

Croatian Traditional Herbal Dyes For Textile Dyeing

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Abstract: Textiles, namely protein fibers, in continental part of central Europe have been traditionally dyed by natural dyes. In the process textile materials were pre or after treated by metal salts – mordants (usually: $KAl(SO_4)_2 \cdot 12H_2O$, $SnCl_2 \cdot 2H_2O$, $FeSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$). Most represented active substances in herbal extracts are flavonoid derivatives, which by complexing with metal ions constitute colored complexes. Depending on herb species and mordant applied, a wide palette of colors is available. Good fastness to processes of textile washing and care implicate to the stability of formed metal complexes.

1. NATURAL DYESTUFF DYEING

Croatia is a country of exceptionally rich ethnographic heritage, best seen in colorful national costumes. Colorful folklore elements of national costumes in specific region were formed using the unity of shapes and color hues (fig. 1). A growing interest in natural dyes application is based on not just the system of national heritage protection and multifunctional properties derived. This interest is found in the fact that a garment dyed by natural dyes holds an alternative economical, touristic as well as humanly, ecological significance. In continental part of Croatia, until the discovery of synthetic dyes, protein fibers were usually dyed by natural dyes [1]. Statistical analysis of military government of “Vojna krajina” data of 19th century revealed authors amazement by the fact that natural dyes and dyed textiles were obtained from a arduous and slow process. At the same time by the second half of 18th century, this tradition has been long abandoned in other European countries, while 19th century was marked by production of synthetic dyes and synthesis of new dyes [2].

However, the end of 20th century was marked by such terms like sustainable development and changes in resources use, investments, technical development, as well as institutional changes in mutual harmony, which would assure fulfillment of needs of present and future generations concerns relationship among humans and their natural, sociological and artificial surrounding habitat.



Fig. 1 “Ćilim” from Slavonija, second half of the 19th century. Exhibit EMZ 14718. “Ćilim” reflects traditional colour palette of era when woolen objects were dyed at home and all dyes were of nature [2].

Beginning of 21st century brings a step forward-intensively pointing to the importance of human ecology, academic discipline that Human ecology researches the interaction of people and human communities with their surroundings and natural life.

This new discipline observes human communities and population exclusively as parts of an eco-system on Earth, often not consistent to classical sociological studies and

research [3, 4]. Definition of natural dyes, as given by the Society of Dyers and Colorists is in accordance to the idea of human ecology theory implying to “unity and harmony with nature”. According to it, natural dyes are dyes and pigments obtained from animal or herbal sources, acquired by using no or minimal chemical treatments [5].

2. DIVISION OF NATURAL DYES

Natural dyes can be classified according to dyeing properties, chemical structure, origin (animal, herbal, mineral), hue or application area (food industry, pharmaceutical industry, textile industry etc.) (Fig. 2) [6-9].

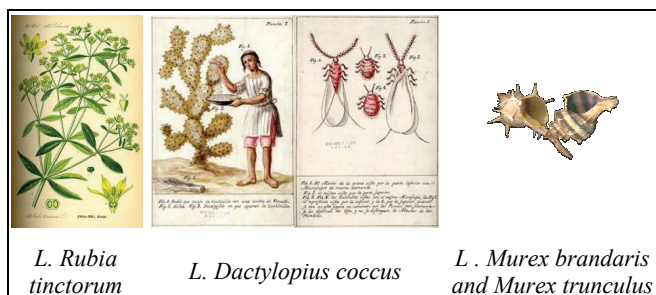


Fig. 2 Exaples of natural dyes origins [7]

2.1. Division of natural dyes according to dyeing properties

In regards to dyeing properties, most natural dyes can be sorted into group of mordant dyes, some can be classified as vat, while a small number of natural dyes belong to groups of direct and basic dyes [5-7].

Complexing with metal salts, mordant dyes give different colorations, while polygenetic properties are prescribed to them. Aluminum, copper, ferrite and tin salts are most usually used mordants. These dyes are usually used to dye protein fibers, with: mordant treatment of fibers (prior to dyeing), mordant treatment carried out in the process of dyeing or after mordant treatment carried out after the dyeing process has been carried out.

Usually used source of dyes are *Rubia tinctorum* cochineal bug (*Dactylopius coccus*), as well as herbs from which most widely used mordant dyes are obtained – flavonoid dyes (fig. 3, 4) [10-15].

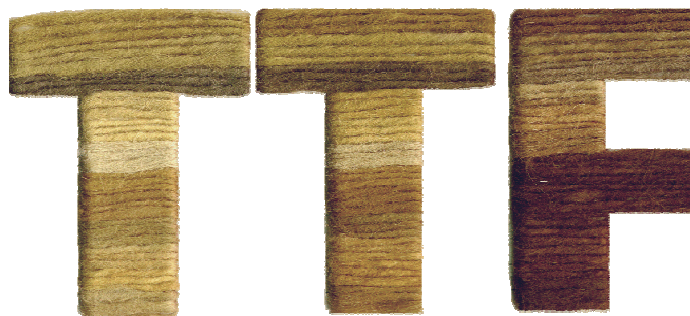


Fig. 3 Typical hue palette of flavonoid dyes



Fig. 4 Woman from Konavle, around 1950. Young woman in ornamented yellow fringes shirt. Yellow color was in Dalmatia obtained from pomegranate fruit or from wild apple tree bark [2]

Second important group of natural textile dyes are in water insoluble vat dyes, which have to be transformed into soluble form with the addition of reduction agent and alkali. Most commonly known representatives of this group are indigo (fig. 5) and purpur 6,6'-dibromindigo dye obtained from murex sea snail (*Murex brandaris*) and lumpy (*Murex trunculus*) [7, 16-19].



Fig. 5 “Rekla” is woman coat from Prkoveci (Slavonija), from the beginning of the 20th century. Exhibit EMZ 20182. “Rekla”-s were made out of wool and dyed by indigo [2]

Among most important natural direct dyes are curcuma and yellow roots (*Curcuma long*, ingredient of curry) and bark or roots of common *Berberis vulgaris* [7, 20, 21].

2.2. Division of natural dyes according to chemical constitution

Division of natural dyes according to chemical constitution is in accordance to botanical nomenclature [7-9].

2.3. Division of natural dyes according to color hue

While classifying natural dyes according to color hue, mordant used during the dyeing process should be regarded. Mediation on mordant type leads to obtaining different color hues [1]. Palette of colors was obtained on woolen samples (coloristic parameters and fastness to washing) dyed by watery herbal extracts. Selection of herbs and mordants was guided by traditional process of dyeing with natural dyes, typical to continental Croatia (tab. 1) [1, 2].

▪ Yellow color hues

Nyctanthes arbor-tristis (Tree of Sorrow, C.I. Natural Yellow 19) dye is extracted from flower (Al as mordant)

Chamaemelum recutica (Chamomile, C.I. Natural Yellow 1) dye is extracted from flowers and leaves (Sn, Al as mordants)

Gardenia jasminoides (Jasmine, C.I. Natural Yellow 6) dye is extracted from fruit (Sn, Al as mordants)



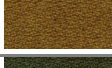





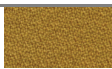



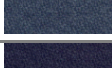
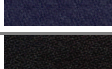
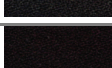
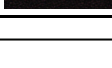

Crocus sativus (Saffron, C.I. Natural Yellow 6) dye is extracted from anthers (Al as mordant)

Calendula officinalis (Marygold, C.I. Natural Yellow 27) dye is extracted from flower (Al as mordant)

Punica granatum (Pomegranate, C.I. Natural Yellow) dye is extracted from fruit scales (Al as mordant)

Fraxinus excelsior (Ashtree, C.I. Natural Yellow 10) dye is extracted from bark (Sn, Al as mordants)

Table 1 Woolen samples dyed by extracts of selected herbs

Herb / Mordant	Colouristic parameters					Washing fastness
	L*	C*	h	a*	b*	
 Sicilian Sumac / FeSO ₄ ·7H ₂ O	49,22	23,90	65,84	9,78	21,81	4/4
 Vine / FeSO ₄ ·7H ₂ O	45,03	23,19	72,69	6,90	22,14	4/4
 Oak / KAl(SO ₄) ₂ ·12H ₂ O	40,70	29,62	73,57	8,38	28,41	4/4
 Walnut-Tree / FeSO ₄ ·7H ₂ O	32,42	13,2	89,56	0,10	13,20	4/4
 Ashtree / FeSO ₄ ·7H ₂ O	42,26	12,74	88,12	0,42	12,73	4/4
 Tree of Sorrow / KAl(SO ₄) ₂ ·12H ₂ O	69,38	35,97	94,52	-2,83	35,86	4/4
 Chamomile / KAl(SO ₄) ₂ ·12H ₂ O	72,41	46,31	91,93	1,56	46,29	4/4
 Jasmine / KAl(SO ₄) ₂ ·12H ₂ O	70,98	63,38	81,93	8,90	62,76	4/4
 Saffron / KAl(SO ₄) ₂ ·12H ₂ O	59,72	40,15	81,99	5,60	39,76	4/4
 Pomegranate / KAl(SO ₄) ₂ ·12H ₂ O	49,92	33,43	77,81	7,06	32,68	4/4
 Marygold / KAl(SO ₄) ₂ ·12H ₂ O	51,44	31,88	77,43	6,94	31,11	4/4
 Juniper / CuSO ₄ ·5H ₂ O	47,53	24,73	46,77	16,94	18,02	3/4
 Madder / KAl(SO ₄) ₂ ·12H ₂ O	42,37	26,30	43,23	19,16	18,01	3/4
 Elder / CuSO ₄ ·5H ₂ O	53,21	21,24	250,21	-7,19	-19,99	4/3
 Elder / CuSO ₄ ·5H ₂ O	41,25	28,87	303,18	15,80	-24,16	3/4
 Oak / FeSO ₄ ·7H ₂ O	23,79	3,67	57,09	1,99	3,08	4/4
 Pomegranate / FeSO ₄ ·7H ₂ O	19,57	5,51	46,11	3,82	3,97	4/4

- Green color hues

Fraxinus excelsior (Ash tree) dye is extracted from bark (Fe as mordant)

Juglans regia L. (Walnut-Tree) dye is extracted from green scales or leaves (Fe as mordant)

- Red color hues

Juniperus Communis (Juniper) dye is extracted from sprouts (Al, Cu as mordants)

Rubia tinctorum (Madder, C.I. Natural Red 8) dye is extracted from roots (Al as mordants)

- Blue color hues

Juniperus Communis (Juniper) dye is extracted from berries (Cu as mordant)

Sambucus Nigra (Elder) dye is extracted from berries (Cu as mordant)

- Purple color hues

Rubia tinctorum (Madder) dye is extracted from roots (Cu as mordant)

Sambucus Nigra (Elder) dye is extracted from berries (Al, Cu as mordants)

- Brown color hues

Rhus coriaria (Sicilian Sumac, C.I. Natural Brown 6) dye is extracted from leaves (Fe as mordant)

Vitis vinifera (Vine) dye is extracted from leaves (Fe as mordant)

Quercus Aegilops (Oak) dye is extracted from bark (Al as mordant)

Picea abies (Spruce) dye is extracted from sprouts (Al, Fe as mordant)

- Black color hues

Quercus Aegilops (Oak) dye is extracted from bark (Fe as mordant)

Rubus fruticosus (Bramble) dye is extracted from fruit (Fe as mordant)

Punica granatum (Pomegranate) dye is extracted from fruit scales (Fe as mordant)

Harmony of color hues obtained from nature enriches textile the material and gives it a new dimension, warmth and quality (fig. 6).



Fig. 6 „Ćilim” from Bačka, 19th century; Exhibit EMZ 14119. Ćilim were dyed with natural vegetable dyes [2]

3. FLAVONOID DYES

The definition of dyeing with natural dyes in Croatia refers to flavonoids. Flavonoids and flavonoid derivatives are most represented compounds in watery herbal extracts (fig. 7).

Flavonoids are found in red wine, chocolate, fruit, vegetables and various other plants and herbs. Today, more than 6500 different flavonoids have been identified [22-25]. Most commonly used dyeing method uses a pretreatment process in which wool is mordanted in watery solution of metal salts, followed by a process of dyeing in the solution of watery extracted natural dyes [1, 7, 22-25]. Depending on chemical structure and chemical-morphological characteristics of the fibers being dyed by flavonoid dyes, following chemical bond are formed: hydrogen bonds are formed among polyphenole hydroxyl groups with free amino and amid groups of the protein fiber; ionic bonds are formed [25-31].



Fig. 7 Until the end of 19th century in Croatia wool and silk were dyed with “materials” of herbal origin: leaves, bark, roots and different herbal seeds [2]

Although, water is the most usual solvent used to prepare natural extract it is being substituted with another solvent (ethanol, methanol) in the aim of increasing the overall amount of the extract, isolation of certain extract components or simply to remove unwanted impurities such as waxes and lipids from watery extracts. According to many researchers, overall amount of can be increased in alkali media. However, selectivity of certain components is lost [32-36].

4. CONCLUSION

Regardless of rich tradition, beauty of the hues, positive effect on health, natural dyes are still competing for their place under the sun. According to literature references, many technologists and scientists deal with the issues and perspectives of applying natural dyes on industrial level. They point out numerous disadvantages brought about by modern industry: unavailability of resources, limited number of dyes, dye exhaustion, complex processes, coloration repeatability, selection of fibers, dye mixture issues, lack of standardization, unacceptable dye fixation degree, water pollution by heavy metals and organic compounds. Other important thing, which should never be neglected, is that natural dyes do not present a substitution for synthetic dyes. Natural dyes have a reserved place on the market; their development is based on tradition, creativity, fashion,

tourism. Possible issues and disadvantages, which may arise from utilization of metal salts, low fastnesses, waste biomass etc. may easily be solved by aimed scientific research. Opposed to disadvantages, numerous advantages are tied to natural dye, such as that they are obtained from renewable resources, health risk free and there is no need for toxic chemicals, which are hard to dispose off.

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