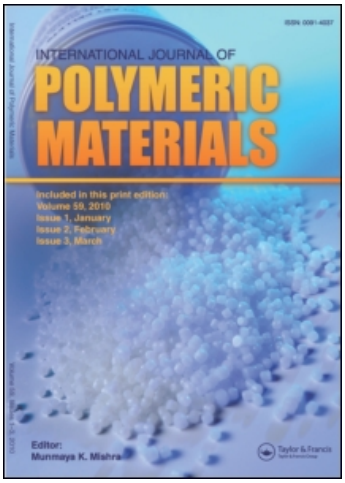

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Plant Dyes and their Use in Restoration of Eastern Manuscripts

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Plant dyes' influence on mechanical and physico-chemical paper properties in different conditions of heat- and light-accelerated artificial aging process was studied. A method of isolating dyeing complexes from plants by regulating solvent and extraction parameters was developed. Problems concerning the production and use of paper dyed according to the proposed method in practical work of restoration paper-based manuscripts, lithographies and documents are discussed.

KEY WORDS Dyes, restoration, paper documents aging.

INTRODUCTION

Considering the continuous aging process of hand-written and printed literary documents, studies dealing with restoration and conservation of documents are becoming increasingly important.

Of special difficulty is the work with Eastern manuscripts. The paper necessary for their restoration should be of the same color as the manuscript and it should be stable over time. However, the choice of dyes suitable for this purpose is rather difficult due to the poorly-studied problem of their influence on paper's physico-chemical properties and its destruction. The use of natural plant dyes to restore the destroyed pages of the printed issues and ancient manuscripts (hand-written books) is of increasing significance. Of special interest in this respect is the rich flora of Middle Asia, especially that of Tadjikistan, where about seven thousand high plants grow, many of which have been used for centuries as dyes for paper, textile and leather haberdashery goods.[1,2]

The aim of the present work is to develop chemical compounds and methods for production of natural plant dyes, and study their influence on paper properties, manufacture and use of dyed paper by the dyes suggested in restoration of Eastern manuscripts.

EXPERIMENTAL

Studies were carried out on six types of paper: with mica basis, restorational paper type 1, subparchment A type, paper for photoelectrographic cylinders, restorational

paper type 2 and restorational paper type 3 to strengthen the document basis differing in thickness. Eighteen sources of plant dyes were used, including staining henna, walnut nut peel, staining basma, dodder, chrome-flower barberry, common St. John's wort, mulberry-tree polypore, sum of dyeing substances of mulberry-tree polypore (SDSMTP), rind of common oak, pome-granate rind, hawthorn fruits, Gleditchia triacanthus fruits, onion peel, etc.

Dyeing solutions were prepared following the methods of the State Pharmacopeia of the USSR.[3] Of the great amount of dyes used in a form of water, water-alcohol and water-acetate extracts, the sum of dyeing substances of mulberry-tree polypore, obtained due to the original methods consisting of raw extraction by water-acetone mixture under different raw-water ratio, is of special interest. Prolongation of extraction period and solvent quantity increase do not significantly influence the amount of staining substances yield, but result only in an increase of solvent use and prolongation of the period of extraction.[4] The process of extraction is carried out under 24°C to avoid destruction of biologically active components. The parameters of the process were determined: the raw-solvent ratio was 1:10, the acetone-water ratio was 1:4, extraction time was 4 hours, and extraction temperature was 24°C.

A neutral powder of dark-brown color is obtained (19.4 g). The qualitative chemical reactions showed that mulberry-tree polypore dyeing substances include phenol compounds and hydrolyzing tanning substances.

To determine physico-chemical and mechanical paper properties standard methods were used: data on break resistance, tear, elongation on stretching, reflection coefficient, pH, capillary paper absorption were analyzed.[5] Solutions and films made of cellulose diacetate (CDA) electron spectra were obtained using "Specord-240 M." The relative viscosity of the stained films in a form of acetone solutions was evaluated by the viscosimetric method.[6] Dyes' effect was analyzed by relative viscosity change of 0.5% acetone solutions received from the stained CDA films before and after irradiation.[7]

The following methods of artificial aging were used in the present work: "moist" and "dry" thermic aging, ultraviolet irradiation and irradiation by day-light lamp.

DISCUSSION

Color and shades of Eastern manuscripts, kept in the fonds of manuscripts in the Institute of Oriental Studies of the Academy of Sciences of Tadjikistan, were studied. The analysis showed that of 2000 books analyzed, the paper of 33% was of grey color, 31% were brown, 17% yellow, 5.3% pink, 5.2% beige, 1.6% violet, and 0.7% displayed green color of different shades. All the colors and shades could be divided into 8 groups and 14 subgroups, which scale may be used to choose natural plant dyes.

The choice of dyes similar in color to those used to stain paper in ancient times is of great importance for the modern restorational science and practical work.

When studying coloristic dye properties it was found that the most suitable for paper dyeing is the products made of walnut nut covering, quercitrol, isoramnetin,

henna extract, barberry root dyes, berberin, SDSMTP, Gleditschia. These are characterized by resistance to heat and light aging as well as ultraviolet irradiation.

The influence of dyes on mechanical and physico-chemical paper properties in a process of different types of artificial aging was also studied. Figure 1 shows that index of break resistance (lg N) of the dyed samples of mica paper basis (No. 2, 3, 4, 5) reduces in a process of moist thermal aging more slowly than that of the undyed paper (No. 1). The unfavorable effect of pome-granate extract on paper strength should be noted because it indicates the presence of agents facilitating the aging process of paper (No. 6). In other stained samples the index of break resistance was stable. The same effect was noted in the stained paper samples of subparchment type A in the process of ultraviolet irradiation, a fact confirmed by comparison with the curves presented in Figure 2.

Evaluation of reflection coefficient (R) change in the paper specimens studied

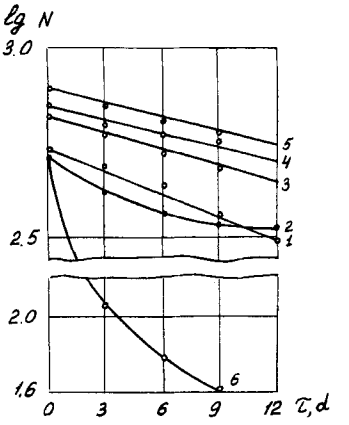

FIGURE 1 Change of resistance index to break (lg N) of the mica paper basis depending on artificial moist thermal aging period (τ). 1—without dye; 2—nut; 3—henna, 4—quercitrol; 5—berberin; 6—pome-granate.

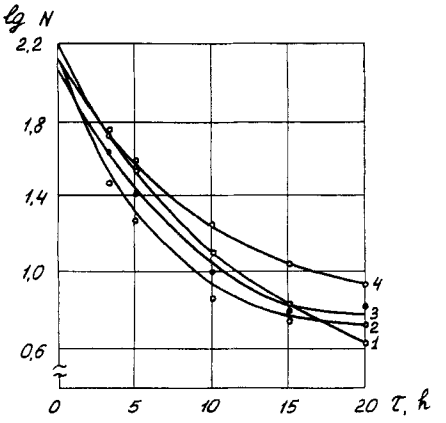

FIGURE 2 Change of resistance index to break (lg N) of the parchment paper type A depending on the time of ultraviolet irradiation (τ). 1—without dye; 2—berberin; 3—henna; 4—SDSMTP.

TABLE I

Reflection coefficient change (R) of the stained paper, subparchment type A, under thermal aging

Type of dye, and its concentration	R		ΔR
	Before aging	After aging	
Without dye	83.3	67.1	16.2
SDSMTP, 1.0%	22.8	21.6	1.2
Quercitrol, 0.1%	53.5	52.4	1.1
Isoramnetin 1:10	45.2	44.1	1.1
Henna 1:10	32.4	30.8	1.6
Berberin 1:500	41.6	39.5	2.1
Nut 1:10	31.3	30.2	1.1
Ginger plant 1:10	64.4	61.1	3.3
Barberry 1:10	45.8	12.9	32.9
Pome-granate 1:10	48.0	14.6	33.4

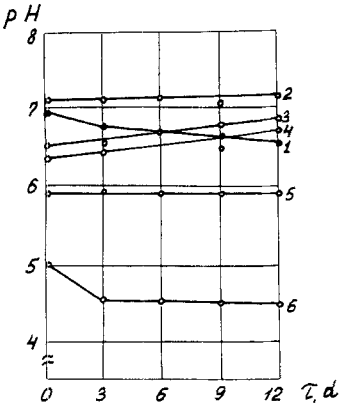

FIGURE 3 pH dependence on the period of thermal aging (τ) for the specimens of mica paper basis. 1—without dye; 2—SDSMTP; 3—berberin; 4—quercitrol; 3—henna; 6—pome-granate.

in the process of thermal and light aging confirmed the advantages of the dyes recommended. Table I shows that minimal difference (ΔR) following artificial aging is seen in paper specimens stained by quercitrol, isoramnetin and nut, and then in order of decreasing effect by SDSMTP, henna, berberin, barberry, pome-granate, and undyed specimens, where the value is 16.2 (Table I).

pH dependence on thermal aging period for the specimens of mica paper basis, stained by certain dyes, is presented in Figure 3. This figure shows that pH remains practically unchanged after aging and is at a higher level compared to control specimens. The index markedly falls (up to pH level = 5.0–4.5) only in specimens dyed by pome-granate extract; the process of acidification is likely to take place in this case, which unfavorably influences paper longevity. And under the influence of SDSMTP, paper pH remains at a neutral level (pH = 7.0), thus showing the basic character of polypore-staining substances.

The same results are observed when studying other paper specimens' pH. Of all the dyes and SDSMTP extracts studied, henna extract, walnut nut cover decoction, decoction of dodder, quercitrol and berberin give paper additional stability in aging

process. This is probably promoted by a hydroxyl group present in the composition of the main dyeing henna substances (lavzone), nut (juglone), quercitrol and berberin staining matter, which are able to interact with cellulose hydroxyls forming hydrogen bonds.[8] Since thermal aging under atmospheric air is connected with oxidation processes, the increase in paper strength may result from the action of such well-known antioxidant dyes as quercitrol, berberin, or henna.[9,10] The neutral nature of the dyes recommended also promotes paper destruction slowing.

To determine light stabilizing dyes' effect, CDA was used as a paper model as it approaches cellulose in its structure, dissolves in organic solvents, and permits to obtain optically transparent films. The data in Table II shows that introduction of plant dyes in CDA solution exerts practically no influence on the relative viscosity of the initial polymer, observed before irradiation. Dyes' light stabilizing activity was evaluated by the degree of preservation of the polymer's viscosity after irradiation (Table II).

Analysis of the data presented in Table II shows that undyed CDA is light unstable and preserves only 7.1% of the initial viscosity after irradiation. Introduction of natural dyes in CDA in all the cases except berberin results in significant

TABLE II

Stained CDA solutions' relative viscosity change during ultraviolet irradiation over 24 hour period

Dyed CDA solutions	Concentration, %	Relative viscosity		Viscosity preservation, %
		Before irradiation	After irradiation	
Without dye	—	1.12	0.08	7.1
Quercitrol	3	1.04	0.74	71.5
Nut	3	1.14	0.74	64.6
Henna	3	1.17	0.73	61.9
SDSMTP	1	1.02	0.59	58.8
Berberin	1	1.10	0.08	7.6

TABLE III

Paper absorption capillary change in the process of artificial aging

Type of dye and its concentration	Capillary absorption, mm/10 min					
	Subparchment			Mica basis		
	Before aging	Thermo-aging, 12 days	UV irradiation, 20 hours	Before aging	Thermo-aging, 12 days	UV irradiation, 20 hours
Without dye	30.0	28.0	30.0	16.0	15.0	15.0
SDSMTP, 1.5%	10.0	8.0	8.0	11.0	9.0	8.0
Berberin 1:500	28.0	28.0	28.0	24.0	24.0	25.0
Nut 1:10	8.0	8.0	7.0	4.0	3.0	4.0
Henna 1:10	10.0	10.0	8.0	6.0	5.0	6.0
Quercitrol 0.1%	25.0	24.0	26.0	18.0	16.0	16.0
St.-John's wort 1:10	16.0	16.0	15.0	27.0	25.0	26.0
Ginger plant 1:10	16.0	16.0	18.0	14.0	14.0	15.0
Dodder 1:10	14.0	14.0	16.0	14.0	14.0	15.0

light stability index increase. Thus all the dyes studied except berberin are light stabilizers. Quercitrol also has its own light resistance.[7]

As a rule, paper of ancient manuscripts has a hydrophobic surface. Thus paper intended for such manuscripts' restoration must also possess some hydrophobic properties. Capillary absorption studies of the paper stained by plant dyes showed that SDSMTP, nut cover decoction, henna extract, as well as that of dodder decreases by 3–4 times the paper capillary absorption. Different methods of artificial aging do not influence the active character of the above mentioned dyes. It might be the result of their tanning substance content, which distinguishes them from pure phytodyes and makes the dyed paper surface hydrophobic.

The analysis of plant dyes' effect on the paper biological stability showed that among all the dyes studied, only berberin diluted as 1:500 and 1:1000 displayed fungicidal action, producing complete inhibition of fungi Phoma growth and sharp retardation of Penicillium verricosum and Stachybotrus atracorda mould fungi growth. The higher the berberin concentration the stronger its antifungal activity. Specimens stained by quercitrol, SDSMTP, henna, nut, ginger plant and dodder extracts markedly inhibited Penicillium verricosum, Poma sp., and Stachybotrus atra corda mould fungi growth in the paper. Other kinds of dyes and extracts do not possess fungicidal and fungistatic properties.

On the basis of the studies performed, composition and method of production of the sum of dyeing substances from mulberry trees were developed and introduced into practical work. Dye made of SDSMTP is recommended for use in paper dyeing in restoration processes. The tests and evaluations made showed that paper stability intended for manuscript and lithography restoration dyed with SDSMTP increases in aging compared with unstained paper.

Dye extracts from nut, henna, dodder, ginger plant, St. John's wort, SDSMTP, quercitrol, berberin and isoramnetin are recommended for paper dyeing in the process of restoring Eastern manuscripts. The methods of paper dyeing have been developed. An expimental lot of restoration paper was manufactured in the St. Petersburg paper factory "Goznak" with the use of dye made from nut covering. The paper produced was tested in the department of storage of the fonds in the Chief Archival Department in Moscow.

CONCLUSIONS

Dyes produced from nut, henna, SDSMTP, barberry roots, dodder, berberin, quercitrol may be used for restoration process; reflection coefficient of the stained paper is insignificantly reduced in the aging process, which shows high stability over time of staining made using the studied dyes. It was shown that the dyes recommended promote stability increase (according to parameters studied) of the paper stained in aging process.

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