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Cyanotype Printing Technique Using Redox System in Application of Printed Hanging Fabrics Designs

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Abstract

The field of hand textile printing, considered as one of the most exciting branches of arts in combining multiple concepts and techniques. Whether it is in terms of its value, artistic originality, ability to form visual images with all its technical and aesthetic values. The field consists of many methods, each with its own broad and unique elaboration capabilities, through which it allows continuous experimental practice of the presented techniques, through creative technical expertise. The use of techniques based on iron ions in the formation of light-sensitive compounds is one of the uncommon techniques in the field of textile printing. It is Experimental printing field based on oxidation and reduction, such as, cyanotype techniques, which are iron-based photographic prints [17, 16]. One of the earliest photographic processes is the blue printing (cyanotype). Blue printing technology is one of the pictorial alternatives known as Siderotype [19]. The main purpose of this study is to overview the uses of non-traditional manual printing techniques in textile printing field (especially, blue printing), in addition to applying this technique on hanging printing fabrics through innovative designs.

Keywords: Cyanotype, Hand Printing, Oxidation, reduction, Hangings

1. Introduction

It is not possible to understand ancient chemistry except in the relationship of cooperation between humans and nature, in which recognizing that the ancient experiments led to an experimental field through which technologies could be developed in a new way. Light-sensitive chemical compounds are considered as an exciting field for the designer , as he relies on them in reusing techniques or raw materials, revealing new plastic visions, which in turn enriches the field of hand printing.

Cyanotype is one of the photographic alternatives known as Siderotype, a group of iron-based photographic prints.

Historically, this technique dates back to 1842 [12], when Sir John Herschel reported to the Royal Society, a chemical method for this technique.

The word cyanotype (blue print) was derived from the word, the Greek name cyan, meaning "dark blue effect"[2].This technology relies heavily on the formation of materials that are sensitive to light and also to the presence of strong ultraviolet rays.

It was widely used for its permission by engineers and architects to reproduce technical drawings. This is the origin of the term "blueprinting", which is now used to describe technical drawing or plan. In this research, we used Blue printing (Cyanotype), as one of the technological techniques, to enrich aesthetic value of cotton fabrics by using innovative designs of bio -architecture.

Where manual printing is considered one of the practical applied arts that is characterized by unlimited richness in techniques and methods, which results in many plastic and aesthetic values, and its applicability to different surfaces and bodies, which makes manual printing one of the best experimental fields, from which an infinite number of special designs can be Distinction, uniqueness, diversity. [3-27] Among the non-traditional printing methods is the blue printing method that many researchers have not dealt with, which is a method that is not used in the field of printing hand textiles, in which some chemicals that consist of iron salts are used, those materials used in the method of photography printing (cyanotype).

2. Experimental

2.1. Materials

2.1.1. Fabrics

100% plain bleached cotton fabrics weight (140 g/ m^2), was used throughout this study. Supplied by El-Mahalla El-Kobra Company-Egypt.

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2.1.2.Chemicals

2.1.2.1. Ferric ammonium citrate.

The Chemical Formula of ferric ammonium citrate is $C_6H_8FeNO_7$.

Ferric ammonium citrate, also known as ammonia-citrate of iron, is an iron-containing compound that is light-sensitive and converts from a ferric (iron III) to a ferrous (iron II) state when exposed to UV light.

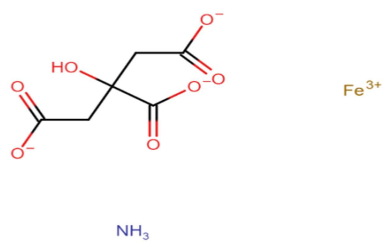


Figure (2): Chemical composition of Ferric ammonium citrate

2.1.2.2. Potassium ferricyanide.

The other component in the sensitizer formula, potassium ferricyanide, produces the blue color when mixed with ferric ammonium citrate and exposed to UV radiation.

Potassium hexacyanoferrate(III) is known by other names, the chemical formula is $K_3[Fe(CN)_6]$.

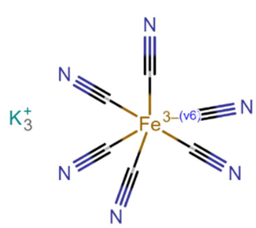


Figure (3): Chemical composition of Potassium ferricyanide

2.1.2.3. Oxalic acid

Oxalic acid has the chemical formula ($C_2H_2O_4$), and its typical form is crystalline.

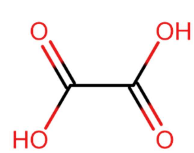


Figure (4): Chemical composition of oxalic acid

2.1.2.4. Acetic acid

The chemical Formula: $C_2H_4O_2$ or CH_3COOH.

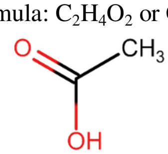


Figure (5): Chemical composition of acetic acid

All chemicals were supplied by: Scientific Company, (Al-Qudai St., Al-Barrad, Shubra Misr Street, Cairo Governorate).

2.2. Methods

The technique works on the broad , premises that iron (III) salts are photochemically reduced to iron (II) salt, which then interacts with potassium ferricyanide (red prussiate of iron) to generate a vividly blue complex. There are several easy steps in the procedure:

1. Coating fabrics or other materials with a solution of potassium ferricyanide and iron (III) salt, for example, ferric ammonium citrate. Because the coating is light sensitive, it must be applied in low light.
2. A layer of sensitive material that has developed is dried in dark place.
3. When making photograms (photograms: an image created without the use of a camera by directly coating chemicals on the surface of a light-sensitive substance, like fabrics, and exposing it to light), the dried, sensitized material is exposed to intense light (the sun or an artificial UV light source) while covered by a negative film or another partially opaque material, typically in a printing frame glass that ensures accurate printing. This is typically done in a printing frame to ensure good contact between the negative and the sensitized material.
4. Test samples are developed in parallel to obtain homogeneity during exposure.
5. To finish the synthesis of Prussian blue in light-exposed portions and dissolve any remaining combination of sensitizing compounds, the exposed material is moved to a water bath. The addition of hydrogen peroxide solution to the bath, can help in the complete development of the blue image.

2.2.1. Preparing chemicals:

a) Both compounds (Ammonium ferric citrate, Potassium ferricyanide) are dissolved using distilled water to make two separate solutions.

Formula for Cyanotype Sensitization

Solution A (ferric ammonium citrate)

- X g. of ferric ammonium citrate. X= (60, 80,100,120,140).
- 2g of oxalic acid
- add water to create a 500 ml solution overall.

Solution B (Potassium ferricyanide)

- X g. of Potassium ferricyanide. X=(20,30,40,50,60).

- 2g of oxalic acid.
- add water to create a 500 ml solution overall.

b) Both solutions are mixed in one cup and make sure that they are homogeneous together, in safe light environment to avoid interaction before treating the fabrics.

also oxalic acid concentration was varied also (Without 1, 2, 3, 4, 5 g.) to determine most suitable concentration in the two solutions, and Change the UV exposure time (5, 10, 15, 20, 25 minutes.) to determine the appropriate time for the printing process.

2.2.2. Fabrics treatment:

Before the treatment process, cotton fabrics were washed in a bath containing nonionic detergent [5 g/l] at 60 ºC for 30 minutes, rinsing in cold water and leave to dry at room temperature.

There are many methods for treatment of the fabrics with the prepared solution, including immersion in the coating solution, or by using brushes, or spraying process. To ensure uniformity, the immersion process was used in this study, in the rate of L: R 1:20 and pick up for cotton =50%, but in the case of achieving texture effects, other methods may be used.

2.2.3. Digital photo negative (print film):

By experimenting and looking to the best to using technology that facilitates and reduces the design process time. The flexibility offered by the digital image through the use of technology continues to impose contemporary designer to move away from the usual design, looking forward to what is new.

The first step is setting up the image to produce a quality digital photo negative.

A B&W 16-bit image work in 16 bit whenever possible to minimize the undesirable effects of multiple adjustment layers, Photoshop setup use is the color space in Adobe RGB [11].

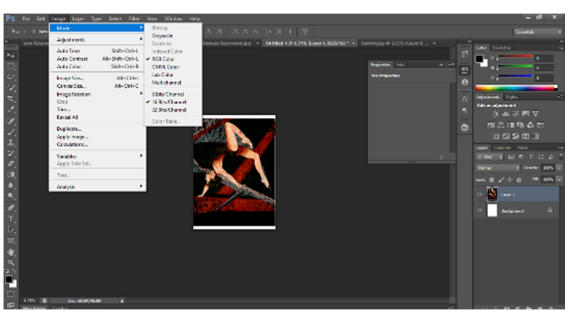


Figure (6): Image is set to 16-bit

1. Design is set to 16-bit

Use Photoshop to edit the design in a photo Photoshop: Image → Mode → 16-bits/Channel.

2. Black and White Image

In Photoshop —> Image —> Adjustments —> Black & White…

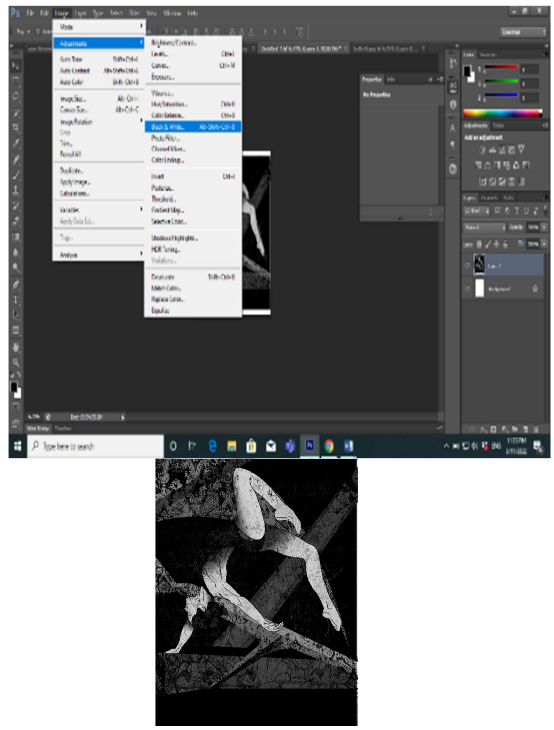


Figure (7): Black & White Image

Other methods include third party B&W conversion tools assure the image remains in the Adobe RGB color space.

3. Negative Image

Creating the Negative

You may apply the exposure correction curves directly to the image or layer upon layer[11].

a) Apply the Correction Curve

In Photoshop: Image —> Adjustments —> Curves

b) Type the curve points in by hand and then save the curve for later use.

c) Make the Negative film.

In Photoshop: Image —> Adjustments —> Invert.

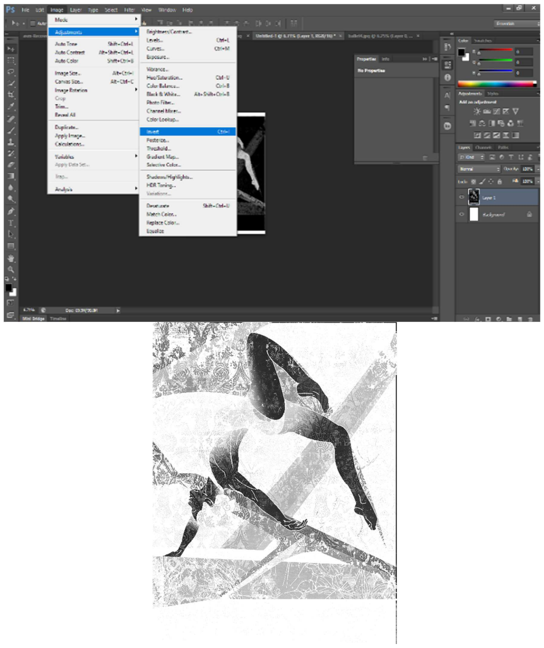


Figure (8): Make the Negative

2.2.4. Exposure

- The light source is a UV lamp exposure.
- Fluorescent lamp with UV-A radiation to around 350 nm (BLACKLIGHT350).
- Wattage: 15 Watts.
- Length: 45cm.
- Diameter: 438mm.
- Product by SYLVANIA Company in Germany

The coated samples were exposed to the UV lamp for 15 minutes.

2.2.5. Washing process and drying:

After exposure time, the fabrics is simply rinsing in water. So white print emerges on a blue background. The final print is dried at room temperature.

2.2.6. Extra Process

Acidic initial water wash both: for Blue printing purpose and to prevent yellow staining of the fabrics substrate (rust formation) from residual ferrous iron created in an alkaline environment, an initial water wash in the rate of L: R 1:20,both was applied in slightly acidic medium using 40 ml/l acetic acid to increase the degree of contrast.

2.2.7.Measurements:

2.2.7.1. Measurement of Color strength (K/S):

The color strength of printing cotton samples were measured using Spectrophotometer model – Japan- in the lab. Of measuring the quality of textile wet processes – Faculty of applied arts – Helwan University.

$$K/S = \frac{(1-R)^2}{2R}$$

The equation used to calculate the color strength. (Kubelka-Munk equation), K is the coefficient of dye absorption, (S) the dyes' diffusion coefficient, (R) the dyed or reflectance coefficient.

2.2.7.2. Measurement of Colorfastness to crocking:

The printing cotton samples were evaluated according to standard test method, AATCC 8, to determine its fastness properties to crocking, in the lab of measuring the quality of textile wet processes - Faculty of applied arts – Helwan University.

2.2.7.3. Measurement of Colorfastness to Light.

To determine colorfastness to light, the printing cotton fabrics samples were tested according to AATCC 16.3 on Xenon Arc – meter equipment in the lab of – National Research Center - Giza - Egypt.

2.2.7.4. Measurement of colorfastness to water.

The printed cotton samples were evaluated according to standard test method AATCC 107, to determine its fastness properties to water, in the lab. of measuring the quality of textile wet processes – Faculty of applied arts – Helwan University.

3.Reesults and Discussions

Previously the traditional used recipe in cyanotype process included two main compounds: ammonium ferric citrate irons (III) (ammonium irons III) and potassium ferricyanide (III) (potassium hexacyanoferrate) [13]. The citrate ions function as electron donors, and transform the ferric ions (Fe^{3+}) to ferrous ions, (Fe^{3+}) [1, 13]. iron (III) and potassium ferricyanide (III) ions are both soluble together, however iron (II) ions cause the iron atom in the complex ion to be reduced to the $^{2+}$ oxidation state. The complex iron ions in potassium ferricyanide (III), which were in the $^{3+}$ oxidation state, are changed to the $^{2+}$ state. This in turn, regenerates the free iron (III) ions, which can then interact with the newly created hexacyanoferrate (II) ions. The insoluble solid, that is produced when iron (III) ions combine with potassium ferricyanide (II) ions, is known as Prussian blue. The dark blue color is produced by transformations of electrons from the Fe^{2+} to Fe^{3+} ions, which are present in this molecule in two different oxidation states [12, 10].

In the current study, we apply the using of oxalic acid with both two solutions. Oxalic acid can be simply replaced with citric acid in the interaction instead of the citrate ion. Oxalic acid is used as an electron donor in the procedure performed in this study. Ammonium Iron(III) Oxalate can be used in place of citrate [12,13] since it is more light sensitive[14], resistant to mold, and capable of penetrating fibers more easily. Besides, the oxalic acid in this experiment assists in keeping highlights clean and bright.

Concerning the mechanism of this interaction, firstly, the iron (III) ions are reacted with the oxalate ion to convert it into iron (III) oxalate.

$Fe\,(III) + 3H_2C_2O_4 \rightarrow Fe_2\,(C_2O_4)_3$.

In the dark, the two iron salts are soluble and don't react together, both citrate and oxalate release CO2 and an electron, when exposed to UV light (undergo photo-oxidation). It is very simple to observe the bond rearrangement and electron loss in oxalate [13, 2].

$C_2O_4^{2-} + UV \rightarrow 2\,CO_2 + 2\,e^-$.

The Fe^{3+} undergoes reduction in the presence of an electron acceptor.

$Fe^{3+} + e^- \rightarrow Fe^{2+}$.

Iron (III) ammonium oxalate is ultimately changed to iron (II) ammonium oxalate. Due to the ability of oxygen to re-oxidize the iron and essentially reverse the reaction, this only causes a very tiny color shift (pale yellow-green to pale yellow-brown) [2, 13].

Despite of the fact that, light-sensitive component is ferric ammonium citrate or ferric ammonium oxalate, Ammonium Iron (III) Oxalate can be used instead of citrate. The initial "film" is made by drying a mixture of potassium ferricyanide, also known as $K_3Fe(CN)_6$, an iron compound, and the oxalate (or citrate) component. When the UV exposed "film" is washed with water during the cyanotype process, the developing and fixing steps happen almost simultaneously. This causes to various modifications:

Firstly: The iron (II), which was initially generated photochemically, is oxidized by the iron (III) in the ferricyanide:

$Fe(CN)_6^{3-} + Fe^{2+} \rightarrow Fe(CN)_6^{4-} + Fe^{3+}$.

Secondly: formation of Prussian blue

Prussian blue is an insoluble salt created when the ferrocyanide $(Fe(CN)_6)^4$ and iron(III) interact. It is a chemical molecule made up of two iron ions in opposing oxidation states:

$3\,[Fe(CN)_6]^{4-} + 4\,Fe^{3+} \rightarrow Fe(III)_4[Fe(II)(CN)_6]_3$

Prussian blue

The presence of iron in the two oxidation states, gives the substrate its deep blue hue. The substance (Prussian blue) stays entrapped in the fabrics substrate because it is water insoluble, this may be due to that ions were immobile in the solid form, so this reaction could not take place.

The above two equations can be reduced to this equation [1, 13]

$Fe^{2+} + K_3(Fe^{III}(CN)_6) \rightarrow K(Fe^{II}Fe^{III}(CN)_6) + 2K^+$

To determine the factors affecting the efficiency of the reactions occurred in blue printing technique, the used chemicals concentrations and the exposure times to light were studied in details.

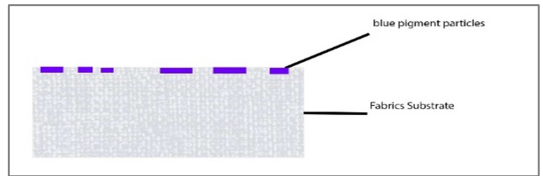


Figure (1): Cross section of a typical Blue printing photograph

3.1 Effect **of Ferric ammonium citrate concentration on K/S of treated samples:**

To study the effect of different concentrations of used chemicals in preparing the solution of padding, only ferric ammonium citrate concentrations were changed (60,80,100,120,140 g) , and potassium ferricyanide concentration was constant (40 g) , In addition to using the amount of 2 g oxalic acid, at both solutions.

From fig. (9) and table (1), it was observed that by increasing in ferric ammonium citrate concentration in the solution, the color intensity of the printings starts to increase in a direct correlation. and reached its maximum by using (100 g), until reached (120 g) hence, the color strength started to decrease and, "bleeding" began to appear in the printed shadow parts [2].

3.2 Effect of Potassium ferricyanide concentration on K/S of treated samples.

To evaluate the effect of Potassium ferricyanide concentration, different concentrations were used to prepare the padding solution (20, 30, 40, 50, 60 g), and ferric ammonium citrate concentration was constant (100 g) which selected from fig. (1) In addition to using the amount of 2 g oxalic acid, at both solutions.

Table (1)
Effect of Ferric ammonium citrate concentration on K/S of treated samples

Potassium ferricyanide/Ferric ammonium citrate.	Concentration 1	Concentration 2	Concentration 3	Concentration 4	Concentration 5
	40/60g.	40/80g.	40/100g.	40/120g.	40/140g.
K/S	15.32	17.09	21.26	16.33	20.01

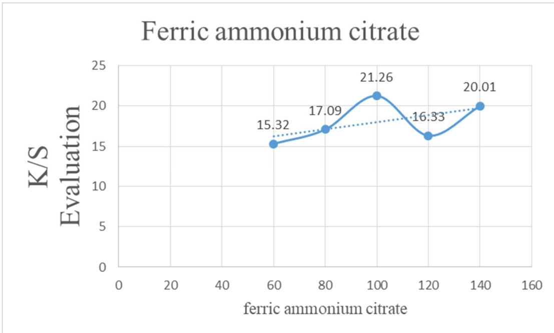


Figure (9): Effect of Ferric ammonium citrate concentration on K/S of treated samples

From fig. (10) and table (2) it was observed that color strength of padded fabrics slightly increased [2] and reached its maximum when using 40 g. of Potassium ferricyanide. So 40 g /l will be the best concentration to be used.

3.3Effect of oxalic acid concentration on K/S of treated samples:

To study the effect of oxalic acid used in preparing the padding solution, different concentrations were used (1, 2, 3, 4, 5 g) in both solutions and the concentrations of both ferric ammonium citrate and potassium ferricyanide were constant (100 g) and (40 g) respectively. These concentrations are determined from the previous results in table (1 & 2).

From fig (11) and table (3) it was observed that, without using oxalic acid in the padding solution, the least color strength (20.46) was obtained, by increasing the concentration of oxalic acid, it will change the intensity of the blue color and change the values of whiteness in the cyanotype patterns, keeping the print bright and highlighted, and increasing color strength of padding samples to (27.13) and more, which resembled about 25% increasing. This may be due the high sensitivity of oxalic acide to light. Also the samples ability to absorption increased [13], when compared with the samples which not containing oxalic acid in padding bath.

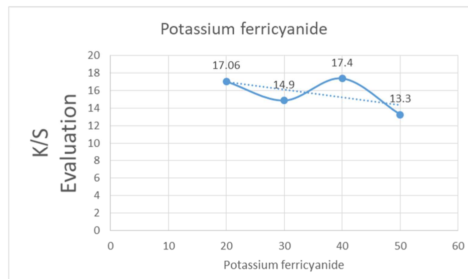


Figure (10): Effect of Potassium ferricyanide concentration on K/S of treated samples

Table (2)
Effect of Potassium ferricyanide concentration on K/S of treated samples

Ferric ammonium citrate/Potassium ferricyanide.	Concentration 1	Concentration 2	Concentration 3	Concentration 4	Concentration 5
	100/20g	100/30g	100/40g	100/50g	100/60g
K/S	17.06	14.9	17.4	13.3	16.1

Table (3)
Effect of oxalic acid different concentrations on K/S of treated samples

Oxalic Acid concentration	Concentration 1	Concentration 2	Concentration 3	Concentration 4	Concentrati on 5	Concentration 6
	Without	1g.	2 g.	3 g.	4 g.	5 g.
K/S	20.46	27.13	25.45	27.47	25.28	24.59

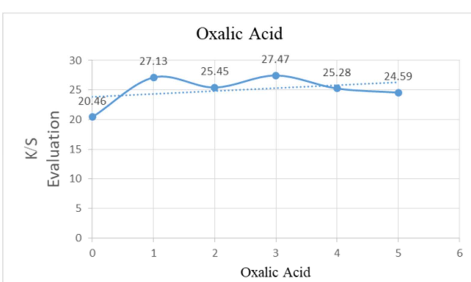


Figure (11): Effect of oxalic acid concentration on K/S of treated samples

3.3.1.4 Effect of exposure time on K/S of samples:

Exposure time to a UV source is an important factor in obtaining homogeneous and stable blue hues. To study the effect of exposure time, different intervals of time were used (5, 10, 15, 20, 25 minutes) after padding and drying samples using of (100 g) ferric ammonium citrate, (20 g) potassium ferricyanide and (3 g) oxalic acid, The time was stopped at 25 minutes to avoid the fading effect of the prints by increasing the exposure time on the fabrics.

From fig. (12) and table (4) it was observed that there is a direct correlation between color fastness (K/S) and exposure time. By increasing the exposure time, the color intensity increases. This result belongs to the beginning of converting iron from its triple state [Fe(III) to the Fe(II)] state, and the formation of Prussian blue on the fabrics[9,18].

Table (4)
Effect of different exposure time on K/S of samples

Time Exposure	Time Exposure 1	Time Exposure 2	Time Exposure 3	Time Exposure 4	Time Exposure 5
	5 minutes	10 minutes	15 minutes	20 minutes	25 minutes
K/S	14.34	16.96	17.6	19.04	20.35

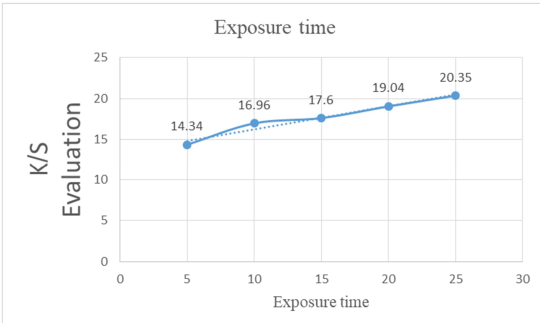


Figure (12): Effect of different exposure time on K/S of samples

3.4 Effect of Acetic acid concentration on K/S of treated samples:

After exposure time, the addition of acetic acid to the wash bath, will intensify the darker shade of blue tones and widen the visible tonal range, also tones in the blue cyanotype will become softer. To study the effect of different concentrations of acetic acid, different concentrations (10, 20, 30, 40, 50 ml) were used in the final washing bath. Constant concentrations (100 g), (20 g) and (3 g) were used of ferric ammonium citrate, potassium ferricyanide and oxalic acid respectively. And the exposure time was (25) minutes. From fig. (13) and table (5) it was observed that there is a direct increasing of K/S of samples accomplished with the increasing of acetic acid conc. Until reach (30 ml), the curve will begin to decline in an inverse relationship with the increase in the concentration of the acid [14, 15].

Table (5)
Effect of Acetic acid different concentrations on K/S of samples

Acetic Acid concentrations	Concentration 1	Concentration 2	Concentration 3	Concentration 4	Concentration 5
	10 ml.	20 ml.	30 ml.	40 ml.	50 ml.
K/S	19.14	21.69	24	22.52	21.86

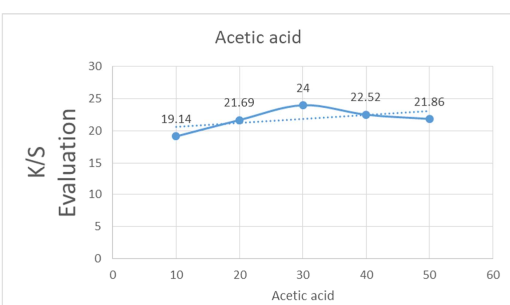


Figure (13): Effect of Acetic acid different concentration on K/S of treaded samples

Finally, we can conclude the optimum recipe for the used concentration of chemicals and exposure time which are:

Ferric ammonium citrate (100g).
Potassium ferricyanide (20g).
Oxalic acid (3g).
Exposure time (25min).
Acetic acid (30 ml).

Also the addition of oxalic acid (3 g) in both solutions, led to an improvement in color strength of the padded samples to 40% approximately.

Figure (14) has shown the overall result of color fastness to crocking (dry and wet), fastness for water, light. Result depicts that, dry crocking is better than wet rubbing, The stability degrees of water also show levels in the case of staining 4-5, while the change in color was given a medium degree = 3, The results also showed poor light fastness.

Color fastness properties with cotton fabrics with cyanotype treated

Crocking fastness		Colorfastness to water		Light fastness
Dry	Wet	Stained	Alteration	(AATCC 16).
4	1-2	4-5	3	3

Figure (14): Color fastness properties

Application of blue print technique on some innovative designs for hanging textiles:

Priented design No. 1 Figure (15)

Dimensions of the applied design	50*70cm
Source:	Museum of Tomorrow, Rio de Janeiro, Brazil.
units and element used:	The design relied on lines and density to show the color gradations as one of the elements of the design foundations
function purpose:	Hanging
Execution method:	Blue Printing (cyanotype).
material type	Cotton

Priented design No. 2 Figure (15)

Dimensions of the applied design	50*70cm
Source:	Kuwait Pavilion.
units and element used:	Architectural units were mainly used in the design, with the addition of color effects
function purpose:	Hanging
Execution method:	Blue Printing (cyanotype).
material type	Cotton.

Priented design No. 3 Figure (15)

Dimensions of the applied design	50*70cm
Source:	Museum of Tomorrow, Rio de Janeiro, Brazil.

units and element used:	The design relied on lines and density to show the color gradations as one of the elements of the design foundations
function purpose:	Hanging
Execution method:	Blue Printing (cyanotype).
material type	Cotton.

Priented design No. 4 Figure (15)

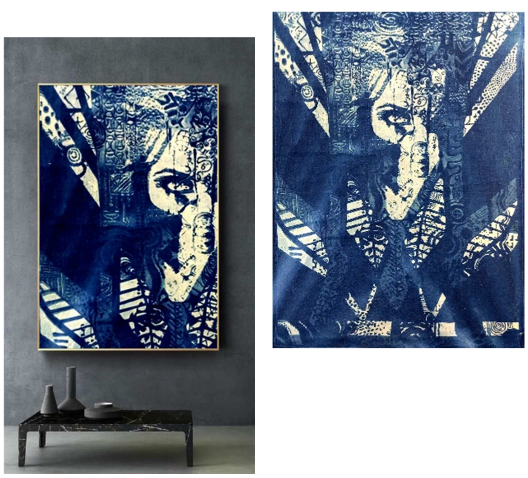
Dimensions of the application design	50*70cm
Source:	Tenerife opera
units and element used:	Human units, plant motifs, and evocative textures were used
function purpose:	Hanging
Execution method:	Blue Printing (cyanotype).
material type	Cotton.

Priented design No. 5 Figure (15)

Dimensions of the application design :	50*70cm
Source:	Milwaukee Art Museum
units and element used:	Human units, plant motifs, and evocative textures were used
function purpose:	Hanging
Execution method:	Blue Printing (cyanotype).
material type	Cotton.

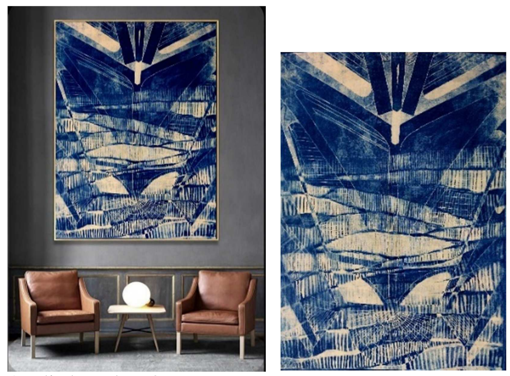
Priented design No. 6 Figure (15)

Dimensions of the application design	50*70cm
Source:	Oceanogràfic Valencia
units and element used:	The architectural units were used represented in the main building with the repetition of some of its parts mixed with elegant patterns of interlocking lines to give more movement.
function purpose:	Hanging
Execution method:	Blue Printing (cyanotype).
material type	Cotton.

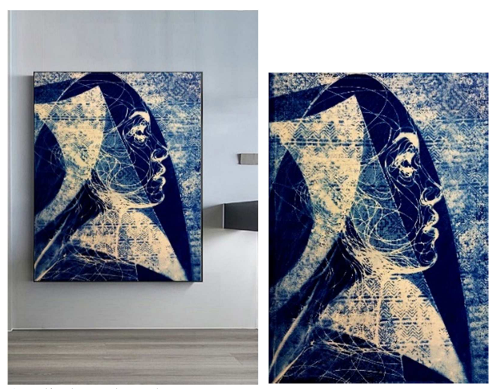


Applied Product 1

Applied Product 2

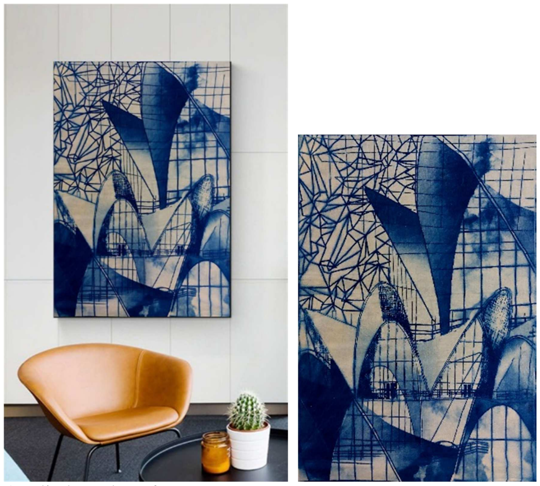


Applied Product 3



Applied Product 4

Applied Product 5



Applied Product 6

Figure (15): Applied Hangings products using cyanotype technique

Conclusion

This study aimed to apply and develop one of the photographic techniques (cyanotype) as non-traditional alternative to textile hand printing techniques, as an experimental approach for hanging textiles. The optimum recipe of immersing bath and exposure time was reached and applied on some innovated designs, created by the researcher and inspired from bio -architecture.

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