Dyeing of Nylon 6 Fibres with Natural Dyes

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“Abstract“

Extraction and application of natural dyes for dyeing polyamide fibre, i.e. nylon 6, were studied in details. Two different natural dyes from vegetable sources were selected for this study, namely: Calendula and Casuarina.

Optimization of dyeing processes was carried out in detail. The amount of natural dyes that exhausted and fixed on the fibre was found to depend on the application conditions. By lowering the pH level of the dye bath the quantity of absorbed dye was found to increase. The optimum pH levels for attaining maximum colour strengths were at pH = 4 and 3 for Casuarina and Calendula respectively. Addition of electrolyte (NaCl) resulted in some decrease in the colour strength owing to its retarding action on the rate of dye absorption. The rate and degree of dye fixation on the nylon was found to increase greatly by raising dyeing temp. up to boiling.

Natural mordants that extracted from some plants were used for post-mordanting the dyed materials since reliable fastness properties were realized.

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Introduction

During the last half of the nineteenth century, synthetic dyes became available because of their wider ranges of bright shades with considerably improved colour fastness properties compared with natural dyes. But in recent years, concern for the environment has created an increasing interest in natural dyes, which are more friendly to the environment than synthetic dyes\(^{(1)}\).

Nearly, all natural dyes, with few exceptions, require the use of mordants such as copper and chrome salts, which cause a serious effluent problem.

On the other hand, the low colour value, long dyeing time and a large quantity of colouring raw materials push the cost of dyeing with natural dyes to be higher than synthetic dyes. The fastness performance is generally not adequate for modern textile.

Natural dyes have many advantages such as lower toxicity and allergic reaction in relation to synthetic dyes.

Dyes from vegetable sources are interesting because of:

1. The colours are very brilliant
2. The toxicity of the dyes is very low

Natural dyes can be divided into two groups:

1. Substantive or non-mordant dyes which produce a fast colour just by boiling without any additives or chemicals and having satisfactory fastness properties\(^{(2,3)}\).

2. Adjective or mordant dyes which require addition of metallic salts to fix the colour on the fibre. These dyes react chemically with the metal to form an insoluble
complex compounds inside the fibre\(^{(1,4)}\). Most of natural dyes are mordant dyes. Some of them are soluble in water and able to dye the more hydrophilic fibres such as cellulose and proteins while some others are water-insoluble with high affinity to hydrophobic or synthetic fibres. The dyer must select the type of dye and method of dyeing to suit specific requirements\(^{(5)}\).

Therefore, a lot of studies have been carried out using natural dyes\(^{(6-10)}\).

Application of vegetable dyes for dyeing different substrates such as cotton\(^{(11)}\), wool\(^{(12-14)}\), silk\(^{(15-16)}\), nylon\(^{(17)}\), and polyester\(^{(18)}\) were investigated to optimize their dyeing conditions.

The present study is a serious trial to optimize the dyeing of nylon 6 with some selected vegetable dyes and to determine the availability of using some natural mordants extracted from vegetable sources.

**Experimental**

1- **Materials:**

Fabric: 100% nylon 6 woven fabric (120 g/m\(^2\)) from Middle East Co. for Textile Industry, Cairo, Egypt was used throughout the present work.

Dyes: The used natural dyes were extracted from uqhuwan (Calendula - officinalis) and Casuarina (Casuarina cunnin – ghamiana).
Mordants: Two natural mordants were obtained from Ward El-Nile (Eichhornia – crassipes), and Khiar shambar (cassia fistula).

Chemicals: Formic acid and sodium carbonate of laboratory grade were used for adjusting the pH of the dye bath.

Hostapal CV-ET (Hoechst), a nonionic detergent for soaping bath. Powdered active charcoal for decolourization the natural mordant.

2-Procedures and Measurements:

2.1. Extraction of Dyes

Calendula:
By soaking 10 g dry plant material in 50 ml water for 12 hr., after which the extract was filtered and completed to 100 ml solution with water.

Casuarina:
By boiling with water (10 g plant material for 100 ml water) for one hr. with 5g/l sodium carbonate. After filtration the extract was completed to 100 ml with water.

2.2. Extraction of Natural Mordants:
The plant materials were soaked in water for 24 hr after which they were boiled for 30 min. The extracts were then, filtered and decolourized using active charcoal to get transparent and clear solutions.

2.3. Dyeing Process:
Nylon samples were introduced into the dyebath containing 60 ml extract/100 ml water at about 50º C. The temperature was gradually raised to the boil and dyeing was carried out
for 60 min. at liquor ratio 1:100. The pH was adjusted at the required value by adding dilute solutions of either formic acid or sodium carbonate. At the end of the dyeing process the dyed samples were removed, rinsed, soaped and rinsed with hot and cold water.

2.4. Mordanting Method:

The dyed nylon fabrics were mordanted in aqueous bath containing the suitable amount of natural mordant and at liquor ratio 1:100. The mordanting process was started at 50º C and the temp. was then fixed for another 40 min. Nylon samples were, then, rinsed and soaped with 2 g/l Hostapal CV-ET for 15 min at 70º C.

2.5. Determination of Minerals:

Total content of Ca, Cu, Fe, Cr, Sn, Zn, Ni and Co were determined in the digested solutions of natural mordants using inductively coupled plasma (400) emission spectrometry (Perkin elemer Emission Spectrometer).

2.6. Measurement of Colour Strength:

The colour strength (expressed as K/S) of the dyed nylon samples was evaluated by reflectance measurements ICS-TEXICON Computerized Spectrophotometer, Model M 520220 (produced by ICS-TEXICON Limited Co., England) Colour strength of the dyed samples are expressed as K/S values. They were calculated from the Kubelka – Munk equation,

\[ K/S = (1-R)^2/2R, \]

in which K and S are the absorption and scattering coefficients, respectively, and R is the reflectance of the dyed fabrics.
2.7. Measurement of Colour Fastness:

Colour fastness to, rubbing, perspiration and light were determined according to AATCC test Methods: (8-1972), (15-1973) and (16A-1971) respectively. Colour fastness to washing was determined according to Test 2 of India Standards (IS) 336/1979

Results & Discussion

Dyeing Polyamide Fabrics with Natural Dyes:

1. Effect of pH of Dyeing on Colour Strength:

Different polyamide samples were dyed in various dyebaths under constant dyeing conditions i.e. conc. of extract, temp., and time whereas the pH level was varied from one bath to another. The colour strengths of the dyed samples were measured and the received data are plotted in Figure 1.

It is well observed, from Fig.1, that pH of dyeing plays a great role in determining the amount of colouring matter that may be absorbed and fixed on nylon fibres. Increasing the acidity of the dyebath is accompanied with higher dyeability of nylon fabric towards natural dyes.

Maximum colour yield is realized on polyamide fibres when dyeing process is carried out at lower pH level (3-3.5) for both of the used dyes. For Calendula the optimum pH value was found to be at pH=3 and for Casuarina at pH=3.5. The high colour yield is realized when dyeing is carried out from strong acidic medium which may be attributed to the electrostatic attraction between the positively charged polyamide fibres
and the anions of the colouring matters. The degree of protonation of polyamide is well known to increase by lowering the pH level of the aqueous medium.

Therefore, it may be concluded that the dyeing mechanism with natural dyes is similar to great extent to its mechanism with acid dyes.

Therefore, the amount of absorbed natural dye will be depended on the degree of ionization of the fibre or in other words will be related to the pH of the dyebath.

**Action of Electrolytes:**

Neutral electrolytes such as common salt (sodium chloride) play an important role in the dyeing operation especially that of ionic dyeing system. The role played by electrolytes differs from one system to another according to the nature of both fibre and dye itself. Electrolytes are used as exhausting agent in case of dyeing cellulosic materials with anionic dyes owing to the similarity of charges on both fibres and dyes. In case of protein fibres and polyamide the electrolytes are considered as leveling agents owing to the unsimilarity of charges on both fibres and dyes.

It is well noticed, from Figure 2, that addition of sod. chloride resulted in some decrease in the colour strength of the two applied dyes. This result is in good agreement with the effect of pH on the colour strength of the dyed polyamide samples.

Polyamides contain a limited number of amino groups at the end of the polymer chains. These amino groups are the available dye sites in the fibre through which the dye anions are attracted to form salt links. Addition of sod. chloride into the dyebath means addition of sodium and chloride ions. Therefore, as a result of the presence of more than one kind
of anions in the same dyebath a competition for the positively charged sites in the fibre will be occurred since one anion being capable of replacing another according to the following equation:

$$\text{Ny-N}^+\text{H}_3\text{Cl}^- + \text{D}^- \rightleftharpoons \text{Ny-N}^+\text{H}_3\text{D}^- + \text{Cl}^-$$

This reaction mechanism is reversible and a dynamic equilibrium is attained. Therefore the final distribution of the dye and inorganic anions will depend upon their relative concentrations. Thus by increasing the relative concentration of chloride anions in the dyebath the reaction mechanism will be shifted towards the replacement of dye anions by chloride anions.

On the other hand, it may be noted also that the equilibrium position of the displacement reaction is governed not only by the relative conc. of the two competing ions but also by their relative affinities for the fibre.

**Effect of Dyeing Temperature:**

It is obvious, from Figure 3 that the rate of dyeing increases gradually by raising the temperature. Maximum dye fixation is achieved at boiling for both Calendula and Casuarina and the rate of dyeing depends to great extent on the nature of both dye molecules and the fibre itself. The rate of dyeing of the colouring matter that extracted from Calendula is higher than that of Casuarina. The magnitude of increase in colour strength is found to be greater in case of Casuarina than that of Calendula under the action of temperature.
By raising the dyeing temp. from 23º C to 40º C the percent increase in K/S is found to be (88 %) for Calendula while it is reached to (124 %) for Casuarina. When the temp. is elevated from 80º C to 100º C, the percent increase in K/S is observed to be about (4.8 %) and (130 %) for Calendula and Casuarina respectively.

It may be suggested that the colouring matters of Casuarina present in the aqueous medium in aggregated form since they need a high temp. to diffuse inside the polymer chains of polyamide. One can notice the great difference in K/S when dyeing is carried out at room temp. (23º C) and at boiling for the two dyes.

It may be concluded from the previous results that Casuarina is more temp.-dependence for attaining maximum K/S than Calendula. High temp., on the other hand, open up the fibre structure and increase the number and volume of voids and thus accelerates the diffusion of dye molecules inside the fibre.

Effect of Dyeing Time:

Dyeing of polyamide samples were carried out for (15, 30, 45, 60, and 90) min. under fixed dyeing conditions i.e. 60 % extract, pH=3, and at boiling. Figure 4 illustrates the effect of dyeing time on the K/S, from which it can be observed that by lasting time of dyeing the K/S is increased for both Calendula and Casuarina. Optimum dyeing time is found to be 60 min. for Calendula and 90 min. for Casuarina.

The colouring matter of Casuarina need longer dyeing time than of Calendula, which may be attributed to its greater molecular size as previously suggested.

Post Mordanting:
Since the aim of the application of natural dyes for dyeing polyamide fibres is to minimize the pollution of environment by using eco-friendly materials therefore mordanting with some harmful and carcinogenic metal salts such as copper sulphate will be of nonsense. Therefore, our new trend is to use some mordants that extracted from suitable plants, such as, Ward El Nile (WN) and Khiar Shambar (KSh). A detailed study was carried out in order to determine and optimize the application conditions of these mordants.

The extraction process was carried out in a similar manner to that of extracting the colouring matters from plants. The received extracts were decolourized by treatment with active charcoal.

Each one of these extracts was subjected to chemical analysis to determine its content of various metals and their concentrations (Table 1). The presence of miscellaneous metals in the extracts may play a great role in determining the efficiency of metal complexing reaction with the colouring matters inside the fibre. The received colour hue as well as the degree of colour fastness properties will depend to great extent on the kind and conc. of the metals.

Effect of pH of Mordanting:

Nylon fabrics previously dyed with Calendula and Casuarina dyes were mordanted at various levels of pH to determine their effect on the K/S and the results are illustrated in Table 2, from which it may be concluded that:

1. The optimum pH values at which maximum dye fixation were attained in case of using (WN) were found to be at pH=5 for Calendula and at pH=8 for Casuarina.
2. The most suitable pH levels available for attaining maximum K/S when using (KSh) as mordant were found to be at pH=4 and 8 for Calendula and Casuarina respectively. Referring to the dyeing properties of the two applied natural dyes, it can be noticed that Calendula dye is very sensitive to the variation of pH value of the dyebath. Maximum absorption capacity was achieved at pH=3. Increasing the pH value from 3 to 8 was accompanied with noticeable decrease in the K/S. This behaviour may give a good idea about the affinity of the dye toward nylon fibres. It may be concluded that the dye of Calendula has a lower affinity compared with that of Casuarina. Therefore, during the mordanting process the pH of the medium will affect the absorption/desorption equilibrium between the fibre and the treatment bath. In the case of dye of low affinity the amount of desorbed dye, i.e. migration of dye from fibre to the bath, will depend greatly on the pH. Mordanting at pH higher than 7 will accelerate the desorption of the dye as in the case of Calendula. Therefore, the optimum pH value for mordanting polyamide fibres dyed with Calendula will be at pH=5 for the two natural mordants. For fibres dyed with Casuarina the most suitable pH for mordanting with (WN) and (KSh) is at pH=8.

Effect of Mordanting Temperature:

Post mordanting of dyed nylon samples were carried out, using a fixed amount of natural mordants, at different degrees of temp. and the results of K/S are illustrated in table 3.
It may be concluded, from table 3, that the optimum temps. for mordanting were found to be at 40º and 80ºC for Calendula and Casuarina dyes respectively in case of Ward El Nile mordant. For Khiar Shamber the most effective temp. was found to be at 100ºC for the natural dyes.

These results are in good agreement with the conclusion about the affinity of the used natural dyes toward nylon fibre and its relation to the adsorption / desorption mechanism.

**Effect of Mordanting Times:**

The rate of mordanting reaction may depend on some various factors:

1. The rate of absorption of the mordant by the fiber.
2. The kind of the mordant itself.
3. The chemical structure of the colour species and their rate of reaction with the mordant to form the metal complex compounds.

For these reasons the duration of mordanting differs from one mordant to another.

Therefore the mordanting time of eco-friendly mordants were studied in order to determine their optimum time.

The dyed polyamide samples were after treated for different durations using fixed amount of mordants and the mordanting process was carried out at pH=6 and 8 for Calendula and Casuarina respectively.

Table 4 indicates the results of K/S as a function of mordating duration.
It may be concluded, from table 4, that the optimum mordanting time with Ward El Nile mordant reaches about 90 min. for both Calendula and Casuarina dyes. Similar results are realized with Khiar Shamber mordant since the most suitable time for mordanting reaches about 60 min. for the two dyes.

**Colour Fastness Properties:**

Nylon fabrics dyed with Calendula and Casuarina natural dyes and mordanted with the two natural mordants were subjected to fastness tests to washing, perspiration, rubbing and light.

Three different metal salts were also used as mordants for comparing the efficiency of mordanting of both types of mordants.

The results of these tests are tabulated in table 5 from which it may be concluded that:

1. **Light fastness:**
   
   Using the grey scale assesses it is evident that the fastness of nylon fabric dyed with Casuarina is higher than that of Calendula.

   It is obvious from the table that the mordanting process either by metal salts or by natural mordants does not affect the light fastness since it reaches (2-3) and (3) for Calendula and Casuarina respectively.

2. **Wash Fastness:**
Unmordanted nylon fabric exhibits very good to excellent (4-5) for Calendula dye whereas it exhibits fair (3) in case of Casuarina dye.

Natural mordants is found to increase the wash fastness especially in case of Casuarina since it reaches (4) grade with Ward El Nile and (3-4) grade with Khiar Shambar mordants.

Similar results were achieved when using metal salts as mordants.

3. Perspiration fastness:

The fastness to acid perspiration (alt.) exhibits fair to good (3-4) for unmordanted nylon fabric in case of Casuarina and from good to excellent in case of Calendula dyes.

For Casuarina the fastness rating is increased as a result of mordanting since it reaches (4-5) with (WN) and (4) with (KSh). Similar results are attained with the different applied metal salts.

The fastness properties to alkaline perspiration are found to improve especially in case of Casuarina by mordanting with (WN) and (KSh). The rating is increased from (3) for the unmordanted dyed fabric to (4) and (3-4) with (WN) and (KSh) respectively. Similar results are observed when mordanting process is carried out with the used metal salts.

4. Rubbing Fastness:

For Calendula no appreciable alteration was observed as a result of mordanting either with natural mordants or with metal salts. For Casuarina slight variation in both wet and dry rubbing fastness was observed in case of using natural mordants.
Conclusion
1-Nylon fabric was successfully dyed with natural dyes, namely: Calendula and Casuarina, and the dyeing conditions were optimized.
2-The behaviour of natural dyes during the dyeing of nylon fabric was found to similar to that of acid dyes.
3-The rate of dyeing was found to increase as the temp. Increase till reached its maximum at boiling for the two applied natural dyes.
4-Temp. break down the aggregate of dyes and increases their solubility as well as opening up the fibre structure and thus accelerates the diffusion of dye molecules inside the fibre.
5-The pH of dyeing was found to play a great role since maximum colour strength was achieved at strong acidic medium which may be attributed to the high electrostatic attraction between positively charged basic groups in the nylon fibre and the dye anions.
6-Eco-friendly natural mordants that extracted from Ward El Nile and Khiar Shamber were used instead of the metal salts since satisfactory fastness properties were realized.

References
11. A.Abdel Keriem; Master Thesis; Textile Printing, Dyeing and Finishing Department, Faculty of Applied Arts, Helwan University, Egypt, 1997.
14. H.S.El Khatib; Ph.D. Thesis; Textile Printing, Dyeing and Finishing Department, Faculty of Applied Arts, Helwan University, Egypt, 2002.
Table 1: Different Metals and their Conc. in the Aqueous Extracts of the Different Plants

<table>
<thead>
<tr>
<th>Plants</th>
<th>Metal Exist in the Extracts (ppm)</th>
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<tbody>
<tr>
<td></td>
<td>Cr</td>
</tr>
<tr>
<td>Ward El Nile</td>
<td>0.043</td>
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<tr>
<td>Khiar Shambar</td>
<td>0.066</td>
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</table>

Table 2: Effect of pH of Mordanting on K/S of Nylon Fibre Dyed with Natural Dyes

<table>
<thead>
<tr>
<th>pH of Mord.</th>
<th>K/S of dyed Nylon</th>
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<tbody>
<tr>
<td></td>
<td>Calendula</td>
<td>Casuarina</td>
<td></td>
</tr>
<tr>
<td></td>
<td>WN</td>
<td>KSh</td>
<td>WN</td>
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<tr>
<td>4</td>
<td>15.22</td>
<td>12.03</td>
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<tr>
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<td>12.98</td>
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<tr>
<td>Temp (°C)</td>
<td>K/S of dyed Nylon fibre</td>
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<tr>
<td></td>
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<td>Calendula</td>
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<td>WN</td>
<td>KSh</td>
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<td>100</td>
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Table 4: Effect of Mordanting Time on K/S of Nylon Fibre Dyed with Natural Dyes

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Table 5: Colour Fastness of the Dyed Nylon Fabrics

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<th>Plant</th>
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<th>Perspiration</th>
<th>Rubbing</th>
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<td>5</td>
<td>4-5</td>
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</tbody>
</table>

Ny. = Nylon  W. = Wool  Alt. = Alteration
Dyeing of Nylon 6 Fibers with Natural Dyes

Figure 1: Action of Dyebath pH on the Dyeability of Polyamide Fabrics towards Natural Dyes

temp. 100 °C, time 60 min. L.R. 1:100
Fig. 2: Influence of Sodium Chloride on the Colour Strength of the Dyed Polyamide Fabrics.

temp. 100 °C, pH=3, time 60 min. L.R. 1:100
Fig. 3: Influence of Dyeing Temp. on the Colour Strength of the Dyed Polyamide Fabrics. pH=3, time 60 min. L.R. 1:100
Fig. 4: Effect of Dyeing Time on the Colour Strength of the Dyed Polyamide Fabrics.
temp. 100 °C, pH=3, L.R. 1:100