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PLANT DYES : PRODUCTION, EXTRACTION AND APPLICATIONS, AN EXPERIENCE IN THE SOUTH-WEST OF FRANCE.

INTRODUCTION :

Our project on plant dyes started in 1994, during a meeting with Henri LAMBERT, who was founding the Bleu de Lectoure company and who wished to set up a production of blue Woad Pigment (*Isatis Tinctoria*). This production would have to developped towards a new range of art products (water colors, gouaches, inks, drawing pencils, … etc.)

To begin with, the works helped restore the extraction methods used for woad. A documentary research and analysis were therefore engaged, using at the same time recent publications as well as written works from the Napoleon period.

The first laboratory tests on a semi-experimental scale allowed to rapidly obtain the first grammes of natural indigo from Woad.

At the same time, the first hectares of Woad were put in production and the Bleu de Lectoure workshop was built.

End 1994, the sampling of the blue pigment in several different activities activated an interest for this sort of pigment and brought forth the necessity to develop other colors, yellow and red.

During a discussion between the AMIFEL* and the LCA/CATAR**, a plant dye production and industrial holding plan was set up and the first contacts were taken with a farming cooperative, as well as with a textile finisher.

The project became definite beginning 1995, around a consortium agreement, associating the different mentionned partners. The consortium obtained a financial support from the ONIPPAM*** and from the Midi-Pyrénées Regional Council.

The project continues today and enters, as far as Woad is concerned, in its agro-industrial development phase, on scale 1.

In order to follow the developpment of the mentionned project, the LCA/CATAR has progressively opened up a specific area of research to natural dyes. Part of the human and equipment means set in place, directly contributes to the scientific and technology advancement of the natural dye production project.

In order to understand the evolution of our project, followed is a report in two parts.

PART ONE : PLANT DYES

1. History of natural dyes :

The known history of natural dyes begins during the prehistoric period with painted frescos done by the first human beeings, around 40 000 years before J.C. The colors were mostly mineral or coming from calcinations (gypsum white, ochras, ashes,….) Since then, the entire human history follows the evolution of the formulation and usage of dyes, first natural, then synthetic.

Certains dates emphasizing this evolution are :

In Egypte, 5000 years before J.C., the egyptians used plant dyes (Madder Root, Weld, Indigo, Kermes, Crimson) for cosmetic preparations (essentially make-up).

1 500 years before J.C., these same dyes were used to decorate the egyptian tombs.

400 years before J.C., the romans used natural colors to artificially dye wine.

Many years later, in 1671, Colbert printed the first book on textile dyeing.

In 1856, at the turning point of the history of dyes,HENRY PERKIN, managed to synthesize the first synthetic dye, the "Mauveïne". This date marks the fall of natural dyes, as in 1859, VERGUIN synthesizes the "Fuscine",
in 1860, GRIESS makes the first azoical dyes,
in 1876, ROUSSIN synthesizes the sulfoned azoics dyes,
in 1869, synthetic alizarin is made by GRAEBE and LIEBERMANN
in 1894, VIDAL manages to make sulphuric dyes
in 1897, BAYER becomes the first to make synthetic Indigo

This evolution will develop faster and faster, pushed by the progress of organic chemistry during the first and mostly the second World War, which on the first hand, will work on new synthetic possibilities and, introduce, on the other hand, new supports to dye. These supports are synthetic polymers, like Nylon fibers, technical papers and textiles, requiring colors with new qualities for inks, textiles dyes, etc. These will have to be adapted to resist machine detergents as well as external agressions, etc.

2. Recent Interest

An increased interest for natural dyes, started several years ago, on the part of the consummers, is just begining to be felt. This interest is difficult to quantify but the Textile Institut of France gives about an 8 % annual increase of the market and several national and international projects are beeing set up to plant different natural plant dyes, aiming to an industrial production of natural dyes.

- European project (Air2.CT94.0981(SC)) / Production / Extraction Methods / Textile Applications (Contact Ulla EGGERS / Livos pflanzenchemie.

- Italian project, region of Venice (1995-1996) - Production / Extraction Methods / Textile, Ink, Paint and Medicinal Applications.

- "Oro Blu" Project (1998-1999) Region of Marches (Italy)

- LINK Program (1995,….) Production / Extraction Methods / Textile, Ink, Paint Applications (David HILL / MAFF Support)

- "Flax"Company Project, which has been growing dye plants for about 10 years.

The need for natural dyes is beeing shown through several non-alimentary activities, such as :

- Art Products
- Decoration Products
- Printing and Computer Inks
- Automobile Paints
- Cosmetic Products
- Leather Goods and Textiles

3 Main Dye Plants and Composed Dyes :

A – Diversity of the sources and chemical structures

The diversity of natural dye sources is quite vast. It spreads out from the mineral world to the animal reign, passing by the superior and inferior plants.
Traditionally, different ochras were extracted near Apt, different areas in the world supply different lapis-lazuli blues (Moroco, Mexico,…)

Animals are highly searched after sources of colors, as early back as ancient history up to now. For example, the case of the Crimson of Tyr coming from a sea shell and its cousins the purpura persica and the purpura patula (red crimsons) or again the hexaplex trunculus (blue crimson).

Certain members of these families, present on the Mexican coasts are today officially protected because of near extinction. During these last few years, the intensive fishing for the crimson has reduced the size of the species, whom are no longer capable of reproducing.

In seaweeds and in mushrooms, the browns, reds and blues are also present. « Fomes » which are superior mushroms give certain twany browns and may be stated as an example.

Finally, the superior plant families, practically all around the world (except perhaps in the north and south poles) carry natural dyes. Certain may be cites as an example :

- The pomegranate tree (Punica Granatum L.), from Asia and the Orient which the barks, fruits, branches and roots bring on beige to yellow colors.
- The roucou (Bixa Orellana L.) from tropical America which the seeds provide a carotenoïde, the "Bixine", starting from a bright yellow to an orange yellow color.
- The Anil (Indigofera Subfructicosa), from central America and which its outside parts provide indigo.

As well as, calendula, amaranth, the dyer's camomilla,…etc.

B – Known Main Plants

Amongst the most well known dye plants, the Weld (Reseda Luteola), Madder Root (Rubia Tinctorium) and Woad (Isatis Tinctoria) distinguish themselves in our region.

These plants are profoundly integrated in the local traditions, keeping them well preserved and planted in a corner of a garden or field. Before their substitution by synthetic dyes, these three plants supplied the three basic colors for making the trichrome capable of obtaining most of all the colors.

The most well known usage, was for military dyeing and in 1811, Napoleon Bonaparte demanded that Puymorens set up an agro-industrial production of woad pigment. This production had to compensate the loss of indigo occuring from the many European blockades that the Empire was going through.

This study which describes the various production processes up to the architectural drawings of an exraction and dyeing unit, became a book published in 1813, which inspired us start the first woad extractions.

a) Weld :

Weld is a bi-annual plant from the resedaceae family, flowering from mai to september. It is present in all of Europe and grown in Central Europe for its yellow pigment. The plants appreciates chalky soils and sunny lots.

- Production Method :

The planting is done with the seeds, in September or in the Spring. The stem of weld plant as such, will not help fight off the weeds by the occupation of the soil. Therefore, it has to be unweeded with the help of a good hoeing and a selectif weeder.

The harvest may be done by a mechanical cut.

- Dyeing compounds :

The main flavonoides that are found come from the luteolin (free or glycosyled) and the apigenin.

The extraction is done in a hydroalcoholic milieu, then follows different precipitation steps and butanol co-extraction, aiming to eliminate the lipidic fraction and to bring a purified extract in flavonoids.

The characterization and quantification may be done by CCM and HPLC.

The productivity in purified extracts is about 4 to 6% by dry weight which would obtain between 20 to 30 % of luteolin-7-glucoside (major composant)

- **Other compounds presenting an interest** :

Besides the flavonoids, the actual works underline the interest for lipid compounds and the glucosinolates found in the external part of Weld.

Weld revealed to be a very rich plant in lipid compounds, particularly in linoleic acid. The glucosinolates showed the antifeedent and insecticidal properties.

b) Madder Root :

Madder Root is a perennial plant from the rubiaceae family coming from Persia and the oriental Mediterranean coast. It was grown in Europe (south and east of France) in the 18th and 19th century, to produce a blood red dye.

- **Production Method :**

The planting can be done either by seeds or by the division of the rhizomes end of April. The weeding is done by mechanic and manual hoeing. It may be completed by weeding products.

The plant doesn’t appear hungry for fertilizers.

The harvest of the roots is done by turning over the earth on 50 cm and manually picking the roots. The harvest may be mechanically on sandy and light soils.

Dyeing compounds :

The Madder Root dyeing compounds which are found in the plant derive from anthraquinons in the shape of aglycons or glycosides.

In 1968, Burnett and Thompson identified 19 in the roots coming to maturity. But, the young roots contain mainly 4 anthraquinons in a free form and in a glycosyled form : the lucidin, the alizarin, the purpurin and the rubiadin.

The compounds are extractable in water or by different cold or heated alcohools.

The anthraquinonic derivatives characterisation and the quantification may be done by several diferent methods : UV, CCM and HPLC.

The productivity is around 3 to 4 % by dry weight of the roots. (Formamek, 1969, 1970).

c) Woad :

Woad is a bi-annual plant of the crucifera family. It grows in every mild region of Europe, Asia and the Unites States. It prefers chalk and rocky soils in the sun.

- Production Method :

The planting may be done with the seeds in October or during the month of May. The weeding is chemical and is necessary during the growth period. The plant requires an azote and phosphate addition.
The harvest may be done by a mechanical cutting at least 4 times per year.

- Dye Compounds :

The main dye compound is a blue double-indoxyle (bis-indoxyle) : the indigo is usually along with a red derivative called indirubine.
The plant contains essentially 2 Indigo precursors, major Isatan B and the Indican, which are both glycosyl and indoxyl derivatives. These derivatives in major give, by oxydation the Indigo and in minority the indirubin in presence of the isatin.

The extraction of Woad indigo is very old and has been described as early as the 3rd century. More recently, in the 15th and 16th century, the art of the woad balls ("Cocagne") and the alchimia of the « agranat » were often used. But the first process aiming to obtain a purified blue pigment in a powder form, dates back to the Napoleon period.

The indigo's unsolvable characteristics in water makes the soluble precursor extractions very much sought after. The chemical and / or bio-enzymatic extraction allows the possibility to extract, from the woad leaves, the precursors that will afterwards be oxydated in an indigo precipitating through the medium.

The productivity in "raw" Indigo is around 1,3 to 2% by weight of the dry leaves.

- Other compounds presenting an interest :
Several different woad extracts were studied in the Thuringen Landesanstalt für Landwirtschaft in order to obtain several products for wood protection. The extracts obtained by the fermentation of woad extracts shows antifungal activity

2 SD PART : AN EXPERIENCE IN THE SOUTH OF FRANCE

After the first works with the Bleu de Lectoure Company, the different consortium partners mentionned in the introduction, began an operation in 2 phases :
- a first feasibility phase, in order to choose different dye plants.
- a second development phase of the exploitation of the dye plants choosen on a larger industrial scale.

1 – First Phase : A Feasibility study (1995-1997) :

This first phase was a feasibility step during which the bibliographic data on the different plants, their productivity on smaller lots inferior to 1 ha, the first laboratory and pilot extraction essays were able to be collected.

More than one dozen plants were regrouped together, grown and analyzed.

From the list, 6 plants were choosen for their availability, their adaptability and the first productivity in dye extracts.

Within these 6 plants, Weld, Madder Root and Woad were the first plants to be grown, but it is mostly with the engaged works on Woad that brought most of the results.

It was thefore decided to bring on the second phase of the project, which is the passage to scale 1, by setting up 10 ha of Woad in November 1998. This step would eventually help plan ahead the same operations for weld and madder root.

2 – Second Phase : The Passage to Scale 1 (1998-1999)

For the planting of 10 ha, it was decided to grow the woad on "planks" in two areas near Castelnaudary.

- **The setting up of 10 ha of Woad : November 1998**

  ploughing of the soil
  Setting up of the planks
  Weeding
  Seed planting
  1 month period for rising
  Fertilization
  Cuts :
  1 st cut beginning July 99
  2 sd cut en July 99
  3 rd cut beginning September 99

  From the first cut, beginning July to the last cut in September, the production per hectare of the fresh green matter went from 5 to 16 tons.

  Follow-up of the pigment content:

  During the months of June and July, a follow-up from the differents lots was regularly done to check the pigment content.

  As early as May, certain plants already contained 2,5% of indigo per dry weight, but the adverage value is around 2 %.

  End of June, a cooling off because of storms, made the content drop to around 1,5%, which stabilized later on.

  It was then decided to make a first harvest July 2sd, with an adverage content of 1,4% of indigo per dry weight of leaves.

  - Harvest

  The harvest was done with the help of a machine equiped with a cutting bar working approximately one hectare in two hours.
  The transport was done by trucks carring a capacity of 3-4 tons of leaves.

  - Extraction :

  In this case, we used the equipments available within the local of a distillery. Around 6 tons of leaves were put in tanks of a capacity of 125 m^3 and filled halfway with water. During this operation, the follow-up of the pigment concentration was constanly checked in order to narrow down th extraction time. The extraction phase lasted 1h30 and the liquid was oxydated, then put in the resting phase.

- Pigment deposit :
The extraction solution is left to deposit during the night at a normal temperature, in 100 m^3 stainless steel tanks.

- Separation, drying and productivity :
The deposit is otained by filtering on a filter press and the final product is dried.

During these first tests, with optimizing, the 40 liters of concentrated suspension, coming from the 2 tons of leaves, brought on around 2 kg of pigment.

CONCLUSION AND EVOLUTION

Towards the end of 1999 and year 2000, the project will evoluate following different directions. First of all, by increasing the surfaces of the grown dye plants. The production of 50 ha of woad represents the next step. During this period, the conditions of the industrial extraction must be improved, keeping in mind the possibility of recycling of the plant extract matter through new valorisations methods.

At the same time, contacts and exchanges with different activities will favor the evolution of these natural plants towards a larger scale of non-food.

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*AMIFEL : Association Méditerranéenne des Régions Productrices de Fruits et Légumes
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