DYEING EXTRACTS AND TANNINS IN THE TEXTILE INDUSTRY

INTRODUCTION

The dyeing extracts and tannins arouse a great interest these days. Their intrinsic qualities are recognized by the most eminent professors and technicians and their field of application, thanks to the modern possibilities, is very vast and it is now recognized that they act complementarily with the artificial dyes.

This is why, based on its strong experience, SCRD proposes in this book to underline what one can obtain with the vegetable dyeing extracts and tannins.

The main sections within this work are the following :

- **The origin, nomenclature and characteristics of the tinctorial extracts and the tannins currently used.**
- **Control methods and equivalences of various qualities.**
- **Characteristics of Logwood in the dyeing of wool.**
- **Requirements to make a solid dyeing, as well as examples chosen of industrial applications concerning the various natural, artificial and synthetic fibres (except for some of the latter, like Tergal, Rilsan, Orlon which have only very little affinity for the mordant dyes).**

You will also find applications such as the weighting and the dyeing of silk with Logwood. We also detail the most economic formulas for printing on cotton and viscose fabrics, and the use of Tanning RTK for the conservation of jute.

Finally, we shall detail the usage of the natural tannins in the mordanting and the printing of the basic dyes as well as their usage in the process of supply of wool, or their use for the washing fastness improvement of the acid and metalliferous dyes applied to nylon.

ORIGIN AND PREPARATION OF THE DYEING EXTRACTS AND THE TANNINS CURRENTLY USED

A- MANUFACTURING PRINCIPLES FOR THE ROUGH EXTRACTS, CLARIFIED OR PURIFIED NOT OXIDISED

The Logwood, for example, (*hematoxylon campechianum*, coloring principle : hematoxyline), cut in fine chips, gives the basic Logwood extract when subjected to a thorough aqueous extraction.

The juices, which come from the extraction batteries, are then concentrated on apparatuses with triple effect, under vacuum, of 3° Baumé approximately, up to 14, 30 or 34° Baumé before or after purification.

For the other vegetable extracts' preparation, the principle of extraction is the same, with some variances in each case.
One uses:

I°- Other dyeing raw materials :

- The wood of *chlorophora tinctoria* or *morus tinctoria* for Yellow Wood extracts (dyeing principles : Morin and Morintannic acid).

- The wood of the *caesalpina crista* for Red Wood extracts (dyeing principle: Brazilwood which gives, by oxidation, the Brazilein).

2°- Other tannic raw materials :

For the preparation of pyrogallic or hydrolysable tannins, lightly colored and purified: the **China Gall nut**, 75% of tannin content, produced by the bite of the aphis chinensis.

For the preparation of the pyrogallic tannins, cheap, but more or less coloured:
- The Sumac leaf : 22 % of tannin content (*rhus coriaria*),
- The Myrobolam nut : 35 % of tannin content (*terminalia chebulia*),
- The Chestnut wood : 8 % of tannin content (*castanea vulgaris*).

For the preparation of the catechic or condensed tannins:
- Mimosa barks : 35 % of tannin content (*acacia decurrens*),
- Quebracho wood : 20 % of tannin content (*aspidospernum*).
- The areca catechu : 8 % of tannin content. The usual results with catechu extracts are a reddish coloring and more marked properties.

The purification of these products is carried out, according to their usage, either by clarification and filtration, or by treatment with alcohol, ethyl acetate or ether to make them perfectly usable.

B- THE EFFECTS OF OXIDATION

In order to obtain the maximum dyeing output, it is necessary, for example in the case of Logwood, to transform the Hematoxylin, latent dyeing matter, into Hematein, the true mordant dye. This transformation requires a spared oxidation of the rough or clarified extracts. Same remark in the case of Yellow Wood.

Lastly, for the catechic tannins, the oxidation determines an insolubilisation of the tannin on the "tanned" or "mordanted" fibre. This is required in the case of the tanning of fishing nets and for giving solid shades of brown.in the dyeing of cotton fabrics in particular

Each of these products, soluble in water or, in certain cases in alcohol, is delivered under atomized powder form.

This leads to the following classification and usages :

C- CLASSIFICATION AND USES OF THE EXTRACTS

NAMES OF THE PRODUCTS	UTILISATION
A. LOGWOOD EXTRACTS a) NOT OXIDISED	
Hematin ESPGP	Weighting of silk. Ink to mark the bags. Dyeing of wool on oxidizing mordant (chromium, copper, sulphuric acid). Dyeing of cotton, flax, jute, ardil, vegetable bristle and hair, nylon, acetate. Felt half-wool for charentaise.
b) OXIDISED	
Hematin HPT	Dyeing of wool combed, spun, and in piece : - on iron, copper and oxalic acid. - on chromium, lactic acid, hydrochloric acid and sulphuric acid. - on chromium and formic acid.

NAMES OF THE PRODUCTS	UTILISATION
B.- OTHER TINCTORIAL EXTRACTS	
Yellow CNOK (not oxidised)	Dyeing of wool in yellow and shading of the blacks in one or two baths. Dyeing of vegetable fibres and silk. Dyeing of wool, reduced mordant. Dyeing of wool, oxidizing mordant. Printing on cotton.
Retan TPC	Tannins extracted with water. Mordanting and printing of cotton for use of basic dyes. Supply of wool.
Gall nut tannin	Increased wash-fastness of some dyes on nylon.
Gall nut tannin	Tannin purified with alcohol. Supply of wool. Manufacturing of inks and pharmaceutical products (Codex in France).
Retan MDI Retan BLK-M Retan STF Tannant TCK	Mordanting of cotton for dyeing with basic dyes.
Mimosa Retan GSK Tannant RTK	Dyeing. Vegetable fibres tanning. Tent Fabric Kaki and brown. Silk weighting.

The evaluation and the comparison of tannins relies on two methods: one uses the Lovibond tintometer for coloring. The official method - adopted amongst others by the French Leather Chemists' Association - for the proportioning of the tannin is described in card 1: *Official method of the quantitative tannic analysis* (or Shake method simplified) p.18. It rests on the absorption of the tannins by a skin powder, slightly chromed.

TANNING CONTENT, ACIDITY pH, TOTAL ACIDITY EXPRESSED IN ACID ACETIC % AND COLOUR OF THE MAIN TANNIN EXTRACTS

Table 1

TANNIN EXTRACTS	Insoluble %	Tannins %	Not Tannins %	Moisture %	pH of the analytical solution	Expressed in acetic acid total acidity % dry residue	Colouring Lovibond J	Colouring Lovibond R
Retan TPC	0.8	82,5	13,9	2,8	3,88	12,5	1,3	0,8
Gall nut tannin (soluble with water)	0,0	77,2	16,8	6,0	3,74	10,6	0,9	0,6
Gall nut tannin (soluble with alcohol)	0,0	90,7	5,7	3,6	3,35	9,90	1,1	0,4
Sumac	2,6	50,9	42,0	4,5	4,13	7,50	7,2	2,2
Retan MDI	1,9	57,0	36,5	4,6	3,33	11,34	11,7	1,8
Tannant TCK	0,0	67,6	28,0	2,7	3,30	9,00	10,0	3,5
Mimosa ME	1,0	69,2	24,8	5,0	4,60	1,40	2,6	1,3
Tannant RTK	5,0	48,4	23,6	23,0	5,59	-	-	-
Retan GSK	9,9	73,5	10,6	6,0	4,90	1,50	-	-

WOOL DYEING

PARTICULARITES OF THE LOGWOOD IN WOOL DYEING

The Logwood blacks were recognized to be the most beautiful and deepest which can be obtained on Wool, Nylon and Acetate. The use of Logwood suffered from the complication of dyeing in two baths, the reputation of low light-fastness and by the inaptitude of Logwood to resist the acid treatments (carbonizing and acid topping).

It is now possible to reconsider these objections thanks to the quality improvements obtained these last years. A few English dyers never have ceased using Logwood to obtain the famous " English black " which matches with the most beautiful draperies manufacture.

We saw that the coloring principle of Logwood (hematoxylin) is extracted from wood to be more or less oxidised in the course of manufacturing - according to the destination of the extract - in order to be transformed into hematein.

The hematein thus obtained, is the coloring product which, exactly as the dyes with chromium do, combines with metal salts (chromium, iron and copper in particular) to form a lake firmly fixed on wool and likely to resist the most severe fuller proof.

Lightfastness

Indeed, the black with Logwood, on chromium mordant, tends to become green after a very long exposure to sunlight. On the opposite, a black obtained with artificial chrome dyes changes, but more towards a vinous reddening.

This is so true that certain dyers use a mixed process : Logwood – chrome black. In this case, each element compensates the other’s correction.

On a scale from 0 to 8 the tests measuring the impact of light exposure give a 5 for the loggwood black on chromium mordant, a 6 on iron and copper mordants, a 6 for a dyeing in alizarin black and a 7 for a black obtained with the black diamond and chromium.

These results could be closer still if the black with Logwood on chromium had been obtained with reduced mordant, in presence of copper for reinforcing light-fastness, or if one had reduced the proportion of Yellow wood (Cuba), while increasing the proportion of hematin and by adding a little alizarin red.

Lastly, on a purely documentary basis, the table 2 (page 8) shows the results of the dyeings obtained with oxidised hematin, on the various industrial mordants.

Is the vegetable dyeing complicated ?

At some time the dyer could not carry out a dyeing with Logwood on oxidizing chromium mordant, without proceeding initially to the mordanting, followed by a long rinse, which had to take place before the dyeing with Logwood in a new bath. This practice had a very remarkable advantage : it left the mordanted goods " to mature their mordant ". This maturation of mordant involved, then, a better production of the lake of Logwood and a splendid black came out of it.

It is now possible to use the English "sequence process" to dye with Logwood. This process means that mordanting and dyeing are made in the same bath, after complete exhaustion of the potash or soda dichromate.

One uses :

1,5 to 2 % of soda dichromate or potash
2,0 to 2,5% of formic acid 85%
1,5 to 2,0% of soda hyposulphite

In France, the dyers prefer to simply use the suitable organic acids, with a marked reducing action. This leads generally to the same degree of exhaustion; moreover, one replaces part of the boiling bath exhausted by fresh water, in order to lower the temperature to 50-60°C, before adding oxidised Logwood, as indicated in the practical examples.

RESULTS OF DYEINGS WITH OXIDISED HEMATIN ON DIFFERENT MORDANTS

Table 2

Mordants	Shades	FASTNESS						
		FULLER			POTTING		TOPPING	
		Light-fastness	Change of hue	Bleeding on wool	Change of hue	Bleeding on wool	Change of hue	Bleeding on wool
Chromium	Dark blue	5-6	5	5	5	4-5	5	3-4
Iron	Blue black	6	5	5	4-5	4-5	2-3	2
Copper	Dark blue	5	4-5	5	1	2-3	1	1-2
Tin	Dark purple	4	3	4-5	2	3-4	2	3
Aluminium	Tern purple	4	2-3	5	1-2	2	1	2
Tungsten	Purple blue	4	2	4	1-2	3	1-2	2
Zirconium	Reddish blue	4	3	5	2	3-4	1-2	2
Nickel	Greyish brown	4	2-3	4-5	1	2-3	1	2
Molybdenum	Dark blue	6-7	1	3	2-3	1	5	1-2
Titanium	Black	4-5	5		4-5	3-4	5	3-4

Light-fastness maximum 8. Other : fastness maximum 5.

Nota. A sample of heavy drapery dyed in Hematin HPT on reduced chromium mordant gave the following results:
Index of lightfastness 5 / 5-6 Index of fastness to the alkalinefuller 5 fingers (4-5).

This method makes it possible, to some extent, to dye with Logwood, on chromium mordant, in only one bath. In this case, and according to C. Seyferth, the losses of force on the dynamometer of a wool dyed in black, would be the following :

Dyeing with:	Loss with the dynamometer:
A- Black diamond P.V.B.	
7% dye 1% acetic acid 10% acetate of ammonia 1% sulfuric acid	
I°- Development with: 3% potash dichromate	1,5 %
2°- Development with : 2% potash dichromate 2% formic acid	1,5 %
3°- Development with : 1,25% potash dichromate 1,25% lactic acid	5,0 %
B – Logwood black.	
10 % Hematin ESPGP	
I°- 3% Potash dichromate 2,5% Tartar	4,2 %
2°- 3% Potash dichromate 1% Sulfuric acid	2,4 %
3°- 1,5% Potash dichromate 1,5% Formic acid	1,5 %

Lastly, we can say that in the case of the yarn and the piece, a dyeing well done with Logwood (on iron and copper mordant), will be more fast to washing and light and won't be more fragile when tested for abrasion-fastness than an ordinary acid black.

A true sensitivity to the strong acids

It is advisable to keep the dyeings in Logwood away from the operations such as carbonizing and topping with sulfuric acid.

The Logwood dyeing also carries clear advantages, compared to artificial dyes.

Cover of the straws

The black with Logwood, which has faculty to link remarkably well, covers perfectly the vegetable impurities fixed on strawy wools.
Thus, by avoiding the obligation of the chemical elimination of straws, it can, in many cases, save this expensive operation.

Wool packaging

Logwood does'nt "dig" wool and preserves its inflating and its nerve, which is very appreciable.

Weight profit

While the dyeing with artificial dyes often involves a waste of weight, Logwood on the contrary, brings a "weight bonus" of about 4 %. This has to be taken into account when comparing both processes.

Beauty of the black

The deepness of the black made with Logwood remains unsurpassable in the sunlight as well as in artificial light.

Let us examine, now, the necessary conditions to carry out the blacks with Logwood, fast to the fuller and abrasion, on iron, copper and chromium mordant.

Conditions to make a solid dyeing

The dyeing of wool, with Logwood, requires some care :

1° The water employed for the dyeing and the rinse must be the less calcareous as possible. If the water is hard, it should be corrected before the start. This is done with hydrochloric acid, at a rate of 20 g of acid at 20° Baumé per cubic meter and degree hydrotimetric- represented by alkaline-muddy bicarbonates- or by the addition of the oxalic acid in the water of the bath which one carries at 60°C,

before introducting the other elements into the dyeing on iron and copper mordant. Without this precaution, insoluble combinations appears, which are prejudicial to the quality of the black color. One will control also the pH of degreased and rinsed wool, which must be close to 7,0. The liquor ratio can vary from 1/20 for common wools to 1/45 for fine wools mixed with rabbit hairs.

2° The wool must be well degreased before dyeing. If not, grease or oil of which is covered the wool will prevent the total fixing of the "Logwood, iron and copper" or "Logwood, chromium and copper" lakes on fibres, compromising the abrasion resistance.

3° For the dyeing on chromium mordant, you shouldn't dye under pH 5, nor beyond pH 6. There is no need to acidify the dyeing baths although they do not appear to be thoroughly exhausted. This coloring is due to products which the Logwood abandons and which separation from hematoxylin would be expensive.

By a strong acidification, these products would go on wool without the chromium could fix them. This would be prejudicial for fastness (to the fuller in particular).

It is the same for the rinse which must be carried out with fresh or purified water. If not, it should be corrected at pH 5/6 with hydrochloric acid with the possible addition of a detergent. However, it is necessary to be wary, in this case, of the " not ionogenic " which are, for the majority, suitable for form insoluble complexes with Logwood and tannins (without speaking about cationic).

As for the mordanting, in the case of the reduced mordant, the bath exhaustion must be total, i.e. colourless and without precipitation with soda carbonate. These conditions are generally met at an approx. pH of 4,3 at the end of the operation with formic acid (the operation goes on for 45 to 75 minutes, according to the boiling). When the wool is raveled and faded, the exhausted bath of mordanting will contain an important quantity of iron salts. The bath should then be completely drained, but it is not necessary to rinse it.

4° For the dyeing with iron, copper and oxalic acid. Bring the bath containing the wool, the Logwood and the oxalic acid to boiling temperature and maintain it at 95/98°C during ten to fifteen minutes. Then let the temperature drop naturally to 60/70°C in twenty minutes just by stopping the steam and keeping the bath moving.

One can then add fixing salts (copper sulphate and ferrous sulphate, beforehand dissolved in soft water) and bring the bath back to boiling temperature which one will maintain during forty-five minutes to one hour: enough for the complete development of the black on wool and the progressive exhaustion of metallic salts. This can be observed by the successive colours of the bath: from gold yellow to brown ale, then back to pale gold yellow at approx. pH of 3,5.

After the dyeing operation, the dyed wool should lay down or drain during at least two hours, so as to help the oxidation and to obtain, with the rinse, little coloured water.

DYEING OF SILK IN BLACK

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 therefore which all require a great experience, particularly when the silk material is to be weighted simultaneously. It would not be feasible to fully describe here all of the dyeing and weighting processes that may be followed. We will therefore limit our work here to only a few ones, likely to give satisfactory results.

We wish to emphasize that, as a rule, solely unoxydized Logwood Extracts, such as powdered Hematin ESPGP, ought to be used for silk tin-weighting.

However, when weighting is of no consequence, or if dyeing on a weighting other than tin-weighting, it becomes possible to use oxydized Logwood Extracts, among which: Hematin HPT.

It is said that silk has been weighted "*au pair*" whenever the loss determined by the degumming process has been recuperated, loss which amounts to approximately 27 per cent.

Any overweight will be expressed in percentage, based on the weighted "*au pair*" silk material. It should be noted that this percentage will, in general, not exceed 90 for tram threads, or:

60 per cent for silk material
30 per cent for Crepe Georgette

Table 3

COMPARISON OF SOME OF THE CURRENT TANNINS USED WITH LOGWOOD AND TIN FOR THE WEIGHTING OF SILK

In order to determine the share of each product in the weighting of silk, the following comparison tests have been carried out on leas of silk weighted with tin:

1°Ashes produced by the calcination of one lea of silk weighted with tin which weighs:
5,722 g = 2,372 G, or : **41,4%**

2° LEAS N°	1	2	3	4
Condensed water. Liquor ratio 1/25 Initial bath density	Tannant RTK	White sample	Retan GSK	Retan CHACK
INITIAL WEIGHT……. Two hours tanning at 70°C, then rinse with cold water. Then, drying and stay out of the drier	5,094 g	4,340 g	5,000 g	4,889 g
WEIGHT AFTER RECOVERY OF MOISTURE…… Compared to silk already weighted with tin, the increase is :……..	5,895 g 17,6 %	4,345 g 0,0 %	5,330 g 6,6%	5,154 g 5,42 %
COLOURING OF SILK	Old brownish gold	White	Old yellowish gold	Flesh
Solution containing by litre: 16 g of Hematin ESPGP 16 g of soap in powder Liquor ratio 1/50……. Reach 95°C in 15 minutes and maintain this temperature for 90 minutes	255 cc	""	250 cc	244 cc
COLOURS		**GARNETS EXTREMELY DARK**		
Wash. Rinse with tepid water, then with cold water. Then: Solution containing per litre: 3 g. of soda nitrite 6 g. of formic acid 80% Liquor ratio1/50…… Cold for 30 minutes Rinse and softening with soap 10 g/l. Drying and lactic acid 10 g/l fifteen minutes at 50°C	255 cc	""	250 cc	244 cc
FINAL COLOUR OF THE SILK		**VERY DEEP BLACKS**		
Drying and recovery of moisture FINAL TOTAL ORGANICS WEIGHTINGS …… WEIGHTING DUE to THE LOGWOOD	61,3 % 43,7%	0,0% 0,0%	54,3 % 47,7%	51,7% 46,3%

CONCLUSIONS : Tanning RTK proves to be the most active tannin, from the point of view of total weighting, in spite of the braking which it causes to the logwood. It should however be announced that the mother solution 1/1 marked only 18,5° Baumé after the elimination of the impurities which it contains normally. On this subject, the experiment of laboratory led to the following results: 100 g Tanning RTK + 100 g hot water give, after dissolution at 70°C, then cooling at 15/20°C and water complement for the return to the initial weight:

Liquid purified ……..118 G
with 18,5° Baumé Residue ……. 82 G

As a consequence, in the absence of Tanning RTK, Retan GSK could be used in atomized powder form.

BLACK DYEING OF ARTIFICIAL AND SYNTHETIC FIBRES

The not oxidised Hematin, or especially treated, penetrates Nylon remarkably well and can be used on bath circulation machines and on beck.
Special Hematin HPT is especially used on jigger.
One can work in followed baths.

It is interesting to add that the dyeing process with Logwood is quite appropriate for the dyeing of the surgical hairs: one does not risk the formation of necroses in human tissues; the dyed hairs support without any discolouration sterilization with steam under pressure (120°C).

The sewing threads for stockings, dyed with logwood, resist to the preboarding without changing nor bleeding on stockings.

Lastly, Nylon dyed with Logwood has a better light-fastness and there is no sublimation during the pleating.

The beauty of the black obtained on Nylon, Perlon and Acetate is really exceptional.

With this work, we have wanted to extend the already existing documentation, not only with regard to the application on followed bath, but also by using different bath volumes, in order to allow the dyeing of miscellaneous articles on the most current apparatuses.

We also wanted to assess the minimum consumption of Logwood in the dyeing process and of soda dichromate for the development of the black.
However, the smoothness of Nylon, in particular, sometimes requires slightly different percentages of hematin or soda dichromate.

One knows that the dyes which do not become exhausted completely during the dyeing (vat dyes, substantive dyes for cotton and logwood for example) require, for an intensity of shade given, a final concentration of bath given. All conditions being equal in addition, it is appropriate then at least, to also take into account the percentage of product fixed on the matter to dye and also of the dilution of the bath resulting from the water brought by the wet matter ready for dyeing.

For this purpose, we use the following equation, made as simple as possible:

Proportions of the various products necessary to the dyeing of nylon in black with Logwood

New bath: $K = (C_2 \times V) + (C_2 \times E) + \frac{(A \times p)}{100}$

In which:
K = Weight in kilos of product for the new bath
C2 = waste concentration required per litre, at the end of the dyeing
V = Volume of water in litres for the new bath corresponding to liquor ratio 1/5
E = Weight in kilos of water brought by the wet matter to dye
A = Weight of dry matter to dye
P = Percentage of product absorbed compared to the wet matter to dye

That is to say that the initial concentration of the bath receiving the wet matter to dye, would be :

$$C1 = \frac{K}{V + K}$$

or a weight of product compared to the initial volume of water being :

$$C = \frac{K}{V}$$

Or, more simply, a total necessary percentage P of products, compared to the dry matter to dye, equaling K when A = 100 kilos. This makes it possible to establish graphs with straight lines for the required percentages.

Note: it should be noted that :

1°- Calcareous water should be avoided as much as possible, because alkaline-muddy salts generally decrease the brightness of Nylon and the beauty of the black. However, if necessary, one could complex it with 1 to 2 g/L of sequestering salt (soda Hexametaphosphate, Calgon or Celon), then acidify to a pH of 5 or alkalize, according to the cases.
The use of calcareous water, with an hematin excess, can lead to a bronzed black, which can be corrected by a sodium sulphide bath.

2°- A defect of acetic acidity during the chromating will lead to a brownish black, i.e. insufficiently developed.

3°- The increase in weight of the dyed matter is about 4,5 % and the dyeing with Logwood preserves the Nylon's remarkable fastness.

4°- A black not deep enough can be reinforced by another dyeing with very reduced proportions of the various products mentioned.

5°- A stained black can be dismounted (partly) in a boiling bath of oxalic acid, then rinsed, alkalized with caustic soda, rinsed again, acidified and dyed with reduced proportions of hematin, dichromate and acetic acid.

In theory, one treats :

- the **spun yard** and the **combed yarn** (cakes, coils or muffs) with a liquor ratio of 1/15 to 1/20 on circulation of bath apparatuses.

- **satin** and **taffeta** with the liquor ratio of 1/3 to 1/8 on jigger.

- the **voile** with the liquor ratio of 1/50 on winch beck.

- **lace**, **stockings** and **jersey**, with a liquor ratio of 1/15 to 1/30 on circulation apparatus, vat or winch beck.

The de-oiling and the desizing of preformed Nylon are carried out either with hot water, or with:

3 to 5 g of caustic soda 36° Baumé per litre
2 g of a modern detergent (beware of the non ionogenic products: they form insoluble complexes with Logwood and tannins)

during one hour at 65°C. Rinse with purified or complexed water. Acidification with hydrochloric acid for pH 5 before dyeing.

Sometimes, one also uses a bath of suitable diastatic product, according to the usual technique, or even very hot purified (or complexed) water with soda carbonate, when it is only a matter of the eliminating an easily soluble slashing (checking by the reaction to iodine for the starch and by the tannin for the gelatine).

Fastness of the dyeings with the ESPGP hematins on Nylon

- Light …….. 5-6 (maximum 8)
- Boiling soap ……. 5 (maximum 5)
- Sweat ……. 5 "

Acid topping

- Acetic……. 5 "
- Sulphuric ……. 4 "
- Ironing (wet and dry)…….. 5 "

COTTON DYEING

In spite of the quantity and the diversity of the artificial black dyes used, certain cotton fabrics have never ceased to be dyed in black with logwood. The reason for this is their perfect harmlessness on the fabrics' fastness.

This is especially true for the dyeing of crossed articles, glazed and calendered percalines, common *clairvaux*, buckrams, lawn for the hat industry etc.

The processes of application of this black vary according to the dyeing factories and especially according to the installations they have; but all can be classified into these two main methods:

a) The one which consists in impregnating fabrics with the colouring matter, then to fix with mordant during a subsequent passage.

b) The other which consists in initially fixing the metallic oxides on the fibre, and then dyeing with colouring matter until saturation.

This last method, though slower than the first method, is certainly more rational: it provides a better black, which bleed less and it is cheaper. Notwithstanding, we will describe the two methods because the first one, in many cases, could be more easily adapted to the existing material in certain dyeing factories.

USE OF TANNINS IN TEXTILE INDUSTRY

Recommendations

The choice of the tannin to be used depends essentially on the colours which one wants to obtain: the various tannins have a different shade, more or less intense. This has to be taken into account when one wants to obtain a bright pure shade, a medium or a darkened one by means of basic dyes in the dyeing or the printing of vegetable fibres or rayons. This is why, in particular, one will prefer the Chinese Gall nut tannin for the bright blues, greens or pinks; the Sumac tannin will be good enough for the medium blues, greens or reds. Retan MDI or Retan CHACK give a much more colorful mordanting and as they are cheaper, they will be preferred for the realization of the brown, tobacco, Havana, otter and black.

For the bright shades, one must of course use water as pure as possible and especially exempt of iron. If the water is calcareous, one will initially correct it by a little acetic acid.

Cotton, for example, must be well boiled off, possibly bleached and rinsed well before undergoing the mordanting with the tannin. After the mordanting and the fixing, one should not leave the goods exposed to the air, in order to avoid them becoming brownish. The dyeing takes place with the chosen basic dyes, in the presence of 1 to 1,5 % of acetic acid. Start at tepid and go up to 60°C.

MOST POPULAR TANNING EXTRACTS

The tanning content analysis, by the Shake method, of the vegetable extracts, gives the following results detalled on Card 1:

Retan MDI ……57,0 %
Retan CHACK …… 50,7 %
Tannant RTK …….. 53,5 %

There are two types of tannins extracted from the Gall nut : one extracted with water, the other one extracted with alcohol.

This latter is considered as an absolutely pure Gall nut tannin and its total solubility in alcohol gives all facilities for the printing of the basic dyes in alcoholic solutions on transparent paper.

OFFICIAL METHOD OF THE QUANTITATIVE TANNING ANALYSIS

(or simplified Shake method)

Preparation of the analytical solution

One will have to employ a quantity of products such as to obtain a solution containing, as exactly as possible, 4 grams of tanning matters per liter, absorbable by the skin powder. In no case it should be less than 3,75 g nor more than 4,25 g. If the analysis result shows a tannin content out of these limits, it should have to be done again.

The weighing of the products to be analyzed will have to be done on a scale with a precision of 0,002 g.

The extracts, weighed in a becher, dissolved in ten times their weight of boiling distilled water, go into a graduated flask of 1000 cc.

Add boiling water up to the 1000 cc gauge. In a fresh water bath, cool as quickly as possible the flask until it reaches 18°C. Finally, top the 1000 cc gauge with cold distilled water.

Dosing of total solid matters

50 cc of the analytical solution are put to evaporate in a bain marie in a tared flat capsule, in silver or stainless steel. After evaporation, dry in an oven at 98,5°C - 100°C. Then, as quickly as possible cool down in the desiccator until it reaches the **constant weight A.**

Dosing of total soluble matters

Filter part of the analytical solution on a Berkefeld candle, especially prepared, under a vacuum of maximum 70 millimeters of mercury. The first 100 cc are to be rejected. Collect the following 50 cc, which must be optically clear. Evaporate, desiccate and weigh them the same way as for finding weight A. **This is weight B.**

Dosing of the non tannins

Use a special skin powder, pre-chromed, available in an Institute for Leather Industries.

In a 250 cc powder compact, introduce a weight of skin powder equivalent to 6,25 g of dry substance (ie, in general 7 G). Add 100 cc of the analytical solution. Close the container with a rubber top. Agitate mechanically the container (80 revolutions per minute) for twenty minutes. After ten minutes rest, filter on a funnel with porous glass filter plate (characteristics n° 172 211 of the Pyrex catalogue), fixed by a rubber top on a 200 cc filtration flask, itself connected to a source of vacuum.

Under a slight vacuum, pour in the funnel the container's contents (skin powder and de-tanned solution). The liquid runs immediately in the flask. With the rubber top, gently press the skin powder on the porous plate, until it's slightly dryed.

Cut the vacuum, collect the slightly turbid de-tanned solution. Put it under vacuum again, on the funnel with the skin powder. The filtrate must be limpid. If needed, make a third filtration.

One esteamates 50 cc of the de-tanned solution, still in the special capsule. Dry in the same way in the oven and weigh quickly until constant weight. **There is weight C.**

Interpretation of the results

Insolubles	= A – B,	brought back to 100 of product
Tannins	= B – C,	" " "
Non tannins	= C	" " "
Water	$= \frac{100 - A}{100}$,	" " "

As for the acidity measure, determine the pH and the total acidity (expressed as a percentage of acetic acid) with the glass electrode. This will lead to the average results given by table 1 on page 5.

SELECTED EXAMPLES OF INDUSTRIAL APPLICATIONS ON WOOL

I°- On "*taupeline*" spun and scoured

(mixture of merino wool and 30% of rabbit hairs)

This material is particularly demanding, **dyeing on reduced mordant.**

Liquor ratio 1/45. Weight of the material to be dyed: 10,040 kg.
Machine with stainless steel propeller.
Purified water: - 450 litres at 50/60°C.
Formic acid 85% in order to correct alkalinity until pH 6,0

Enter goods, insure the circulation for a few minutes. Add pre-dissolved:

	3 % Sodium dichromate ……	0,300 kg
then:	4 % Lactic acid 50% ……	0,400 kg

Make the bath circulate. Heat to the boiling point in fifteen minutes approximately. Maintain this temperature for one hour and a quarter until complete exhaustion of the chrome. The bath should be colorless and shouldn't precipitate the lead acetate or the ammonia or the soda carbonate any more, except in the presence of calcium salts. Empty the colorless bath (pH 4,3). No need to rinse.

Fill with purified water. Add at 50°C:

14 % Hematin HPT……	1,400 kg
1,5 % Yellow CNOK ……	0,150 kg

Go to boiling temperature within fifteen minutes. Dye during forty-five minutes. Rinse during ten minutes at 50°C with purified water, then allow a second rinse at 50°C with 2 g/L Teepol (anionic wetting agent). Lay down, spin-dry and dry.

The "*taupeline*" will then have a very soft touch, a perfectly black shade with full and bluish sheen, without any felting, perfectly uniform and no dirtying under abrasion.

Increase in weight with deduction of the scouring loss : 5,05 %.

2°- Wool in flock (washed thoroughly, 1/2 fine), **combed wool:**

a) Control of the reaction on the batch of wool by means of the universal indicator :

Enter the scoured and dry wool. Soft water and, if necessary, 1 % of wetting agent. Suitable detergent, in the dyeing apparatus. Heat and make the bath circulate during a few minutes. Bring the pH to value 7-8:

pH 4,0 = orange red
pH 5,0 = orange
pH 6,0 = yellow
pH 7,0 = greenish yellow
pH 8,0 = yellowish green
pH 9,0 = green
pH 10,0 = greenish blue

If an acid pH is obtained, for example of 4 (case of carbonized and insufficiently neutralized flock wool), it is necessary to neutralize with 0,5 % of soda carbonate, dissolved beforehand in hot water, so as to obtain, after five to ten minutes of circulation, a pH of 7,5 approximately. This is the normal reaction for white wools of Mazamet (if the pH is higher than 8, it is possible to acidify).

Then carry out the mordanting and the dyeing.

a) Mordanting and dyeing (Dyeing on reduced mordant) :

Liquor ratio 1/20 or 1/25. Soft water.
Apparatus in wood or stainless steel, with propellers.
120 kg of common wool (white and Burel) pH 8.

In the bath at 50°C, dissolve :

1,8 % Sodium dichromate (2,160 kg)

Make the bath circulate during five minutes then add successively:

1,1 % Formic acid 85% …….. 1,320 kg
0,5 % Copper Sulphate…….. 0,600 kg
and : 1,1 % Formic acid 85%…….. 1,320 kg

Then go up to boiling point in twenty minutes. Maintain for 60 to 75 minutes. Colorless bath, pH 4,5 with the universal indicator.

Empty 2/3 of the bath.

Refill the bath with soft water, readjust the temperature at 60°C. Add, beforehand dissolved in an boiling water bucket (provided with a steam wash-bottle) :

6 % Hematin HPT
and 0,3 % Yellow CNOK dissolved in hot water

It is possible to replace part of Yellow CNOK by 0,2 to 0,3 % of alizarin red.
Heat to boiling point, maintained for forty-five minutes. Empty. Rinse with soft water at 55 °C. Spin-dry and dry.
For **combed yarn**, after rinse with soft water at 55°C, put into the smoothing machine (water, ammonia, neutral soap, rinse).

3°- Multicoloured shoddy wool, for 100 kg (dyeing on oxidised mordant) :

This dyeing is carried out with an oxidying mordant in order to destroy, as much as possible, the basic colours insufficiently fast with the fuller.

Sodium dichromate……2 %
Sulphuric acid 65° Baumé…….2 %
Copper sulphate……0,4 %

Enter at 60°C. Add dichromate. Insure circulation for ten minutes, then introduce the sulphuric acid and the Copper sulphate, dissolved beforehand. Go to boiling temperature and maintain for ninteen minutes.
Refresh. Cut down. Start another mordanting operation.

The batches of mordanted wool are put on side then rinsed thoroughly with the circular washing machine and one proceed with the dyeing in a new bath with:

Hematin ESPGP……. 3 to 5 %
Yellow CNOK……. 0,1 to 0,2 %

In order to shade the black.

Start at 60°C then go up to boiling temperature. Maintain the temperature for one hour. Then lay down and put to dyeing another mordanted and rinsed batch, as already indicated.

After the dyeing, the wool is thoroughly rinsed, spin-dried and dried.

Remark - In the case of batches of shoddy and faded wools, dye on chromium reduced mordant as indicated for flock wool and scoured wool.

DYEING OF WOOL RAGS

Dyeing of multicolored woolen rags, scoured, and possibly faded

Mordanting

Soft water.
Liquor ratio 1/25 at 40 to 50°C.
2,2 % of potash dichromate or sodic dichromate

Then, after five minutes of impregnation, add :
2,2 % of sulphuric acid 96% diluted in cold water
0,4 % of Copper sulphate
and reach boiling temperature maintained for fifteen minutes.
Cool at 85/90°C and add :
2,2 % Lactic acid 50%

Go back to boiling temperature and then maintain for an hour.

Lastly, empty the bath completely and refill it again. Let the water circulate during a few minutes because the waste mordanting bath contains impurities, lime salts in particular which can be very awkward in the following operations.

The dichromate treatment is necessary to destroy or fix basic colourings which would not be fast enough to the fuller.
In the case of faded rags, same observation as for faded shoddy wool.

Dyeing

Bring the bath to 50°C. Add :
4 % Hematin HPT
Go to boiling temperature and maintain during forty-five minutes to one hour.

In the course of dyeing, if necessary, correct the acidity in excess (yellow shade of the bath) by addition of 0,5 to 1 % of Soda carbonate, so that the bath has a colour " old Bordeaux " (without being purple) ; i.e. at pH 5 approximately. Then, bring cold water in order to gradually reach 25/30°C. Empty the bath and rinse again with clear water if necessary.

Nota : Fastness of Logwood black: (See table 2, page 7)
Light ……5-6 (maximum 8)
Fuller ……..5 (maximum 5)
Carbonizing ……2-3 (maximum 5)

DYEING OF MOHAIR WOOL IN BLACK

1st Method :

a) Scouring – fifteen minutes at 50°C, with :

5 % of Ammonia
4 % of Teepol
1 g/litre of soda Hexametaphosphate

Rinse with soft water until complete elimination of alkalinity.

b) Mordanting – Seventy five minutes at **boiling temperature** with :

Products added in this order to the bath at 60°C	1,8 %	Sodium dichromate
	1,2 %	Formic acid 80%
	0,5 %	Copper sulphate
	1,1 %	Formic acid 80%

Empty the **completely exhausted bath**. No need to rinse. One can even, if necessary, simply refresh the bath at 50°C with fresh water.

c) Dyeing – One hour at the boiling temperature with :

Products dissolved beforehand and added to the bath at 50/60°C	7 %	Hematin HPT
	0,3 %	Yellow CNOK

Empty the bath. Fill of soft water. Circulate for ten minutes and rinse a second time.

2nd Method :

Same formula as 1°, without scouring. It can be noticed that the distribution of chromium is less regular than on scoured wool.

3rd Method :

Same formula as 1°, but while using for the dyeing:

Products dissolved together in boiling water	Hematin ESPGP	8 %
	Borax	1 %
	Yellow CNOK	0,1 %

It is then noticed that the waste bath, after rest and decantation, does not leave a blackish residue.

DYEING OF FELTS FOR THE HAT INDUSTRY, WOOL AND RABBIT HAIRS, LIGHT FELTS

1°- Impregnation

During one night with:

Soft water at 50°C. Liquor ratio 1/20.
Sodium dichromate …… 3 %
Soda carbonate…… 2 %
Teepol……..3 %

2°- Mordanting

Add to the bath of impregnation at 50°C :

Formic acid 60 %…….. 4 %
Copper sulphate……1 %

Bring to boiling temperature. Maintain for nineteen minutes (practically complete exhaustion).

3°- Dyeing

Empty the waste exhausted mordanting bath. Fill with soft water. Heat at 60°C and add:

	Very thick and tight felt	Light felt
Hematin HPT	25 %	15 %
Yellow CNOK	1 %	1 %

Heat to boiling temperature. Maintain for two hours and a half, and, during the dyeing, add a little soda carbonate (0,3 to 0,5 % of the felt weight) so as to maintain a “brown beer” color, a little reddish, sign of a low acidity.

4°- Rinse

Lay down and give two rinses with soft water, very hot, so as to eliminate excess of logwood not fixed.

WOOL IN PIECE
(Dyeing with iron and copper mordants)

Common wool.
Stainless steel winchbeck.
Proportions % of beforehand dissolved products in hot water
Liquor ratio 1/20
Scoured and rinsed wool, brought to pH 6 or 7.
Purified water brought to pH 6 with 0,3 g/litre of ordinary hydrochloric acid.

Start at 60/70°C and add in this order :

New bath

1°	Oxalic acid……..	2,8 % to 3,0 %
	Hematin HPT……..	4,2 %
2°	Hematin ESPGP……..	2,8 %
	Yellow CNOK……..	0,5 %

Bring to boiling temperature within fifteen to twenty minutes. Maintain for ten to fifteen minutes. Stop the steam while still letting the winch turn, so as to let the bath cool to 60/70°C in twenty to thirty minutes. Then add :

3°	Crystallised iron sulphate……..	3,3 %
	Crystallised copper sulphate…….	1,7 %

Go back to boiling temperature. Maintain for forty-five minutes to one hour.

The bath will go from a “yellow gold” color to a “brown ale” and then to a “pale gold yellow” at pH 3,3 - 3,5. The wool will go little by little from “yellow gold” to brown and the “blue black”, which will be accentuated thereafter.

Then, lay down flat, leave to rest for two hours approximately. Rinse during fifteen minutes at 50°C with purified water, corrected at pH 5 or 6 with oxalic acid (150 g approximately per cubic meter). Empty and rinse again with cold water (purified if possible). Lay down, spin-dry and dry.

Old bath

Same process as with a new bath, but empty 1/3 of the old bath, replaced with water corrected with 0,3 g/litre of ordinary hydrochloric acid.

Oxalic acid…… 2,8 %
Hematin HPT…… 3,4 %
Hematin ESPGP…….. 2,2 %
Yellow CNOK…… 0,4 %
Iron sulphate crystallised……..2,3 %
Copper sulphate crystallised…… 1,2 %

Logwood on iron and copper mordants, in particular when applied to woolen fabrics and knitting wools, gives more fastness guarantees than an ordinary acid black.

WOOL IN PIECE
(Dyeing on reduced chrome mordant)

(which is often preferred to that which is carried out with iron and copper)

The duration of the dyeing corresponds, in this case, to that of an operation with a chromium black. Independently of the beauty of the black and the good “hand" given to the fabric, one can avoid, in many cases, the expensive operation of the chemical elimination of straws.

Example:

For several heavy pieces (*gabardine* for example) weighing 142,5 kg. Volume of the bath: 2 600 liters. **Water purified** at 13°H.T.(lime and soda carbonate). Correction of water with 0,2 g/litre of ordinary hydrochloric acid ; 520 cc for pH 6. Winchbeck in wood. Enter at 50/55°C and add in this order :

1,7 % Potash dichromate (or soda dichromate)…… 2,425 kg

Stir for ten minutes, then :

2 % Lactic acid 50%…… 2,850 l
0,4 % Copper sulphate…… 0,570 kg
2 % Formic acid 80%…… 2,850 l

Bring to boiling temperature in fifteen to twenty minutes. Maintain this temperature for one hour, in the case of very green wool. Colourless bath. pH 4 approximately. Refresh until 25°C. Empty. Refill.

Heat at 50/55°C and add at the same time, sprinkling in the partition:

0,5 g/L celan " A "…… 1 300 g

Check the pH (5 approximately) and add, beforehand dissolved in very hot water :

0,5 % Hematin ESPGP…… 715 g
5,0 % Hematin HPT…… 7 125 g
0,3 to 0,4 % Yellow CNOK…… 1 280 g

Bring to boiling temperature in fifteen to twenty minutes. Maintain this for forty-five minutes. Cut the steam. Sampling, if good shade, refresh at 25°C with purified water. Empty. Refill. Add 0,3 g to 0,4 g/litre of hydrochloric acid for pH 4,5 approximately. Heat at 30°C. Refresh at 20°C, and lay down.

OBSERVATIONS

The experiment's results are :

1°- Wool pieces in vat with winch: when mordanting with 1,7 % of potash (or soda) dichromate and 0,4 % of copper sulphate, one cannot obtain a sufficiently reduced mordanting (green) and a colourless bath not precipitating with lead acetate after one hour of boiling, without making use of 2 % of lactic acid (50%) in addition to the 2 to 2,2 % of formic acid 80%. This last quantity is usually considered to be sufficient in the case of flock wool of Mazamet on circulation apparatus.

This difference in behaviour can come from the usage of a less reducing wool, from a liquor ratio sometimes larger (1/35 in the place of 1/20) or from a contact of the piece to the air at pH 3,9 approximately at the start and 4,1 approximately at the end of the operation.

2°- Under these conditions, if the reduction is sufficient (green-grayish wool) with a colourless bath, one can observe, on the other hand, a slight precipitation with ammonia and especially with carbonate soda. This shows the presence of a small proportion of chromium lactate and formiate. These are soluble and of an extremely pale greenish colour, which gives the impression that the waste bath is absolutely transparent seen through a test tube, whereas it is not.

Thus, in the case of the dyeing of the pieces and after mordanting, one cannot simply refresh the exhausted bath with fresh water until 50°C before the introduction of Logwood. This would mean taking the risk of later determining the formation of a certain proportion of black lake in the dyeing bath. This would be prejudicial to the abrasion fastness ; more especially as it would be suitable to bring back the reaction bath's pH from 4,2 to 4,8 by an addition of ammonia.

This partial neutralization would be likely to fix chromium hydrate on the pieces, more or less uniformly and superficially, causing unlevelness and a possible hardening of the wool.

It is thus advisable to completely empty the waste bath, after a progressive cooling to 30°C, in order to avoid the breaks.

By using 1,7 % of $Cr_2O_7K_2$ while mordanting, one will find, through the dyed wool analysis, a percentage of chromium corresponding to 1,44 % of $Cr_2O_7K_2$ or approximately 1,52 % compared to the weight of wool before dyeing (for a liquor ratio 1/30).

3°- The water purified partially with lime and soda (12°H.T.), although less alkaline than rough water or permuted water, is still likely to produce, with Logwood, an alkaline-muddy lake, also prejudicial to abrasion fastness and also to the aspect of the black (black a little russet-red) especially if the Hematin amount is around 6 %. One can, fortunately, avoid these defects by " complexing " the muddy alkaline salts with 0,5 g/litre of Celan or soda Hexametaphosphate, for example. Then, adjust to pH 4,8 and add the Logwood to the 50°C bath. One thus obtains a dyeing bath with a

bright brownish-yellow shade (brown ale) and perfectly clear. The wool is quite black with blue reflection and has a very good abrasion fastness in industrial operations, after rinse with corrected water at pH 4,5 with hydrochloric acid.

It has to be added that, under these conditions and while starting at 50°C, the black will develop on mordanted wool a little slower, which is preferable for the penetration, the fastness, the levelness and the beauty of the blue-black.

4°- As a matter of safety, the simultaneous use of Hematin ESPGP and Hematin HPT (oxidised with high concentration and dried with an atomizer) is possible, if the mordanting isn't completely reduced. This would act as a shield against the over-oxydization of Hematin. However, as the Hematin HPT is oxidised only at 80% (15% of natural oxidation for Hematin ESPGP), if it is made sure a full green mordanted wool is obtained with a colourless bath, we estimate that alone, the Hematin should be enough, with an addition of Yellow CNOK.

The Hematin alone gives a dark blue, approaching the black by increase in the fixed quantity. Yellow CNOK leads to a "racing green" or to a "crow black", following the proportions employed.

The addition of Yellow CNOK must be as weak as possible, that is to say 0,2% to 0,4%, in order to preserve a proportion of Hematin HPT close to 5 to 5,5 %, to ensure a lightfastness close to 5,5. Other fastnesses (except sulphuric topping and carbonizing) being always maximum.

5°- Finally, with regard to the rinse:

- When one deals with soft water (mountain rainwater), it is enough to ensure the effectiveness by a progressive fresh water supply.

- When water is even slightly calcareous, it is advisable to refresh initially until 25°C approximately, then to empty, refill with water at 30/35°C, corrected with 0,3 to 0,5G/litre of hydrochloric acid for pH 4,2 to 4,5, stir ten minutes and bring back to 20/25°C with fresh water before laying down.

DYEING PROCESS FOR " MIXED BLACK "

The " mixed blacks " have an excellent air resistance and light-fastness, **higher** than that of the acid black and than that of Logwood which constitute them. Indeed, the acid black has a strong tendency to redden with the light, while the Logwood black tends to become green. By the association of these two blacks, the defects are offset (green being the complementary colour to red), the resulting black will only change very little with the air and the light.

Very important - Apart from that, these blacks are solid to washing, abrasion, decating, to sweat (and therefore to acid) and they make it possible to obtain the good weight, the beautiful reflection and the touch that is appreciated with Logwood.

Dyeing

Above all, it is important to correct the water used: because the dyeing is done with oxalic acid which doesn't put up with calcareous waters.

The simplest process is to previously correct the water with hydrochloric acid : 20 cc of hydrochloric acid 22° Baumé industrial per hydrotimetric degree and per cubic meter of water. Thus for 1 cubic meter of water at 20° hydrotimetric, one will add to the dyeing vat 400 cc of hydrochloric acid, before any other addition.

Stir then dissolve in this order :

according to shade and intensity of the black needed

- 2 to 4 % of acid Black
- 3 to 4 % of Hematin HPT
- the quantity of Yellow CNOK necessary for the shading
- 5 to 10 % sodium sulphate
- 2 to 3 % Oxalic acid

Introduce the wool at 60/70°C, go up in half an hour to boiling temperature, maintain for forty-five minutes. The aniline dye is then exhausted and the bath should only have a brown-yellowish colour. If this isn't the case, it means that the exhaustion is incomplete and you should add :

0,5 to 1 % oxalic acid

and let it boil for another quarter of an hour.

Then add :

2 to 4 % of iron sulphate
1,5 to 2 % of copper sulphate

Keep it boiling for thirty to forty-five minutes.
Haul, ventilate, rinse.

OPERATING CONDITIONS FOR THE APPLICATION OF DIRECT LOGWOOD BLACK ON FELT
(Multicoloured wool, reinforcment cotton)

Proportions are in percentage of kilos of dry felt. Liquor ratio 1/20-1/30. Fresh or purified water. Scoured felt. Winch batch.

OPERATING PROCESS n° 1

a) Dyeing

	new bath	old bath
Acid Black Logwood Black ESPGP	12 to 15 %	9 %
Copper sulphate	2 %	1,2 %

b) Chromating

Sodium or potash dichromate	1 %

Enter the dyeing bath at 60°C. Stir for fifteen minutes. Add the dye and then the _ dose of copper sulphate. Stir for twenty minutes and add the remainder of copper sulphate. Go to boiling temperature and maintain it during forty-five minutes.

Then, haul the pieces, let them drain, lay on a tray to the air, to allow the development of the black, for at least ninteen minutes.

Lastly, make a thirty minutes chromating at 60°C with 1% soda dichromate (each time in a new bath). Haul, let drain, rinse thoroughly with the two roller washing machine, spin-dry, one face finishing (if necessary) and dry.

OPERATING PROCESS n° 2

Liquor ratio 1/25-1/35, soft water.

a) Dyeing

	new bath	old bath
Soda carbonate Solvay	1 %	0,5 %
Oxalic acid	1,2 %	0,5 %
Hematin ESPGP Direct synthetic black	10 %	6,0 %
Copper sulphate	1,4 %	1,1 %

b) Chromating

	new bath	old bath
Sodium dichromate or potash	1 %	

Enter the 80°C dyeing bath containing soda oxalate. Add the dissolution of direct black H.M. Bring to boiling temperature. Cool the bath down to 70°C, while maintaining the movement. Then add through the partition the copper sulphate dissolution. Go back to boiling temperature and maintain for an hour.

Then, haul the pieces, let them drain, lay on tray in the air during one hour thirty to two hours, in order to allow the development of the black.

Lastly, make a thirty minutes chromating at 50°C with 1 % soda dichromate, each time in a new bath. Then, haul and let drain. Rinse thoroughly and spin-dry, one face finishing (if necessary) and dry.

Notes

The soda oxalate obtained by the combination of soda carbonate and oxalic acid (in preliminary 10% solutions) is used because the presence of this salt improves the solubility in the dyeing bath of the Logwood / Tannin / Copper sulphate lake.

In addition, in order to obtain a better distribution of the cupric complex, it is advisable to begin the dyeing at 80°C without the copper sulphate. Bring to boiling temperature, let the bath cool to 70°C before adding the metallic salt. Go back to boiling temperature and maintain it during forty-five minutes to one hour.

In general, under these conditions, the wool and the cotton are well covered and the bath will stay at approx. pH 5,5, if the felt is neither acid, nor alkaline, while entering the dyeing process.

The mixture of Hematin ESPGP and direct dye is preferred **to the sole direct dyes** (substantives) in the dyeing in black of felts for slippers. This is due to the fact that these articles require not only a very black shade and a sufficient cover of cotton, but also an improvement of the swelling and firmness of the material.

BROWN SHADE ON MULTICOLOURED WOOLEN FELT, WITH COTTON REINFORCEMENT
(Felt for slippers)

Liquor ratio 1/20.
Proportions for 100 kg of felt
NEW BATH on beck

Tannant RTK	40 %

Enter the bath at 50/60°C. Maintain for one hour. Lay down. Rinse with cold water on another beck to eliminate the excess in Tanning RTK, not fixed. Then, add in the rinse bath, brought to the volume desired :

Acetic acid 80%	1 %
Soda dichromate	2 %

Go up to 70°C. Maintain this for half an hour.

Then empty and rinse thoroughly.

On FOLLOWED BATHS, do not use more than 10 % approximately with this Tanning RTK.

Such a treatment is required in order to give a better firmness to this kind of felt and to reduce the weight loss during the dyeing.

WEIGHTING AND DYEING OF SILK WITH LOGWOOD

WEIGHTING OF SILK

Operate on silk carefully scoured with soap and soda carbonate. 100 kg of scoured silk, equals approximately 130 kg of greige silk.

After scouring, silk is rinsed with tepid **pure water** (30/35°C) during a quarter of an hour.

Silks in floats
Tin-dichloride and soda phosphate weighting

As an example, here is a process that gives heavy weighting :

Use a tin bath containing tin dichloride at 30° Baumé and 15°C of which ratio:

$$\frac{\text{Acid found with the analysis}}{\text{Theoretical Acid}} = 10{,}25$$

Process

First tin bath : The tin bichloride bath is obtained from Pinksalt at 55° Baumé, lowered to 30°C through the addition of soft water. The tin bath volume is equal to about fifty times the silk weight.

The silk material is entered into the tin bath at 30° Baumé and 18°C. This temperature is to be maintained, trough refrigeration if necessary. Operations should, if possible, be carried out in a semi-darkness.

Dye silk material four times within one hour, then let it drip and wring out.

Rinse : The material is to be carefully rinsed with cold water at 18°C. Water should titrate **at a maximum** of 7°HT.

Four washings of 15 minutes each will be carried out in different waters. The silk will then be lifted, wrapped in a piece of Tulle material, placed into the dryer and then phosphate-treated.

First phosphate bath : Prepare a sodium phosphate bath at 6° Baumé, with distillated water or water purified at 0° HT containing per liter :

130 g of Sodium Phosphate, Bisodic PO_4Na_2H, 12 H_2O

6 g of Sodium carbonate CO_3Na_2, 10 H_2O

Enter silk at 65°C. Dye for five minutes and then bring the temperature to 70°C. Dye for 25 minutes, keeping the temperature at 70°C, then lift, drip and rinse.

Rinse : The material must be rinsed with special care, with water at 0° HT. Silk will be given four washes :

1st washing at a temperature of 35°C
2° " " 25°C
3° " " 15 to 18°C
4° " " 15 to 18°C

Drip and dry silk in its Tulle cover and proceed to brightening.

Brightening : To be carried out during 10 minutes, in water at 0° HT, with 2 cc pure Hidrochloric Acid 20° Baumé per liter of water.

Maintain temperature at 20°C. Lift material, drip, wring out completely without rinse.

Second tin bath : Use the same tin bath, now of approx. 28° Baumé. Raise to 30° Baumé through addition of Pinksalt at 55° Bé.

The process now is identical to that of the first tin bath.

Second phosphate bath : Another Phosphate bath is to be prepared with subsequent operations remaining as previously described, with a careful rinse and a brightening.

Third tin bath : The old bath is approximately 29° Baumé. Raise to 30° Baumé (addition of Pinksalt at 55° Bé) and process as described for the first and second bath.

Third phosphate bath : Prepare a third phosphate bath and process as for the first and second phosphate baths. Rinse, wring out and dry.

No brightening nor soaping ought to be carried out at this stage.

Tin-weighting is now over. The silk will then be weighed after it has recaptured ambient humidity.

The tin-weighting percentages obtained, based on the weight of the degummed silk, averages from 70 to 75 %.

Once the phosphate bath has been carried out, the silk will, if necessary, be treated for 40 minutes, at 50°C, in a bath containing Sodium Silicate at 2° - 5° Bé. A 30 minutes soaping will follow, at 50°C, with a solution containing 20 per cent soap.

Rinse, wring out and dry, if required.

WEIGHTING AND DYEING WITH LOGWOOD

Once the silk has been tin-weighted, prepare the logwood bath, with the percentages stated below, **based on the weight of the tin-weighted silk** :

80 % of Hematin ESPGP
80 % of household soap

Dissolve Logwood Extracts in **lukewarm soft water** and then add the soap solution, priorily dissolved in **water at 0° HT** and 100°C.

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

Enter the silk material at 50/55°C. Dye for 30 minutes. In the meantime, weigh and dissolve separately:

2 to 5 % of Methylene Blue (according to the quality of this product and of the colour wanted).

Add to dyeing bath approx. 1/3 of the dissolved Methylene Blue. Dye and raise temperature to 60/65°C. Dye for 15 minutes. Add another of the Methylene Blue solution, dye on and then add the remaining portion of the Methylene Blue solution.
Raise to 90/95°C while dyeing for one hour 30 minutes to two hours.

Lift silk material and drip. Rinse twice in water at 30°C, then at 15°C and oxydize in a fresh bath, as cold as possible, in which 3 to 5 g Sodium Nitrite (NO2Na) will have been dissolved beforehand and to which 6 to 10 g Formic Acid **per liter of liquor** have been then added.

Enter material and dye continuously for 30 minutes. Rinse twice with tap water.

Brighten and soften according to usual process (soap bath at 10 g/l, for 15 minutes at 50°C). Wring out. Then enter the silk into a bath at 50°C containing approx. 5 % Lactic Acid 50%, during 15 minutes.
After exhaustion, rise, spin-dry and dry.

For lower tin-weightings, reduce proportionately the number of passages and the quantities of Hematin, but two tin-passages –as a minimum– will however remain necessary.

According to the bath volume, the guideline for this process would require :

- for 10 to 20 % of weighting: 60 % of hematin with 2 tin baths
- for 25 to 35 % of weighting: 80 % of hematin with 2 tin baths
- for 40 to 50 % of weighting: 80 % of hematin with 3 tin baths
- for 55 to 65 % of weighting: 115 % of hematin with 3 tin baths

above weighting percentages are based on the weight of raw silk material.

One can also use the methylene blue after the weighting and the dyeing with Logwood on silk weighted with tin.

For that, one uses initially only the hematin and the soap. Then, after the nitrite bath and the rinses, one enters in a cold bath containing :

1,9 % of Methylene blue
2,5 % of lactic acid 50%
} % of the weight of the weighted silk

Then, bring the temperature slowly to 70/80°C.

After exhaustion, rise, spin-dry and dry.

DYEING IN PIECES
Logwood black on tin mordant

Degumming : As usual.

Weighting : take into account that the blacks also increase by N % of their weight in dyeing.
For the China crêpes, the weighting with tin phosphosilicate are :

Weightings Weight for weight (W.F.W)	**Number of tin passes**	**Silicate bath**
0 to 10 %	1 to 28° Baumé	1° Baumé
10 to 20 %	2 to 20° Baumé	1/2° Baumé
20 to 30 %	3 to 20° Baumé	1° Baumé
30 to 40 %	1 to 28° Baumé 2 to 20° Baumé	1/2° Baumé
40 to 50 %	3 to 28° Baumé	1/2 or 1° Baumé

(For the tin weighting, refer to the indications given for the weighting of silk in floats).

Dyeing

Plunge the pieces in a bath at 60°C containing :

50 % soap and for Weightings	**W.F.W. and 0 to 10**	**10 to 20 and 20 to 30**	**30 to 40**	**40 to 50**
Methylene Blue	2,5 %	3,5 %	4 %	5 %
Hematin ESPGP	20 %	30 %	40 %	50 %

The Methylene blue being put in several times and only half an hour after the beginning of the dyeing with Hematin ESPGP and the soap.

Gradually heat so as to achieve 80/85°C in one hour thirty. Then make two washes with soft water and one washing while making an overflow.

Oxidation : In a water bath as cold as possible, one dissolves successively:

2,5 to 5 g of soda nitrite
then : 5 to 10 g of formic acid
by litre of bath.

Agitate the silk in this bath for half an hour. Give two washes with hard water, revive and soften as usual.

SILK DYEING ON IRON MORDANT

The silk is put in an iron nitrate bath at 30° Baumé during one hour, removed, twisted and left in a heap for the night. Then, it is washed thoroughly and put into calcareous water heated at 90/95°C during twenty minutes.

Put the material in a bath with 10 % of Yellow CNOK for half an hour at 60/70°C, and a then in a Logwood bath composed of 20 % of Hematin HPT and 20 % of household soap.

Enter at 55°C, turn for fifteen minutes, go up to 65°C in fifteen minutes, then to 75°C. Dye for fifteen minutes. Rinse and revive.

The weighting is approximately 15 % of the degummed silk's weight.

If the quantity of oxidised hematin is 40%, this weighting is approximately 20%.

SILK DYEING ON MIXED MORDANT

Logwood Black on iron mordant gives a bluish shade which is difficult to reproduce on tin mordant.

It is however possible to reproduce a given “iron black” with a heavy tin-weighting. We recommend to follow the process which is described hereunder :

For a final weighting of 45 %, start with a tin-weighting of 33 %. Immerse the silk into a bath containing:

3,5 % of Hematin ESPGP
13 % of Yellow CNOK

Dye for 20 minutes at 60/65°C, then add the following ingredients, separately dissolved :

12 % iron sulphate
2 % copper sulphate

The relative proportions of these two mordants can vary according to the shade to be obtained.

Dye for one hour and 30 minutes at 65 to 70°C. Lift material. Dye for a further 60 minutes in an other vat, at 70/75°C, with :

30 % of Hematin ESPGP or HPT (according to shade and deepness of black desired)
25 % soap

The weighting thus obtained through the dyeing alone is 12 %.

DYEING OF NOT WEIGHTED SILK ON CHROME MORDANTS

The Logwood black on silk, degummed and mordanted with iron, requires concentrated iron nitrosulphate baths but produces a beautiful black with approximately 15 % weighting.

The logwood black on silk, degummed and mordanted with chromium, gives also a very beautiful black but with a shade which is more blue.

The produced weighting is 12 %. It is thus very close to the previous one.

The process number 1 comprises :

1° A mordanting with chromium and a rinse
2° A dyeing with a mixture of oxidised and not oxidised hematin
3° A rinse with cold water
4° A chromating and a rinse
5° The usual softening and reviving

One operates under the following conditions with fresh or purified water, and a liquor ratio of 1/25 for example.

OPERATING PROCESS NUMBER 1

1°- Mordanting

Enter at 50°C.
Furnish, in this order, for 100 kg of degummed and thoroughly rinsed silk :

Sodium dichromate	1,7 %

then, five to ten minutes after :

Lactic acid 50%	2 %

Then :

Copper sulphate	0,4 %
Formic acid 80 %	2 %

Bring to boiling temperature and maintain for one hour. Empty. Rinse.

2°- Dyeing

Enter at 55/60°C. Add :

Hematin HPT	10 to 15 %
Hematin ESPGP	10 to 15 %

Go to boiling temperature and maintain for one hour. Empty.

3°- Rinse with soft cold water until the bath is only very weakly coloured.

4°- Chromating

Enter in a cold bath, furnish :

Sodium dichromate	3 %
Acetic acid 80%	1 %

Go up to 60/65°C. Maintain thirty to forty-five minutes. Empty. Rinse.

5°- Softening and reviving

Enter the bath at 50°C containing 10 g of soap per litre. Turn for fifteen minutes. Haul, spin-dry and enter directly in a bath at 50°C containing:

5 % of lactic acid 50 % (of the weight of the silk)

Turn for fifteen minutes. Haul. Spin-dry.

OPERATING PROCESS NUMBER 2

This process only uses chromium alum for the mordanting instead of dichromate and organic acids used in the operating process 1.

LOGWOOD BLACK ON SILK NOT WEIGHTED, MORDANTED WITH CHROMIUM ALUM

Proportions in % of kilos of dry silk.
Soft water. Liquor ratio 1/25-1/30.

1°- Degumming or degreasing

Two soap baths of half an hour to one hour at 95°C with 20 % of household soap.

Thorough rinse, pH 6,5/7,0.

2°- Mordanting

20 % of crystallised chromium alum.

Enter at 55°C. Go up to 95/98°C. Maintain for one hour at this temperature. Rinse thoroughly with soft water or corrected water at pH 6,5/7,0.

3°- Dyeing

10 % Hematin ESPGP
10 % Hematin HPT

Enter at 55°C. Go up to 95°/98°C. Maintain for one hour at this temperature. Rinse thoroughly with soft water.

4°- Fixing complement (chromating)

Enter in cold water, furnish with :
2 % Sodium dichromate
1 % Acetic acid 80 %

Go up to 65/70°C.Maintain this temperature for thirty to forty-five minutes. Empty.

5°- Rinse

Rinse with soft cold water for five minutes.
Rinse with soft water at 50°C with 1 g/L of CO_3Na_2, during five minutes. Carry out a final rinse with soft water during five minutes.

6°- Spin-drying and drying

DEEP BLACK AND DARK SHADES ON SCHANTUNG SILK (Nanshan natural)

Greige silk

Weight by meter in 0,87 m width = 74 g.
Reaction to iodine: none.
Ashes : 2,7 % soluble in HCI and which are precipitated by ammonium oxalate after neutralization.

Elimination of lime salts and grease contents

Liquor ratio : 1/50.
Water at 70/80°C.
Hydrochloric acid 20° Baumé = 1,5 g/L (7,5 %).
Agitate during fifteen minutes, two rinses with water at 50°C, then :
Degreasing during fifteen minutes with purified water at 60°C, ordinary ammonia 1,5 g/L.
Two rinses with purified water. It is possible to spin-dry and dry.

Mordanting

Liquor ratio : 1/10.
Impregnation of the fabric (dried) in a ferrichromic liquor at 31/32° Baumé. Spin-dry and make a second passage in the same mordanting liquor. Spin-dry. Rest for one hour, then proceed to the methodical rinses, i.e. :

- three rinses for five to ten minutes with ordinary cold water, corrected with 0,3/0,4 g per litre of hydrochloric acid 20° Baumé. Liquor ratio 1/50-1/60 so as to neutralise, as exactly as possible, the rough water's alkalinity.

- a fixing in a purified water bath with soda carbonate : 2 to 3 % of the silk's weight, so as to obtain pH 6,5 to 7,0 with the universal indicator.

Start at 40°C and go up to 80°C.
Then, spin-dry and another mordanting like previously but on the worn bath at 30° Baumé. Carry out the rinses and the fixing as indicated above.

Lastly, soaping is possible with :

20 % of household soap (deep black)

Enter at 50°C, go up to 90°C. Maintain for half an hour. Rinse and dry through spreading or Hot flue if necessary.

The final density of the mordanting bath is 28° Baumé.

The mordanting liquor is prepared from :

41,750 kg of ferrous sulphate
30 litres of hot water
7,250 kg of sodium dichromate
4 litres of water
10 kg of sulfuric acid 96 % and complementary water to make 100 kg at 44° Baumé.

The mordanting liquor contains :

Fe = 8,41 %
Cr = 2,53 %
That is to say a ratio : $\frac{Fe}{Cr}$ = 3,32 and an alkalinity of 24,3 %

Dyeing

Liquor ratio 1/50.
Purified water.

The mordanted fabric is entered the dyeing vat at 40/50°C. Introduce the acetic acid necessary for the correction of alkalinity, then the dyeing products, dissolved beforehand in hot condensed water.

Then, proceed as follows : (see table on the following page)

MEDIUM BLACK	BROWN
10 % of Yellow CNOK 2 % of Synthetic green Turn 1/2 hour at 90°C Cooling to 70°C 3 % acetic acid 80 % 15 % Hematin Turn for 1 hour at 90°C Rinse. New bath. 5 % Hematin 5 % Yellow Cuba CNOK 2 % Acetic acid 80%. Turn for 3/4 of an hour at 90°C Rinse. Spin-dry, dry Finishing. Drying.	15 % Yellow CNOK 3 % Acetic acid. Turn for 1 hour at 90°C Rinse. Spin-dry. Dry Finishing Drying
BLUE BLACK	**DEEP BLACK**
20 % Hematin HPT 5 % Yellow CNOK 3 % Acetic acid 80 %. one hour at 90°C Rinse, new bath. 1,5 % Sodium dichromate . 3,0 % Acetic acid 80 %. Enter in cold water. Go up to 70°C Maintain for _ hour. Rinse. New bath. 0,6 % Methylene Blue. 0,6 % Vésuvine. 2,0 % Acetic acid 80 %. Enter in cold water. Go up slowly to 90° Maintain for 20 minutes Rinse. New bath. 2,5 % Hematin HPT 2,5 % Yellow CNOK 2,0 % Acetic acid 80 % Enter at 60°C. Go up to 90°C Maintain for _ of an hour. Rinse. Spin-dry. Drying and finishing.	20 % Hematin HPT. 5 % Yellow CNOK 5 % Acetic acid 80 % One hour at 90°C Rinse. New bath. 1,5 % Sodium dichromate. 3,0 % Acetic acid 80 %. Enter in cold water. Go up to 70°C Maintain for 1/2 hour. Rinse. New bath. 0,8 % of Methylene Blue. 0,8 % Vésuvine. 2,0 % Acetic acid 80 %. Enter in cold water. Go up slowly to 90°C. Maintain for _ hour. Rinse. Rolled up rest for the night. Rinse. Spin-drying. Drying. Finishing.

Finishing : impregnate the dry fabric with a solution at 40°C containing, per litre :
20 g fair Dextrin.
21 g soda sulphoricinate.
2,5 g Tanning TCK.
Spin-drying and drying with a weak tension in the fabric.

DYEING WITH LOGWOOD BLACK ON ARDIL ARTIFICIAL FIBRE

This fibre gives acidity before dyeing and one needs 2,5 % approximately of soda carbonate in order to neutralize at pH 3 to pH 6.

The fibre is easily mordanted by sodium dichromate and formic acid in an boiling bath.

It also fixes strong quantities of Hematin ESPGP in hot baths. However, in order to obtain a suitable black, by development with sodium dichromate, according to the process used for Nylon and Acetate: it is especially necessary to strictly stick to 2 or 2,54 % of sodium dichromate in hot baths and without addition of acetic acid, at least for remaining around pH 5 to 5,4.

The increase in weightafter the dyeing is low, even with the Logwood.

Dyeing Formulas

1°- With preliminary mordanting :

Soft water. Liquor ratio 1/20
Proportions for 100 kg of Ardil, additions to be made in this order, with circulation:

Water at 60°C	2,000 litres
Solvay Soda carbonate	2,500 kg
Sodium dichromate	2,000 kg
Formic acid 80%	1,250 kg
Copper sulphate	0,500 kg
Formic acid 80 %	1,250 kg

Bring to boiling temperature. Maintain for one hour. Exhausted chromium bath. Final pH : 3,97.

	Blue Black	**Black**
Water at 60°C	2,000 L	2 000 L
Hematin HPT	5 %	8 %
Yellow CNOK	0,2 %	0,2 %
Solvay Soda carbonate	1,75 %	1,75 %
Final pH of the baths of dyeing	5,25	

Bring to boiling temperature. Maintain this for forty-five minutes. Rinse. Spin-dry and dry.

2°- With subsequent chromating :

Soft water at 70°C	2 000 L
Solvay soda carbonate	2,5 %
Hematin ESPGP	7 %
Acetic acid 80 %	1 %

Go up to 95/98°C. Maintain this for one hour. Haul. Drain.
Rinse until the coloration of the water is weak, then :

Cold water	2000 L
Sodium dichromate	2 to 2,5 %

Go up to 90/95°C in fifteen minutes. Maintain this for forty-five minutes and rinse with hot water, then lay down, spin-dry and dry.

LOGWOOD BLACK ON VISCOSE

1°- Iron mordanting

Enter an iron nitrate solution at 9/10° Baumé. Turn for one hour. Haul. Spin-dry and put directly in a cold bath of soda carbonate at 5 g/L. Turn for fifteen minutes. Haul. Spin-dry.

Give a first rinse with water at 60/70°C during fifteen minutes, then a thorough rinse with cold water.

2°- Dyeing

After having “complexed” the bath water during ten minutes with 1 g/L of soda hexametaphosphate and 0,3 g to 0,5 g of ordinary hydrochloric acid, for pH 5,5 approximately if the water is calcareous, furnish at 40°C with:

15 % Hematin CFHK
5 % Yellow CNOK

Enter the mordanted viscose. Slowly heat until 60°C. Turn for forty-five minutes.

3°- Rinse

With very hot water and, if necessary, softening with 1% of Céranine H.C. 39 (Sandoz) at 30°C, during fifteen minutes and drying.

The Céranine must be diluted beforehand by making a paste, in water at 50/60°C and slightly acidified with the acetic acid for pH 5,5 approximately, especially if the water is calcareous.

NOTA. - To dye pieces with a continuous process, it is naturally necessary to have a sufficient number of “vats for course” provided with nip rolls so as to have, as in the case of the logwood dyeing of cotton fabrics:

- one or two vats for mordanting.
- five vats for the iron fixing, the rinses and the dyeing.
- one or two vats for the final rinse.

DYEING IN BLACK OF NYLON AND PERLON WITH NOT OXIDISED HEMATINS

New bath :

Here is the equation giving the proportion of the various products necessary to the black logwood dyeing of Nylon:

New bath : $K = (C_2 \times V) + (C_2 \times E) + \frac{(A \times p)}{100}$ (see p.14)

One takes A = 100 kg

For a **vigorous black** (*) in vat, winch beck, machine with circulation or jigger with direct or indirect heating, and purified water corrected with hydrochloric or acetic acid, or not very calcareous water complexed with Celon, soda Hexametaphosphate or another sequestering salt and corrected to the desired pH (1 g Celon per 0,100 g of calcium).

a) Dyeing

(pH = 4,5 approximately)
E = 100 litres for 100 kg of Nylon supposed dry
C2 = 5 g Hematin ESPGP per litre (jigger)
p = 6,5 % absorptive Hematin ESPGP
C2 = 0,5 g Acetic acid 80% per litre
P = 1,3 % Acetic acid 80% employed

b) Chromating

(initial pH 3,5)
(final pH 4,5)
E = 100 litres for 100 kg of dry Nylon.
C2 = 0,8 g sodium or potash dichromate per litre for Hematin ESPGP
p = 3 % of dichromate for Hematin ESPGP
C2 = 1,5 g Acetic acid 80% per litre for ESPGP
p = 3 % Acetic acid 80% for Hematin ESPGP

Remark : for Nylon dyeing on jigger (taffeta, satin) one uses Hematin HPT. In this case, the proportion of dichromate is a little higher than for Hematin ESPGP.

(*) The indicated % can be reduced by 10 % in the case of dyeing on tulle and with closed machines, heated through serpentine.

Thus **in grams per litre,** according to the **liquor ratio** :

$$\mathbf{Lr} = \frac{\text{Nylon weight}}{\text{bath volume}}$$ (given table 4)

Table 4

Liquor ratio (Lr)	HEMATIN DYEING		DEVELOPMENT			CHROMATING	
			Acetic Acid 80 %	Sodium dichromate		Acetic acid (80 %)	
	HPT (1)	ESPGP(2)		(1)	(2)	(1)	(2)
1/3	25,7	-	5	13,2	-	14,3	-
1/5	17,2	-	3,2	8,3	-	9,36	-
1/10	10,8	12,0	1,8	4,59	3,88	5;58	4,65
1/15	8,7	9,6	1,4	3,36	2,85	4,32	3,6
1/20	7,6	8,5	1,17	2,75	2,34	3,69	3,07
1/30	6,6	7,3	0,95	2,13	1,82	3,06	2,55
1/50	5 ,8	6,4	0,77	1,64	1,41	2,56	2,13

Tables 5 and 6 : **proportions of the various products necessary for the dyeing in a new bath and in an old bath, as well as for the development of a strong black by chromating on** preboarded, de-oiled or desized **Nylon :**

Table 5

	ON JIGGER		ON WINCH VAT OR CIRCULATION APPARATUS				
LIQUOR RATIO (Lr)	**1/4**	**1/8**	**1/16**	**1/20**	**1/30**	**1/50**	**1/60**
A. DYEING							
a) New bath							
EDTA……..	0,5g to 1g	0,5g to 1g	0,5g to 1g	0,5g to 1g	0,5g to 1g	0,5g to 1g	0,5g to 1g
Hematin ESPGP							
% of the dry nylon weight…...	8,15%	9,95%	-	-	-	-	-
or g/litre……	20,4 g	12,4g	-	-	-	-	-
Hematin ESPGP %							
% of the dry nylon weight…..	-	-	15%	17%	22%	32%	37%
or g/litre ……	-	-	9,3 g	8,5g	7,3g	6,4g	6,4g
Acetic acid 80%							
% of the dry nylon weight…..	1,55 %	1,75%	2,15%	2,35%	2,85%	3,85%	4,35%
or g/litre……..	3,88 g	2,19g	1,34g	1,17g	0,95g	0,77g	0,72g

Old bath :

Whatever the chosen liquor ratio, eliminate 350 to 400 L of the used bath per 100 kg of Nylon. Then garnishing of the equivalent quantity of corrected water, 8 to 9 % of Hematin and 1,6% of acetic acid 80% of the weight of Nylon. I.e., for the liquor ratio of 1/4, the old bath must be eliminated each time and for the liquor ratio of 1/8, there is hardly any interest in preserving it.

c) Rinses with cold water (20 to 30°C)
Soft or purified water.

1st rinse
Water corrected with a sequestering salt 0,5 g to 1 g/litre and acetic or hydrochloric acid (0,2 to 0,3 g/litre) for pH 5 to 5,5.

2nd et 3rd rinses
Water corrected with acetic acid, for pH 5 to 5,5 (slightly coloured water) or continuous rinse with overflow. If the water is very soft, there can be a light re-heating with steam, if necessary.

Table 6

	On Jigger		On vat with winch or circulation apparatus				
LIQUOR RATIO (Lr)	**1/4**	**1/8**	**1/16**	**1/20**	**1/30**	**1/50**	**1/60**
C. CHROMATING (New bath each time)							
Sodium dichromate, % of the weight of dry nylon……..	4,05%	4,41%	4,36%	4,68%	5,48%	7,08%	7,88%
or g/litre……..	10 g	5,51 g	2,72 g	2,34 g	1,82 g	1,41 g	1,31 g
Acetic acid 80%, % of the weight of dry nylon……..	4,5%	5,22%	5,55%	6,15%	7,65%	10,65%	12,15%
or g/litre……..	11,2 g	6,5 g	3,46 g	3,07 g	2,55 g	2,17 g	2,02 g

d) Rinses

1st rinse : with water at 20/30°C

2nd rinse : with water at 50°C complexed beforehand with 0,5 g to 1 g of sequestering salt and alkalized with 1 g of soda carbonate per litre.

3rd rinse : with water at 20/30°C or with continuous rinse with overflow and a light steam re-heating.

OPERATING PROCESS

Water : Water purified and corrected at pH 5 with a little hydrochloric acid (0,2 to 0,4 g/l) or not very calcareous water complexed with a sequestering salt and also corrected at pH 5.

Dyeing :

Nylon preformed, de-oiled or desized is entered, drained, into the dyeing bath at 60°C. It is then heated to 90/95°C within fifteen to thirty minutes and maintained at this temperature for one hour in a vat or a circulation apparatus and for two hours in a jigger.

Then, empty and let drain for a few minutes. The Nylon has then a colour of blond tobacco.

On old baths preliminary elimination of a certain quantity of waste bath (400 litres for 100 kg of Nylon) before the addition of the required percentages of hematin and acetic acid.

Cold rinses :

Give a five to ten minutes rinse with water purified and corrected to pH 5, or water complexed and corrected to pH 5. Empty and let drain.

Then, give a five to ten minutes rinse, also with corrected water at pH 5 with 0,2 to 0,4 g of hydrochloric acid per litre. Empty and let drain. The water is clear, practically colourless.

Chromating :

The dyed nylon, rinsed and drained, is put in the cold chromating bath, which is carried to 90/95°C within twenty-five minutes approximately and then maintained for three quarters of an hour to one hour at this temperature.
The nylon changes little by little (especially after 60°C) from the tobacco colour to brown, then to a black with blue reflections.
Empty, let drain and rinse.

The chromating is carried out each time in a new bath.

Rinses :

A rinse with cold water during five to ten minutes. Empty. Let drain.
A rinse with water at 40°C added with 1 to 2 g of soda bicarbonate.
Or, a five to ten minutes rinse with water at 50°C purified or complexed with 0,5 to 1 g/L of sequestering salt and alkalized with 1 to 2 g of soda carbonate per litre, in order to eliminate completely the excess of sodium dichromate and the fatty particles. Then, empty, let drain and give a final rinse with cold water to eliminate the soda carbonate in excess. Finally, lay down and dry, on screen for lace, and on tenter frame for the taffeta and the satin.

LOGWOOD BLACK ON PERLON
HOSIERY SPUN YARN (Bleached)

Liquor ratio 1/20. Water not very calcareous (D.H.T 10/12°)

1° Degreasing : fifteen minutes at 50°C with:

Teepol	2 g/l
Caustic soda 40° Baumé	1,5 g/l

Thorough rinse for pH 7 to 8.

2° Dyeing : new bath. Proportions for 100 Kilos of perlon:

Water at 50/55°C	2000 l
Soda hexametaphosphate	0,5 g/l
Acetic acid 80%	2,4 %

Leave a few minutes for the reaction to start, then add :

Hematin ESPG	17 %

Go up to 95/98°C and maintain this temperature for one hour. Haul. Drain. Rinse three to four times with cold water (until a very weak pink colouring is reached).

3° Development – Fixing

Water at 20/25 °C.
Acetic acid 80% …… 6 %
Sodium dichromate …… 4,7 %

Go to 90/95°C in 10/15 minutes and maintain this for forty-five minutes. Haul. Drain.

4° Rinse

First time with cold water, second time with hot water at 40°C added with:

1 to 2 g of soda bicarbonate per litre and a third one with water at 40°C.

Haul. Drain. Spin-dry and dry. Lastly, if necessary, give a softening treatment with 2 % of Céranine H.C. 39 (Sandoz) for example.

For this, plunge the Perlon in the Céranine bath at 25/30°C corrected at pH 5 with acetic acid. Then go up slowly to 50°C. Maintain this for 5 to 10 minutes while turning. Haul. Drain. Spin-dry and dry.

First of all, a mother solution of Céranine H.C. 39 is carried out by adding, little by little, water at 50/60°C until a stable homogeneous solution is obtained. This is then diluted at will.

MIXTURE OF NYLON AND COTTON

For the **Nylon and cotton** articles, this is a formula which is, for example, used for **black laces** fast dye.
Liquor ratio 1/30. Purified water.
Weight of preboarded and "finished off" lace containing 90% Nylon and 10% cotton : 68,200 kg.

Nylon Dyeing on winch beck or circulation apparatus :

New bath :

Soft water at 60°C …… 2 050 L
Hematin ESPGP ……..15,680 kg
Acetic acid 80% - 2,87 %…… 1,900 kg

Go to 95°C in fifteen to twenty minutes. Maintain this for one hour.

Chromating :

Water at ordinary temperature ……2 050 L
Sodium dichromate 5,00 %……3,410 kg
Acetic acid 80% - 7,08 %…… 4,830 kg

Go to 90/95°C in fifteen-twenty minutes. Maintain this for forty-five minutes to one hour, then give 3 rinses :

A five minutes rinse with soft water at 50°C. A five minutes rinse with soft water at 50°C, with 1 g of Solvay soda carbonate per litre. Finally, a rinse with not calcareous cold water.

Topping or cotton sulphur black dyeing, on beck or bath with circulation apparatus (for example at the same time as a pass of material containing a lot of cotton).

New bath :

Soft water at 90°C : Liquor ratio 1/20 -1/30
Sulphur black: 15 %
Crystallised sodium sulfide: 30 % (or 15 % in flakes)
Crystallised sodium sulfate: 30 %

The dye is initially dissolved with sodium sulphide in very hot water (no copper) and the lot is put into the hot water of the dyeing apparatus with some of the sodium sulfate. Then, one introduces the laces to be dyed at the same time (or conversely, the bath).

One works safe from the air, or one has the bath circulate during five minutes, then heated at 95°C. Then, the remainder of the quantity of sodium sulfate is added.

The temperature of 95°C is kept during fifteen minutes and then brought down to approximately 90°C during one hour.

Then, in a water beck, rinse immediately with soft water during five minutes, empty, give a second rinse under the same conditions, then a third rinse for five to ten minutes in water added with 0,5 g per litre of acetic acid 80%.

Finally, spin-dry, finish and dry on screen.

LOGWOOD DYEING OF A MIXTURE OF 60% STAPLE FIBRE OF NYLON AND 40% HAIRS OF ANGORA RABBIT

In order to obtain a beautiful black, fast to all tests (except carbonizing and topping in presence of sulphuric acid), it is necessary to operate as follows, with purified water:

Liquor ratio : 1/30 to 1/40.

Degreasing : at 50°C with 2 g/L of Solvay soda carbonate + 2 g/L of Teepol during approximately one hour, then rinse thoroughly.

Mordanting :

Enter at 60°C. Add:

1,5 % Sodium dichromate
3 % Formic acid 80%

Go up to boiling temperature. Maintain this during one hour fifteen minutes to one hour thirty. Empty. Rinse.

Dyeing :

Enter at 60°C. Add :

20 to 25 % Hematin ESPGP
0,7 % Acetic acid 80%

Go up to the boiling temperature. Maintain for one hour. Empty. Rinse with cold water until the water has a light pink coloration.

Development and fixing :

Enter cold. Add:

4 % of Sodium dichromate
4 % of Acetic acid 80%

Go up to 80°C. Maintain between 85 and 95°C during forty-five minutes. Empty. Rinse during five to ten minutes : once with cold water, and once at 45°C with 1 g/L of sodium bicarbonate and once again with cold water.
Cut down. Spin-dry and dry.

DYEING IN BLACK OF MIXTURES OF WOOL AND NYLON

PROCESS A

1°- Degreasing : rinse with soft or purified water.

2°- Mordanting :

Liquor ratio 1/20 soft water.
Add in this order :

1,5 % Sodium dichromate
then, 3 % Formic acid 80%.

Enter at 60°C, go up to the boiling temperature, maintain for one hour and a quarter for a complete exhaustion, empty, rinse once.

3°- Dyeing impregnation :

Liquor ratio 1/20, soft water.

15 % Hematin ESPGP

Enter at 60°C. Go up to boiling temperature. Maintain for one hour. Empty or keep the bath for another operation. Give two rinses with soft cold water (until the water has no color any more).

4° - Development fixing :

Liquor ratio 1/20.

4 % Sodium dichromate
4 % Acetic acid 80%

Enter cold. Go up to 80/90°C. Maintain for thirty to forty-five minutes. Empty. Rinse with tepid water. Then, rinse with ammoniated water at 50°C. Finally, rinse with tepid water.

Notice. - It is necessary to mordant beforehand in order for the Hematin ESPGP not to discharge into the development bath and so that the wool does not take a brown colour.

The 4 % of dichromate and 4 % of acetic acid 80% seem to be necessary for the bath of development not to take a pronounced brown colour while the wool and the Nylon become perfectly black with a bluish reflection.

PROCESS B

1°- Degreasing : rinse with soft or purified water.

2°- Dyeing :

Liquor ratio 1/30 -1/50.
Enter at 60/70°C and add in this order :

Hematin HPT…… 5 %
Hematin ESPGP …… 5 %
then :
Oxalic acid …… 3 %

Go up to boiling temperature. Maintain this for half an hour. Let cool to 60°/70°C. Add : **dissolved together**
Iron sulphate …….. 3,5 %
Copper sulphate …… 1,7 %

Bring to boiling temperature once more. Maintain this for one hour and a quarter. Haul. Drain. Empty. Rinse with cold water.
Fix in a new bath with :

Potash dichromate ……. 2 to 3 %
Acetic acid 80% …… 1 to 2 %

Enter at 50°C. Go up to 90°C. Maintain this for forty-five minutes. Rinse with hot water. Spin-dry and dry.

DYEING IN BLACK HEMATIN OF CELLULOSE ACETATE

PROCESS A

a) Determination of the quantities of products to use according to the same formula as the one used for Nylon and mixtures nylon/cotton. In this case, the use of the **sodium sulfate is absolutely essential** to obtain in the chromating stage the required very beautiful black shade for which :

$$Q = (V + E)\ C_2 + p$$

	Dyeing with hematin		**Chromating on hematin**	
	HPT	ESPGP	HPT	ESPGP
In volume of water brought by 100 kilos of acetate (or bath left)….	100 L	100 L	100 L	
V= volume of water corresponding to liquor ratio……	V/L	V/L	V/L	V/L
C_2= waste concentration of hematin……	10 g/L	11 g/L	-	-
or waste concentration of dicromate……	-	-	3,2 g/L	2,7 g/L
or waste concentration of acetic acid 80%…….	0,5 g/L	0,5 g/L	0,6 g/L	0,6 g/L
P= percentage of hematin necessary……..	5,5%	6,0%	-	-
or percentage of dicromate necessary…...	-	-	3,2%	2,7%
or percentage of acetic acid 80% necessary…….	1%	1%	1,2%	1,2%
Concentration of sodium sulfate crystallised…….	-	-	55 g/L	55 g/L

	DYEING WITH HEMATIN	CHROMATING ON HEMATIN
Duration	1 hour thirty to 3 hours	1 hour thirty to 3 hours
Temperature	75/80°C	75/80°C
initial pH	4,2	4,5
final pH		5,0 to 5,5

Observations : For the dyeing of Acetate on **jigger** one uses Hematin HPT and the proportion of dichromate is a little bit higher than for Hematin ESPGP.

UNBLEACHED RHODIA TAFFETA ON JIGGER (normal type, in stainless steel) CHROMATING WITHOUT MONOSODIUM PHOSPHATE

for 80 to 130 kg

Desizing :

Begin the process using dry material with soft water at 30°C. Two passes at 30°C. Empty, then :

Water at 50°C …….. 400 L
Soap….. …… 2 kg
Crystallised trisodium phosphate …. 1 kg

Table 7

	HEMATIN Dyeing with one or the other			DEVELOPMENT (CHROMATING)				
Liquor Ratio (Lr)	Hematin		Acetic acid 80%	Sodium dichromate for (1) or (2)		Acetic acid 80% for (1) or (2)		Crystallised sodium sulphate
	HPT	ESPGP		(1)	(2)	(1)	(2)	
1/3	31,7 g/l	-	4 g/l	14,9 g/l	-	4,8 g/l	-	55 g/l
1/5	23 g/l	-	2,6 g/l	10,2 g/l	-	3,1 g/l	-	55 g/l
1/10	16,5 g/l	18,1 g/l	1,55 g/l	6,7 g/l	5,67 g/l	1,86 g/l	1,55 g/l	55 g/l
1/15	14,3 g/l	15,7 g/l	1,2 g/l	5,5 g/l	4,67 g/l	1,44 g/l	1,2 g/l	55 g/l
1/20	13,2 g/l	14,5 g/l	1,0 g/l	4,95 g/l	4,18 g/l	1,23 g/l	1,0 g/l	55 g/l
1/30	12,1 g/l	13,4 g:l	0,85 g/l	4,37 g/l	3,84 g/l	1,02 g/l	0,85 g/l	55 g/l

Allow 1 passage at 50°C
" 1 " 60°C
" 3 " 80°C and empty.
Water at 50°C …….. 400 L
One passage and empty.

Twice {
Soft water at 60°C …….. 400 L
Borax in powder …….. 250 g
One passage and empty
}

Remove the possible filth on the vat wall, then :

Water at 40°C …….. 400 L
Borax in powder …….. 500 g
Sodium Hexametaphosphate…… 400 g

Three passages and empty.

Twice {
Water at 40°C …….. 400 L
One passage and empty
}

If necessary, treat the bath with :

Correctan …….. 1 g
Oxalic acid …….. 2 g
Grease-remover DCT……. 1 cc
Cyclo hexanol …….. 0,5 cc
} per litre

during two hours at 45/50°C, in order to eliminate the spots from ferruginous dirty oil, and rinse.

Observations- It is necessary to carry out, in a particularly neat way, the operation of desizing.

While operating during a too long time in a too hot and a too alkaline surrounding, one must indeed fear an appearance modification of the taffeta (reduction of the brightness of certain Rhodia fabrics and *moiré* efect).

For the desizing, it is thus recommended to apply the following treatment :

1° - Bath at a maximum of 35/40°C containing 3 g/L of a desizing anionic agent (Exencol) during one hour thirty, followed by :

2° - A bath at 60/70°C during one hour thirty containing for 400 liters of purified water:

2 kg of Household soap
1 kg of crystallised trisodium phosphate

3° - And three to four rinses in water at 40/45 °C containing 0,5 to 1 g/L sodium Hexametaphosphate, thus approximately 12 to 13 "passages" in five hours of treatment, including the preparation and the heating of the baths.

Dyeing :

Soft water at 60°C : 400 litres. Add in two sequences if required 1 g per liter of Celon. Give two passages at 60°C.

Add half of the quantity of Hematin dissolved in hot water and half of the quantity of acetic acid indicated further. Agitate well. Give a passage.

Add the remainder of Hematin and the remainder of acetic acid. Heat to 65°C. Agitate the bath.

Give a passage.

Heat at 70°C. Give 1 passage
" 75°C. Give 1 "
" 80°C. " 1 "

and stir for one hour, between 75° and 80°C. It means ten passages in three hours thirty approximately.

Rinse :

3 times { soft water at 25°C, 400 l
one passage. Empty

The last time, the water must be close to colourless.

Chromating :

Water at 60°C …… around 100 L

Add all the prepared quantity of crystallised sodium sulphate.
Heat to 50°C. Stir well for complete dissolution.

Add the necessary cold water for the 400 L, then half of the dissolution of dichromate and half of the solution of acetic acid. The dissolution has been carried out in stainless containers. Agitate well.

Make one passage.
Add the remainder of dichromate and the remainder of acetic acid. Agitate the bath well. Make a passage without heating any more, then :

Heat up to	45°C.	Make	1	passage
"	50°C	"	1	"
"	60°C	"	1	"
"	70°C	"	1	"
"	80°C	"	1	"

Turn during one hour at 75/80°C. This means nine passages in hot during three hours approximately, including two hours at 70/80°C.

Rinse :

Water at 50°C …….. 400 L

Make a passage and empty.

Water at 50°C …… 400 L
Borax in powder or soda carbonate,
In two times …… 500 g

Make two passages and empty.
Water at 25/30°C. Continued alimentation with overflow.
Make two passages and haul the material.
Pass in the running water padder for spin-drying, preparation of the tenter drying.

Guarnishings :

With a **constant** initial bath volume of 400 L approximately, or 30 cm height, for the **jigger** for example, or 1 600 L for the **circulation apparatus**.
(see table 8 page 67)

DYEING IN BLACK HEMATIN OF ACETATE CELLULOSE WITH A CHROMATING COMPRISING MONOSODIUM PHOSPHATE AND SODIUM SULFATE

PROCESS B in which the following points must be clarified :

1° - The Hematin substantivity for Acetate is weaker than for Nylon. This forces to dye in more concentrated baths.

2° - Hematin is fixed on Acetate less strongly than on Nylon. This leads to chrome in presence of an electrolyte.

3° - The solidity of the chromium lacquer and the beauty of the black depend on a well defined pH value as indicated by the following table :

Dyeing of acetate in black hematin, lightfastness according to the pH value

Chromating bath 4 g/L sodium dichromate and:	pH	shade obtained	Light fastness	Melting point °C	Acetone solubility
Hydrochloric Acid 22° 4 cc/l …….	1,5	Reddish-brown	1	269	insoluble
Formic acid 80% 4 cc/l ……..	2,5	Reddish-brown	2-3	280	insoluble
Frozen acetic acid …….	3,0	black brown	4-5	350	insoluble
Sodium acetate (aa. Acetic acid)4g/l	3-4-5	black	5-6	360	partially soluble
Monosodium phosphate 4 g/L ……..	4,5-5,5	Deep black	6-7	308	solvent chlorine
disodium phosphate (aa sodiumbicarbonate) 4g/l	5,5-6,5	black gray		298	50% soluble
Sodium carbonate 4 g/l	9,9	gray		239	100% soluble

The pH value increases gradually during the chromating. It is influenced by :

- the volume of the bath
- the quantity of buffer salt
- the Hematin concentration in the Acetate
- the duration and temperature of the chromating

Finally, the following process patented by S.A. Rhodiacéta for a liquor ratio 1/8 :

18 g/L atomized Hematin powder
0,5 cc/L icy acetic acid
0,2 g/L Alcoyl naphthalene soda sulphonate
1 g/L Sodium hexametaphosphate

Begin the dyeing at 60°C. Go up in half an hour to 80°C and to dye for another hour and a half at this temperature.

Evacuation or recovery of the bath (if one works in followed bath) then rinse with cold permuted water until the washing water has a weak colouring (four fifteen minutes rinses approximately on circulation apparatus).
Limit the compressions of the textile in order to improve the washing.

The chromating bath, also of volume 1/8, is loaded as follows :

6 g/L Sodium dichromate
4 g/L anhydrous monosodium phosphate
40 g/L anhydrous sodium sulphate
0,2 g/L Alcoyl napthalene sodium sulphonate

The chromating begins at the ordinary temperature during fifteen minutes. One then raises the temperature to 80°C in forty-five minutes then proceed to the treatement during one hour and a quarter at this temperature.

The pH of the chromating bath, which at the beginning is 4,5, reaches 5,5 at the end of the operation.

After the chromating, rinse with tepid water then with permuted water until elimination of any yellow colouring due to the dichromate. Then, soap during forty-five minutes at 65°C in a bath containing 5 g/L soap (but this soaping is not essential). Finally, one rinses.

Table 8

WORK ON	JIGGER					CIRCULATION APPARATUS		EXAMPLES
Bath volume …..	400 l	400 l	400 l	400 l	400 l	1 600 l	1 600 l	
Liquor ratio (Lr)	1/3	1/4	1/5	1/6	1/8	1/12	1/16	
Weight of acetate	130 kg	100 kg	80 kg	66 kg	50 kg	133 kg	100 kg	(300 l+100l)10 g
								+ 5 500 g = 9 kg
DYEING (l)								5 %
Hematin HPT %	9,5%	10,5%	11,5%	12,5%	14,5%	-	-	
or g/L ……	31,7 g/l	26,2 g/l	23 g/l	20,8 g/l	18,8 g/l	-	-	9 500g =31,7 g/l
Hematin ESPGP %	-	-	-	-	-	20,3 %	24,7 %	300 l
or g/l……	-	-	-	-	-	16,8 g/l	15,4 g/l	
Acetic acid 80%, %	1,2 %	1,25 %	1,3 %	1,35%	1,45 %	1,65 %	1,85 %	
or g/l……..	4 g/l	3,1 g/l	2,6 g/l	2,25 g/l	1,8 g/l	1,37 g/l	1,15 g/l	
EDTA ……	1 g/l	1 g/l	1 g/l	0,5 g/l	0,5 g/l	0,5 g/l	0,5 g/l	
CHROMATING								(300 L + 100 l)
Sodium dichromate %	4,5 %	4,8 %	5,1 %	5,4 %	6,0 %	6,2 %	7,3 %	3,2 g +
or g/L ……..	14,9 g/l	12 g/l	10,2 g/l	9 g/l	7,6 g/l	5,1 g/l	4,55 g/l	3 200 g = 4 kg
Acetic acid 80%, %	1,44 %	1,5 %	1,56 %	1,62 %	1,74 %	1,65 %	1,85 %	480 %
or g/l……..	4,8 g/l	3,7 g/l	3,1 g/l	2,7 g/l	2,17 g/l	1,37 g/l	1,16 g/l	4 480 g =14,9 g/l
Crystallised sodium sulfate g/l……	55 g	55 g	55 g	55 g	55 g	55 g	55 g	300 l

(l) Or 9,5% x 1 530 = 14,5% of liquid Hematin HPT 35° Baumé for the liquor ratio 1/3.

Desizing of the acetate yarn:

Agent de desizing, 2 g/l
Crystallised trisodic phosphate 3 g/l

One hour at 65°C. Thorough rinse with permuted water.

Desizing of the acetate fabric :

20 g/L Household soap, or initially :

Bath of desizing agent (2/3 g/l) during one hour thirty at 35/40° maximum. Then soap bath with 5 g/L and crystallised trisodium phosphate at 2,5 g/L during one hour thirty to two hours, at 60/70°C without exceeding this temperature in order to avoid the matification.

Then, rinse thoroughly at 45/50°C with soft water, or permuted and complexed with 1 g/L soda hexametaphosphate in order to eliminate any soap trace.

Instructions for the use of emetic tannin on Nylon, dyed with acid or metalliferous dyes, in order to improve washing and light-fastnesses

The acid and metalliferous dyes have, on Nylon, very good wet fastnesses. However, in certain cases, it is necessary to still improve these solidities, for example when one wishes to carry out shades which resist to a washing at boiling temperature.

These results are obtained, after dyeing, by a fixing treatment with the emetic tannin-tartar. This treatment is all the more effective when its application temperature is high. Practically, it is better to operate at a temperature close to boiling.

Operating process :

The dyed material is treated during 15 minutes at around 100°C with :

0,75 % soda pyrophosphate
3% Gall nut tannin - water extracted (China)
1 % icy Acetic acid

One adds then:

2% emetic tartar

and one continues the treatment during fifteen more minutes at the same temperature. Rinse and dry.

This treatment also has a favorable influence on the light-fastness of the acid and metalliferous dyes.

DYEING OF COTTON FABRICS IN LOGWOOD BLACK

BLACK BY SUBSEQUENT FIXING

This is generally carried out in a series of course tanks. The dry unbleached cloths go through a first tank containing a boiling solution of Logwood extract or a mixture of Logwood and a tanning extract, duly alkalized. After this, they are folded back on tip trucks where they rest during five or six hours at least.

Thus they go in a second tank containing a tepid solution (40 to 50°C) of iron salt, then, after a new rest of a few hours, in a third tank with two compartments. The first one is for liming and the second one is for the rinsing.
It is then enough **to bring** these parts in a **hot alkalized solution of Logwood**, either on jigger or in a fourth tank.

When the bottoming is carried out exclusively with Logwood, the first tank must be assembled in a bath containing 8 to 10 kilos of extract at 30° Baumé and 250 to 300 g of Solvay soda per hectolitre of water. The addition of a tanning extract is made in substitution of a part of the Logwood extract, and the proportion of each can reach 50/50.

The second tank, for fixing, is built with a solution of iron salt (pyrolignite, sulphate or nitrosulphate). At the beginning, the bath must indicate 3° Baumé. During the process, one nourishes it by addition of a strong solution, capable to maintain the initial iron content. One often uses a mixture of the above mentioned salts, especially the pyrolignite and the nitrosulphate.
For the liming, the first compartment of the third tank is filled with whitewash heated at approximately 80°C. One must maintain the bath milky enough to be assured that it constantly contains free lime, essential condition for the fixing of ferric oxide.

BLACK BY DYEING ON MORDANT FIXED BEFOREHAND

This method consists in mordanting directly the dry unbleached cloths by impregnating them with iron pyrolignite at 5° Baumé, heated at 50/55°C.

When the operation is done on pad, one should make at least three passages in order to ensure a good penetration of the mordant. If the process is carried out in a course tank, two passages are enough thanks to the intermediate rest. The fabrics thus mordanted are dried either by suspending them on slats in a drying room, or by passing them through a hotflue.

Once dry, the mordanted pieces, sewn end to end, are degummed, at the speed of 40 meters per minute, in a course tank containing a whitewash heated to a temperature close to boiling. Take care to nourish the bath during the process, by addition of more concentrated whitewash when each seam comes by.

Coming out of liming, the degummed fabrics are immediately a thorough washing while passing in ropeform. One separately folds back each piece for the dyeing which is also carried out in ropeform, in tanks known as "*à garancer*".

Each one of these tanks contains ten pieces tied without end, each one separately. They turn during nineteen minutes in a Logwood bath slightly alkalized with one liter of Logwood extract 30° Baumé for 10 kg of fabric.
Raise the temperature little to little, through a steam bubbler, so as to come to a boiling temperature after one hour. Then one continues the dyeing during half an hour, with a moderate bubble.

The bath is then emptied and the tank is filled with fresh water for the rinse and the cooling of the fabrics which one then racks with an untwister or a scutcher, in order to be able to dry them on rolls, before giving them the finish.

CONTINUOUS DYEING

This process is based on traditional method (b) of preliminary ferric oxide fixing on the fabric. It consists :

1° - to impregnate the fabric with iron pyrolignite
2° - to dry it
3° - to degumm it with lime water
4° - to rinse it
5° - to dye it with Logwood
the whole operation in only one passage

If one does not have the necessary installation, work can be stopped in some of its phases, without the process ceasing to be continuous.

The facilities which have drying yarns, can continue to dry the parts mordanted with pyrolignite and then to clean them and to dye them in the five compartment of the course tank which constitutes the principal advantage of the continuous process.

Mordanting :

The unbleached cloths, dry and roasted if necessary, are impregnated directly by a passage in a course tank containing iron pyrolignite 5° Baumé, heated at 45/50°C.

After two successive squeezings, the goods are folded back in tip trucks. Then, after a few hours rest, in order to finalize the fibre penetration, the fabric passes in a pad whose basin contains pyrolignite of same concentration, so as to equalizing the impregnation and to express it very strongly.
The mordant excess thus recovered is used to supply the impregnation tank. If drying is made through the hotflue, this exprimor pad must be in the front and uninterrupted with the drier. On the other hand, if one dries through drying room, the pad must roll up the mordanted fabrics into transportable rollers.

Drying of the mordanted pieces :

As already mentioned, the two most suitable drying methods for this are : the hotflue and the drying yard. The advantage of the first system is to allow a continuous process, without having to un-stitch the parts. As for the second, it is does not require heating but requires a surplus manpower compared to mechanical drying. **Let us add that the colours obtained by mordant dyeing dried by contact always come out more or less two-sided, and that the iron oxide thus fixed, losing its affinity for the colouring matters, draws badly in dyeing and gives only a bronzed and very thin black.**

Liming, rinsing and dyeing :

These three last phases of the continuous dyeing take place in a course tank with five compartments. This tank is made of coated with roll of brass turning ; it is surmounted by five couples of squeeze rolls whose inferiors are covered with brass shirts, and the superiors of half-hard rubber shirts. Streching screws, turning to wrong way of the walk of fabric, are to the entry of each of the five groups of squeezers infallibly opening all the folds of fabric and the rolled edges.

The first compartment (lime degumming) is heated by a bubbler. The two following compartments are used for washing; they are laid out in cascades. The water squirts to the entry of the squeezers, runs out in the opposite direction of the walk of the piece and is evacuated by overflow.

The last two compartments are used for dyeing ; they are at different levels so that the overflow of the fifth can run out in the fourth. In the bottom there's a copper steam coil, fit with a drain cock, which heats the two baths by contact, in order not to dilute them with condensed water of the steam.
Here is the process with the five compartment tank :

The fabrics, mordanted and dried, enter the boiling lime bath which purpose is to supplement the iron oxide fixing on the fabric, and to peroxidize it. Afterwards, the pieces go into the two washing compartments where they get rid of all the soluble salts. Finally, in the two dyeing compartments, they are impregnated with alkalized Logwood, in sufficient quantity to saturate the fixed mordant.

When coming out of the machine, the goods are folded back in tip trucks where they rest for the necessary time to get a perfect combination of hematein and ferric oxide. This combination, favoured by the heat of the passage in boiling bath, can be regarded as perfect after a two hours rest. One can then proceed to the final rinse which is given on a squeezer exprimor. Then the pieces are dried in drums.

With regard to **liming**, one cannot indicate exactly the proportions of lime to use. One starts by filling the tank to clean up almost entirely with boiling water. Then, add to it 20 to 25 liters of a whitewash, prepared by watering 25 kilos of quicklime in 500 liters of water. Then, during the operation, one nourishes the bath by addition of 4 to 5 liters of whitewash, each time that it does not contain enough free calcic hydrate to

be able to easily neutralize the acids which the drying did not eliminate and which still exist in a sub-salt state in the fabric to clean up.
However, one easily witnesses the disappearance of the lime hydrate, first when the bath loses its milky aspect, and then when, by degumming, the greenish-gray colour of the mordanted fabric does not change as quickly any more into a dark rust shade, evidence of a good fixing of the ferric oxide. It is necessary, however, to avoid an excess of lime.

Regarding the **dyeing**, the preparation is made by mixing 22 kg of pure Logwood N.O. extract diluted in 50 liters of water with a solution of 1 kilo of soda salt, in a barrel containing enough boiling water to give a 200 liter preparation.

One prepares, once and for all, the two dyeing tank compartments by introducing a sufficient quantity of water to cover the inferior rolls. This is heated and in each compartment are added 25 liters of the above-mentioned preparation. Then, for each incoming piece, 5 liters of the same preparation are shared between the two compartments. Of course, the quantity of logwood necessary to nourish and maintain the concentration of the dyeing bath is correlated with the quality of the fabric. The proportions indicated above are for parts weighting 10 to 11 kilos for 100 meters. They will have to be increased according to the weight of the fabrics.
During the whole process, the Logwood bath must be maintained close to boiling temperature. One thus activates considerably the formation of black lacquer in the fiber and the excess dye which the fabric takes with it makes it possible to perfect the ferric oxide saturation during the rest.

Undoubtedly, the level of the dyeing baths is increased by the mixture of the preparation and the water taken by the pieces when coming out after the rinse. It must be stabilized by the overflows which pour from the fifth tank into the fourth and from this one into a barrel. This evacuated bath is used for new preparations.

There comes a time when the Logwood bath, having accumulated impurities of all kinds (layers of sediment, Logwood lacquer, etc) needs to be renewed. In this case, one empties of its content the compartment N°4 and, after having cleaned it well, one siphons the limpid part of the contents of N° 5, while avoiding touching the deposit which is then evacuated. After cleaning, one fills up this last compartment with a fresh bath.

Through this process, the consumption of products and work force is as reduced as possible, considering nothing is lost. One counts, for the dyeing of 10 kilos of cotton fabrics in intense and tight black, approximately :

- 3 L iron pyrolignite 16-17° Baumé
- 120 g of quicklime
- 475 g of pure Logwood N.O. extract
- 35 g of Solvay soda salt

The lining articles, dyed through the continuous process, offer a beautiful solid black, with no change of shade in the stores. Furthermore, the beauty and the resistance of this black are still increased when one slightly colours the finish of these articles by adding, for 500 liters : 1 liter of Logwood extract 30° Baumé, 75 g of sodium dichromate and 75 g of copper sulphate.

Stiffened articles and lawns for hat industry:

In the production of certain black articles very strongly finished, requiring consequently the application of a lot of very coloured finishes, the light fabrics are dyed only with a black of little intensity (ie to some extent a very dark gray).

In this case, the application of the first two operations of the process of dyeing in black by subsequent fixing, described page 69, is quite indicated. It can be summarised as follows : impregnation of the fabric in alkalized Logwood, rest, fixing with iron pyrolignite, rest, final rinse. There is no need of other treatment.

DYEING IN GRAY OF COTTON FABRICS WITH LOGWOOD

Before the discovery of the artificial gray dyes, the various shades of gray on cotton fabrics were produced, almost exclusively, by means of Logwood more or less mixed with tanning matters and yellow vegetable colouring matters.

The advantages of this method are :

- production of full shades on fabrics not dug
- a great regularity of the shade
- a competitive cost.

Moreover, by dyeing this gray through an uninterrupted process, one adds to these advantages:

- a larger and faster production, with reduced work-force
- a very significant saving in colouring matters
- total suppression of stained or un-evenly dyed parts.

However, before describing this method, it is advisable to recall the processes which are of an everyday usage for the dyeing of the Logwood gray, on jiggers or pads, wherever there is no possibility of a continuous process.

DYEING ON JIGGERS :

In practice, one proceeds on two jiggers located so that the fabrics can go from one to the other. On the first one, the wet and well squeezed fabrics first get impregnated with Logwood through three passages in a cold bath. Then, on the second jigger, one fixes the dye through two passages in a cold iron bath. One then empties the bath and washes on the same jigger with two passages in cold ordinary water. This washing must be supplemented by an energetic rinse on squeezer exprimor with three cylinders provided with two water sprinlers.

The following table shows, stated in liters, the proportions of Logwood and iron sulphate 1/10 solution to be used in order to produce a range of five traditional shades. The prescribed quantities correspond to the dyeing of a roll carrying 300 to 350 meters of average fabrics. The quantity of water necessary to keep a constant volume in the baths must be indicated by a gauge mark set in the jigger's basin.

Intensity of the gray		1	2	3	4	5
1st apparatus	L.E. Preparation ……. Lit.	1	2	4	7	12
	Water …… "	69	68	66	63	58
2° apparatus	Ferrous sulphate 1/10 … "	1	2	3	4	6
	Water …… "	79	78	77	76	74

L.E. preparation : Logwood extract preparation

To get a very dark gray by this process, it is necessary to proceed to two successive operations of gray N° 5, by thoroughly washing in between, in order for the second Logwood bath not to precipitate.

The L.E. preparation is carried out in a series of smashed barrels, by dissolving 10 kilos of pure Logwood N.O. extract in 400 liters of boiling water, and by adding to it a quarter of liter of ammonia. If one wishes a less “purple” gray, one adds to this preparation one kilo of yellow Cuba extract 40° Baumé or 0,400 kg approximately of Yellow CNOK.
Some dyers, in spite of an over-cost of transportation and housing, preferably use for their gray our clarified Logwood extract, from which the resin is completely removed, and which gives gray shades as fresh as the wood decoction.

DYEING ON PAD :

The use of Logwood extract makes it possible to dye the gray on pad, in shorter baths, therefore more concentrated, than on jigger. However, some companies, after having tested the two systems, continue to use the jiggers because of certain dyeing defects such as : ends of parts stained, darker edges, etc which occur on pad.

One must, however, make an exception with the very dark grays which, on pad, require much less bath than on jigger, and which even implie only one operation for dyeing and mordanting. The economy is made even bigger owing to the fact that, by preserving it and by suitably nourishing it after each operation, a strong Logwood bath needs to be renewed only after it has impregnated three or four fabric rolls.

To dye on pad, one uses the same quantities of colouring matters and mordant than on jigger. But because of the smaller capacity of the pad’s basin, one makes shorter baths by adding only the quantity of water necessary to complete the dyeing bath to 50 liters and the iron bath to 60 liters, instead of 70 and 80 liters respectively. It is necessary to make the first passage in ferrous bath without exerting any other pressure than that of the pad cylinders’ weight, so that a premature squeezing will not be exerted on colouring matter still insufficiently fixed.

“Ashy” grays :

Apart from traditional grays, one produces more or less “ashy” grays, by mixing to the L.E. preparation bigger quantities of Yellow CNOK extract and even tanning extracts such as Sumac, Retan MDI, Retan GSK, etc.

Some very deep back shades of tone, the “mouse” gray for example, are very often dyed without any Logwood, either with Sumac extract alone (for the light shades) or with a mixture of Retan MDI and yellow and red extracts. In any case, the operating process does not change.

CONTINUOUS DYEING:

This machine is composed of a coated sheet tank forming three surmounted compartments of three couples of squeeze rolls which inferiors are covered with a brass ring, and the superiors of a half-hard rubber shirt. In front of the entry of each couple exprimor, a streching screw out of brass, driven in opposite direction of the walk of fabric, easily opens the folds and the rolled edges of the fabric. Roll of turning of the three compartments are out of brass, those which surmount the second must be placed to give to rather high the race of fabric a sufficient development to ensure the fixing of the dye by the mordant. At the bottom of the first compartment a serpentine provided with a steam trap is to ensure the heating of the dye bath without diluting it. The food of the dye bath and the fixing bath is done by filter pipes provided with a funnel. The last compartment is laid out in cascade and is useful for the first rinse: water is distributed there by a perforated jet placed to the entry of the third couple exprimor, and it is evacuated by overflow after having carried out its rational course. The ordering of the machine is done by progressive movement.

For such an apparatus to be practical, it is necessary for the higher level of the tank not to exceed 0,90 m and that its depth does not exceed 0,80 m.

In order to facilitate the preparation of the Logwood bath, the upholding of its level and the modifications required by the changes of tone and intensity of the colours to produce, one must be able, at any moment, to know the contents of this bath. For this reason, one uses a twenty liter gauge. It is then, by a simple calculation, very easy to go from a clear shade to a darker one and reciprocally.

Preparation of the baths :

One runs water in the first two basins of the machine, so that the lower rolls are only scarcely covered. One then heats the first at 90°C, then one adds to it the prescribed quantity of LC preparation. The second one is only heated at 35°C before receiving the ferrous sulphate solution.

Preparation LC is made by dissolving 10 kilos of pure Logwood N.O. extract, 1 kilo of Yellow CNOK extract and 200 g of Solvay soda salt in 400 liters of boiling water.

The ferrous sulphate solution is prepared 1/5, i.e. 200 g of iron sulphate (green vitriol) per liter of water.

Dyeing :

To dye, for example,in a medium gray (N°3 in the chart).

One introduces, to start with, in the first basin, as many time four liters of preparation LC as it contains twenty liters of water, and in the second basin four liters of a ferrous sulphate 1/5 solution.

During the process, for each passing of piece, one adds in the distributor of the first basin 1,25 liter of preparation LC and in the second basin 0,75 liter of ferrous sulphate 1/5.

It is necessary to nourish the baths during the process, only at the moment when a seam must leave a compartment to enter the following.

At their exit of the machine, the dyed fabrics are folded back in bundles of two or three pieces which must rest during half an hour at least, in order to ensure the equal development of the shades, before undergoing the final rinse on squeezer exprimor.

The light and medium grays are dyed on wet and well squeezed fabrics. It is the water which they bring which weakens the Logwood bath and which obliges to maintain it to its initial concentration by nourishing it the concentrated preparation.

The fabrics to be dyed in dark gray enter dry in the bath. One thus avoids the use of too concentrated baths. As in this case the dye is consumed without weakening significantly, one will maintain its level by addition of a bath of equal concentration which one holds in reserve. As it takes also more time for the iron mordant to fix a very dark gray, one does not rinse it continuous in the washing compartment, but it must be rinsed twice on the squeezer exprimor, after exiting the dyeing machine.

The proportions being well established for each different shade of gray, one easily goes from a shade to another without emptying the baths. One can base oneself, for these baths, on the proportions indicated in a table for dyeing on pads. The gauge having measured the volume of remaining bath, one knows how much it contains of preparation LC and the quantity which will be necessary to add for the colour to follow.

If, on the contrary, it is a question of going to a clearer shade, the gauge will indicate how much water the bath will have to be added. If the difference is too big, one will take away first a part of the bath so that one has dilute only the necessary quantity.

However, it is always preferable to follow a progression. For this reason it is advisable to classify the shades to dye in advance and to start with the clearest.

The dyeing baths of a certain intensity, which are worth to be preserved, can be stored in a reserve and be used again, either for dark gray, or for black.

All the shades of “ashy” gray, greenish gray and beige can be dyed in continuous. The same applies to the backgrounds for being dyed again in basic dyes for very bright dark shades well nourished.

Gray on unbleached cottons :

Certain lining articles such as calendered *percalines* and *poltaises*, the “*clairvaux*”, the “*scraped finettes*”, etc. are dyed on simply unbleached fabrics. The dyeing of these pieces is also done through a continuous process ; but the Logwood preparation should then contain 10 kg of pure N.O. Logwood extract and 400 g of Solvay soda for 400 liters (Yellow CNOK being of no use in this case).

MIXED BLACK ON COTTON

The " Mixed Black ", sulfur and sumac dye, plus iron, produces very strong blacks with an increase in weight of 7 to 8 %.

Moreover, the purpose of this treatment is to prevent the deterioration of the fibre by oxidation, which is always to fear with sulfur blacks.

One stirs the pieces during two to three hours, at ambient temperature and, in the case of hanks, one can leave in contact during the night, with 12 % of liquid Sumac or 5 to 6 % of Sumac K extract in powder (% of the material's weight).

Then, one very strongly squeezes the material and one fixes the tannin by a passage through an iron pyrolignite bath at 2,5° Baumé, during forty minutes, at ambient temperature.

Lastly, one rinses thoroughly.

DYEING OF FLAX AND COTTON YARNS, FINISHED OFF, WETTED ON BECK

New bath for shades	Tobacco	Catechu
for 100 kg of dry matter:		
Purified water at 75°C ……..	2 000 L	2 000 L
Soda oxalate …….	5 kg	5 kg
Tannant RTK (brown-red element)…….	40 kg	64 kg
Yellow CNOK (yellow element)…..	10 kg	8 kg
Hematin ESPGP (blue element)…….	0,500 kg	3 kg
Crystallised soda acetate …….	1,700 kg	1,700 kg

Enter at 70°C, smooth for half an hour approximately, while letting the material cool down towards 50/60°C. Haul, then add :

Copper sulphate …….	1,500 kg	1,500 kg

dissolved beforehand in hot water, acidified with acetic acid. Heat at 90°C and smooth for one hour.

Let it cool down then heat at 90°C and smooth for one hour. Ring strongly and make a pass in the dichromate **development bath**.

On followed baths, one will use for 100 kg of material (these proportions can vary according to the machinery used) :

Soda Oxalate …….	0,750 kg	0,750 kg
Tannant RTK	3,000 kg	4,800 kg
Yellow CNOK .....…….....	0,750 kg	0,600 kg
Hematin ESPGP …….	0,050 kg	0,220 kg
Soda acetate ……..	0,750 kg	0,750 kg
Copper sulphate …….	0,600 kg	0,600 kg

Development chromating on new bath each time :

Purified cold water …….	2 000 L	2 000 L
Acetic acid 80% ……..	1 L	1 L
Sodium dichromate …….	2 kg	2 kg

Enter in cold bath, smooth for half an hour, then go up slowly to 45°C and smooth again for half an hour.

Rinse with tepid water, then with hot water.

Spin-dry and dry.

DYEING OF COTTON AND FLAX CLOTHS FINISHED OFF, WETTED ON JIGGER

New bath for brown colour.

For 100 kg of dry material :

Purified water at 75°C ……..	400 L
Tannant RTK ……..	25,600 kg
Yellow CNOK…….……	3,200 kg
Hematin ESPGP ……..	0,800 kg
Sodium acetate ……..	0,900 kg
Copper sulphate ……...	0,800 kg

On followed baths (proportions to refine, on the spot, according to the machinery used) :

Tannant RTK ..……..	4,800 kg
Yellow CNOK ……..	0,600 kg
Hematin ESPGP ……..……	0,220 kg
Sodium acetate ……..	0,700 kg
Copper sulphate ……..	0,600 kg

Enter at 75°C. Make some passages at this temperature. Then, while letting the bath cool towards 50/60°C, add in several times the very diluted solution of copper sulphate (carried out in condensed water or acidified with acetic acid).

Heat to 90°C, turn for one hour, while letting it cool down towards 70°C. Squeeze and pass in the jigger of **development**.

Development chromating, each time in a new bath:

Cold water ……..	400 L
Acetic acid 80% ……..	0,500 kg
Sodium dichromate ……..	1 to 1,500 kg

Enter in a cold bath, make several passages while raising the temperature until 45/50°C within thirty to forty-five minutes.

Then : rinse, squeeze, roll up and dry.

DYEING IN KAKI, FOR TENT FABRIC

FORMULA n° 1

The cretone pieces are initially prepared on pad at 55/60°C with diastases - 5 g per liter - that is to say for 100 liters to 60°C, 0,500 kg of Rapidase.

The parts thus treated remain in a heap for several hours well covered. Then, one washes on jigger with boiling water.

Squeeze strongly then make two passages (cold) in the pad with :

40 litres {
- 10 litres of Tannant RTK solution at 10%
- 6 litres of Yellow CNOK solution at 10%
- 24 litres water

One leaves the parts rolled up during twelve hours and one chromes cold in the jigger. Three passages with :

6 liters of dichromate solution at 10%
6 liters of solution of copper sulphate at 10%

for 100 liters of bath, corrected with acetic acid.

Then, one washes, squeezes and one passes in an iron bath, that is to say two passages on pad with :

2 liters of iron pyrolignite at 15° Baumé
48 liters of cold water

Let it rest for one night before rinsing thoroughly.

Lastly, one proceeds at the impermeability with alumina acetate and soap or other products.

FORMULA n° 2

This dyeing can be also obtained, with a great facility, through two jiggers only.
One prepares a mother solution with :

20 kg of Tannant RTK
10 kg of Yellow CNOK
1,5 kg of Hematin ESPGP

in 200 liters of boiling water.

The **1st jigger** is filled for 300 liters of bath and 100 kg of fabric (well prepared) with:

30 liters of the above mentionned mother solution
and 0,750 kg of copper sulphate

One gives two passages in the boiling bath.

For the 2nd passage, one refills with :

15 liters of the mother solution
and 0,375 kg of copper sulphate

and for the following passages with :

7 liters of the mother solution,
and 0,180 kg of copper sulphate

The pieces are squeezed and come out lemon-yellow.

The 2nd jigger or of fixing is furnished with :

300 liters of water at 70°C
2 to 2,500 kg of sodium or potash dichromate

Two passages are made.

One empties the bath, gives two rinses, squeezes and one then goes to the finishing operations.

DYEING OF THE COTTON, FLAX OR HEMP HANKS

For 100 kg of cotton, flax or hemp:

Dissolve 7 to 10 kg of Logwood HPT in the smallest possible quantity of water but with enough however so that the pieces can soak in the bath which must be hot. After the hanks have gone through this solution, ring. Let the material oxidize with air during one night. Then fix in the following bath at 40°C :

Copper sulphate ……. 5 kg
Potash bicromate …….. 1 kg
Water : sufficient quantity to be able to stir

Expose to the air for two hours. Rinse and enter again in the Logwood bath at 40°C. Rinse and then give a soap and oil bath.

Notice- for dark blacks, it is better to add to the Logwood approximately 5% of Yellow Wood extract.

DYEING OF COTTON LACES

1) <u>Basic articles</u> (ie 400 kg of cotton to dye in black on which one wants to obtain a weighting of 35 %)

The quantity of water to use is important ; one needs approximately twenty liters of water for one kilo of cotton.

Fill a tank with the necessary quantity of boiling water. Add :

30 kg of Hematin ESPGP
80 kg of Retan CHACK 25° Baumé (or 80 kg of pure Retan GSK, 25° Baumé)
10,300 kg of Yellow CNOK

It is advisable to add 2 kg of Solvay soda (anhydrous carbonate).

Enters the goods in the boiling bath, smooth them for one hour approximately. Then immerse them in the bath without heating any more; leave the bath until the following day.

Haul, ring, and without rinsing, carry the load in another tank filled with tepid water, in which one dissolves 80 kg of iron sulphate and in which one puts in suspension 40 kg of well pulverized chalk. Agitate and bring in the goods which one smoothes during one hour at 30/40°C.

Haul, ring, rinse and place the materal in the first bath, heated at 80°C. Smoothe during one hour, haul, let it oxidize one or two hours in the air, rinse and dry.

2) <u>Fine articles</u> (25 % weighting) One operates as for the basic article with smaller quantities of products in the baths.

For 400 kg of cotton, the dyeing bath is topped with :

30 kg of Hematin ESPGP
or 30 kg of Retan CHACK dissolved in 30 liters of water
or 30 kg of Retan GSK dissolved in 30 liters of water
6,450 kg of Yellow CNOK

and the fixing bath with :

60 kg of iron sulphate
30 kg of pulverized chalk

COLOURING OF THE BLACK FINISHINGS FOR COTTON THREADS

To dye the finishings in black, one uses not oxidised Logwoods.
For 400 liters of finishings, prepare :

2,520 kg of Hematin ESPGP
0,200 kg of Yellow CNOK
0,250 kg of crystallised iron nitrate
0,150 kg of Potash bicromate

To get a really “bluish” black, one can decrease the quantity of Yellow or even remove it completely.

For the finishing of the cotton dyed in black with sulphur, one also uses, for 50 kg of threaded cotton and one cubic meter bath :

0,300 kg of starch
0,250 kg of lard
0,500 kg of soda sulphoricinate
0,630 kg of Logwood HPT

Heat to boiling temperature, stop the steam, enter the cotton, stir for half an hour, haul, and add in this bath :

0,075 kg of Sodium dichromate

Enter again and let it half an hour at 75°C. Bring the material out and let it drain.

FINISHING OF GLAZED YARNS

Here are two standard formulas :

Formula n° 1

Starch ……..	8 kg
Vegetable wax …….	0,500 kg
Coconut oil ……..	0,500 kg
Water …….	100 litres

One colours as indicated hereafter : one finishes, dries, moistens, rubs on heated calender; one makes the glazing.
The vegetable wax is often replaced by paraffin.

Colouring of the finish

For 400 liters of finish, dissolve beforehand :

3,150 kg of Hematin ESPGP
0,285 kg of Yellow CNOK

One adds the dissolution in the finish, stir well, then one incorporates little by little, on trickle, without ceasing to stir :

0,350 kg of iron nitrate 40° Baumé
and 0,150 kg of Potash bicromate

dissolved in a little water

Formula n° 2

For 400 liters of finish, one mixes :

40 kg of corn starch
10 kg of potato starch
with 300 liters of hot water

One then adds, dissolved beforehand :

2,500 kg of Hematin ESPGP
0,285 kg of Yellow CNOK

Stir well and, little by little, add the dissolution of :

0,350 kg of Copper sulphate
and 0,200 kg of Potash bicromate

Heat the lot at 60°C with steam while strongly stirring. During this time, one dissolves in 30 liters of water the following fatty mixture :

1 kg of tallow
1 kg of borax
1 kg of yellow wax
0,250 kg of adragante gum
0,500kg of Cologne strong glue

One adds this mixture to the previous one and the lot cooks until the finish begins to thicken. One then stops the steam and stirs well. Let it boil another five to ten minutes, while agitating until the mixture appears mucilaginous. One then adds condensation water to come to 400 liters. This mixture is made at hot temperature.

One can increase the brilliance by putting more wax or by adding paraffin ; one increases the hardness by raising the quantity of adragante gum and glue.

THE USE OF TANNINS IN TEXTILE INDUSTRY

(Some application formulas)

A - Mordanting of Boiled off cotton

a) Threads in beck or pieces with the winchbeck

Use 2 to 6 % of powder tannin according to the intensity of the shade to reach later with the basic dye(s) chosen.

Leave the cotton in contact with this bath, during two hours at 50-70°C and for the dark shades, let it immersed during a whole night.

Ring and treat (without a preliminary rinse) in another bath with 1 to 3 % (of the cotton weight) of emetic during thirty to forty-five minutes at the ordinary temperature.

Rinse in a bath very slightly alkalized with sodium bicarbonate (0,2 % approximately), so that the pH is brought to 7,0 approximately at the end of the neutralization. The bath starts cold and ends at 45/50°C for fifteen to twenty minutes. Lastly, dye with the desired quantity of the selected basic dye(s).

For the dark shades, one can replace the emetic by iron pyrolignite in a solution at 1 or 2° Baumé or by iron sulphate (4 to 10 % of the dry cotton weight).

The mordanting and fixing baths do not fully exhaust in this case and one can fill again the old baths for the following batch with approximately the three quarters of the original quantities. It is advisable then to neutralise the increase in acidity of the fixing bath.

b) Mordanting in jigger

Make four to six passages at 70°C with 1 to 5 % of tannin and let rest in roll for two hours. Squeeze, then make two passages with 0,5 to 3 % of emetic or in a pyrolignite or cold iron sulphate bath. Rince and dye.

c) Mordanting in pad.

Immerse the fabric twice in a very hot solution containing 3 to 20 grams of tannin per liter. Roll up the fabric. Let it cool and fix by a passage in an emetic bath with 1 to 5 grams per liter. Rinse and dry. Soak again and dye.

B - Formulas for printing with basic dyes

1-

Crystallised purple in fine powder ……	20 g
Boiling water ……	46 g
Acetic acid 80% ……	92 g
Acetine ……	80 g
Lactic acid 50% ……	3 g
Glycerine ……	10 g
Phenol ……	14 g
	265 g

2- Solution of arabic gum 1/1 ……**500 g**

3-

Gal nut tannin (grinded powder) ……	105 g
Boiling water ……	92 g
Acetic acid 80 % ……	35 g
Lactic acid 50 % ……	3 g
	235 g

TOTAL ……**1 000 g**

Thoroughly dissolve 1 and 3 separately, then mix 1 and 2 before adding 3.

The finished color is sieved before use, to eliminate any foreign substance.

After printing, drying in a hot room or to the air, then steaming in order to volatilise the acetic acid and to allow the insolubilisation of the coloured lacquer on the fibre.

The steaming is carried out, for example, during one hour, with 200 g of pressure under bump grays.

One then fixes in a bath at 35°C with 5 to 10 ‰ emetic during thirty minutes. Then one washes to eliminate the thickener in washing machines.

The fabric is then dried on drums.

In the preparation of colors, it is by direct experiment that one determines the relative proportions of thickener, dyes, mordant and additional products.

One examines, after fixing, which is the mixture which gave the best results for intensity, brightness, washing and soaping resistance.

APPLICATION OF THE RTK TANNINS IN COMBINATION WITH THE SHADING TINCTORIAL EXTRACTS FOR THE DYEING OF COTTON IN BROWN AND KAKI

As exposed previously, these dyeings can be easily obtained with two jiggers only. For example :

for a greenish kaki shade, one prepares a mother solution with :

20 kg of RTK tannin
25 kg of Yellow CNOK at 23/25° Baumé
2,5 kg of Hematin ESPGP

in 200 liters of boiling water.

The first jigger is filled with 300 liters of boiling water (purified water) and, in two steps :

30 liters of the mother solution described above
and 0,750 kg of copper sulphate dissolved separately

One makes two passages at boiling temperature for a roller of 100 kg fabric. For the following batches, one refills with :

2nd batch : 15 liters of the mother solution
and 0,375 kg of copper sulphate

3rd and following batches : 7 liters of the mother solution
and 0,180 kg of copper sulphate

The fabrics come out of this bath light lemon-yellow.

The second jigger (fixing) is filled with:

300 liters of water at 70°C
and, in two steps : 2,500 kg of potash bicromate (addition at each end)

Give two passages. Empty the bath and make two rinses.

N.B. - The RTK tannin gives the brown-red element, the Yellow CNOK the yellow element, and the ESPGP Hematin the black-blue element.

To obtain a brown, one will use, for example, under the same conditions as above, the following proportions for 100 kg of dry cotton, boiled off :

New bath:

Water …… 300 to 400 %
RTK tannin ……..…… 20 %
ESPGP Hematin ……..…… 2,1 %
Copper sulphate ……..……..0,8 %

and in addition :

Sodium dichromate …….. 2,5 %

with a reduction of 20 % of these quantities **on an old bath**.

DYEING IN BLACK OF OSTRICH FEATHERS

1st PROCESS :

a) Degreasing

For 100 liters of water, 2 liters of ammonia at 22° Baumé.
Immerse the feathers for one hour. Haul. Add another liter of ammonia. Immerse and leave in contact for another 3 hours. Haul. Rinse

b) Dyeing

Dissolve the following products in 80 liters of water corrected with Acetic Acid and heated at 70/80°C :

0,400 kg Potassium Ditartrate
0,250 kg Potassium Bichromate
and 0,200 kg Copper sulphate

} dissolved separately in the prescribed order.

Leave the feathers in this bath for six hours and let slowly cool down. Then haul and spin.

Dye in another bath at 90°C with :

10 % Hematin ESPGP
3 % Yellow Cnok

until the required shade is obtained.

2nd PROCESS :

For 1 kg of feathers :

Soak for one night in a sodium solution (1% solution) at 35°C. Haul. Leave in an ammonium carbonate solution at 2% for two hours. Haul and rinse.

Immerse for six hours in an iron nitrate bath at 10° Baumé. Haul and rinse. Dye as described above in a bath at 90°C until the required shade is obtained.

DYEING IN BLACK OF PIG BRISTLE AND HORSE HAIRS

This dyeing can be done in one or two baths but the method in two baths seems preferable for the brush-factory.

In both cases, the hair must be carefully degreased by a passage in an alkaline bath (soda or ammonia) and rinsed well.

Process in one bath :

Carefully degrease the animal hair with an ammonia solution at 2%, during half an hour, at 50/60°C. Thoroughly rinse.

Then dye at boiling temperature, during fifteen minutes approximately, with :

6 % Hematin ESPGP
1 % Yellow CNOK

then add :

2,5 % Oxalic acid

and finally, after another quarter of an hour :

3 to 4 % Iron sulphate
1,5 to 2 % Copper sulphate

Keep the boiling temperature for one hour, then stop the heating let the immersion go on for another two hours. Haul. Drain for one night in order for the black to develop. Ring and dry.

Process in two baths :

After degreasing, one mordants at boiling temperature with :

2 % Sodium dichromate
2 % Sulphuric acid 65° Baumé

Haul, rinse and dye in another bath, during one hour at boiling temperature with :

6 % Hematin ESPGP
0,5 to 1 % Yellow CNOK

Haul and rinse.

DYEING OF VEGETABLE BRISTLE

Black with pure Logwood :

First, treat the vegetable brislte with :

10 % Sodium
and 2 % Resin soap
during one hour at boiling temperature.

Rinse thoroughly to eliminate the coloured resinous matter which coated the fibres.

Then dye for one hour at boiling temperature with :

2,5 % Hematin ESPGP
0,25 % Sodium
0,75 % Copper sulphate
} dissolved beforehand and added separately one after the other

Leave the bristle immersed for two hours. After dyeing, haul, drain in order to let the black develop. Then, rinse and dry.

Combined black :

Start at 45°C in a bath with :

3,5 % Direct Black
1,5 % Ammonia 20%
1,0 % Sodium
4,0 % Hematin ESPGP
0,4 % Yellow CNOK
5,9 % Sodium sulfate, crystallised.

Build up to boiling temperature which one maintains for two hours. Stop the heating and continue the immersion for one hour thirty.

Haul. Drain. Immerse in a bath at 30°C of iron pyrolignite at 5° Baumé. Stir for one hour.

Haul. Drain in the open air for the black to develop and rinse thoroughly. The dyeing bath is then refilled with half of the proportions indicated above, for other operations.

DYEING OF TAMPICO

1°- With Logwood

Dye in a first bath with 6 % Hematin ESPGP (of the weight of the material) and 1,5 to 3 % of ammonia 22° Baumé.

Enter the goods at boiling temperature and let them soak for one night, the penetration being slow.

Haul on the following day and drain. Collect the bath which will be used for the following batches.

Develop the black in another bath, tepid, containing 5 % iron sulphate. Leave for two to three hours. Haul and rinse.

The Logwood bath is used for the following batches while refilling it only with 8 % of pure Logwood N.O. Bath volume : approximately 9 times the weight of Tampico (Lr 1/9). The iron bath must be changed each time in order to have clean goods.

An addition of 2 to 3 % of liquid Yellow Cuba will darken the bath.

2°-Mixed black

One uses for 100 kg of material :

3 kg black direct
1,5 kg to 3 kg Hematin ESPGP
0,6 kg Yellow CNOK extract

Enter at 70°C. Bring the bath to boiling temperature. Maintain for two to three hours. Haul, drain and immerse in an iron pyrolignite (4 or 5° Baumé) bath at 30/35°C. Lastly, haul, drain for several hours and rinse cold.

JUTE DYEING

(proportions % kg of matter)

Black

Jute being very acid, treat the threads in a bath made of :

3 % of soda carbonate

during fifteen minutes at boiling temperature, then add :

3 % of copper sulphate.

Maintain the boiling temperature for forty-five minutes and, in the same bath, add :

5 to 6 % Hematin ESPGP
1 % Copper sulphate
0,25 to 0,5 % Yellow CNOK

Dye for one hour at boiling temperature. Haul and rinse.

Yellows and browns

Bath at 70°C with 8 to 10 % Yellow CNOK, according to the desired shade. Immerse the jute and leave for half an hour. Add 3 % of copper sulphate or 5 % of alum, according to the shade to obtain.

The alum gives a purer yellow. Dye for one hour while heating until boiling temperature.

By a subsequent passage in a bath with 2,5 % of iron sulphate, one obtains olive colours, while with 1 to 2 % of sodium dichromate at 50/60°C, one will obtain a more or less dark brown, after half an hour of treatment.

Red

According to the mordant, the shade varies : bluish red on alumina, purple gray on iron, red with tin salts.

Most usually, one passes the jute in a tannin decoction at 5 %, or in a decoction of sumac at 2° Baumé, and then in a cold solution of alumina sulphate, which one makes basic by an addition of soda carbonate. One dyes in a tepid bath with 2 to 6 % Red, according to the shade to obtain and a little Yellow CNOK if one wants an orange red.

INK FOR PRINTING THE BAGS

Dilute 90 g of Logwood CPMK in one liter of water at 70/80°C, then add in this order :

1,600 liter of cold water
0,300 kg Iron sulphate.

Stir well and keep in a wooden or glass container, tightly sealed.