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Theoretical and practical basics of the mordant dyeing for the restoration of museum textile

Annotation. This article launch theoretical and practical research round for union cataloging of dyeing formula textile museum pieces with plant adjective dyes. Part 1 is devoted to theoretical and practical basics of the textile dyeing with adjective dyes. The attempt of plant dyes usage for museum textile restoration is well substantiated.

Keywords: natural plant dyes, mordant rouge, adjective dyes, dyeing, textile, fabrics, restoration.

Formulation of the issue. During the renewal of museum textiles restorer often faces the need of fabric loss completion to provide the exhibit a good appearance. Such losses as a result of damage caused by insects, microorganisms, tissue destruction with air oxygen, ultraviolet light, etc. For strengthening the destroyed cloth after cleaning is dubbed with modern backing (depending on the material of the original the backing can be made of silk, wool, linen, cotton or viscose). For a better look the backing fabric is usually painted in a color close to the original. Textile goods requiring restoration usually have dull colors. However, using natural plant dyes in the painting can result in colors that are very close to the tone of the original. In addition, according to the principles of modern restoration, coloring of backing fabric with plant dyes is more preferable than with artificial ones.

Relevance of research. Until the second half of the nineteenth century, before the invention of cheap and easy to use aniline dyes, only plant dyes had been used. Bright industrial dyes have soon replaced soft shade plant dyes. However, this very plant dyes feature makes them appropriate for use in restoration work. Soft dyeing of fibrous materials for duplication and strengthening of museum textiles and loss supplement is a daily challenge for restorers of historical textiles. Natural dyes give a nice stable colors with a broad mix of soft shades, enabling the most accurate and complete exhibit restoration. Restoration work usually requires plenty of colors and shades but industrial dyes not always give such an opportunity. Therefore revival of forgotten technologies and using of natural plant dyes for coloring of various fibrous materials [1] is very important.

Relation of the author's contribution to important scientific and practical problems.

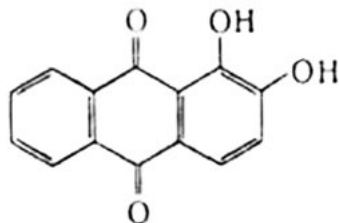
Latest research do not fully cover diversity of plants that can be used as plant dyes for museum textiles, providing a wide range of colors.

Analysis of recent research and published works. Painting with plant dyes was widely known since ancient times. Four thousand years BC China many dyes from plants and animals were used, such as sandalwood blue, red Kermes and Chinese green or Lokao. The first mention of painting and coloring technology and even recipes can be found in the work of the Greek historian Pliny's «Natural History», which is almost two thousand years old.

One of the oldest textile dyeing methods to produce resistant to wet treatments textiles is mordant dyeing, which means use of metal hydroxides to form chemical bond between cloth and dye. Thus, for centuries fabric painted in bright red color with a substance of the madder plant roots had been produced using aluminum hydroxide as a binder or «mordant».

It was proved that the main organic component of that plant dye is 1,2-dihydroxy-9,10-anthracenedione also known as alizarine [4]:

Mordant dyes are used for dyeing wool, cotton, silk and viscose. The chemistry of the dyeing process is quite complex: fiber is treated with a solution of metal salts in the presence of a weak alkali and wetting agent; at this conditions fiber and metal cation form complex compound due to chemically active peptide groups (wool, silk) or aldehyde and carbonyl groups of cellulose (cotton, viscose). Then reacts the dye, which also interacts with the metal cation and form on the fiber an insoluble complex salt (varnish) which absorbs certain wavelengths of visible light (400-800 nm), which leads to visual perception of a certain color. Salts of many metals, but most often of copper, aluminum, iron and chromium can be used as mordants. Mordant dyes usually contain acidic phenolic groups and electron-acceptor groups in the neighboring position, which perform the same function as a carbonyl group in Alizarin. Due to chelate structure of colored layer these chemically active groups can form stable complexes with metal cations. Dye structural formula: intra-complex



compounds of alizarin in which the metal cation is located between fiber and dye. Most mordant dyes are exceptionally resistant to sunlight [2].

We know that on the territory of Ukraine cloth dyeing with plant dyes was particularly prevalent in Hutsulia [3]. Having no scientific knowledge, craftsmen and craftswomen used practical skills acquired by age-old experience. Woven items which were manufactured with dyed yarns are known since the XVIII–XIX centuries. Dyes are made from various plant materials, which

Podolia is rich for: bark and leaves of wild apple trees, stems, flowers and seeds of hypericum, green walnut husk, onion peels and many others. Craftsmen obtained the variety of shades in different ways: not only white, but gray and cream wool was used for coloring; there were also different methods of etching. Pickled cabbage brine, cucumbers, whey were used as mordants. The color is also fixed by spring water curing or sun bleaching. Thanks to that a wide range of shades of different colors was made.

Importance of the unsolved aspects of the general problem which are studied in the article. Despite the diversity of plant dyes [6] they are still little used in the restoration of museum textiles [7] where, as in other areas, direct dyes [8] are more common. This is primarily due to the lack of ready-made vegetable mordant dyes and as a result, the lack of sustainable textile color reproduction when using same recipes.

Novelty of the research. The aim of the cycle of studies that will consist of several interconnected stages, is an attempt to create a catalog of recipes of plant mordant dyes and their ordering by resulting color for intended use in restoration of museum textiles.

Methodological value of present work. By this time there were no reliable methods of plant mordant dyes manufacturing for textile museum with well producible and wide color range.

Presenting of the main substance. In this work practical methodology to be followed in the preparation and coloring of fibrous materials with plant dyes is summarized.

Water and chemicals used for coloring with plant dyes [5]:

1). Water. Natural water can have different degrees of hardness caused by the presence of different metal salts (calcium, magnesium, iron, manganese, copper and other).

Water quality can affect the stability and uniformity of color, dyes and ancillary materials consumption. Hard water contains metal salts that can interact with the dye, which may change the color tint of color. Therefore, water should be soft, use boiled water or rain (snow) water, you can also add soda ash, if it is required by the dyeing procedure.

2). Salts of metals - alum.

Salts of aluminum - potassium alum.

$KAl(SO_4) \cdot 12H_2O$ is used for etching, it provides bright, clean colors: yellow, lemon, light brown.

Salts of copper and chromium.

Copper sulfate (copper vitriol, blue vitriol) $CuSO_4 \cdot 5H_2O$;

Potassium dichromate $K_2Cr_2O_7$;

Sodium dichromate $Na_2Cr_2O_7$.

Salts of copper and chromium are used for wool etching. They provide intensive bronze, old gold, mustard and brown colors.

Iron salts: iron sulfate (green vitriol) $FeSO_4 \cdot 7H_2O$. Using it for wool etching results in gray, dark brown and walnut hue.

3). Plant row material.

This study deals with plants that grow within Ukraine only. But this restriction did not prevent from getting a wide range of colors from bright yellow to rich red, from gray to brown and green. Coloring chart comprises almost all colors of the spectrum except blue. We have not used for dyeing plants which have some kind of indigo, because it's fundamentally different way of painting – so-called vat dyeing.

Substances called pigments – are complex organic compounds, coloring substances of plants that are located in different plant parts. Natural plant dyes can be produced from roots or stems, bark or leaves, flowers or fruits. Chemical composition of plants to some extent depends on its age, place of cultivation, soil composition, weather conditions during the growing season and on harvesting season. Plants should be picked on a clear day, preferably in the morning, picked material should be free of accidental plants.

Flowers and aerial parts of plants should be picked during the flowering period. Yield of raw plant material after drying is 20–30%. Leaves are harvested in early summer. Yield of raw plant material in this case reaches 30–35%. The plant roots are harvested in the spring and autumn. Dug roots are washed and dried. Exit of raw plant materials varies from 20 to 60%. Fruits and berries should be harvested in dry weather in ripe or unripe condition, whichever is suitable for painting. The bark is harvested in late spring and early summer (April-May). During this period, the bark is easily separated from the trunk, and contains the largest amount of coloring agents. The bark of valuable wood species is gathered at lumbering areas (oak), which yields in 40-50% of raw plant material.

The plants should be dried in dry shady place at 25–40 ° C. The shorter is drying period – the better coloring properties of plants are kept. The dried plants should have a natural shade of color, otherwise they are unsuitable for dyeing. Keep picked raw plant material in canvas bags or glassware. Keep dried plants no longer than one year: they lose their coloring properties during prolonged storage.

Many dye containing plants also have medicinal properties. This is due to the presence of alkaloids that are both dyes and medicines. Many of these plants can be bought at a pharmacy or herbalists. If the dye is a pharmacological agent, then use pharmacy packaging weighing 200 g. That is very convenient, because in pharmacology plants are harvested, dried and stored according to the standards. Therefore, stage of the plant material preparation does not affect painting result.

Preparation of dyeing solution: before making dyeing solution thoroughly grind the plant material? particles should be larger than 4–5 mm.

Coloring solution can be prepared by various methods.

1). Plant raw material is pre-soaked for a day in soft cold water. Then it is boiled in the same water within 15–20 minutes. Take 1–2 liters of water per 100 g of the raw material. Filter the broth in dyeing vessels. For full dye extraction boil plants another 15–20 minutes in 1–2 liters of water. Mix the first broth with the second to get ready coloring solution.

2). The plant raw material is soaked for a day in the soft cold water and boil in the same water for 1–2 hours; the hot broth is filtered through a sieve or cloth and cooled. For more intensive dye action the broth sometimes is let turn sour.

3). If the broth is made from fresh plant material, leaves, stems, roots, flowers, fruits, buds, bark or seeds are preliminary soaked a day long in a soft cold water (1–2 liters of water per 100 grams of plant material) and then are boiled in the same water for 15–20 minutes. The broth is filtered in a dyeing vessel. For complete extraction of dye the plants are boiled for another 15–20 minutes in 1–2 liters of water, which is mixed with the broth.

4). To make broth with fresh fruits a juice cooker can be used (elderberry, mountain ash, blueberries). The resulting juice is mixed with water at a ratio of 1: 2 or 1: 3 and the solution used for dyeing.

Prepared cloth is colored at a dyeing bath module of 50: 1 (mass ratio of coloring solution to the mass of cloth to be painted). The process takes place in a glass, earthenware or enameled vessel, under constant stirring with glass or wooden rod.

The brightest and most intense shades can be obtained by dyeing with dyes contained in fresh plants. But Ukrainian climate makes it possible only for five months a year. Therefore it is necessary to pick plants for their further use in advance. Store dried raw plant materials in shady place to retain the natural plant color. Wash plant roots before drying. The dried roots can be stored in a sealed container indoors or better in a dry place in living room.

Thoroughly clean textile materials (fiber, yarn, fabric, knitwear) to be colored to get even and fine shade after dyeing. Textile materials should not have any natural and technological impurities, systematic and random contamination, they should be hydrophilic.

The presence of contaminants and impurities in the textile material would lead to unstable and uneven color. The easiest way to prepare a textile material for painting is washing. For washing of 1 kg of textile take about 1 piece of laundry soap, crush it and dissolve in a little volume of hot water. The washing solution is poured into warm water and whipped to a foam, then it could be used for textile washing, while it is slightly squeezed and turned. Do not wring the cloth out, as this could deform it or form folds, which cannot always stretch after painting. Change soapy water 2–3 times. It should be warm because the hot water may turn the color darker. The use of synthetic detergents is undesirable, because they may change color tone, as our experiments showed. Cotton yarn or fabric undergoes coloring with plant dyes worse than woollen cloth, therefore it should be boiled in soap-soda solution for 1 hour before dyeing. To prepare the soap-soda solution completely dissolve 6–8 grams of soap in 1 liter of soft water, then add soda ash. During boiling the cloth should be completely covered by the solution (take 2–3 liters of solution per 100g of cloth).

After washing or boiling rinse the cloth twice or thrice in warm water, to remove the rests of soap, which would impede uniform coloring. Textile drying after washing or other preparatory procedures is not required. The cloth should be wet when it is immersed in a dye bath, immersing the dry cloth can lead to an uneven or spotty

color. If the cloth is dry, it is necessary to soak it in water before dyeing. For all types of fibers, soaking time is 10–15 minutes.

Etching (fixing) of plant dyes: most coloring substances contained in plants require etching with salts of different metals (mainly aluminum, copper, iron and chromium) for stronger bonding with textile fibers. Salts of these metals are well absorbed by textile fibers from aqueous solutions and during the dyeing process form solid colored compounds called varnishes on the fibers. Process of chemical bonding of metal salts with textile fibers during the coloring is called etching and those metal salts – mordants. Furthermore, mordants change colors and shades of colors, which makes it possible to get a wider range of colors in the same coloring solution. Etching makes the painted material considerably more stable to wet treatments and light.

Using concentrated dye solution with fewer mordant amounts will result in light shades, and with a larger amount of the mordant – dark ones. Adding more mordant to a weak coloring broth will result in a darker color. If the resulted color is too dark, the cloth should be boiled in soap-soda solution (5 g/l of soap and 1 g/l of soda) until the lighter shade is reached.

Prepare a 1% solution of metal salt (alum) or copper sulfate or iron vitriol or salts of chromium (in our case – potassium chromate K_2CrO_4) for etching.

Alum etching gives an opportunity to get light, clear shades of yellow and beige colors. Copper sulfate helps to get red, various shades of green and brown colors. Iron vitriol provides gray, grayish-brownish-green shades, and tartaric acid – beige and light brown ones.

There are 3 ways of etching:

1. Preliminary etching. Chemicals are dissolved in water. The solution is heated to 40 °C, then the wet washed material to be colored is put in and slowly brought to a boil; boiled for 15–20 minutes with occasional stirring. After that the cloth is removed and not wringed out, immersed in a cold solution of the dye, slowly brought to a boil and boiled for 45–60 minutes. After coloring the dye bath is cooled, the cloth removed and rinsed in warm water (40–45 °C), washed in soapy water and then rinsed with warm, then – with cold water again.

Mordant solution can be used for processing the next batch of cloth. To get a wide range of colors you can use mordant mixture or mixtures of dyes. However, this method consumes considerably more dye.

2. Simultaneous etching and dyeing. It is the most convenient and the most common way of dyeing. First fixing agents are dissolved in the dye bath under thorough stirring. The cloth is immersed in the resulting solution, constantly turned, and the solution is brought to a boil and boiled for 45–60 minutes. Boiling should not be very intensive. Subsequently the cloth is rinsed with warm water, washed in soapy water and once again rinsed with warm and then with cold water.

3. Etching after dyeing. Cloth is treated in dye solution for 1 hour. After that the cloth is removed, the bath is cooled to 40–45 °C, and a solution of acid or mordant is poured in. Then the clothed is immersed into the bath, gradually brought to a boil and

boiled for 30 minutes. After the etching the cloth is removed, rinsed with warm water, washed in soapy water and repeatedly rinsed with warm and next with cold water.

Natural plant dyes, as mentioned above, can be used to paint wool, silk, cotton and linen. The best results in plant dyeing can be reached with wool and silk, far worse with cotton and especially linen fabrics. Thus, the etching is particularly important for dyeing of cotton and linen textiles. They should be boil longer (note that linen textiles are boiled for 3 hours), and then alkali (soda ash) should be added into the dyeing solution.

It is difficult to obtain saturated colors on cotton fabrics, but the tint can be intensified with more concentrated dyeing solution or in case of repeated dyeing procedure. For this material is not rinsed after dyeing but just dried, then dyed in the same solution. This sequence can be repeated few times to reach the desired shade.

There was already published some information about other fixing agents for plant dyes, such as salt, vinegar, sauerkraut brine, cucumbers brine, alkaline solution of birch ash.

To prepare an alkali from birch ash take a large amount of ash and a small amount of boiling water (100: 1) and stir. After the water is cooled, ready clear alkali solution is poured into another bowl. There is also a number of folk ways of etching: steam etching; steaming in the oven, when wet painted cloth is wrapped in burlap and kept warm in oven; bright shades can be fixed by bleaching of the wet dyed cloth in the sun.

If the paint is badly stuck, the cloth can be additionally rinsed in hot strong juniper berries decoction [7].

Below you can find a list of plants used for dyeing in this research: oak (bark, acorns), *Rubia Tinctorum* (roots) chelidonium (leaves), alder (bark, leaves, aments), wormwood (whole dried plants), tansy (leaves, roots), horse chestnut (husk inflorescence), stinging nettle (fresh or dried stems and leaves), walnut (leaves, green husks), onion skin normal and blue, Japanese *Sophora* (flowers), peppermint (leaves), thyme (leaves) and many others.

Conclusions. As a result of this work, a large map of mordant dyes was arranged, which has been successfully used in the restoration workshop of the National Museum of History of Ukraine. Painting showed good lightfastness during museum exhibition, derived color palette complies with restoration tasks.

Students of the restoration works of sculpture and decorative art branch have been taught during the present study, which would facilitate their future individual work with historical textiles.

Prospects for the use of the research results. In addition, mordant dyeing can be used in different design applications, especially those requiring ethnographic color recreation.

Soft and wide range of dyes derived during this work makes them appropriate for further study and use in restoration, where exhibits are unique and do not require any large amount of the dye, but soft shades and light stability of colors is needed.

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Теоретичні та практичні засади протравного фарбування тканин при реставрації музейного текстилю

Марія Джулай

Анотація. Ця стаття є результатом теоретичних і практичних досліджень, пов'язаних зі спробою створення каталогу рецептур протравних рослинних барвників та систематизації їх за кольорами фарбування для цільового використання під час реставрації музейного текстилю. У статті розглянуто теоретичні засади протравного фарбування, наведено узагальнені практичні методики, яких слід дотримуватись вповодж всього процесу фарбування, обґрунтована доцільність спроби використання рослинних барвників при реставрації історичного текстилю.

Ключові слова: рослинні барвники, протрава для фарбування, протравні барвники, фарбування, текстиль, тканини, реставрація.

Теоретические и практические основы протравного крашения тканей при реставрации музейного текстиля

Мария Джулай

Аннотация. Эта статья является результатом теоретических и практических исследований, связанных с попыткой создания каталога рецептов протравных растительных красителей и систематизации их по цвету выкрасок для использования в реставрации музейных тканей. В статье рассмотрены теоретические основы протравного крашения, приведены усредненные практические методики, которых необходимо придерживаться во время всего процесса крашения, обоснована целесообразность использования натуральных красителей при реставрации древнего текстиля.

Ключевые слова: растительные красители, протрава для крашения, протравные красители, крашение, текстиль, ткани, реставрация.