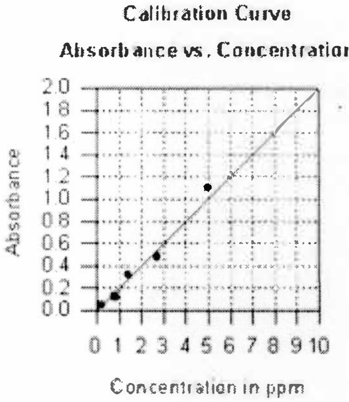


Figure 23. Calibration Curve Absorbance vs. Concentration.

The absorption spectrum of a compound is a plot of the relationship between absorbance and wavelength (Figure 24). Notice that the absorbance is at a maximum when the wavelength is 525 nm. The wavelength of maximum absorbance, λ_{max}, is usually the wavelength chosen to read absorbancies for a calibration curve. This is because the potential for error in the reading the absorbance at the relatively flat peak is smaller than in the steeply rising part of the spectrum.

If the sample is a mixture of two absorbing substances, the resulting absorption spectrum is the sum of the two individual absorption spectra.

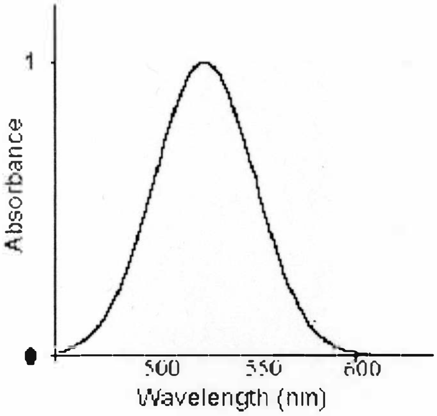


Figure 24. An Example of an Absorption Spectrum.

For example, if species A has λ_{max} at λ_1 and species B has λ_{max} at λ_2, then the total absorbance of the mixture at λ_1 and λ_2 is expressed by equations (14) and (15).

$$A_{\lambda_1}(\text{total}) = A_A\lambda_1 + A_B\lambda_1 \quad (14)$$

$$A_{\lambda_2}(\text{total}) = A_A\lambda_2 + A_B\lambda_2 \quad (15)$$

For the absorption of the individual substances, the Beer's law quantities can be substituted (16, 17).

$$A_{\lambda_1}(\text{total}) = \varepsilon_{A\lambda_1} l c_A + \varepsilon_{B\lambda_1} l c_B \quad (16)$$

Where $\varepsilon_{A\lambda_1}$ is the molar absorptivity for substance A at λ_1, l is the pathlength, and c_A is the molar concentration of A and $\varepsilon_{B\lambda_1}$ is the molar absorptivity for substance B at λ_1, l is the pathlength, and c_B is the molar concentration of B.

$$A_{\lambda_2}(\text{total}) = \varepsilon_{A\lambda_2} l c_A + \varepsilon_{B\lambda_2} l c_B \qquad (17)$$

Where $\varepsilon_{A\lambda_2}$ is the molar absorptivity for substance A at λ_2, l is the pathlength, and c_A is the molar concentration of A and $\varepsilon_{B\lambda_2}$ is the molar absorptivity for substance B at λ_2, l is the pathlength, and c_B is the molar concentration of B.

The molar absorptivities of A and B can be calculated from calibration curves of the individual substances at each wavelength, so when the absorbance of the mixture has been measured, then above mentioned equations can be solved for the concentrations of substances A and B in the mixture.

CHAPTER III

STATEMENT OF PROBLEM AND OBJECTIVES

The re-use of spot colors is very difficult. Every spot color is unique, generated by blending individual pigments to fulfill a customer's wish. In the gravure process, there always has to be more ink manufactured than is needed and consumed. The handling of excessive ink left from process after accomplishing the work, also called "press return", or "work back" ink, is difficult. To store it and wait for another customer who would use the same spot color as somebody had before him would be impractical and very costly. A wiser way is to re-blend the work back inks. Work back ink could serve as a base for future custom color. This is a cost effective and environmentally practical option.

However, presently the re-use of press return inks in this manner is difficult, time consuming, and highly variable. The commonly used way is to dilute the press return ink with extender and start building the new spot color. In this method, much more ink is blended than necessary. Also, currently available color matching programs enable only approximate construction of the desired spot color. Human eye is needed to make the ultimate judgment.

Several re-adjustments are necessary to finally match the color. The challenge is to find a method to analyze the blend and to repeatably and inexpensively either prepare or reformulate it.

The objective of this work is to analyze the spectral curves of spot color pres-return inks qualitatively and quantitatively using UV/VIS or near infrared region of electromagnetic spectrum. Qualitative analysis will enable to find out inks, used to construct the spot color. Further goal is to find a mathematical model, which will facilitate the best fit in quantitative analysis. The ultimate goal of this work is to utilize press return spot color inks in further printing jobs as a portion of desired spot color. Press return ink will be quickly qualitatively and quantitatively analyzed and a mathematical model will be used to calculate the necessary amounts of discrete inks to construct the desired spot color.

CHAPTER IV

EXPERIMENTAL DESIGN AND METHODOLOGY

Preparation of Ink Blends

Following commercially available isopropyl acetate product gravure inks were used.

Ink A	-	13Y892	Yellow ink 1
Ink B	-	13N751	Brown ink
Ink C	-	13Y762	Yellow ink 2
Ink D	-	13Y852	Orange ink
Ink E	-	13R859	Red ink

Three virgin inks A, C, E, and extender were mixed using various weight fractions in order to prepare two different blends, each containing the mix of two different virgin inks (Table 1) at their varying concentrations.

In further experiments, three virgin inks B, C, D, and extender were blended together according to weight fractions indicated in Table 2 with the aim to prepare mixtures containing three virgin inks at their altering concentrations.

Table 1

The Weight Ratios of Virgin Inks and Extender Employed in the Two Ink Mixtures Preparation

Inks Used	Parts of Inks in Blend	Concentration of Ink A (%)	Concentration of Ink C (E) (%)	Parts of Extender in Blend
A+C A+E	80	10	90	20
	80	20	80	20
	80	30	70	20
	80	40	60	20
	80	50	50	20
	80	60	40	20
	80	70	30	20
	80	80	20	20
	80	90	10	20

Blends of total amount of 50g were prepared. After the inks and extender were put into the beaker, a multi-purpose, variable-speed blender (Morehouse-Cowles Model CM-100) was utilized to mix the blend. The blender was set for 15 minutes at 500 RPM that ensured adequate time and force to disperse and mix inks and extender. After mixing, the running viscosity was adjusted by the isopropyl acetate to 25 seconds using a Shell cup #2.

Table 2

The Weight Ratios of Virgin Inks and Extender Employed in the Three Ink Mixtures Preparation

Inks Used	Parts of Inks D+B in Blend	Concentration of Ink B (%)	Concentration of Ink D (%)	Parts of Ink C in Blend	Parts of Extender in Blend
B+C+D	60	10	90	20	20
	60	20	80	20	20
	60	30	70	20	20
	60	40	60	20	20
	60	50	50	20	20
	60	60	40	20	20
	60	70	30	20	20
	60	80	20	20	20
	60	90	10	20	20

Printing

Prints were made by means of gravure laboratory K-Printing Proofer equipped with 150 lpi (lines/inch) solid engraving and 100-90-80-70 % tone wedges. The K- Printing Proofer was adjusted to optimum printing conditions. Specialty coated paper was used as a printing substrate in all experiments. In order to ensure repeatability of the printing process, a reference sample was printed after each 10 impressions.

Spectrophotometric Measurements

Spectrophotometric Measurements With Perkin Elmer UV/VIS/NIR Spectrometer LAMBDA 900

Spectrometric measurements were performed using a Perkin Elmer UV/VIS/NIR Spectrometer LAMBDA 900 equipped with UV WinLab 3.0 software. Two illumination sources, a deuterium lamp and a halogen lamp covered the working wavelength range in which the readings were taken (190-2000nm). Integration time for UV/VIS (Ultraviolet-Visible) region was set for 0.32 sec while for NIR (Near Infrared) it was set for 0.56 sec. The lamp change from halogen to deuterium was at 319.20 nm and the grating change of the monochromator was at 862.50 nm. The interval for spectrometer data collection was set to 5 nm.

Measurements were taken at 100 % tone ink film on two different areas. The results were averaged and recalculated to absolute reflectance values.

Recalculation to Absolute Reflectance Values

Recalculation of obtained reflectance values to absolute ones was done by employing the formula (18).

$$R(abs) = R(act(S))*(R((scan(S))/R(base\ (S))*R(sample) \tag{18}$$

Where: R(abs) = Absolute Reflectance Value of the Sample (%)

R(act(S)) = Actual Value for the Scanned Standard "99" (from the calibration certificate) (1)

R(scan(S)) = Scanned reflectance of the standard "99" read by the instrument (%)

R(base (S)) = Reflectance for Spectrometer's Standard (after autozeroing the instrument) (%)

R(sample) = Reflectance of the sample (%)

Spectrophotometric Measurements With Datacolor International Spectraflash SF600

Spectrophotometric measurement of the samples was done employing a Datacolor International Spectraflash SF 600 spectrophotometer equipped with ColorTools ver. 2.2

software. Spectraflash SF 600 is a dual-beam diffuse/8° spectrophotometer with concave holographic grating. A Pulsed Xenon lamp was employed as a light source. Its spectral range output is from 400 nm to 700 nm with reporting interval 10 nm.

During the measurements, the instrument was set to large area viewing (LAV) aperture. Specular gloss was excluded. The number of lamp flashes was set for five. Current Illuminant/Observer mode was D65 10deg.

Measurements of reflectance and color coordinates L*a*b* were taken at 100% tone ink film on ten different areas and the results were averaged.

Retroengineering of Gravure Spot Color Inks

Retroengineering was done employing software MS Excel 2000 with installed Solver (tool for statistical analysis).

MS Excel was used to solve for weight fractions of the employed virgin inks in the mixture, based on their linear combination in order to fit the measured spectrum of the blend with the smallest possible total difference (distance). The total difference was set as the sum of weight differences for each wavelength (D).

The weight difference for each wavelength (D) was calculated according to formula (19).

$$D = W^*(C-M)^2 \qquad (19)$$

Where D = weight difference (distance) between measured and calculated reflectance for particular wavelength (%^2)

W = employed weight (dimensionless)

C = calculated reflectance (%)

M = measured reflectance (%)

During the process of linear combination, three different weights were utilized. They were calculated for each wavelength as follows:

Weight (I) - the weight was set as 1

Weight (II) - 100/%R

Weight (III) - 100/(100-%R)

Where %R is the value of the reflectance for particular wavelength.

The linear combination solving was done under the following conditions:

- The sum of calculated weight fractions of employed virgin inks has to be one

- Each of calculated weight fractions has to be equal or greater than zero.

CHAPTER V

RESULTS AND DISCUSSION

The press return product gravure inks create a big economical problem. What to do with them? Most often reformulation of press return ink into desirable spot color takes place. Technology offers spectrophotometric measurements such as CIE L*a*b* values. Even then, when the L*a*b* values are reasonably close, there is a need to "visually adjust" the color, which is time consuming and often takes several steps to converge to acceptable color. The goal of this work was to analyze press return inks and according to the shapes of their UV/VIS or NIR spectra to be able to calculate their composition. To accomplish this, the first step was to analyze the virgin inks used for blending spot colors.

Each of examined virgin inks exhibits different reflectance at certain wavelength typical only for itself (Figure 25). This is, of course, a necessary condition for achieving the desired color different from the others in the set.

Ink A shows the highest reflectance values out of all inks in the upper half of the visible spectrum (550-800 nm). Coming to shorter wavelengths its reflectance is increasing with its maximum of 89% at 570 nm, followed by a steep decrease to 11% at 450 nm. In UV region, this ink does not show any significant maximum or minimum.

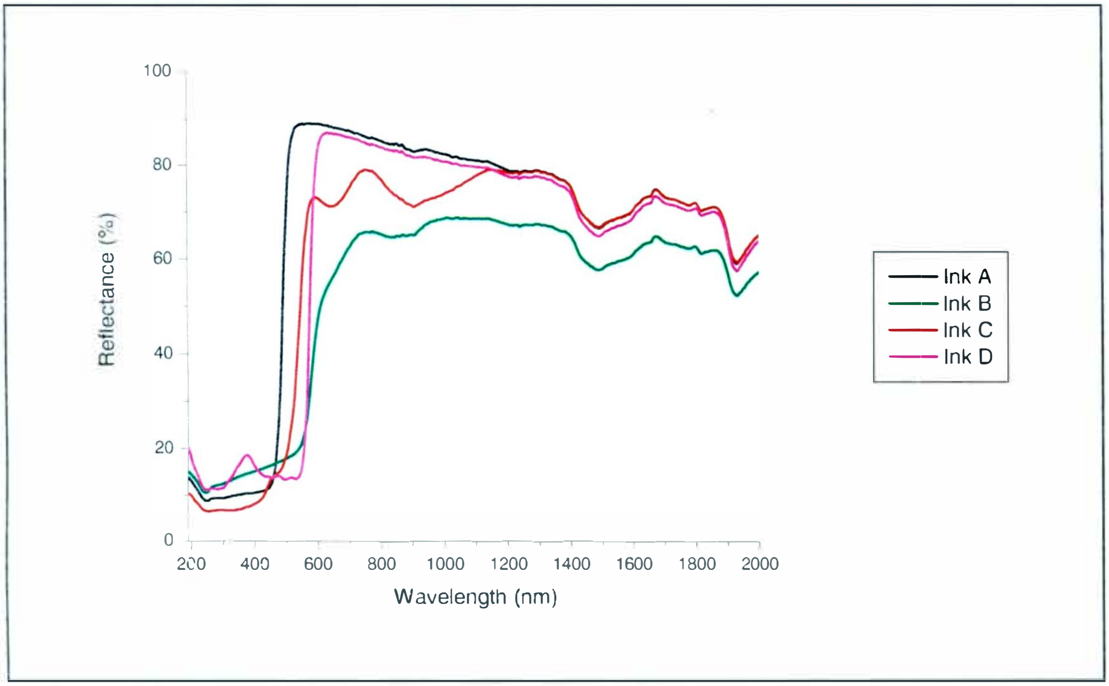


Figure 25. UV/VIS/NIR Spectra of Virgin Inks.

Ink B exhibited the lowest reflectance values with its maximum of 68% at 765 nm and steep decrease to 20 % at 540 nm. In the range of 540 nm - 410 nm it gives the highest reflectance of all inks with slight transition decrease into the UV with the reflectance of 9.5 % at 245 nm without any significant peaks in the UV region. Ink C is easily recognizable due to its maximum of reflectance of 79 % at 755 nm, followed by the minimum 72 % at 645 nm, and second maximum of 73 % at 590 nm. Afterwards a sharp decrease in reflectance takes a place to the value of 15 % at 475 nm. There are no significant deviations in the UV region demonstrating the presence of molecules absorbing in this range of wavelengths. Regarding the spectrum of ink D, it exhibits the maximum reflectance of 86 % at 620 nm followed by a sudden decrease to 14 % at 540 nm. Very unique is its local maximum of 19 % at 375 nm. This peak is considered to be distinctive for ink D.

Figure 26: NIR Spectra of Virgin Inks.

The spectra of all inks taken in the near infrared region (NIR) of 800-2000 nm (Figure 26) are very similar, to each other, thus the analysis of mixture based on NIR spectra is not practical. Therefore, NIR will not be considered any more. The same applies for spectra taken in ultraviolet (UV) range of 190-350 nm (Figure 27).

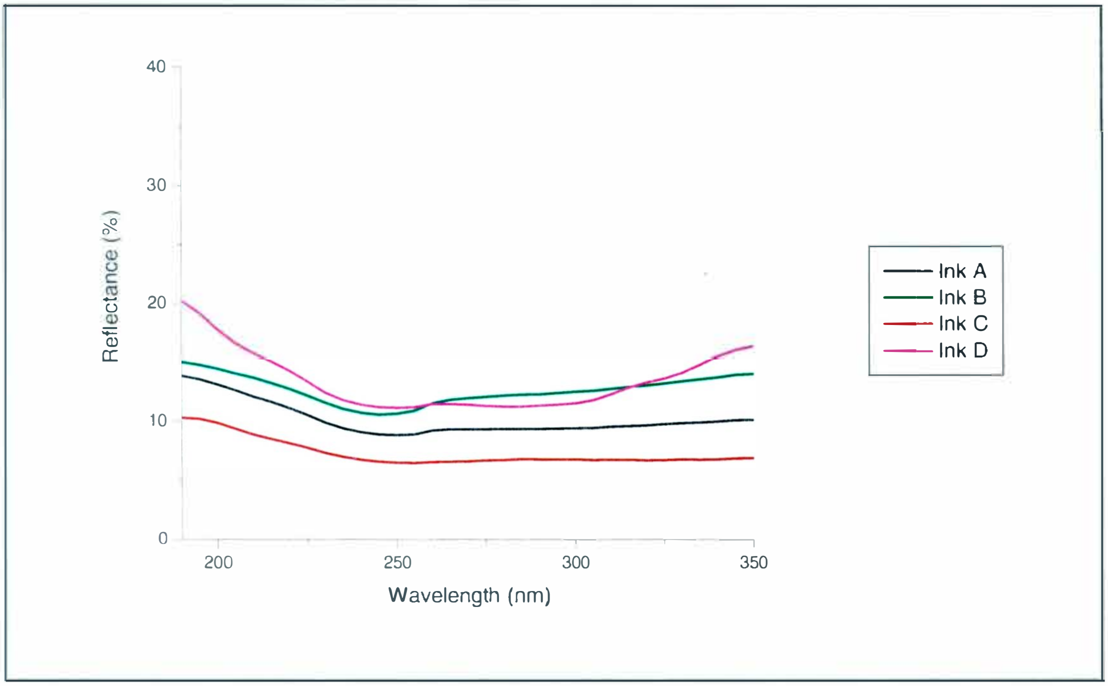


Figure 27. The UV Spectra of Virgin Inks.

The range from 355 nm to 800 nm gives the most valuable information (Figure 25); therefore it will be more closely studied in further analysis. Unfortunately, the spectrophotometer in our laboratory, the Datacolor SpectroFlash 600, does not take the readings in such wide interval, thus the advantages of taking readings below 400 nm and above 700 nm will be lost.

The Analysis of VIS Spectra of Two Ink Mixtures

In two ink mixtures analysis, the inks A and C and A and E were blended as documented in Table 1 (Figure 28).

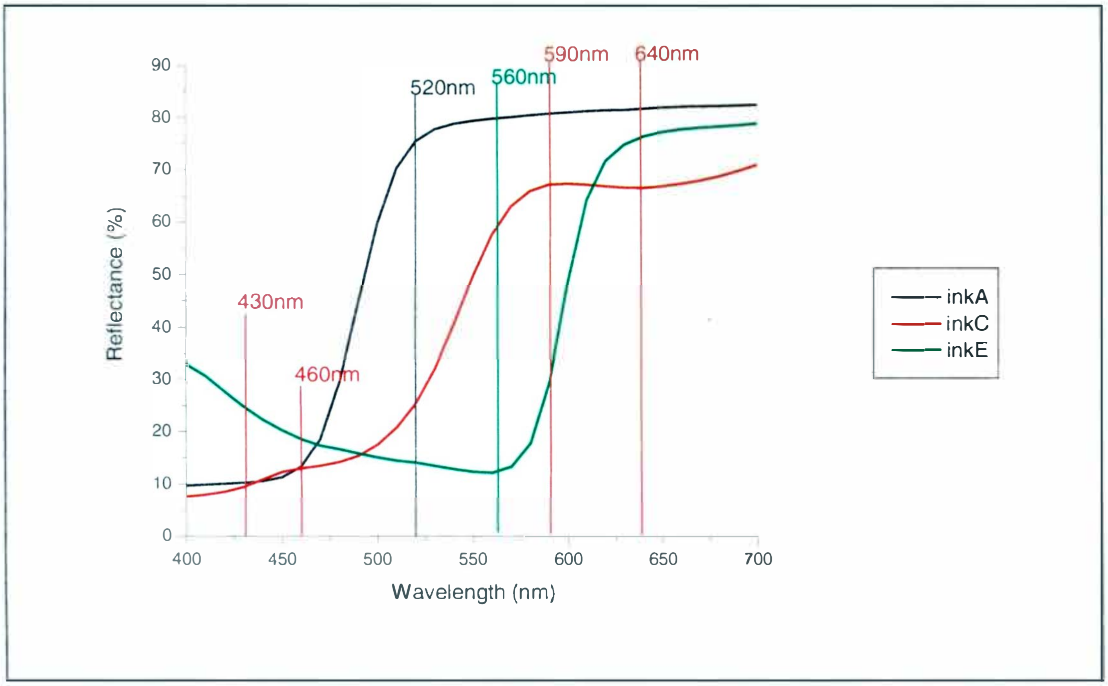


Figure 28. VIS Spectra of Virgin Inks A, C, E.

Ink A represented by the black line does not show any significant maximum or minimum of the reflectance in the range of 400-460 nm. When coming to the longer wavelengths, there is a steep increase in reflectance values from 13% at 460 nm to 75% at 520 nm. Ink A exhibits the highest reflectance values out of all inks in the upper half of the visible spectrum (520-700 nm). For ink C represented by red line, there are two inflection points at 430 and 460 nm in the high-energy part of visible spectrum (shorter wavelengths). Afterwards, slight increase in reflectance occurs from 13 % to 66 % in the range of 470-580 nm. Ink C is easy recognizable due to its local maximum at 590 nm followed by the local minimum of reflectance at 640 nm. Although ink E exhibits decreasing reflectance from 400 nm to 560 nm where reaching its minimum, it shows the highest reflectance values in the range of wavelengths from 400 nm to 470 nm out of all examined inks. After reaching its minimum, there is a steep increase of reflectance to 77% continued by its maximum reflectance values in the range from 640 nm to 700 nm.

Spectra of various mixtures of ink A, E, and extender were analyzed (Figure 29). The contribution of both inks to the reflectance values of blends can be easily recognized. The change in reflectance in the blue region of the visible spectrum was caused by the change of concentration of yellow ink A, which absorbs in this region. Increasing the concentration of yellow ink A results in lower reflectance in the blue region of 400 - 450 nm. Similarly, the changes in reflectance of the blends in the green region of the visible spectrum were caused by the presence of red ink E. By increasing the percentage of red ink E, the reflectance values in green region decrease (Figure 29)

In further experiments, the mixtures of ink A, C, and extender were investigated (Figure 30). Because of the fact that these inks have a similar hue (yellow), they absorb in the same range of wavelengths. Thus, it is hard to distinguish them from one another and it was the challenge of this experiment.

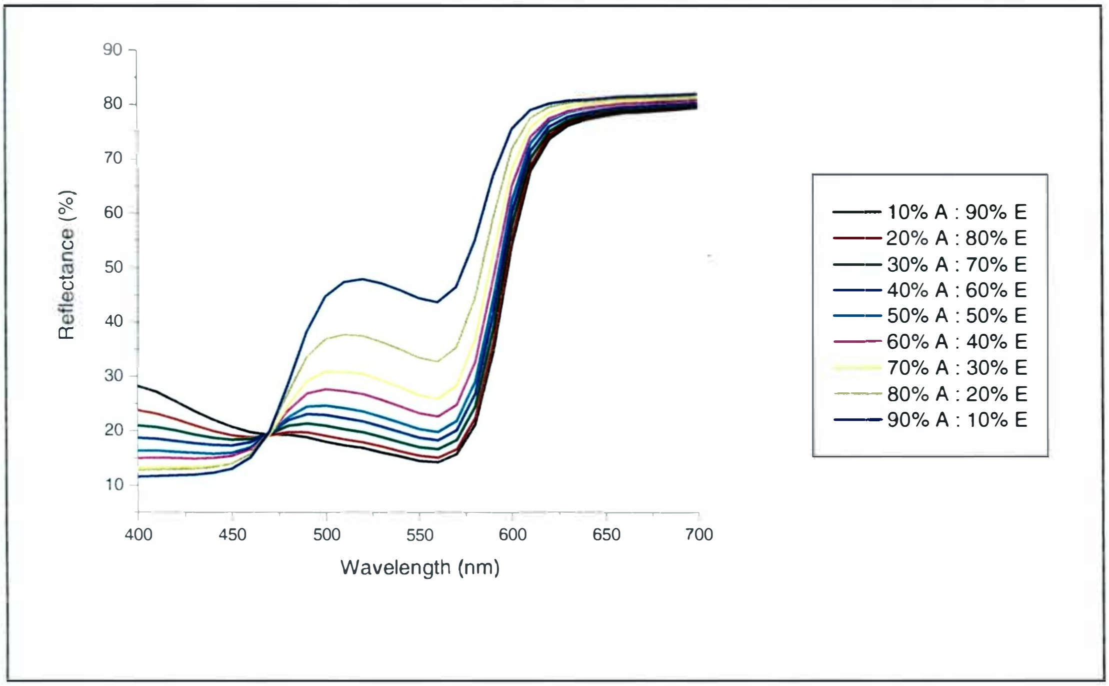


Figure 29. VIS Spectra of Ink A, Ink E, and Extender Mixtures.

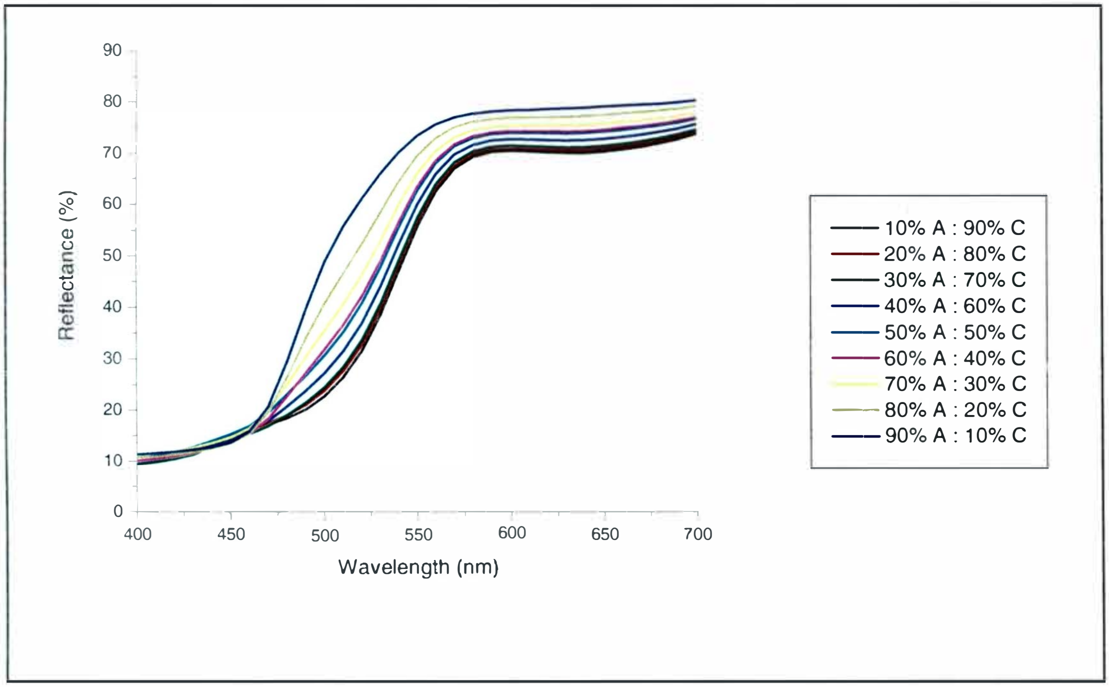


Figure 30. VIS Spectra of Ink A, Ink C, and Extender Mixtures.

In order to better demonstrate the presence of inks A and C in the blend, the mixture 50%: 50% of inks A and C, was analyzed (Figure 31). In the blend represented by green line one local maximum at 590 nm and one local minimum at 640 nm were identified. These local extremes are characteristic for ink C (Figure 31). Ink A shifts the reflectance to higher values in the region of 500 - 700 nm (Figure 31).

Analyzing the mixture of inks A and C at varying concentrations (Figure 30), it can be concluded that the contribution of each of them is highly concentration dependent. Starting with the blend containing 90 % of ink A, the reflectance values are the highest and the course of spectrum is very similar to the one of the pure non-mixed ink A. As the concentration of ink A is decreased and the part of ink C is increased in the blend, reflectance values are slightly decreasing and the spectrum of the mixture is becoming more similar to the one of pure non-mixed ink C.

The decrease in reflectance of the mixture of the inks A and C caused by the increase in concentration of ink C at any chosen wavelength where reflectance-minimum occurs is linear (Figure 32). So, qualitative analysis was done by analyzing characteristic peaks and valleys of individual inks and matching them to the spectral curves of their mixture.

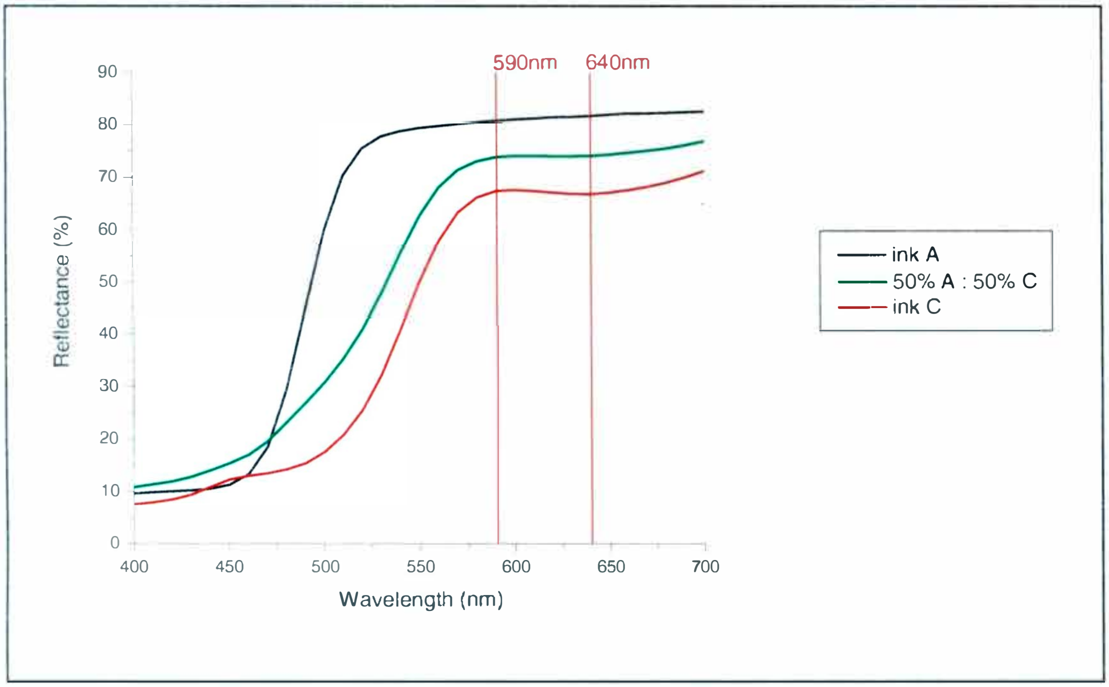


Figure 31. Qualitative Analysis of A, C Ink Blend.

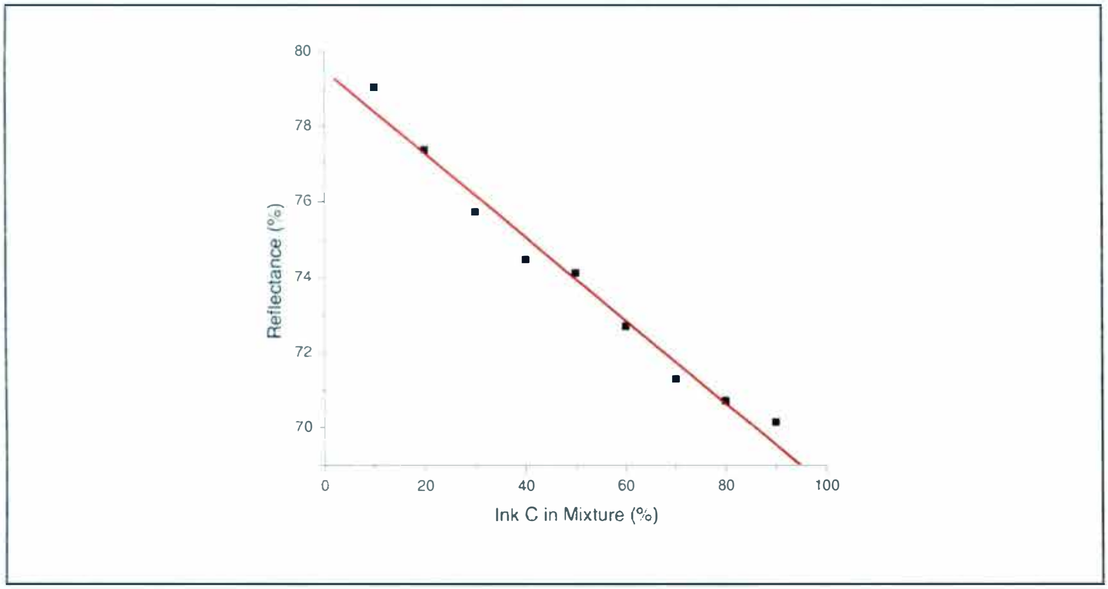


Figure 32. Reflectance of Ink C at 640 nm.

According to Beer-Lambert law, if a sample is a mixture of two absorbing substances, the resulting absorption spectrum is the sum of the two individual absorption spectra [19]. If it is assumed that absorption of the sample and its reflectance are related and proportional, then if the sample is a mixture of two reflecting substances, the resulting reflectance spectrum is the sum of two individual reflectance spectra.

Due to the Beer-Lambert law, reflectance is additive and every reflectance value of the mixture at any wavelength is the sum of reflectance values of individual components. In other words, after the subtraction of individual spectra at the correct concentrations from the spectrum of the mixture, the resulting spectrum should be approaching the zero line. This subtraction was made with known mixture of inks A and C (Figure 33).

The black line (Figure 33) represents the reflectance spectrum of the mixture 30% ink A and 70% ink C. Line B displays the spectrum of the mixture after subtracting the reflectance values of ink A at 30% concentration. After the deduction of reflectance values of ink C at 70% concentration from reflectance values represented by line B, values represented by line C were calculated.

When investigating line C (Figure 33), the calculated reflectance in the range of wavelengths from 475 nm to 550 nm is reaching negative values. This phenomenon was observed for all but one two ink mixtures throughout the process of subtracting the individual spectra of virgin inks at their employed concentrations from the spectral curves of blends. It is believed to be due to the steep decrease in reflectance values of the analyzed blends in this range where the readings of instrument are not that accurate as in the case of linear regions. For this particular set of inks another possible cause could be some favorable ink-pigment packing because of their different particle sizes.

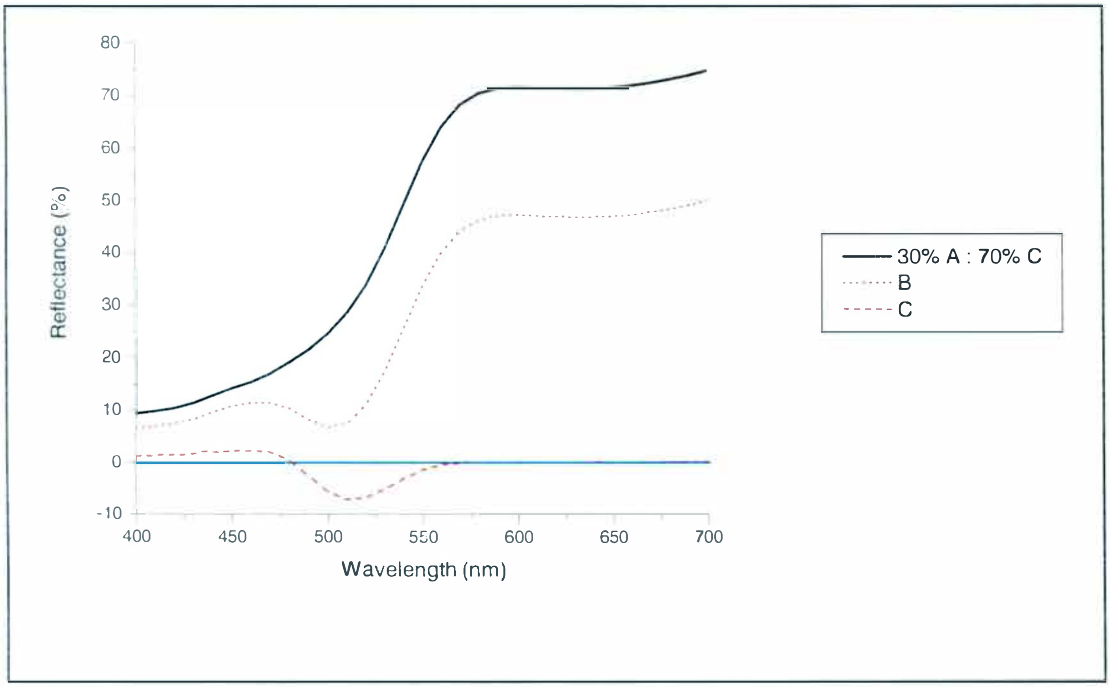


Figure 33. Quantitative Analysis of Mixture 30 % Ink A: 70 % Ink C.

Analysis of VIS Spectra of Three Ink Mixtures

In three ink mixtures analysis, the inks B, C, and D were blended. The spectra of these inks are illustrated at Figure 34.

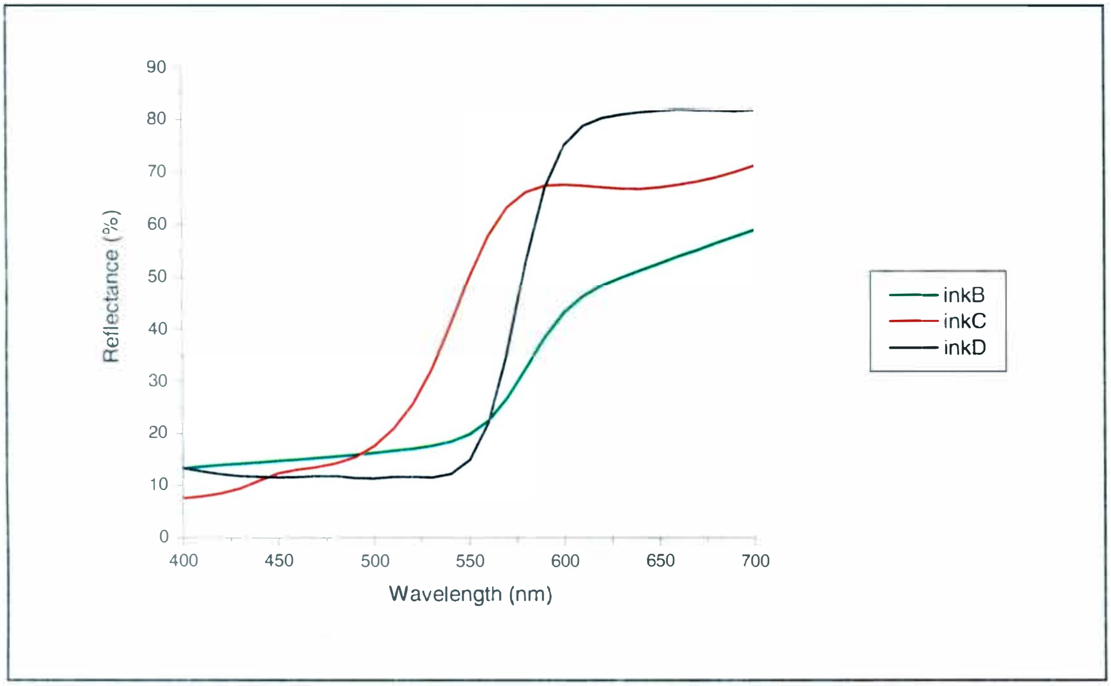


Figure 34. VIS Spectra of Virgin Inks B, C, D.

Ink B did not exhibit any significant peaks or valleys throughout the whole investigated range of wavelengths. The reflectance values from 400 nm to 550 nm are fluctuating around 15% and afterwards there is a slight increase in the range from 550 nm to 700 nm. The course of ink C spectrum was already described in previous discussion. Spectrum of ink D slightly decreases in the range from 400 nm to 540 nm where it reaches its minimum 12%. Afterwards follows steep increase of reflectance values to 80% at 620 nm. In the rest of the visible spectrum, ink D exhibits the highest reflectance of all examined inks.

The VIS spectra of the three ink mixtures containing 60 parts of ink B and D at varying B and D ratio, 20 parts of ink C, and 20 parts of extender were measured (Figure 35).

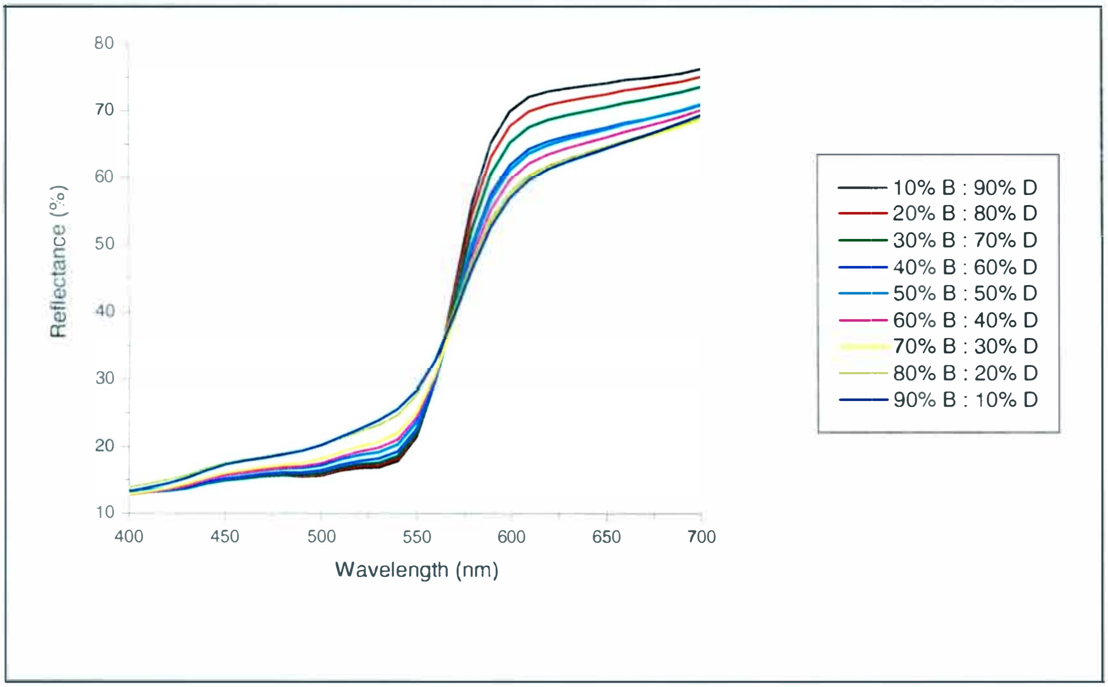


Figure 35. VIS Spectra of 60 Parts (Ink B, Ink D) + 20 Parts Ink C + 20 Parts Extender.

Investigating the spectra of three ink mixtures (Figure 35), the blend containing 90% of ink D has the highest reflectance values in the upper half of visible spectrum (570 nm - 700 nm) and it is similar to the spectrum of pure virgin ink D. The mixture containing 90% of ink B is on the other side similar to pure virgin ink B and exhibits the highest reflectance values in the lower half of the visible spectrum (400 nm - 570 nm).

The qualitative analysis of three ink mixture is difficult from the analysis of two ink mixture. In order to begin qualitative analysis, the mixture of 60 parts (50% ink B: 50% ink D), 20 parts ink C, and 20 parts extender was chosen (Figure 36).

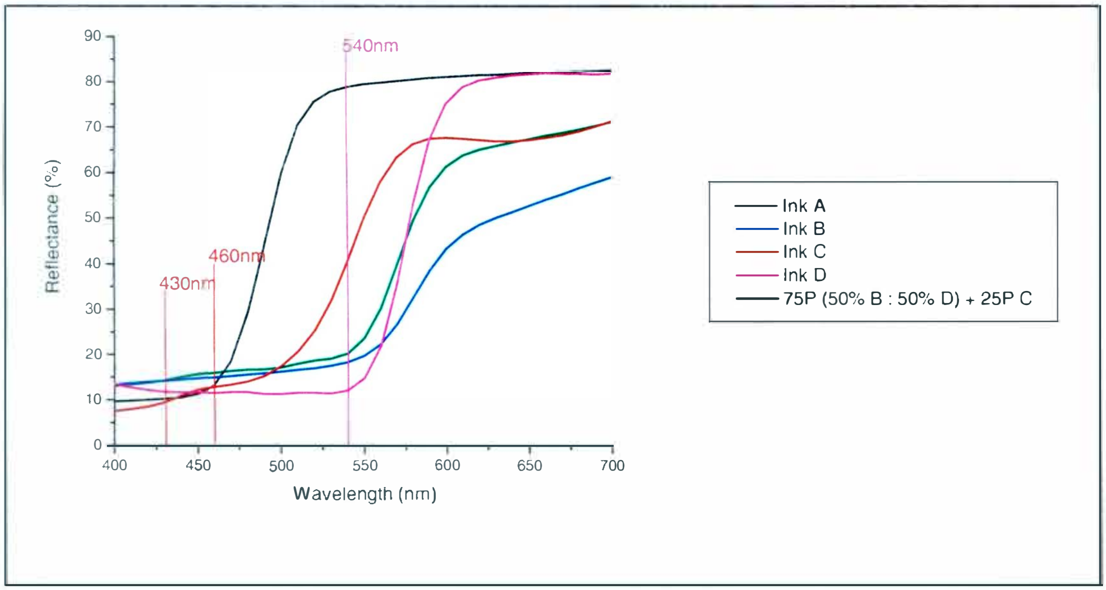


Figure 36. Qualitative Analysis of 75 Parts (50 % Ink B: 50 % Ink D) + 25 Parts Ink C.

Due to the fact of neglecting the reflectance contribution of the extender, current 80 parts of the inks in the blend were considered to represent 100%. Initially, the search for unique characteristic signs, (peaks/valleys, course of the spectrum) specific for each of the inks has to begin.

According to spectrum of the mixture containing three pigments in the abovementioned ratios represented by the green line (Figure 36), the characteristic maximum at 590 nm and the minimum at 640 nm for ink C are not apparent. The spectrum of the mixture in the range of 605-700 nm rather follows the course of ink B. Regarding the ink C, its presence in the blend can be demonstrated by the obvious similarity of the courses of the spectrums between 540-600 nm and with the local minimum at 430 nm followed by the increase in reflectance values to the local maximum at 460 nm. Both, the presence of ink B and ink D could cause the reason for local minimum at 540 nm. The shift of the minimum to shorter wavelengths was most likely due to the ink D. The presence of ink A in the mixture would obviously shift this minimum of reflectance to even shorter wavelengths.

After qualitative analysis of the three-colorant mixture, quantitative analysis was done using the same procedure as in the case of two-colorant mixture. The black line (Figure 37) represents the reflectance spectrum of the mixture containing 75 parts of the inks B, D at their ratio 70 %: 30 %, respectively, mixed with 25 parts of ink C. After the subtraction of the reflectance values of ink B at 70 % concentration in 75 parts from the spectrum of the mixture, line A was created. Line B represents the spectrum of the residual mixture (line A) after subtracting the reflectance values of ink C at 25 % concentration. Lastly the D ink was deducted at 30 % concentration in 75 parts. The reflectance values for line C were calculated.

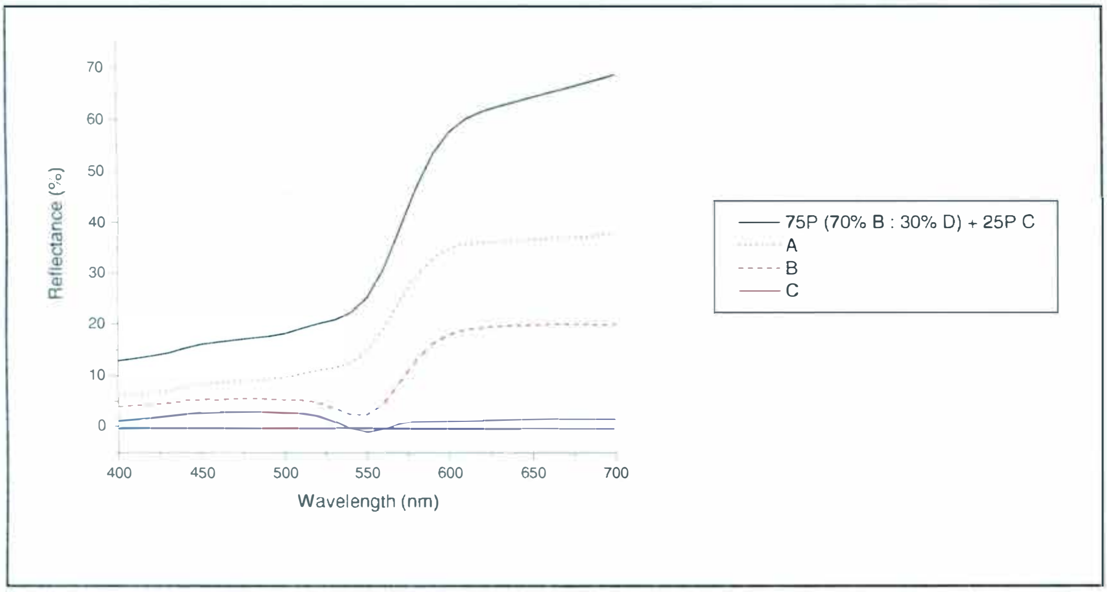


Figure 37. Quantitative Analysis of Mixture 75 Parts (70 % Ink B: 30 % Ink D) + 25 Parts Ink C.

Examining the line C (Figure 37), the same phenomenon as in the case of two ink mixtures is observed. Calculated reflectance values for line C for all but two three ink blends are having negative values in the range from 525 nm to 570 nm. This could be caused by the non-accurate readings of the instrument due to the steep decrease of the analyzed blends reflectance values in this range or due some favorable ink pigments packing for this particular set.

Retroengineering of Mixtures

The reflectance spectra of inks were taken in the range of wavelengths from 400 nm to 700 nm with reporting interval 10 nm. That means that for each ink spectrum was measured 30 reflectance values. Let these 30 values represent 30-dimensional space. This 30-dimensional space depicts all colors, which is possible to display and describe by these 30 wavelengths. In the experiment, maximal number of inks blended together was 3. These 3 mixed inks produce a 3-dimensional subspace of this 30-dimensional one. Each of these inks and their mixtures belong into this space characterized by 30 wavelengths according to the vector space theory [20].

The aim is to distinguish the right subspace, which is created by employed inks. In real life, this subspace is already given substantially by the inks. The goal of this is to mathematically generate the model, which would approach the existing subspace as close as possible. Decision has to be made according to the number of different mixtures. The higher the number of mixtures blended at different ratios of virgin inks, the more precise the model would be.

Retroengineering of Ink Mixtures Using Linear Combination Model

According to the Beer-Lambert law, which states that the resulting absorption spectrum is the sum of the two individual absorption spectra and there is a linear relationship between absorbance and concentration, the linear combination model was chosen. Basically, this was supposed to lead us to the point where it will be possible to predict the final color obtained after the mixing of the virgin inks at known ratios. If this process was likely to be accurate, there would not be a problem. Unfortunately the inks do not behave ideally.

In the linear combination analysis, the main dilemma is between the "real" and "theoretic" color. How close is close enough and how to calculate the distances between the "real" and "theoretic" color? If the system was characterized only by one value (at one wavelength), the problem would not be there. The distance could be calculated by a simple Euclid metric relationship. But if there are 30 values characterizing the spectrum of a sample, is the reflectance value at particular wavelength more, less or equally important as the reflectance at different wavelength?

The answer can be given by investigating of influence of various weights on the final calculated composition of the mixtures [20].

In order to calculate the composition of the mixture based on its measured reflectance spectrum, linear combination employing three different weights (I), (II), and (III) was done.

Through the process of combination, weight (I) gives each wavelength the same importance. Weight (II) assumes that the small difference of reflectance at particular wavelength makes this wavelength of higher importance in comparison to the wavelength at which higher difference of reflectance occurs. Weight (III) is proportional to the reflectance what means that the higher the differences in reflectance at particular wavelength, the more important this wavelength is for linear combination.

Columns “Weight (I)”, “Weight (II)”, and “Weight (III)” stand for the results when weights (I), (II), and (III), respectively, were employed in the calculation of the composition of the blends.

Columns Δ Weight I, II, and III were calculated as the absolute value of the difference between real and calculated weight fraction for each ink. Real weight fraction is meant to be the employed weight fraction of the ink during the process of preparation of the blend and the calculated weight fraction is the one obtained from the linear combination.

Two Ink Mixtures

The results of linear combination for mixtures containing 10 % of ink A and 90 % of ink C, 50 % of ink A and 50 % of ink C, and 10 % of ink A with 90 % of ink E are shown in Tables 3, 4, and 5, respectively.

Table 3

The Comparison of Values of Weight Fractions for Mixture 10 % Ink A With 90 % Ink C To Their Values in Blend Calculated Employing Three Different Weights

Ink	Real	Weight (I)	Weight (II)	Weight (III)	Δ Weight (I)	Δ Weight (II)	Δ Weight (III)
A	0.10	0.16	0.16	0.18	0.06	0.06	0.08
B	0	0	0	0	0	0	0
C	0.90	0.82	0.79	0.80	0.08	0.11	0.10
D	0	0.02	0	0.02	0.02	0	0.02
E	0	0	0.05	0	0	0.05	0

Analyzing data for the mixture 10 % A with 90 % C (Table 3), the closest match seems to be given by linear combination utilizing weight (I). The same cannot be concluded when investigating the mixture of 50 % ink A and

50 % ink C (Table 4). Both weight (I) and weight (II) gave the calculated values with more than 0.10 differences between the real and calculated weight fractions for ink A. The closest match was calculated for weight (III).

Table 4

The Comparison of Values of Weight Fractions for Mixture 50 % Ink A With 50 % Ink C To Their Values in Blend Calculated Employing Three Different Weights

Ink	Real	Weight (I)	Weight (II)	Weight (III)	Δ Weight (I)	Δ Weight (II)	Δ Weight (III)
A	0.50	0.38	0.39	0.41	0.12	0.11	0.09
B	0	0	0	0	0	0	0
C	0.50	0.59	0.54	0.56	0.09	0.04	0.06
D	0	0.03	0	0.03	0.03	0	0.03
E	0	0	0.07	0	0	0.07	0

In regards of mixture containing 10 % ink A with 90 % ink E (Table 5), the closest match seems to be for weight (I) if the calculated 0.07 for ink D is not considered.

All calculated weight fractions are similar without any significant deviations. The differences in utilizing various weights in the process of solving the spectrum of the mixture are very small. For better demonstration, the graphs of real and calculated spectra for investigated two ink mixtures are displayed (Figure 38, 39, 40).

Table 5

The Comparison of Values of Weight Fractions for Mixture 10 % Ink A With 90 % Ink E To Their Values in Blend Calculated Employing Three Different Weights

Ink	Real	Weight (I)	Weight (II)	Weight (III)	Δ Weight (I)	Δ Weight (II)	Δ Weight (III)
A	0.10	0.04	0.04	0.04	0.06	0.06	0.06
B	0	0	0	0	0	0	0
C	0	0	0	0	0	0	0
D	0	0.07	0.04	0.08	0.07	0.04	0.08
E	0.90	0.89	0.92	0.88	0.01	0.02	0.02

From graphs it can be concluded, that all calculated spectral curves have very similar shapes. This is the reason why the weight fractions obtained from linear combinations are close. Actually no one weight resulted in the correct qualitative analysis of the mixture. In all cases, linear combination included a third ink along with two basic ones.

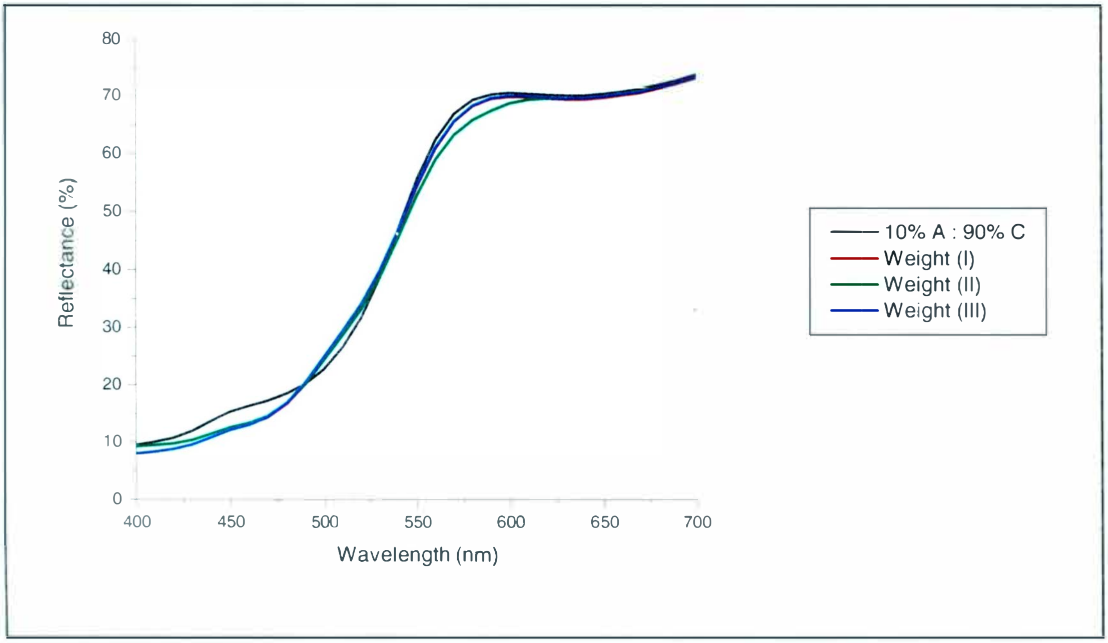


Figure 38. The Measured VIS Spectrum of Mixture 10 % Ink A + 90 % Ink C and of Calculated Spectra for Weights I, II, III.

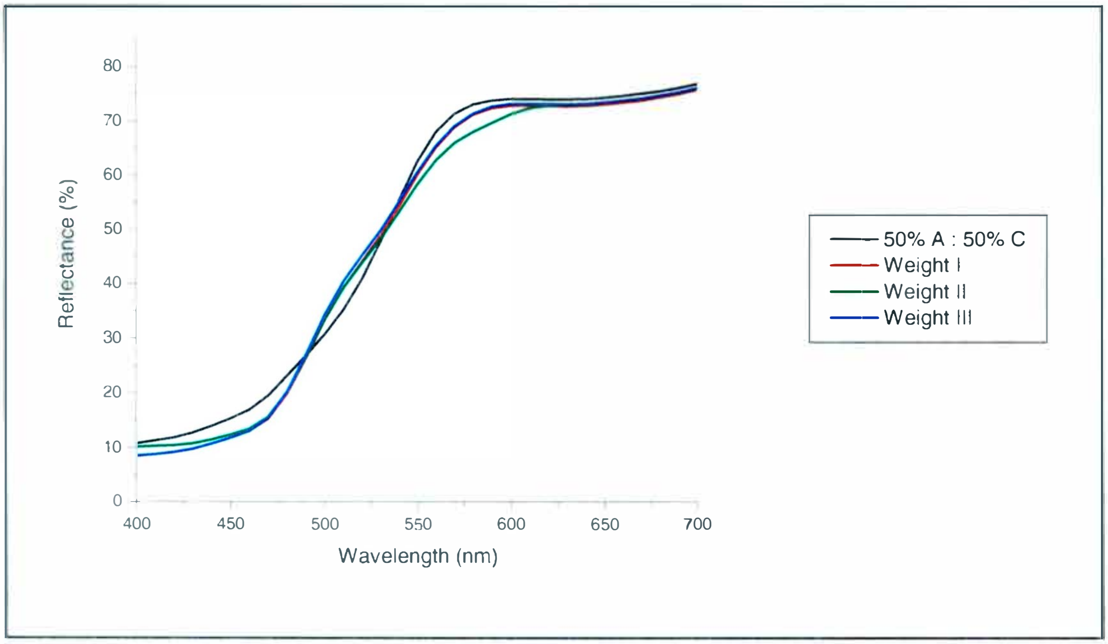


Figure 39. The Measured VIS Spectrum of Mixture 50 % Ink A + 50 % Ink C and of Calculated Spectra for Weights I, II, III.

However, the concentrations of the third ink were generally negligible. In case of A, C mixtures, it was the inks D and E, in case of A, E mixture the ink D. The false addition of ink D might be explained by the similarity of spectra between the inks D and A (Figures 28, 34).

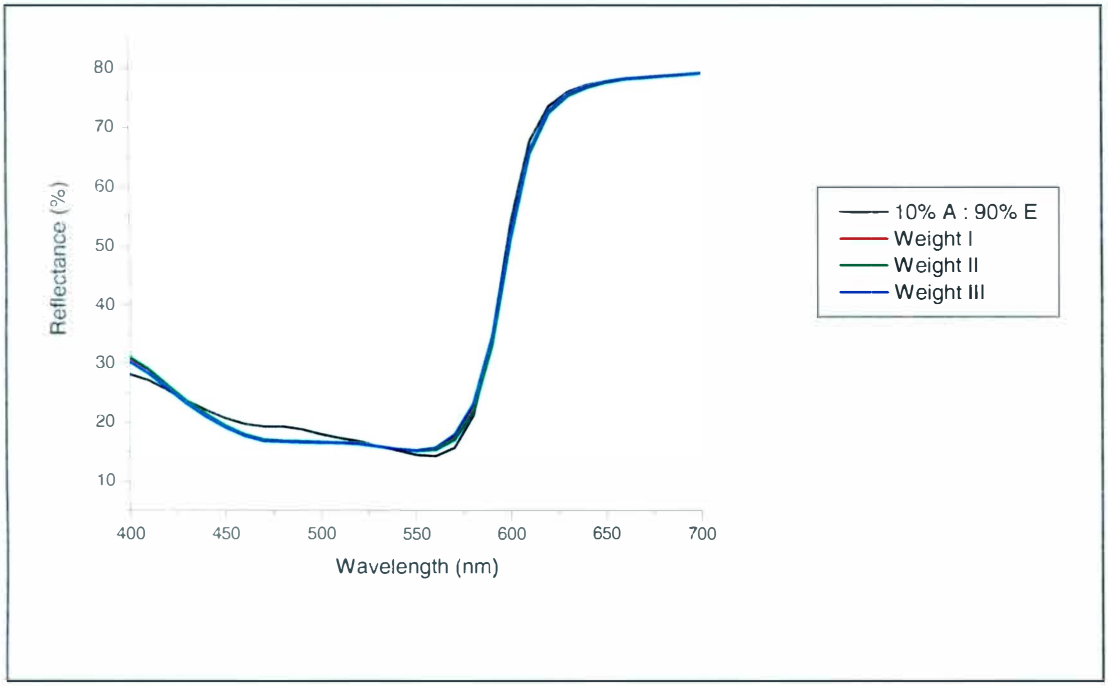


Figure 40. The Measured VIS Spectrum of Mixture 10 % Ink A + 50 % Ink E and of Calculated Spectra for Weights I, II, III.

Three Ink Mixtures

In three ink mixtures retroengineering process, the following blends were chosen as model mixtures:

60 parts (10 % B : 90 % D) + 20 parts (C) + 20 parts (extender)

60 parts (20 % B : 80 % D) + 20 parts (C) + 20 parts (extender)

The results of mathematical analysis employing linear combination for three ink model mixtures are shown in Tables 6 and 7. Due to the fact of neglecting the reflectance contribution of the extender, current 80 parts of the inks in the blend were considered to represent 100%.

Table 6

The Comparison of Values of Weight Fractions for Mixture of 75 Parts (10 % Ink B: 90 % Ink D) With 25 Parts of Ink C To Their Values in Blend Calculated Employing Three Different Weights

Ink	Real	Weight (I)	Weight (II)	Weight (III)	Δ Weight (I)	Δ Weight (II)	Δ Weight (III)
A	0	0.035	0.040	0.023	0.035	0.040	0.023
B	0.075	0.152	0.135	0.137	0.077	0.060	0.062
C	0.25	0.16	0.14	0.21	0.09	0.11	0.04
D	0.675	0.653	0.620	0.63	0.022	0.055	0.045
E	0	0	0.065	0	0	0.065	0

In both cases the weights (I) and (III) added also ink A to the present inks in the mixtures. As in linear analysis of two ink mixtures, this could be explained by the similarities of spectra of inks A and D. Weight (II) is considered to be the worst in this case due to the fact that besides the false addition of ink A to the mixture it also adds the ink E, which was also not employed in the formulation.

Table 7

The Comparison of Values of Weight Fractions for Mixture of 75 Parts (20 % Ink B: 80 % Ink D) With 25 Parts of Ink C To Their Values in Blend Calculated Employing Three Different Weights

Ink	Real	Weight (I)	Weight (II)	Weight (III)	Δ Weight (I)	Δ Weight (II)	Δ Weight (III)
A	0	0.03	0.04	0.02	0.03	0.04	0.02
B	0.15	0.22	0.20	0.20	0.07	0.05	0.05
C	0.25	0.16	0.14	0.20	0.09	0.11	0.05
D	0.60	0.59	0.57	0.58	0.01	0.03	0.02
E	0	0	0.05	0	0	0.05	0

Investigating Figures 41 and 42, it was found that the calculated and real spectra of mixtures are similar to each other.

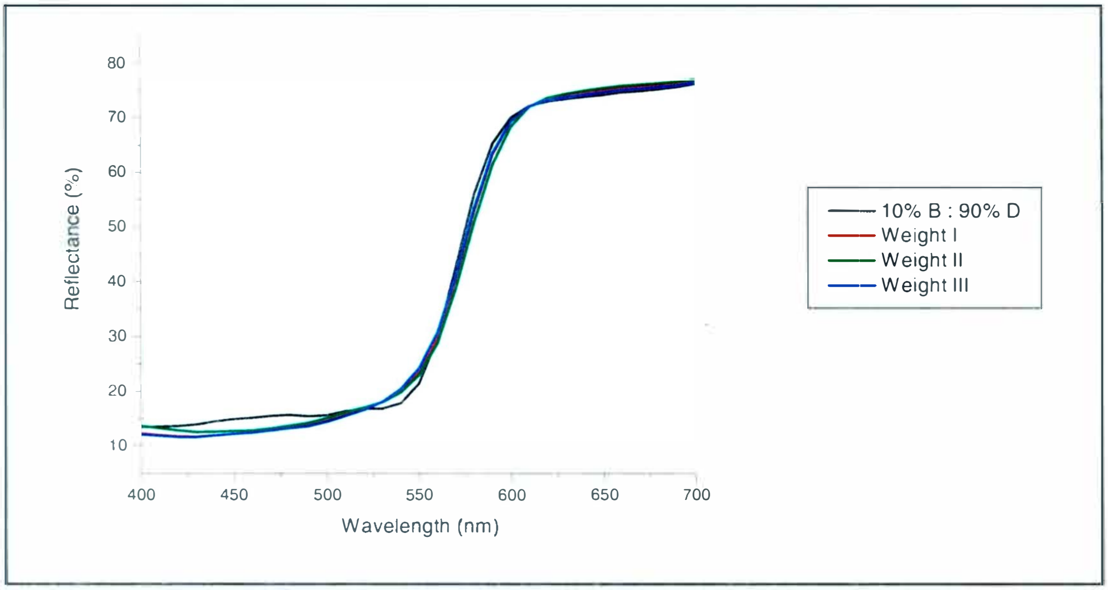


Figure 41. The Measured VIS Spectrum of Mixture 75 Parts (10 % Ink B: 90 % Ink D) With 25 Parts of Ink C and of Calculated Spectra for Weights I, II, III.

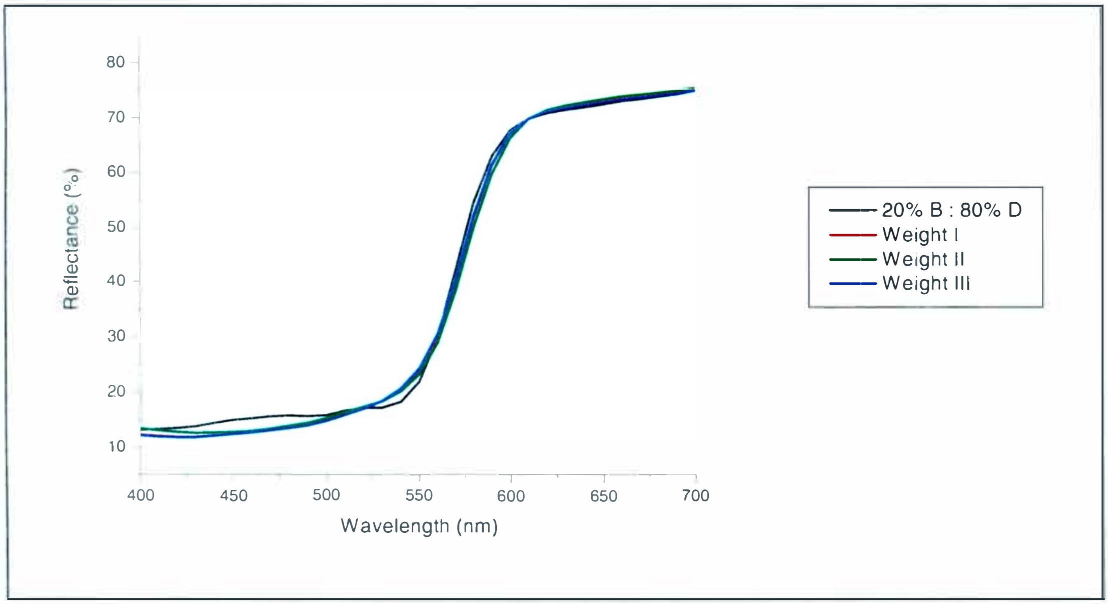


Figure 42. The Measured VIS Spectrum of Mixture 75 Parts (20 % Ink B: 80 % Ink D) With 25 Parts of Ink C and of Calculated Spectra for Weights I, II, III.

This is why the values obtained from linear combination analysis are generally close to the real ones and also comparable to each other.

Generally, the numbers resulting from the linear combination analysis of the inks are in the range within 10 % from real weight fractions utilized through the process of blending the inks.

Table 8

The Comparison Between Analyzed and Calculated Model Mixtures 60 Parts (20 % Ink B: 80 % Ink D) With 20 Parts of Ink C and 20 Parts of Extender

Mixture	L* AVG	L* VAR	a* AVG	a* VAR	b* AVG	b* VAR
ANALYZED	62.34	0.12	32.96	0.19	30.59	0.35
CALCULATED	59.39	0.05	32.77	0.03	30.71	0.05

In order to relate the similarity of real and calculated blends, the total color difference (ΔE) between the analyzed model mixture and the mixture newly prepared, was calculated. Real blend and calculated one (weight III, see Table 7) were chosen as the model mixtures. Mixture calculated utilizing weight (III) was chosen due to its smallest Δ weight (Table 7).

From the displayed values in Table 8, the total color difference ΔE was calculated according to the formula (7) as 2.96. This match can be considered as a very close. Analyzing L*a*b* values, the calculated mixture is darker, slightly greener, and yellower.

The Application of Spline Functions in Two Ink Mixtures Analysis

In case of two ink mixtures, the resulting color has to be the combination of reflectance values of employed virgin inks. If only reflectance values of pure virgin inks were given that makes at certain wavelength 2 points. The only possible mathematical solution would be to draw the line crossing these points. Due to the fact that mixtures of two inks at varying concentrations were prepared, more than 2 points are available. If including 2 points from virgin inks plus 9 points obtained from their differently concentrated mixtures, it adds up to 11 points. With 11 points, the utilizing of linear, quadratic, and cubic splines will be discussed [21].

Linear Spline Functions

Using of linear splines means that each pair of adjacent points is fitted by a linear function. In this case, 11 points will be fitted with 10 linear functions. In order to fit adjacent two points, the reflectance values for both of them, or reflectance value for one of them plus one derivation (direction of the line) have to be set. The fitted 11 points by the linear splines function is displayed on Figure 43 (black line).

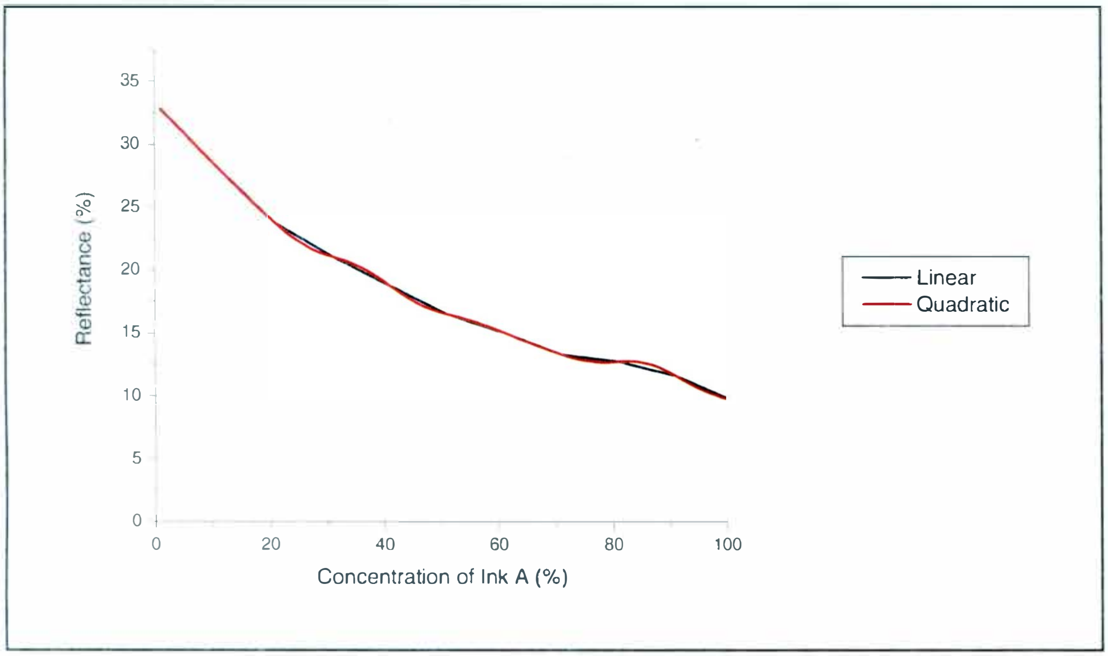


Figure 43. The Linear and Quadratic Splines Utilized for the Mixture of Inks A and E at 400 nm.

Quadratic Spline Functions

In this case, each pair of adjacent points is fitted by quadratic function. The fit is displayed on Figure 43 (red line). To fit points with quadratic splines, the reflectance values for three points, or for two points plus one derivation is required.

When comparing linear and quadratic spline functions, their courses are very similar. It is believed that last linear spline (90% - 100 % ink A) is more accurate than quadratic. This is due to the fact that for the calculation of quadratic spline, there are no three points available. Thus, the combination of two points plus one derivation had to be chosen. The derivation of left side of first spline (0 % ink A) has to be set. Any error caused by this choice is transferred to the next spline and the total error is accumulated at the last spline (90 % - 100 % ink A).

Cubic Spline Functions

The error caused by quadratic splines would be eliminated if cubic splines were employed. For cubic splines, there have to be four points available or three points plus one derivation or two points plus two derivations. It would be the choice either I want to set first derivative at the beginning and second derivative somewhere else, or I will choose two derivations of second order, the first one at the beginning and the second one somewhere else. At the derivations of the second order very often applies that the most sufficient number to pick is 0. Thus, the application of cubic splines in this case would be probably the most convenient.

However, MS Excel does not solve the cubic spline functions and the programs calculating them are not commonly accessible or easily manageable.

The Application of Spline Functions in Three Ink Mixtures Analysis

In order to be consistent with accuracy obtained from two ink mixtures, for three ink mixtures there would have to be 11^2 different mixtures prepared. Such number of mixtures is not reasonable and therefore the use of spline functions was not considered in three ink mixtures analysis.

Linear Combination Versus Linear and Quadratic Fits in Two Ink Mixtures Analysis

The quantitative analysis of mixture containing 80 parts of inks A and C at their concentrations 30 % and 70 %, respectively mixed with 20 parts of extender is displayed in Figure 33. As mentioned before, the calculated reflectance values represented by the line C (Figure 33) reach negative values in the range of wavelengths from 475 nm to 550 nm, approaching minimum of -7.091 % at 520 nm. Thus, reflectance values at this wavelength were chosen for further processing in order to bring the calculated value of reflectance at this wavelength closer to zero line.

Instead of linear combining of two reflectance values for pure virgin inks, the linear and quadratic fit for both, the reflectance values of pure inks A, C together with the reflectance values of their mixtures, will be employed. The employed reflectance values are shown in Table 9.

Table 9

The Reflectance Values of the Mixture 80 Parts Inks (A+C) With 20 Parts of Extender at 520 nm

Concentration of Ink A in the Mixture 80 Parts Inks (A+C) with 20 Parts of Extender (%)	Reflectance at 520 nm (%)
0	20.786
10	31.582
20	32.877
30	33.785
40	37.011
50	40.862
60	42.173
70	46.342
80	52.278
90	61.069
100	70.276

Based on functions obtained from linear and quadratic fits, the reflectance value was calculated (Table 10).

Table 10

The Functions and Reflectance Values Based on Linear and Quadratic Fits for the Mixtures 80 Parts Inks (A+C) With 20 Parts of Extender at 520 nm

Fit	Function	Calculated Reflectance (%)
Linear	%R = 22.0 + 0.41*(conc(Ink A))	-5.758
Quadratic	%R = 26.11 + 0.13914*(conc(Ink A)) + 0.00273*(conc(Ink A))^2	-4.199

When the simple linear combination was used the 'difference' value for this wavelength was -7.091 %. This difference was reduced when the linear fit function was used (-5.758 %) and the quadratic fit function was used (-4.199).

Generally, applying of fit functions calculated based on higher number of reflectance values than two gives more desirable results in terms of getting reflectance closer to 0 % value. However, the final gain from applying more complicated procedures, in this case linear and quadratic fits, in the process of ink mixtures analysis was not significant.

CHAPTER VI

CONCLUSIONS

In this work, spectral analysis of product gravure spot color inks was done with the aim to improve and speed-up the spot-color matching process and the application of press return inks.

First, the reflectance spectra of virgin product gravure solvent-based inks were analyzed with a Perkin Elmer UV/VIS/NIR Spectrometer LAMBDA 900 in the range of 190-2000 nm. The readings were taken each 5 nm. The spectra of all inks did not significantly differ from each other in the spectral ranges of 190 to 350 nm and 800 to 2000 nm. It was found that the range from 355 nm to 800 nm gives the most valuable information.

Further analysis was done based on readings obtained from spectrophotometer Datacolor International Spectraflash SF600. Unfortunately, SF600 has spectral range output from 400 nm to 700 nm with reporting interval 10 nm. Thus, the advantages of taking readings in wider ranges and shorter intervals were lost.

Characteristic peaks and valleys of individual virgin inks spectra were closely analyzed in the range of 400-700 nm.

Qualitative analysis of both two and three pigment mixtures was done by analyzing representative maxima and minima of individual inks and matching them to the spectral curves of mixtures. This method was reliable and all components in the mixtures were identified.

It was found that the Beer-Lambert law is applicable in the quantitative analysis of product gravure ink mixtures. Based on the results of qualitative analysis and application of Beer-Lambert law, the calculation of concentrations of individual components was completed.

Further aim was to develop and test a mathematical model, which would quantitatively describe the measured spectra of the ink mixtures as close as possible. According to Beer-Lambert law, linear model was chosen. In order to solve the composition of unknown blends, MS Excel with installed solver was utilized. Also the influence of different weights in the linear combination analysis on the calculated weight fractions of the inks was investigated.

It was found that in the case of two ink mixtures all utilized weights give similar results. In the case of three ink blends, the used weight (III) gave the most accurate results.

According to calculated weight fractions, a new blend was prepared and compared to the analyzed one. The total color difference ΔE between both of them was 2.96 (D65 10deg).

From the discussion regarding linear, quadratic, and cubic spline functions, for the retroengineering of the ink mixtures, employing of the cubic splines would be the best choice. However, MS Excel Solver is not suitable for calculations of cubic spline functions. For these calculations, more advanced programs would be necessary.

BIBLIOGRAPHY

1. GAA, Profile Survey of the U.S. Gravure Industry, GAA, Rochester, NY, 1994, 87-127

2. Leach, R. H., The Printing Ink Manual, Van Nostrand Reinhold, 4th Edition, 1988, 94-149

3. Laden, P., Chemistry and Technology of Water Based Inks, Blackie Academic & Professional, 1st Edition, 1997, 111-153

4. Society of Dyers and Colorist, Bradford, Yorkshire, BS1 2JB, UK

5. American Association of Textile Chemists and Colorists, Research Triangle Park, NC, USA

6. Patton, T.C., Pigment Handbook, Wiley, volume 1, 1973, 983

7. NPIRI Raw Material Data Handbook, NAPIM Publications, volume 4, 1983

8. Lewis, P.A., Organic Pigments, Federation of Societies for Coating Technology, Philadelphia, 1988

9. Kubelka, P., and Munk, F. Z. Tech. Physik 12, 1931, 593

10. Wendlandt, Wesley, W., Modern Aspects of Reflectance Spectroscopy, Plenum Press, New York, 1st Edition, 1968, 27-45

11. Instrumental Color Systems Ltd., Handbook of Industrial Color Technology

12. McLaren, The Quantification of Color Differences, Chapter 10

13. Commission Internationale de l'Eclairage (CIE) Proceedings 1931, Cambridge University Press, Cambridge, 1932

14. Brode, Wallace, R., Chemical spectroscopy, J. Wiley & Sons, 2nd Edition, 9th printing, 1962, 278-289

15. Rao, C.N.R., Ultra Violet and Visible Spectroscopy Chemical Applications, Butterworths, London, 2nd Edition, 1967, 175

16. Parker, Sybil, P., Spectroscopy Source Book, McGraw-Hill, New York, 7th Edition, 1988, 137

17. Davies, Mansel, Infra-Red Spectroscopy and Molecular Structure, Elsevier Pub. Co., Amsterdam, 1st Edition, 1963, 111

18. Tompson, B., Printing Materials: Science and Technology, Pira International, UK, 1998, 402-411

19. Clark, B.J., Frost, T., Russel, M.A., Techniques in Visible and Ultraviolet Spectrometry, Chapman & Hall, 1st Edition, volume 4, 1993, 52-54

20. MacLane, S., Birkhoff, G., Algebra, ALFA, Bratislava, 1st Edition, 1974, 266-300, 475-516

21. Babusikova, J., Slodicka, M., Weisz, J., Numericke Metody, ALFA, Bratislava, 1st Edition, 2000, 37-43, 45-51