COMPAGNIE FRANÇAISE DES EXTRAITS
MAISON WESTPHALEN

LE HAVRE, LE

S U M M A R Y

.../...

S U M M A R Y (Cont'd)

* * * * * *

N A T U R A L C O L O U R I N G M A T T E R S . . .

AND THEIR APPLICATION IN THE DYE FIELD

BY JEAN JACQUES RODIER,
CHIEF CHEMIST,
COMPAGNIE FRANCAISE DES EXTRAITS,
MAISON WESTPHALEN,
LE HAVRE, FRANCE

* * * * * *

In spite of the considerable development taken by the industry of synthetic colouring matters in all parts of the world, some natural colo ing dyestuffs, although in a reduced number, are still being widely used within the various fields of industry.

Natural colouring matters will be obtained mainly from the vegetab kingdom, only a few, rare specimens originating from the animal kingdom.

Among the vegetable colouring substances extracted from wood, the main one is the LOGWOOD EXTRACT.

Logwood Extract is obtained from a tree of the leguminous family, named Haematoxylon Campechianum. This extract contains a leuco-derivati designated as Haematoxylin.

Haematoxylin, through humid airblowing oxydation or chemical oxyda will be transformed into Haematein, whereby losing two hydrogen atoms:

HAEMATOXYLIN	HAEMATEIN
C 16 H 14 06	C 16 H12 06 + 2 H

This Haematein happens to be the colouring principle of Logwood. Thus, and depending on the intended application, non-oxidized, moderatel oxidized and oxidized extracts will be industrially supplied.

Haematein in solution gives a deep red colouration with strong min acids. Thus, the test may easily be carried out for identification of Hematine dyed materials.

LOGWOOD EXTRACT is a colouring matter requiring the use of a morda It has therefore a limited affinity for textile fibers. Its use as a dy will depend on the property offered by Haematein to form complexes with metals.

The shade, deepness, fastness of the dye will depend on the type o metallic salt used as a mordant.

.../...

There follows an indication of the shades obtained with the most usual metals :

Chrome	. . . . .	Blue to Black
Iron	. . . . .	Blue to Black
Copper	. . . . .	Blue
Aluminium	. . . . .	Blue-Violet

Nowadays, wool materials will be entirely dyed on a chrome mordant and silk materials on an iron mordant, chromed skins requiring iron or iron/copper mordanting, and Persianer iron/copper mordanting equally. For nylon and acetate materials, a chrome mordant will be used.

It should be noted that chrome and iron are being used as mordants for numerous applications, such as wool dyeing, metal bronwing, vegetable fibre dyeing, and so on.

Oxydation Degrees

Hematines will be manufactured with various oxydation degrees, so as to meet the requirements of a range of quite special dye processes. This oxydation degree corresponds to the percentage of total colouring matter which was oxydized to become Haematein.

Example : An Haematein 80 percent oxydized signifies that, for a total dye value as contained in the extract, 80 percent Haematein and 20 percent Haematoxylin are present. Tanning and glucosides are also present in Logwo Extract.

There are various Hematine Grades available for commercialization, -
with 15 percent oxydation: HEMATINE MEX-NOK
HEMATINE MEX-NOSK

with 60 percent oxydation: HEMATINE MEX-CFHK

with 80 percent oxydation: HEMATINE MEX-HCK

The oxydation degree will be chosen according to the type of dye to b carried out. The choice of the oxydation degree of a given Hematine will b linked to the choice of a mordant. A type of mordant with oxydizing properties will have to be used with HEMATINE MEX-NOK or NOSK, whereas HEMATINE MEX-HCK will require the use of a mordant with no oxydizing properties. These various grades of Hematines find their application in dyeing and printing operations involving various materials such as wool, silk (whether filled or not), rayon, acetate, nylon, chromed leather, hair, Mexican fibre, jute, furs, buttons of all kinds, wood, paper, straw. Beside, such Hematines may be used for the preparation of inks and pigments Finally, pure Haematoxylin finds its application in the Histology field (for microscopy staining and to serve as an analytical reagent, for colorim determination of aluminium).

.../...

I - APPLICATION OF VEGETABLE TINCTORIAL EXTRACTS IN THE TEXTILE FIELD

A - WOOL DYEING

Logwood Blacks are known as being the most beautiful and the deepest ones that may be obtained on wool. Haematein is the dye principle which, in combination with metallic salts, forms a lacquer solidly fixed on wool and able to resist the most severe drum test.

Fastness to Light

Rigorous comparative tests resulted in the following ratings:

(1) Logwood Black on Chrome Mordant 5

(2) Logwood Black on Iron/Copper Mordant 6

Precautions

In order to carry out a satisfactory dyeing, it is advisable to take some precautions, such as :

- Using a water as soft as can be, so as to avoid insoluble combinati with Haematein

- Degreasing wool material before dyeing

A.1. Wool in Rolls

Dyeing is to be carried out in two baths - % wool -

Liquor ratio = 1/30 (or, 3,000 liters bath for 100 kilos wool)

Mordanting

Sodium Bichromate	1.7 %
Lactic Acid 50 %	2.0 %
Copper Sulphate	0.4 %
Formic Acid 80 %	2.0 %

The wool pieces will be entered into the bath at 60° C. The temperature will then be raised to 100° C and maintained until the liquor appears colourless, with wool turning from yellow to a greenish brown.

Duration : between 45 and 60 minutes

A progressive rinse is required to avoid creasing

.../...

Dyeing

Hematine MEX-HCK = 6 to 9 %, according to wool fineness.

The colouring matter, priorily dissolved in ten times its weigh of water at 80° C, will be introduced into the bath at 40° C. The temperature will be raised directly to 100° C and maintained for 45 minutes.

The rinse with cold water will be progressive.

A.2. Wool Thread and Combed Wool

Liquor ratio = 1/10 - 100 kilos wool for 1,000 liters bath

The dye process is identical to that previously described but, at the time of introducing the dyestuff into the bath, an homogeneisa of said bath will be necessary, with circulation being allowed throug the material for ten minutes.

Comments :

When using an autoclave, which permits dyeing at temperatures above 100° C, the duration of the dye operation will be notably curtailed:

Mordanting	30 minutes
Intermediate rinse	
Haematine dyeing	25 minutes

Decompression will however have to be controlled, as well as cooling to 60° C and the full outflow rinse.

A.3. Raveled Wool and Rags

Liquor ratio = 1/10 to 1/15 - 100 kilos wool for 1,000 to 1,500 liters bath

Most of the time, raveled wool and rags will be carbonized in the oven, through the action of Hydrochloric gas, in a bath containing Sulphuric Acid 4° Baumé, followed by one pass in a room heated to 105° C, and then washed and neutralized.

The material is introduced into the dye apparatus and the water poured out and heated to 60° C. At that point, introduce :

Oxalic Acid	3 %
Hematine MEX-HCK	3 to 4 %
Hematine MEX-NOSK	3 to 4 %

The bath having been circulated for ten minutes, the temperatur will be raised to 100° C and cooled, fifteen minutes later, to 70° C through exterior circulation of the cooling water.

.../...

At that temperature, the following ingredients will be added :

- Iron Sulphate	3.4 %
- Copper Sulphate	1.7 %

The temperature having been raised to 100° C must then be maintained for 45 minutes. A rinse is then progressively given or the residuary bath is being transferred to the reserve vat. It should be noted that the bath, replenished with 2/3 of the required elements upon each dyeing, may be reused four times before being run out.

Comments :

(1) Cooling of bath from 100° to 70° C is possible by addition of cold water to the dye float. The ratio will be adjusted subsequent to the addition of the cooling water.

(2) The dye bath colour will serve as a pH indicator :
- a blue-black coloured bath (Basic pH) will require the addition of a small quantity of Oxalic Acid,
- a light yellow coloured bath (Acid pH) will require the addition of Sodium Carbonate to obtain a yellow-brown colour.

(3) Dyeing raveled wool and sulphuric acid carbonized rags:
May be carried out immediately upon the release, out of the carbonizer, of the wool material which is then acid and dry. Water will be poured over the rags and the bath will be circulated for 10 - 15 minutes, while loading itself with sulphuric acid.

The temperature must reach 60° C and the following will then be added :

- Sodium Bichromate	2 %
- Copper Sulphate	0.4 %

The bath is then circulated for 5 minutes and its temperature raised to 100° C. Thirty minutes later, 1.5 % Lactic Acid will be added in fractions, with a temperature being maintained at 100° C for 20 minutes. The material is then rinsed with progressive cooling to 40° C, adding to the fresh bath :

4 to 6 % HEMATINE MEX - HCK

The rags are introduced at 40° C, the dye apparatus run for 10 minutes, the temperature raised to 100° C and maintained for 45 minutes. A rinse is then to take place.

.../...

B – DYEING NYLON AND MIXED FABRICS CONTAINING NYLON

HEMATINE MEX _ NOSK is recommended for Nylon dyeing, this grade be non-oxidized and solubilized. Using Hematine MEX-NOSK for this type of material will result economical in price while insuring a good fastness to light and dry or wet rubbing of the material. Moreover, no sublimati nor creasing need be feared.

It is interesting to note that dye processes involving the use of Hematines are perfectly adequate to surgical suture thread dyeing, since there exists no risk of necrosis forming into human tissues, or of any decolourization occurring at the time of sterilization with water vapor under pression (120° C).

Treatment is to be carried out in two phases, namely :

- Dyeing properly said with Hematine MEX_NOSK in acid media
- Developing of Hematine with Bichromate

The quantities of Hematine, Acetic Acid and Bichromate to be used will depend on the quantity of material involved and on the bath volume; they must, however, correspond with the following, general formulations :

Dyeing (pH 5)

HEMATINE MEX – NOSK	6.8 % on the weight of the material + 5.3 grams per liter of bath
Acetic Acid 80 %	1.3 % on the weight of the material + 0.5 gram per liter of bath (pH 5)

Developing (pH 4)

Developing HEMATINE MEX – NOSK requires the use of :

Sodium Bichromate	3.2 % on the weight of the material + 0.85 grams per liter of bath
Acetic Acid 80 %	3.0 % on the weight of the material + 1.5 gram per liter of bath

B.1. NYLON ON THE JIG

Liquor ratio = 1/3 to 1/5 – for 100 kilos of material
= 300/500 liters of bath

(1) Dyeing

- Dissolve Hematine in very hot water
- Bring bath pH to 5.0 with Acetic Acid
- Sieve the Hematine solution
- Enter the Nylon material and give :

  - one end at 60° C
  - one end at 75° C
  - two ends at 85° C
  - two ends at 95° C

- Rinse (two ends)

.../...

(2) Developing

- Pour out Acetic Acid (pH 4) and then the Bichromate in solution
- Enter the material and give :

  - one end at 40° C
  - one end at 60° C
  - two ends at 85° C
  - two ends at 95° C

- Rinse (two ends)

NOTE :

Dyeing will be carried out in about 5 hours - 5 hrs. 30'

B.2. NYLON ON THE BEAM

Liquor ratio : 1/8 - 100 kilos material = 800 liters of bath

(1) Dyeing

Hematine and Acetic Acid having been priorily prepared, dyeing will start at 60° C. The temperature will then be raised directly to 110° C and maintained for 15 minutes, then cooled to 80° C for 20 minutes. A quick rinse will be given.

(2) Developing

Bichromate being priorily dissolved, the pH will be adjusted to 4.0 by addition of Acetic Acid. The temperature will then be raised to 90° C and maintained for 30 minutes. The material will be rinsed.

NOTE :

Total duration of operations : approximately 2:20 hours

B.3. TEXTURIZED NYLON THREAD PACKAGES

Helanca thread on spools, or packages

(1) Carry out dyeing in autoclave under pressure as described under B.2 above (dyeing on the warp beam)

(2) Dyeing in autoclave without pressure will be carried out along the process described below :

.../...

After introduction of HEMATINE MEX - NOSK, the temperature must be raised to 95 - 100° C. Forty-five minutes later - and with temperature maintained - the bath will be run out and a rapid washing will be made.

Development starts qt 40° C, in a fresh bath. The temperature is raised to 90 - 95° C and maintained for 45 minutes. The material is then rinsed.

B.4. NYLON-VISCOSE IN MIXTURE

In order to carry out a satisfactory dyeing, the mixture must be very precisely determined, as well as the liquor-ratio used.

Examples :

For a mixed fabric containing 80 % Nylon and 20 % Viscose :-

- in a jig ... Liquor-ratio = 1/5 - Nylon will be dyed in a liquor-ratio of 1/6
- in autoclave : Liquor-ratio = 1/15 - Nylon will be dyed in a liquor-ratio of 1/19
- in a winch .. Liquor-ratio 1/25 - Nylon will be dyed in a liquor-ratio of 1/30

For a mixed fabric containing 10 % Nylon and 90 % Viscose :-

- in a jig ... Liquor-ratio = 1/5 - Nylon will be dyed in a liquor-ratio of 1/50

Dyeing may be carried out according to three different processes:

(a) Dyeing Nylon Alone and Direct Black Crossdyeing

The quantity of Hematine required for Nylon will be determined on the basis of the general formulation and considering exclusively the weight of the Nylon material and its liquor-ratio.

The viscose portion of the mixed fabric will be dyed in a second bath, with a direct black, in the proportion of 6 percent on the weight of the Viscose part. This second bath may be reused for several passes.

(b) Dyeing Nylon and Black Sulphur Cross-Dyeing

The process to be followed is identical to that described under (a) above, for Nylon.

The Viscose portion is to be dyed subsequently, in a second bath, with a sulphur colouring matter, in a proportion of 8 percent.

.../...

(c) Simultaneous Dyeing of Both Fibres

For this purpose, a chromable direct dyestuff will be used which will be mixed, dissolved with Hematine MEX-NOSK, in a proportion of 10 % on the weight of the Viscose portion.

Dyeing will be made with pH = 5 - Acetic - following the method described hereunder :

- Temperature raised to 90° C and maintained for 45 minutes
- Cooling in 30 minutes after addition of 20 g per liter of Sodium Sulphate
- Rinse

Nylon now is of a brown colour. Viscose is of a blue colour.

Development with Bichromate will be identical to that specified for Nylon alone.

B.5. MIXED FABRICS, NYLON/ACETATE

The condition under which a satisfactory dyeing may be carried out is the determination of the fabric components. It is also essential to know how much mat the fibres of the material concerned are.

If the Nylon proportion is above 50 percent, the formulation corresponding to Nylon dyeing will be chosen. On the contrary, the formulation adapted to Acetate dyeing will be preferred if Nylon percentage is inferior. In either case, it will be imperative :

- not to exceed a temperature of 87° C

- to add to the developing bath an electrolyte (such as Sodium Sulphate or Sodium Chlorid) so as to block the Hematine over the Acetate portion.

B.6. NYLON FOR UMBRELLAS

Dyeing is to be carried out in the same manner as was described for jig-dyeing or warp beam-dyeing (see B.1 and B.2). However, to avoid any bluish transparency, the following ingredient will be introduced at the same time as Hematine itself, or:

- 0.8 to 1.5 percent Chrome Orange dyestuff (synthetic colouring matter)

.../...

C - DYEING ACETATE AND MIXED FABRICS CONTAINING ACETATE

As in the case of Nylon dyeing, one particular Hematine grade will be deemed proper to Acetate dyeing, namely :

HEMATINE MEX - NOSK, non-oxidized, solubilized

Treatment will be carried out in two phases :

(1) Dyeing in acid media with Hematine

(2) Developing Hematine with Sodium Bichromate

The quantities of Hematine, Acetic Acid and Bichromate to be used depend on the weight of the material to be dyed and on the bath volume. The determination of such quantities is based on the following formulation

- Dyeing - pH 4.0

HEMATINE MEX-NOSK	6 % on the weight of the material + 11 grams/liter of bath
Acetic Acid 80 %	1 % + 0.5 gram per liter of bath

- Developing - pH 4.5 - 5

Sodium Bichromate	2.7 % + 2.7 grams/liter of bath
Acetic Acid 80 %	1.2 % + 0,69 gram/liter of bath
Sodium Sulphate	40 grams/liter of bath

Sodium Sulphate is indispensable when developing Hematine with Bichromate, in order to fix the Hematine on the fibre until it is blocked through the action of the Bichromate, which occurs above 70° C.

C.1. ACETATE DYEING ON THE JIG

As a rule, liquor-ratios will be nearing 1/3 to 1/5 for :

- 100 kilos Material
- 300 to 500 liters of bath.

The fabric must be priorily desized with some anionic detergent and ammonia.

Dyeing

The bath having a temperature of 45° C, Acetic Acid 80 % is poured out, followed by the colouring matter (Hematine MEX-NOSK), priorily dissolved and sieved (pH = 3.5 - 4.0).

.../...

The material is then entered and one end is given at above temperature, followed by :

- one end at 65° C
- four ends at 85° C

The bath is then emptied and two more ends are given for rinsing under running water.

Developing

A fresh bath is prepared, heated to 80° C, temperature at which the Acetic Acid 80 % will be poured in, followed by the Sodium Sulphate and the Bichromate dissolution, sieved.

The material is entered, with :

- one end at 30° C
- one end at 50° C
- one end at 70° C
- two ends at 85° C

The bath is run out, two more ends are given for rinsing with water at 40° C.

Special Treatment

After rinsing, a treatment must be effected, using some anionic detersive agent, to which 1 to 2 grams per liter of Sodium Carbonate will be added. The purpose of this operation is a complete elimination of Bichromate. A last rinse with tepid water terminates the treatment.

C.2. ACETATE ON THE WARP-BEAM

Acetate fabrics may also be dyed on the warp-beam under pressure, at a maximum temperature of 90° C. The liquor-ratio is of 1/8, approxima ly. A temperature of 87-90° C will be reached directly and maintained fo one hour.

The bath will be cooled to 65 - 70° C, before being run out and a r given.

Fordevelopment, it will be necessary to insure that the temperature does not exceed 90° C at any moment.

Time needed for the dye operation : 3 hours.

.../...

D - BLACK ON SILK MATERIAL

Silk is the most precious of all natural textile fibres in existence. As a rule, silk dyeing will be performed under conditions very much alike those applicable to wool dyeing. Black dyeing, however, is in itself part of a very special field. Dyeing will be carried out almost exclusively with Logwood Extracts.

There exist quite a few processes therefor which all require a great experience, particularly when the silk material is to be filled simultaneou ly. It would not be feasible to fully describe here all of the dyeing and filling processes that may be followed. We will therefore limit our work here to only a few ones, likely to give satisfactory results.

It should be pointed out, in any case, that as a rule solely Logwood Extracts, non-oxidized, such as HEMATINE MEX-NOK Powder ought to be used for tin filling. But, whenever dyeing without making any attempt to filli or if dyeing is being carried out upon some other charge than a tin charge, then oxidized Logwood Extracts may be used, such as :

HEMATINE MEX - HCK
HEMATINE MEX _ CFHK

D.1. DYEING TIN-LOADED SILK WITH LOGWOOD EXTRACTS

After tin loading, prepare a filling bath with Logwood Extract. This extract must be dissolved in soft water at 30° C, soap being then added which was priorily dissolved in soft water at 95° C.

The filling bath volume is of about fifty times the silk weight. Proceed as described below :

Enter the silk material at 50 - 55° C. Leave immersed for 30 minute In the meantime prepare, separately, a dissolution of 2 to 5 % of Methylen Blue. Add approximately one third of the Methylene-Blue solution to the dye-bath. Raise temperature to 90 - 95° C. Allow to settle for 1:30 hour 2 hours. Then lift the silk material, allow to drip, rinse twice with water at 30° C, then with cold water. Carry out oxydation in another bath as cold as may be in which 3 to 5 grams Sodium Nitrite and 6 to 10 grams Formic Acid by liter of bath will have been priorily dissolved.

Enter the material (30 minutes)

Rinse twice with ordinary water

Brighten and soften in a soap bath in the proportion of 10 grams per liter, for 15 minutes.

Dry and then leave in a bath at 50° C containing about 50 % Lactic Acid 50 %, for 15 minutes.

.../...

There follows a scale of percentages of Hematine to be used, depending on the importance of the charge desired :

- For 10 to 20 % charge ..... 60 % HEMATINE MEX - NOK + 2 tin baths
- For 25 to 35 % charge ..... 80 % HEMATINE MEX - NOK + 2 tin baths
- For 40 to 50 % charge ..... 80 % HEMATINE MEX - NOK + 3 tin baths
- For 55 to 65 % charge ..... 115 % HEMATINE MEX - NOK + 3 tin baths

The charge percentages should be understood based on the weight of raw silk material.

D.2. DYEING SILK ON IRON MORDANT

The silk material will first be treated in a bath containing iron nitrate at 30° Baumé, for one hour and then lifted, twisted and heaped up for the night. It will be thoroughly washed the next day and rinsed with hard water, heated to 90 - 95° C, for 20 minutes.

The silk material will then be introduced into a bath prepared with 10 % CUBA MEX - NOK POWDER, for 30 minutes, at 60 - 70° C, and then into another bath, prepared with Logwood Extract, or 20 % HEMATINE MEX - HCK, plus 20 % household yellow soap.

Enter the material at 55° C. Stir up for 15 minutes, raise to 65° C in 15 minutes and then up to 75° C. Dyeon for 45 minutes, rinse and brighten.

The charge is equal to about 15 % of the total weight of the degummed silk material.

For a quantity of HEMATINE MEX - HCK equalling forty per cent, the charge will near twenty per cent.

D.3. DYEING SILK ON MIXED MORDANT

Logwood Black on Iron Mordant results in a bluish shade which it is difficult to reproduce on tin mordant. Nevertheless, if the reproduction of a given iron black is desired over a strongly tin-loaded material, the following process will be recommended:

- Start with silk tin-loading
- Immerse silk into a bath prepared with :

  3.5 % HEMATINE MEX - NOK
  13.0 % CUBA MEX - NOK

- Dye for 20 minutes at 60 - 65° C, then add dissolutions (prepared separately) of :

  12 % Iron Sulphate
  2 % Copper Sulphate

- Dye for 1 hour 30 minutes, at a temperature of 65 - 70° C. Lift the material.
- In another vat, dye for 1 hour at 70 - 75° C, with :

  30 % HEMATINE MEX - NOK or MEX - HCK (depending on the deepness of black desired)
  25 % Soap (Charge obtained through dyeing only = 12 %)

.../...

D.4. DYEING SILK ON CHROME MORDANT

Using Logwood Extract on degummed and iron mordanted silk necessitates concentrated liquors of ferrous nitrosulphate, the final result being, in any case, a beautiful black with approximately 15 per cent charge.

Logwood Black on chrome mordanted material also gives quite a beautifu - although bluish black. Moreover, the charge obtained, of 12 per cent, is comparable to that cited above. The process recommended contains operations used for wool in flocks and is also similar to that to be followed for Nylon on circulation apparatuses. These operations are being detailed hereunder.

. Soft Water)
. Liquor-ratio 1/30) 100 kilos silk material for 3,000 liters of bath

D.4.1. - Degumming

Two soap baths of each 30 minutes to 60 minutes at 95° C, with 20 % household soap (on the weight of the silk material).

Rinse - pH = 6.5 - 7.0

D.4.2. - Mordanting

20 % Chrome Alum, crystallized

Enter material at 55° C. Raise to 95 - 98° C. Maintain for 1 hour and rinse thoroughly with soft water, eventually corrected to pH 6.5 - 7.0.

D.4.3. - Dyeing

HEMATINE MEX - NOK	10 %
HEMATINE MEX - HCK	10 %

Enter material at 55° C, raise to 95 - 98° C, maintain for one hour at this temperature and rinse with soft water.

D.4.4. - Chroming

Enter cold. Prepare bath with :

Sodium Bichromate	2 %
Acetic Acid 80 %	1 %

Raise temperature to 65 - 70° C, maintain for 30 to 45 minutes.

Empty bath.

D.4.5. - Rinsing

Give one rinse with cold, soft water - 5 minutes.
Give one more rinse with soft water at 50° C, to which 1 g/liter Sodium Carbonate has been added - 5 minutes.
Give one final rinse with cold water - 5 minutes.
Drain and dry.

.../...

D.5. SILK PRINTING

After printing, with IRON BLACK NUMBER 7, silk remains soft.

Compounds of IRON BLACK No, 7

HEMATINE MEX - NOK	25 kilos
ACETIC ACID 80 %	10 kg 400
IRON SULPHATE	8 kg 300
PYROLIGNITE OF IRON 20° Baumé	15 kg 600
SODIUM BISULPHATE 35° Baumé	8 kg 300
CHROME ACETATE 20° Baumé	2 kg 800
WATER	30 liters
	100 kilos

Process for a Deep Black

Reduced Iron Black No. 7	40 kilos
Sodium Chromate	1 kilo
Thickening (Tragacanth)	59 kilos
	100 kilos

Sieve. Print. Dry. Spray for 15 minutes (MATHER PLATT). Dry.

E. COTTON DYEING

E.1. Black on Cotton, Linen and Hamp Skeins

For 100 kilos of any of the above materials :

- Dissolve 10 kilos HEMATINE MEX - NOK in as reduced a quantity of water as may be possible, but nevertheless sufficient for the material to be immersed in bath.

- Plunge the skeins into the solution and drain

- Allow to oxidize in the open overnight

- Fix in a bath at 40° C containing :

  . Copper Sulphate 5 kilos
  . Sodium Bichromate 1 kilo
  . Water (quantity sufficient to move the material within the solution)

- Leave material in the open for two hours

- Rinse. Enter material once again into the Logwood Liquor at 40° C

- Rinse and give one bath with oil and soap

.../...

NOTE: To obtain deep blacks, it will be found advantageous to add 5 per cent CUBA MEX - CNOK to the Logwood solution.

E.2. Cotton Shoe-String Dyeing

This common article of great consumption and of a reduced cost price will be dyed according to a simplified and more economical formulation.

The quantity of water used is of importance since about 20 liters will be required for one kilo cotton material. The vat, already containing the appropriate quantity of water at 100° C, will be filled with :

HEMATINE MEX - NOK	25 kilos
GAMBIER EXTRACT GSK	40 kilos
CUBA MEX - CNOK	10 kg 500
SODIUM CARBONATE	2 kilos

Proceed as described below :

- Enter material at 100° C
- Leave immersed for approximately 1 hour
- Then leave on, without heating, until the next day
- Lift, drain but without rinsing and transfer into another vat, at 30° C, in which 80 kilos Iron Sulphate will have been dissolved and, in suspension, 40 kilos of pulverized chalk
- Stir up
- Enter material anew, for 1 hour, at 30 - 40° C
- Lift material, drain, rinse and introduce again into the first bath, reheated to 80° C
- Leave in for one hour, then lift and allow to oxidize in two hours, in the open
- Rinse and dry

E.3. COLORATION IN BLACK OF FINISHING AGENT FOR SPUN COTTON

For this operation, it is recommended to choose non-oxidized Logwood Extracts. For 400 liters of the product, use :

HEMATINE MEX - NOK	2,500 kilos
CUBA MEX - CNOK	0,200 kilos
CRYSTALLIZED IRON NITRATE	0,250 kilos
POTASH BICHROMATE	0,150 kilos

Reduce - and eventually eliminate - CUBA MEX-CNOK in order to obtain a blue-black shade.

.../...

When dealing with sulphur black dyed cotton, use following proportions for 100 kilos of spun cotton and 2,000 liters of bath:

Starch	0 kg 600
Lard	0 kg 500
Sodium Sulforicinate	1 kg 500
HEMATINE MEX-NOK	1 kg 200

Raise temperature to boiling point. Stop steaming.

Enter the cotton material. Stir up for 30 minutes. Lift. Add 0 kg 150 Sodium Bichromate to bath.

Enter material anew and leave in bath for 30 minutes, at 75° C.

Take material out of bath for dripping.

F. DYEING LIBERIAN (AND SIMILAR) FIBRES BLACK

F.1. Dyeing Jute Material (Proportions % Kilos of material)

Jute material being strongly acid, the spun fibres must be treated in a bath containing :

3 % Sodium Carbonate, during 15 minutes at boiloing point,

with subsequent addition of :

3 % Copper Sulphate

Maintain to the boil for 45 minutes and then add to bath :

6 %	HEMATINE MEX - NOK
1 %	Copper Sulphate
0.5%	CUBA MEX-CNCK

Dye in one hour, at boiling point, lift material and rinse

F.2. Dyeing Coco or Coir Fibers Black

If a very fast black is desired, the best result will thenbe obtained with a diazotable direct black. For an ordinary black, it is recommended to use HEMATINE MEX - NOK. The material must be immerse directly into the bath which is to contain:

....	10 %	HEMATINE MEX - NOK
....	0.5%	CUBA MEX-CNOK
....	4 %	Sodium Carbonate, calcinated
....	0.5%	Coco Soap

The material is entered at 40 - 50° C and dyed in 30 minutes at 95 - 100° C. The ratio required between the weight of the fibre and the volume of the bath is of 1/10. This bath, which does not exhaust, may be keeped for subsequent dyeings.

.../...

Take material out, drain and allow to oxidize in the open overnight.

The next day, develop, at 60° C, with :

3 %	Iron Sulphate
0.15 %	Formic Acid 80 %

The purpose of using Formic Acid is a solubilization of the salts contained in the water.

The material is next rinsed with current cold water.

F.3. Dyeing Sisal Material and Manila Hemp Black

Black dyeing is carried out through the combination of a Direct Black stuff with HEMATINE MEX _ NOK, subsequently iron-fixed. The proportions required are given below:

3 %	Direct Black
2 %	HEMATINE MEX - NOK
4 %	Sodium Sulphate
0.75 %	Sodium Carbonate calcinated
0.25 %	Ammonia 22° Baumé

The material is entered at 100° C and boiled for 3 hours. It is to remain for one hour in the cooling bath, then taken out and allowed to oxidize overnight in the open.

Hematine is to be fixed onto the material through immersion in a bath of Iron Pyrolignite at 3.5° Baumé, for one hour, at 25° C.

Lift the material and expose for 12 hours in the open. Rinse thoroughly.

Hematine facilitates grandly fibre penetration and its fastness to tear and wear will reveal much better than if using a Direct Black alone.

F.4. Dyeing of Vegetable Fibre

F.4.1. Black with Pure Logwood Extract

The fibre must be priorily treated with :

10 %	Soda flakes
2 %	Soap

One hour at 100° C

Rinse thoroughly to eliminate the resinuous matter coating the fibres. Dye at 100° C, in one hour, with :

2.5 %	HEMATINE MEX - NOK	
0.25%	Soda flakes	) Priorily dissolved and added
0.75%	Copper Sulphate	) separately, one after the
		) other

.../...

Leave the fibres immersed for 2 hours. At the end of the dye operation, wash, drain for development of the black colour. Rinse and dry.

F.4.2 Combined Black

Enter material at 45° C into a bath containing :

3.5 %	Direct Black
1.5 %	Ammonia 20 %
1.0 %	Sodium
4.0 %	HEMATINE MEX - NOK
0.4 %	CUBA MEX - CNOK
6.0 %	Sodium Sulphate, cyrstallized

Raise to the boil. Allow to remain immersed for 1 hr 30 '.

Lift and allow to drip. Pass through a bath at 30°C containing Pyrolignite of Iron 5° Baumé. Stir up for 1 hour. Lift material and allow to drip in the open for development of the black colour. Rinse thoroughly.

The dye bath will be later on reinforced with half the proportions indicated above, to serve for further operationa.

F.5. Dyeing Tampico Fibre

F.5.1. With Logwood Extract

Carry out dyeing in a first bath containing (based on the weight of the material) :

8 %	HEMATINE MEX - NOK
1.5 to 3 %	Ammonia 22° Baumé

Enter material at 100° C and leave immersed overnight, penetration occurring only slowly. Lift material the next day and allow to drip, collecting the liquor that may be reused for the following operations.

The black colour is to be developed in a different bath at 30° C containing 5 % Iron Sulphate. Leave in contact for 2 - 3 hours. Lift and rinse.

The dye bath will then be reloaded with half of the proportions indicated above, to serve for future operations. The iron bath, however, must be replaced each time so as to obtain a material correctly dyed and offering a good fastness to rubbing. An addition of 2 to 3 per cent CUBA MEX - CNOK will darken the bath colour.

.../...

F.5.2. Combined Black

For 100 kilos material, the following quantities will be necessary:

3 kilos Direct Black
1.5 to 3 kilos Ammonia 22° Baumé
10 kilos HEMATINE MEX - NOK
0.6 kilo CUBA MEX - CNOK

Enter material at 70° C, raise to 100° C, maintain for 2 - 3 hours.

Lift. Drip. Pass material through a bath at 30 - 35° C of Iron Pyrolignite 4-5° Baumé.

Lift. Allow to drip in several hours. Rinse thoroughly.

F.6. DYEING ALFA MATERIAL BLACK

Dyeing will be carried out through a combination of a direct black dye and of a non-oxidized Logwood Extract. The bath will contain:

3 % Concentrated Direct Black
10 % Ammonia 22° Baumé
4.5% HEMATINE MEX - NOK
0.5% Yellow CUBA MEX - CNOK
! % Chestnut Extract TCK

Heat bath progressively to boiling point. Maintain for 3 hours and 30 minutes at this temperature. Take fibres out and leave overnight in the open, to expedite oxydation of the Hematine, then plunge the fibres into a bath of Pyrolignite of Iron 5° Baumé, heated to 35° C. Lift and allow the material to oxidize in the open, for several hours. Rinse thoroughly with cold water.

* * * * *

II - APPLICATION OF NATURAL TINCTORIAL EXTRACTS TO PELTRY ITEMS

The Natural Tinctorial Extracts were the first dyestuffs to be used for pelt dyeing. At the present time, only extracts obtained from Logwood, Yellow Fustic Wood and Redwood are still being used on an industrial scale.

II.1. Dye Method

It is recommended to use non-oxidized Logwood Extracts (HEMATINE MEX - NOK), Pyrolignite of Iron, Copper Acetate, Ammonia salts.

Curcuma is also being used at times which penetrates leather less than hair. On the contrary, if it is desired for the skin to acquire some hand, the use of Gambier and Sumac Extracts will be preferred.

The bath pH, however, will always be of approximately 3.8.

A non-oxidized Logwood Extract (HEMATINE MEX - NOK) will be preferred to oxidized grades because, in combination with ferrous salts, the non-oxidized grade remains practically entirely soluble, hence an easy penetration of priorily degreased hair.

Pyrolignite of Iron will be preferred to Ferrous Sulphate, in order to obtain prettier blacks.

Finally, Copper Acetate favours development of blacks through successive oxydations, particularly at the time of exposure to the air.

As concerns bath temperature, it is in principle nearing 35° C. The luster will be acauired subsequent to dyeing through scouring in the drum filled with non-resinous sawdust.

II.2. Dyeing

Only the dye principles may be described here, since each dyer has his manufacturing secrets. Solely experience - and a multitude of tests - will permit users to find out which process is best suited to his equipment. Dyeing will be carried out through immersion, or dipping, along the two processes described below:

II.2.1. Dyeing Black through Dipping, with prior Mordanting

The pelts, first carefully scoured, will be mordanted for 3 hours at 35° C, in a bath containing, per liter :

2 grams Sodium Bichromate
2 grams Copper Acetate
0.5 gram Sulphuric Acid 60° Baumé

The pelts will then be lifted, thoroughly drained and allowed to oxidize overnight. The next day, dyeing will be carried out in 4 hours at 35° C, in a bath containing, per liter :

.../...

25 - 30 grams HEMATINE MEX - NOK
2 - 3 grams YELLOW CUBA MEX - CNOK

The pelts will be lifted and allowed to oxidize for six hours in the open. If it is deemed that the black so obtained is not deep enough, a second mordanting will be required, followed by q second dyeing.

N O T E : By reducing the quantities of Hematine and by eliminating the addition of CUBA MEX - CNOK, a whole range of gray shades will be had.

II.2.2. Dyeing Black in the Paddle Wheel, with preliminary Mordanting followed by a subsequent treatment with Metallic Salts

The pelts, first carefully degreased, will be stirred for 4 hours at 35° C, in a bath containing, per liter :

20 - 25 grams HEMATINE MEX - NOK
2 grams YELLOW CUBA - CNOK
2 grams Copper Acetate

The pelts will then be lifted, drained and allowed to oxidize in the open overnight. The next day, they will again be dipped into the bath to which the following ingredients will have been added (per liter of bath) :

4 grams Pyrolignite of Iron 14-15° Baumé
4 grams Sodium Sulphate
1 gram Sulphate of Aluminium

The pelts will be drummed for 4 hours, lifted and allowed to oxidize in the open overnight.

The next day, they will be rinsed and the black will be developed in a bath of Sodium Bichromate (5 grams per liter).

This process is well adapted to woolen skins (sheep, lambskins). It is also adequate when handling haired skins (rabbit and deerskins). In the case of haired skins, however, the mixed method will be preferred which comprises: Aniline Brushing and Logwood Dyeing in the paddle wheel.

II.2.3. Mixed Black

Carry out six brushings with Chlorhydrate of Aniline, followed each by drying at 35° C in an oxydation room. When hair shows a deep black, immerse the skins into a bath containing, per liter :

1 cc Ammonia 22° Baumé
0.5 grams Detergent

in order to achieve complete neutralization of hair acidity. Introduce skins again into the paddle wheel containing a bath made of :

12 - 15 grams HEMATINE MEX - NOK per liter

Enter the skins at 35° C, stir up for one hour, then add :

1 gram Copper Acetate

.../...

Stir up again, for three hours, lift, allow to oxidize in 12 hours in the open.

Plunge skins again and expose in the open for one night.

Rinse thoroughly to complete the operation.

The black so obtained will be superb, sufficiently fast to light and the process will reveal economical.

III - APPLICATION OF NATURAL TINCTORIAL EXTRACTS TO TANNERY WORK

The use of fine coloured skins has developed considerably over past years, with the result that skin dyeing still represents a field within which the consumption of colouring matters remains important.

Natural, vegetable dyestuffs, in the form of spray dried powders, will be used in great quantities for this type of dyeing. As a rule, vegetable dyes differ essentially from what specialists in the field are used to classify as Colouring Matters. While the greatest number of artificial dyes (acid, direct, basic dyes) give an intense, immediate colouration, exhausting in acid dyebath, vegetable tinctorial extracts are classified as latent colouring matters which must be oxidized and combined with a metallic mordant to develop colouration.

Vegetable dyes play an important part as ground colour in dyeing fine skins for glove and garment making. Since a few years, they have become more and more indispensable with the presence, on the market, of resins and synthetic tannins, products which, as is widely known, wash the colour away, giving less vivid shades and poor dye penetration and evenness.

Vegetable colouring matters will be particularly recommended for ground colouration of chromed leathers, because many acid dyes, and especially the basic ones, only have a limited affinity for chrome leather.

The vegetable dyes acting as vehicles, their use facilitates the fixation of aniline dyestuffs. They play the part of mordants, improving the evenness of synthetic colouring matters. Such vegetable dyes are perfectly adequate for fine, luxury skins, their use improving the action of aniline dyes on imperfect skins. Finally, they offer the advantage - not to be neglected - of increasing the adherence of pigments onto chrome leathers.

In combination between themselves or eventually with artificial dyes, vegetable colouring matters permit to achieve the production of shades most currently sought on chromed or semi-chromed skins.

A vegetable colouring matter universally used in Tannery Works is a semi-oxidized Logwood Extract, known as HEMATINE MEX - CFHK.

.../...

III.1. HEMATINE MEX - CFHK

This is a semi-oxidized Logwood Extract containing Haematoxylin, Haematein, Glucosides and Tannins, the latters having been edulcorated by means of a gradual chemical oxydation. The purpose of such a chemical operation is :

(a) the transformation of part of the Haematoxylin into Haematein

(b) the partial destruction of Glucosides, thus eliminating part of the tanning properties of the extract

In fact, Haematoxylin, under the influence of chemical oxidizers, loses two hydrogens and is being transformed into Haematein. Upon acidification at the end of the dye operation, this Hematine will not return to its primary state of glucoside. Part of the tanning properties have been lost, which is particularly suitable for use in the making of fine skin garments due to the satisfactory and tempered filling which the skin will then acquire. Moreover and because it is only lightly oxidized, no over-oxydation needs be feared which would result in a reduction of the dye value.

For given productions, the low contents in tannins remaining will be considered an appreciable advantage since it helps avoiding the so-called " Bas de Fleur " (or irregular uptake of dye by the leather), while causing a slight tannage.

pH = 1/10 = 7.8

Penetration into leather : rapid and perfect

Colouration on chrome leather :

- With treatment with	iron sulphate	Blue, Black
	aluminium sulphate	Indigo Blue
	copper sulphate	Navy Blue
	Potassium and Titanium Oxalate	Brownish Black

III.2. Applications

To all chromed leathers paddle-dyed or brush-dyed, intended for clothing, gloving, upholstery, upper shoe and Morocco leathers.

To all alumn tanned skins.

To vegetable tanned leathers, brush-dyed.

To all Chamois-dressed leathers.

.../...

III.3. Fastness Properties

	Ratings
To Light	3
Perspiration	5
Soaping	5
Levelling	5
Dry rubbing	5
Wet rubbing	4-5

III.4. Process

It is extremely simple : HEMATINE MEX - CFHK may be used in all proportions with acid, direct or metalliferous dyes. It exhausts in acid bath and metalliferous salts (iron, copper or titanium salts) will be used for lacquering.

HEMATINE MEX - CFHK lacquers the basic colouring matters; this is in fact a remarkable property of Tinctorial Extracts. For this very reason, Hematine and basic dyes should in no case be used simultaneously; dyeing - on the contrary - should start first with Hematine and acid or direct dyes, then a fresh bath should be prepared, reintensified in basic dyes with an addition of metallic salts.

III.5. Shades obtained

With HEMATINE MEX - CFHK, in mixture with Synthetic Dyes :

- Black
- Blue
- Violet
- Brown - Gray
- Dark Brown

IV - DYEING WOOD WITH NATURAL TINCTORIAL EXTRACTS

Wood may be dyed along two entirely different processes and according to the use which the wood is intended for. Whenever a deep penetration of the dye is sought, vacuum dyeing will be carried out in a hot bath(autoclave) to permit the tinctorial solution to penetrate wood pores. In operating alternatively in the autoclave and under a pressure of 2 kilos per square centimeter, perfect through-dyes will be achieved.

If such a thorough penetration is not desired, and if only already transformed wood is being handled, dyeing will then be carried out either by dipping or brushing or, again, with the paint brush.

.../...

IV.1. Dipping Method

Plunge wood, thoroughly soaked, into a bath containing, per liter :

HEMATINE MEX - NOK	50 g
Sodium Carbonate	25 g
Anionic Detergent	3 cc

Temperature : 50° C. Duration : 4 to 24 hours, based on the penetration desired and the wood specie considered.

Take wood out of bath and drip. Allow to oxidize in 24 hours and then immerse into a bath containing Iron Pyrolignite 5° 5 Baumé, for 4 hours or longer, if required, at room temperature. Wash and dry.

If the black is not deep enough, give one extra pass into a bath of Hematine, and then into a bath of Pyrolignite of Iron, oxydation being in any case necessary subsequent to Hematine impregnation.

IV.2. Paint-Brush Dyeing Process

The paint brush dyeing process will rather be used for colouration of household utensils. For example, several coatings being applied to wood items with the solution recommended below will give quite a beautiful black, with good fastness to light :

2 liters 500 HEMATINE MEX - NOK 30° Baumé
1 liter YELLOW CUBA MEX - CNOK 25° Baumé
5 grams Sodium Carbonate

Allow to dry in the open. Then apply a fresh solution prepared with :

7.5 g Sodium Bichromate
3.0 g Copper Sulphate

Repeat operation four times in order to obtain a beautiful black, deep and even.

IV.3. It is possible to obtain an excellent varnish or lacquer highly shining, destined for wooden footwear and also for shoes made out of cardboard such as : clogs or sabots, galoshes, slippers, by using the following solution :

IV.3.1. 7 kilos 500 HEMATINE MEX - NOK) per liter
3 kilos YELLOW CUBA MEX - CNOK)

which are dissolved in 35 liters water at 70° C. Once the solution has cooled to 40° C, add :

25 liters Pyrolignite of Iron 14 - 15° Baumé
6 liters Acetic Acid 80 %

IV.3.2. Separately, have the following ingredients dissolve very slowly in a double boiler:

4 kilos Wax (in 8 liters water at 95° C)
2 liters Ammonia 22° Baumé

.../...

Pour the wax solution into the tinctorial solution, little by little, and then stir up energetically for perfect homogeneisation of all ingredients.

Appply the solution with paint-brush or brush over the wood articles, thoroughly dry and offering a perfectly degreased surface.

V - BUTTON DYEING

V.1. Natural Rawmaterials

V.1.A. Corozo

This vegetable substance, which can be worked on easily on the lathe and which permits the production of beautiful buttons, may be dyed black with Logwood Extract. To begin with, the material must be mordanted for 2 hours at 30° C, with :

2 % Sodium Bichromate
5 % Hydrochloric Acid 20° Baumé
(based on the weight of the material)

Rinse thoroughly.

Dye in a fresh bath containing, per liter :

20 - 25 g HEMATINE MEX - NOK
2 g YELLOW CUBA MEX - CNOK

in two hours at 90° C.

V.1.B. H o r n

This material will be dyed black with Logwood Extract especially. Horn buttons will be boiled for 30 minutes in a solution containing :

1.5 % Sodium Bichromate
3.5 % Chlorhydric Acid 20° Baumé
(based on the weight of the material)

Rinse thoroughly

Dye in a fresh bath containing, per liter :

15 - 20 g HEMATINE MEX - NOK
2 g YELLOW CUBA MEX - CNOK

in one hour, at 80° C

Considering that horn may soften at high temperatures, it is recommended not to exceed the degrees indicated above.

.../...

V.1.C. Bones

Direct dyes on this kind of material will give acceptable blacks, but Logwood black still remains unbeatable, because of the deepness of the shade obtained.

The buttons must be mordanted in a bath containing 5 grams Sodium Bichromate oer liter, then after dripping, dyed in a fresh bath containing 50 grams per liter of HEMATINE MEX - NOK, in 30 minutes to one hour, at boiling point.

V.2. Artificial Rawmaterials

No application possible with Logwood Extracts

VI - COLOURATION OF MICROSCOPIC SECTIONS IN HISTOLOGY

To obtain a maximum result, several colourations will be carried out in laboratories specializing in biological chemistry, the purpose of which being to clearly define the various elements of human skin.

In this particular field, several kinds of colouring matters will be used, namely :

Pure Haematoxylin, crystallized, H P X
Pure Haematein, crystallized

Both Extracts are the dye principles of Logwood.

* * * * *