



TECHNICAL ANALYSIS OF NATURAL PRINTING INKS FROM NATURAL PIGMENTS PRODUCED FROM INDIGOFERA TINCTORIA L. AND ITS PRINTABILITY SPECIFICATIONS

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ABSTRACT

Natural organic dyes and natural organic lake pigments were used in the dyeing, printing, frescoes, etc. from prehistoric times to end of 19th century. Natural printing inks from obtained organic lake pigments have advantages since their production implies renewable resources causing minimum environmental pollution and has a low risk factor in relation to human health. Natural organic printing inks do not pollute the environment. They are neither toxic nor carcinogenic, and some also have antibacterial and antimicrobial properties. Most of the natural pigments are weak organic acids. The Indigo (Indigofera Tinctoria L.) plant dye is used to be for preparing inks. The natural pigments have been prepared from plant dyes Indigo (Indigofera Tinctoria L.) qualitatively identified by using HPLC-DAD measurements.

After the preparation of printing inks with organic pigment of Indigo (Indigofera Tinctoria L.) plant dye and other organic compounds, with this ink were performed to print with various weight of paper and different printing pressure. It is used two different paper and both of them are used three different weightiness.

The identification of natural pigments and printing inks from produced in organic pigments and compounds are one of the most important targets aimed for in the scientific examination of paintings, textiles, illuminated manuscripts and printing materials. Thus, several techniques have been used, for example brightness and color values of Indigo (Indigofera Tinctoria L.) plant dye natural printing ink values were determined by CIE L*a*b* color space system.

In the study reported here, for the analysis and printing of natural printing properties of inks obtained from Indigo (Indigofera Tinctoria L.) plant dye pigment an analytical method was developed. Identifying the color value, glossy, lightfastness, surface energy and how much influence printing force of CIE Lab values. Finally, we believe that printing with prepared natural pigments and compounds inks can be an important advantage for environmental processes and food printing, child book printing and also etc. So in this study refer to pigments of obtained from insects and plants suitable or not for the offset printing inks.



1. INTRODUCTION

The term “natural organic dyes” refers to dyes obtained from certain dye plants, dye insects and snails. The use of dyestuffs and pigments from the roots, stems, leaves, flowers and fruits of plants is as old as humanity itself. The use of dye plants is known from wall paintings and the dyeing of textile fibers dating back to 4000 years B.C. However after synthetic dyestuffs were discovered in the early 20th century, the use of dye plants began a decline that brought it to the brink of disappearing entirely. When it was determined in the 1980s that a large percentage of synthetic dyes were toxic, carcinogenic and/or led to environmental pollution, natural dyeing once again gained importance.

Nowadays, dyes is produced by chemical method and the chemical compounds are used in its. But a lot of pigments can be used to produce organic inks, whether used in the preparing of printing ink with only natural methods. This mean that, all the components should be created of natural substances. Using special methods to bring together printing and dyeing technology, the laboratory used natural organic dyestuffs to support the production of new non-toxic, non-carcinogenic printing products with natural antibacterial and antimicrobial properties.

The aim of this study was two fold. (i) To obtained natural organic pigment from Indigo (*Indigofera Tinctoria L.*) plant in order to identify and determine the colour values of the printing ink which is produced from this pigments. The latter produced printing inks with its by using other organic compounds. The identification of these pigments was carried out by a printing test machine (IGT C1) with under the different pressure. (ii) At second stage include the investigation of effect of the different amounts of printing pressure on the colouring scale, glossy, CIE Lab of the printing inks by using of cochineal pigment.

2. EXPERIMENTAL

2.1. MATERIALS

Dye Plants, Dye Insect and Chemicals

Dye plants Indigo; *Indigofera tinctoria L.*

Colors Obtained; Dark Blue, Blue, Green

Dye Ingredients; Indican (*Indigo*)



Figure 1: IGT C1 test

Indigofera tinctoria L. is a perennial of the pea family that can grow to seven feet. The leaves are pinnate: nine to thirteen small leaflets grow from a common leaf stem. The insignificant white-red flowers grow in stocky clusters. This indigo plant is probably native to India , but because it can be easily cultivated, it has become widely distributed; under the Arabs and it went as far as Moorish Spain. Shortly before the plants blossom, in the early morning - often before sunrise - they are cut above ground. The branches are bundled and placed whole in masonry containers. After perhaps three-foot-high layer of vegetation has been trodden down and weighted with segments of tree trunks, it is covered with water. At temperatures greater than 30°C (86°F), a fermentation process begins.

Dye plants Indigo (*Indigofera tinctoria* L.) is a perennial of the pea family that can grow to seven feet. Indigo dyes were obtained from leaves of the indigo plants *prepared for inks dye*. Natural indigo (*Indigofera tinctoria*) were provided from Turkish Cultural Foundation Natural Dyes Research and Development Laboratory. Cochineal dyes were obtained from insect of the cochineal insect *prepared for inks dye*.

Dye plants Indigo (*Indigofera tinctoria* L.) is a perennial of the pea family that can grow to seven feet. Natural indigo (*Indigofera tinctoria*) were provided from Turkish Cultural Foundation Natural Dyes Research and Development Laboratory.

Papers:

Six different paper were provided from UPM-Kymenne (İstanbul, Turkey, www.upm.com). These are shown below. (Table 1)

Table 1: Using papers and weights in a test prints.

Sample Papers	Basis Weight
UPM Digi Finesse Gloss	350 g
UPM Digi Finesse Gloss	170 g
UPM Digi Finesse Gloss	115 g
UPM Digi Color Laser	250 g
UPM Digi Color Laser	160 g
UPM Digi Color Laser	100 g

IGT Printability Tester C1

The IGT C1 tester prints all sorts of coated and uncoated materials like paper, board, plastic film, cellophane, laminate, metal, etc. Inking time: inking section 45 s and printing disc 15 s. The inking time of the printing disc is 15 s.

After the printing force has been applied, the print is made automatically. The printing force can be set in 19 steps between 100 and 1000 N. It is used three different amount of printing pressure force this study: 200N, 300N and 450N.



Figure 2: IGT C1 test printing

2.2. METHODS

Formation of Indigo (*Indigofera Tinctoria L.*) plant dye pigment:

2 g of powdered indigo plants was weighed and placed in a beaker. 150 mL distilled water was added in it and mixed well. The mixture was heated up to 100°C, then held at low temperature. 10, 50 mL % 4 FeSO₄·7H₂O solutions and 150 mL of plant extract solution were heated separately to 90°C and 60°C, respectively. 10 mL from FeSO₄·7H₂O solutions at 90°C were added to indigo plants pigments solution at 60 °C. Pink coloured alum-indigo pigments were observed. Afterwards, 0.1 M K₂CO₃ solution was added to neutralize the mixture.



The mixture was cooled to room temperature to precipitate the alum-indigo pigments. After setting down, the mixture was filtered and the precipitate was washed with distilled water. The residue was dried on filter paper at 101°C for a while. The dried alum-indigo pigments was powdered.

Formation of printing inks which is used Indigo (*Indigofera Tinctoria* L.) plant dye pigment:

In this study Indigo (*Indigofera Tinctoria* L.) plant pigments was mixed with the other organic raw material based on vegetable fat. This organic raw materials obtained from DYÖ (Manisa, Turkey, www.dyo.com.tr) printing inks inc. Ink formulation is as follows. (Table 2)

Table 2: Formulation of printing ink which is used Indigo Pigments

Chemicals	Concentration
COCHINEAL Pigment	24 g
OM1212	20 g
AN-440	156g

Printing procedure and method:

The papers were subsequently conditioned for at least 24 h at 23 °C and 50% RH (relative humidity) before printing and subsequent measurements were made. Printing technics were used according to TAPPI T494-014-88 standard using C1 offset IGT. Offset IGT printing force was evaluated three diferent amount of printing pressure 200N, 300N and 450N.

Measurement methods of the printed samples

Spectrofotometer, Color measurements of the printed samples were conducted in accordance with the CIE L*a*b* system using TECHKON SpectroDens reflectance spectrophotometry and Spectra Connect additional software modules. Polfilter: off, white reference: Absolute, illuminant: D50, observer: 2°. For the purpose of the measurements, an 2° observer and a D50 light source were also used. Handsheets were measured according to Technical Association for Pulp and Paper Industry TAPPI standard.

The color distance ΔE^* is displayed with two digits. Additionally the components ΔL , Δa and Δb can be seen. But in printing industry is accepted $\Delta E < 3$. The measurement function ISO-Check enables the fast check of a print with regard to the compliance with the ISO standard values ISO 12647-2.

Glossmeter, also gloss values of printed samples were analyzed with BYK Gardner, Sheen Instrument, UK with glossmeter. They were analyzed in terms of measurement as 20°, 60° and 85°. The lightfastness tests against the light were performed according to standard ISO-B02. ISO 2813 and ASTM D523 (the most commonly used standards) describe three measurement angles to measure gloss across all surfaces. All gloss levels can be measured using the standard measurement angle of 60°. This is used as the reference angle with the complimentary angles of 85° and 20° often used for low and high gloss levels respectively



Fastness Determination blue wool textile fading cards or kits typically consist of 8 swatches of blue wool dyed to various levels. They consist of eight strips of wool mounted side by side on a small card; each strip or reference is colored with a blue dye that fades after exposure to a known amount of light. These scales are used for paint lightfastness testing under international standard ISO 105-B. Exposed samples which exposed 80 hrs are then rated in comparison to the behavior of the fabrics.

Surface Tension and Surface Energy, the contact angle between the liquid and tested materials was measured using a PG-X goniometer with printed samples. Tests were carried out at an ambient laboratory temperature of $T \sim 22\text{ }^{\circ}\text{C}$ and at quasi-constant relative humidity (HR $\sim 45\%$). The equilibrium contact angles were measured after 20 s from water drop depositions. It was performed according to standard ASTM D5725-99 (2008) and parameters defined in standard ISO 4287.

3. RESULTS AND DISCUSSION

3.1. Gloss Values in various printing pressure

In this study, printings were performed in three different printing pressure that were 200N, 300N and 450N. They were analyzed in terms of measurement as 60° . Because of the universal and standard measurement angle, this angle were used there. This 60 degree angle is used as reference angle for all printing products.

Between printed papers in 200N printing pressure was monitored UPM Digi Finesse Gloss-350g. have the most gloss value than the others. This paper both the gloss value and the highest weight of the other papers. (Fig.1)

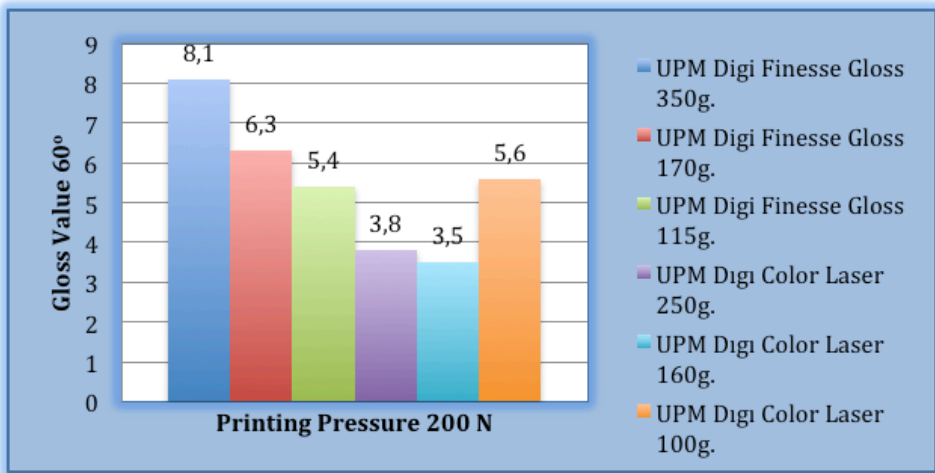


Figure 3: Gloss values of the printing ink prepared with indigo pigments in 200N printing pressure

In the printing pressure 300N, more gloss value was observed of UPM Digi Finesse Gloss-350g. and 170g. (Fig. 2)

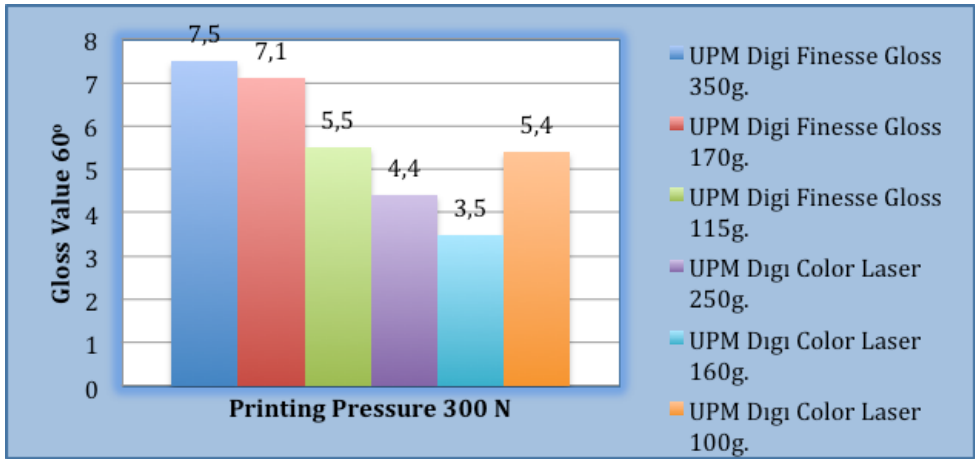


Figure 4: Gloss values of the printing ink prepared with indigo pigments in 300N printing pressure

In the printing pressure 450N, in the paper with the highest brightness and weight gloss value was observed much more that was UPM Digi Finesse Gloss- 350g.(Fig. 3)

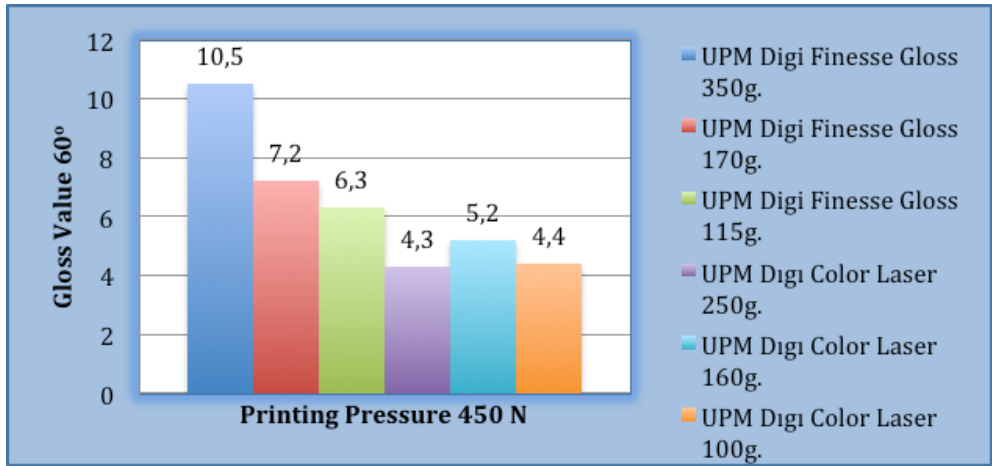


Figure 5: Gloss values of the printing ink prepared with indigo pigments in 450N printing pressure

3.2. Lightfastness, CIE L*A*B* And Gloss Values Changes Of Printing Inks With Organic Pigment Of Indigo (*Indigofera Tinctoria L.*) Plant Dye

Printing was performed in both virgin paper and coated paper with printing ink produced from indigo pigment. The assessment as the value of printing pressure which results in optimum printing pressure of 200N was conducted.



Lightfastness value was observed between 5 and 6. This value is suitable for printing ink industry. Looking at the CIE L*a*b* values after 80 hours exposure, major changes were observed of the L*a*b* values. ΔE value of virgin paper was calculated as..... and ΔE value of virgin paper was calculated as..... Both of ΔE change indicate too much. (Table 3,4)

Table 3: Lightfastness, CIE L*A*B* and Gloss Values Changes of The Virgin Paper

Ink from INDIGO/ 100 g./ Virgin paper/ 200N					
Light Fastness	5 ; 6				
CIE L*a*b*					
	Before		After		ΔLab
	L	62,64	L	65,92	-3,28
	a	-1,23	a	-5,62	-4,39
	b	-56,06	b	-49,42	-6,64
Gloss value					
	Before		After		
	20°	0,6	20°	0,7	
	60°	5,6	60°	5,7	
	85°	14,4	85°	14,7	

Table 4: Lightfastness, CIE L*A*B* and Gloss Values Changes of The Coated Paper

Ink from INDIGO/ 115 g./ Coated paper/ 200N					
Light Fastness	5 ; 6				
CIE L*a*b*					
	Before		After		ΔLab
	L	69,17	L	71,99	-2,82
	a	-6,82	a	-10,47	-3,65
	b	-55,28	b	-49,46	-5,82
Gloss value					
	Before		After		
	20°	0,7	20°	1,1	
	60°	5,4	60°	10	
	85°	12,5	85°	24,2	



3.3. Surface Energy Values Of Printing Inks With Organic Pigment Of Indigo (Indigofera Tinctoria L.) Plant Dye

In general the advancing angle, which remains relatively constant over a wide range of coverage, is slightly lower than the intrinsic contact angle of (50-100%). Low contact angle where the resulting contact angle was as below (Table 5) and good wetting properties can be observed for the printed samples.

Table 5: Surface Energy and Contact Angle Values of The Printed Paper

SURFACE ENERGY		
	Contact Angle with water	Total Surface Energy (mj/m2)
100gr Virgin paper 200N Indigo	49,9	47
115gr coated paper 200N Indigo	42,5	49,7

Under 200N printing pressure of printed on the virgin papers contact angle degree was observed as 49.9 and surface energy value 47; coated papers contact angle degree was observed as 42.5 and surface energy value 49.7. These values are in compliance with standards. And thus a good wetting when printing in offset print are available. Thus ink is not affected much from water. (Fig. 4)

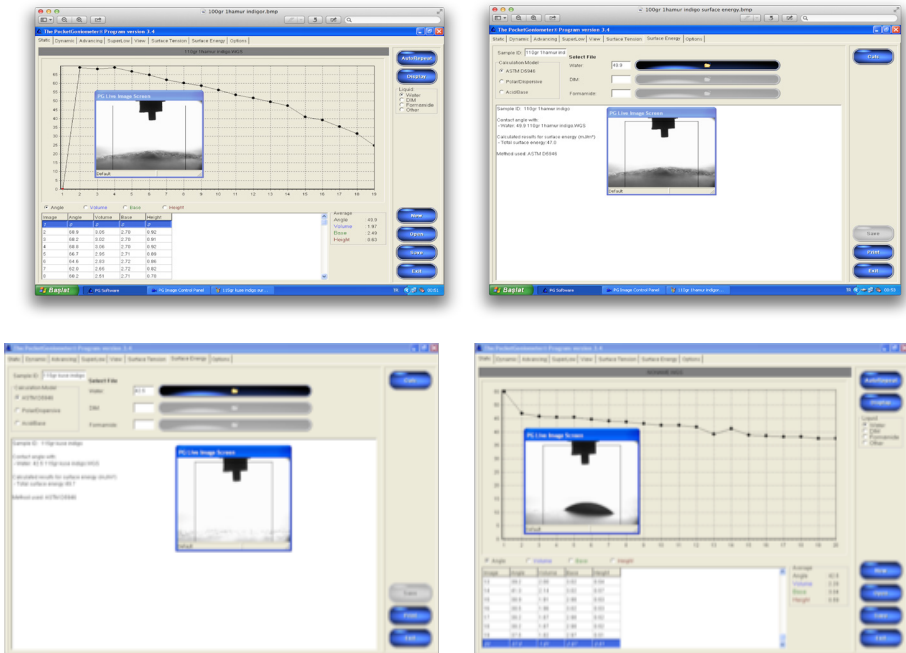


Figure 6: Contact Angle and Surface Energy Values of the printing ink prepared with indigo pigments in 200N printing pressure (I) Virgin Paper, (II) Coated Paper



3.4. CIE L*a*b* Values Of Printing Inks With Organic Pigment Of Indigo (Indigofera Tinctoria L.) Plant Dye

Analyzing the printed samples which was lightfastness test in 80 hr, L*a*b* values ranged too much. Despite the fact that good lightfastness, change in the color of their value is very high. L*a*b* exchange has been at the very top of the ΔE value. (Fig 6)

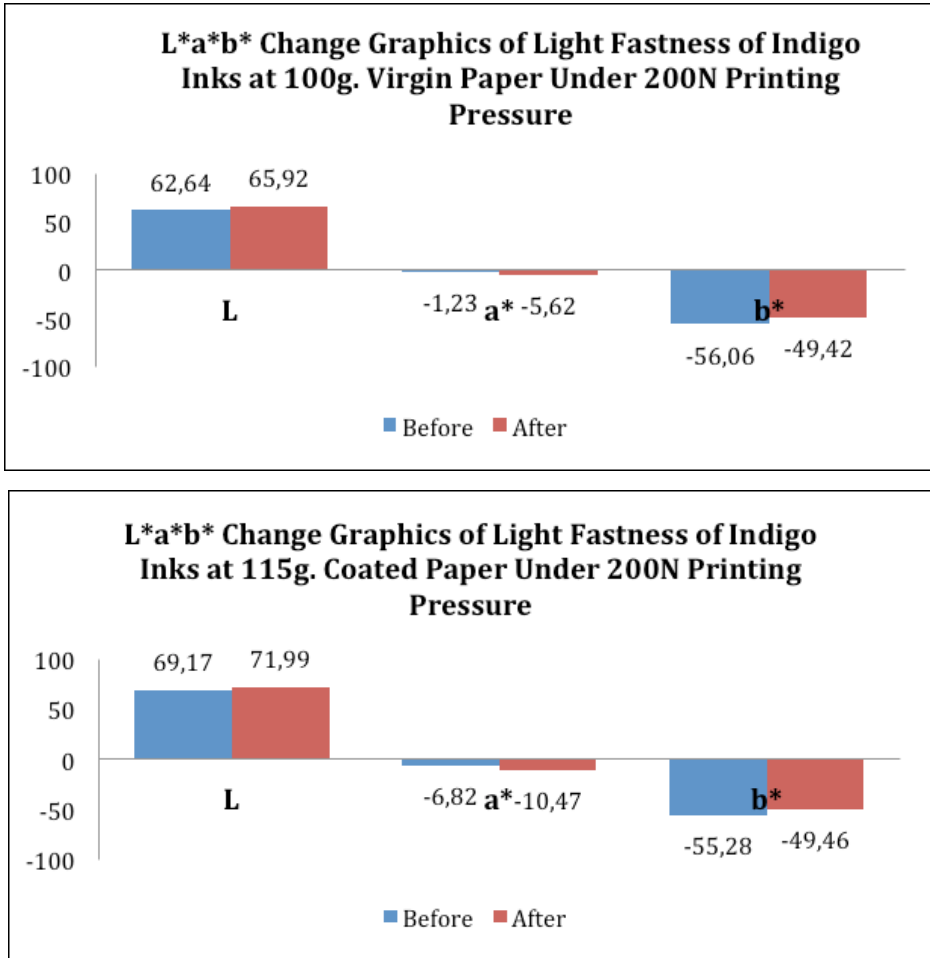


Figure 7: CIE L*a*b* values changes of the printing ink prepared with indigo pigments in 200N printing pressure (I) Virgin Paper; (II) Coated Paper)



CONCLUSION

In the study reported here, for the analysis and printing of natural printing properties of inks obtained from Indigo (*Indigofera Tinctoria* L.) plant dye pigment an analytical method was developed. Identifying the color value, glossy, light fastness, surface energy and how much influence printing force of CIE Lab values.

Besides in trials should be done with high weight coated paper and adjusting the printing pressure as 200N. In this way the best results will be more accurate. Especially, indigo pigments' lightfastness is excellent. Discolouration may remain between 15-50 years.

Finally, we believe that printing with prepared natural pigments and compounds inks can be an important advantage for environmental processes and food printing, child book printing and also etc. A chemical method has been developed for the determination of printing ink from indigo pigments. Chemical method rearrange with different amounts of metals of making pigment.

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