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Phototendering of wool sensitized by naturally occurring polyphenolic dyes

Gerald J Smith[a,*], Ian J Miller[b], Vincent Daniels[c]

[a] *New Zealand Institute for Industrial Research, P.O. Box 31310, Lower Hutt, New Zealand*
[b] *Carina Chemical Laboratories Ltd, P.O. Box 30366, Lower Hutt, New Zealand*
[c] *Conservation Department, Royal College of Art, Kensington Gore, London SW7, UK*

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Abstract

A number of naturally occurring polyphenolics have been used since antiquity to dye wool. These colourants, originally extracted from plants and insects, can be fixed to wool fibres by a metal ion mordant with the free carboxylic acid and sulphydryl groups present in wool protein providing the necessary metal ion binding sites.

Wool undergoes a variety of chemical reactions induced by exposure to UV radiation which eventually manifest themselves as changes in the tensile strength and elasticity of the fibre (phototendering). It is expected that UV-absorbing dyes applied to wool fibres provide some photoprotection to the fibres by partially screening them from this damaging radiation. However, it was found that when mordanted by some metal ions, the natural polyphenolic dyes madder, alizarin and weld which contains the flavonoid, luteolin, exacerbate phototendering compared with undyed wool or fibres which had been treated with the mordant metal ions alone. Several metal ions used as mordants since antiquity such as ferric, cupric, stannic and aluminium have different effects on the rates of this phototendering of dyed wool fabric.

Keywords: Dye; Polyphenolic; Wool; Metal ion; Mordant; Phototendering

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1. Introduction

Polyphenolic dyes such as the hydroxylated anthraquinones and flavonoids represent a large group of chromophores that bind to cationic groups associated with textile fibres. The binding sites for these dyes are frequently metal ions which are complexed to anionic groups present on the fibre surface. Many dyes of the presynthetic era were polyphenolics extracted from plants and insects. For example, madder, which is a mixture of hydroxylated anthraquinones extracted from the root of the plant, *Rubia tinctorum*, was one of the first "mordant" dyes to be used in the Mediterranean region. As early as c. 1760 B.C., a Babylonian tablet records that wool was dyed with madder and alum [1] and Egyptian textiles of the 21st Dynasty (c. 1000 B.C.) have been reported to be similarly dyed [2]. A chemically related dyestuff extracted from *Dactylopius coccus*, cochineal, mordanted with tin was used until as recently as 50 years ago to produce the bright scarlet colour of British Army dress tunics [3].

A range of colours can be realized from a single compound by using different metal ions as mordants that form change-transfer complexes with strong, bathochromically shifted absorption bands [4–6]. The spectral positions of these bands are determined by the differences in the redox potentials of the metal ion and the complexed polyphenolic [7].

Wool is an excellent textile substrate for polyphenolic dyes because these proteinaceous fibres readily bind mordant metal ions, principally through amino acid bearing side carboxylate groups, i.e. aspartic and glutamic acid residues or the sulphydryl groups of cysteine residues [8].

Undyed wool is subject to a number of types of degradation such as changes in tensile strength, loss of elasticity and yellowing upon exposure to sunlight [9–11]. These changes result from photochemical reactions initiated by the absorption of ultraviolet radiation by aromatic amino acid residues,

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[*] Corresponding author. Tel.: +64 4 3913 231; fax: +64 4 5690 132.
E-mail address: g.smith@irl.cri.nz (G.J. Smith).

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their oxidation products and the disulphide groups of cystine residues in the proteinaceous fibre [9–11]. Dyes, as well as fulfilling their intended function of decoration, also absorb and thereby screen some of the damaging UV radiation. However, previous investigations of the photolysis of wool dyed under acid conditions, pH < 3, with synthetic alizarin sulphonate (alizarin is the principal chromophore in madder) showed that this hydroxylated anthraquinone participates in a number of UV and visible induced reactions with the fibre substrate. This is inferred from the increases in the tensile strength of alizarin, acid-dyed wool resulting from irradiation with simulated solar radiation compared with undyed wool [12]. There have also been reports that the presence of metal ions bound to undyed wool can sensitize the UV-induced production of free radicals and photoyellowing of the fibre [13,14]. The metal ions used as mordants in this work, when applied to wool fibres at pH ≥ 4, exist as hydroxides and/or oxides formed by hydrolysis in aqueous conditions [15]. However, when wool treated with these metal ions is subsequently dyed with a polyphenolic molecule, the hydroxyl groups are progressively displaced by phenolate ligands [16].

The purpose of this work was to elucidate the combined effect of natural polyphenolic dyes fixed to the wool by dye-metal ion mordant complexes on the phototendering of wool. The particular dyes chosen for study are representatives of each of the two types of naturally-occurring polyphenolic compounds used as dyes; viz. madder which is principally the anthraquinone, alizarin, and weld which contains the flavonoid, luteolin.

2. Experimental

2.1. Materials

The samples of wool were a plain woven fabric with a mean fibre diameter of 20 μm, weighing 154 g/m^2, provided by the Wool Research Organisation of New Zealand. The weave was open, to allow reasonably uniform exposure to light when the fabric was irradiated from both sides.

The madder, *Rubia tinctorum*, and weld, *Reseda luteola* L., dyes were extracted from 3% dried weight of plant material in water at 90 °C for 2 h, after which the solution was filtered, and applied immediately to the fabric in the way described below. Ferric chloride, stannic chloride, copper chloride, aluminium sulphate and alizarin sulphonate were supplied by BDH. All reagents were used without further purification.

2.2. Methods

Irradiation of 10 cm × 10 cm samples of the standard wool fabric was carried out in a reflecting, aluminium chamber containing two banks of fluorescent tubes (Truelite 40W, 48 in) that closely approximate the solar spectrum without producing excessive heat. Each bank of lamps consisted of four parallel fluorescent tubes mounted 1 cm apart and the banks were positioned on opposite sides of the fabric sample at a distance of 7 cm. Immediately behind the banks of lamps were aluminium reflectors open at the top and bottom to allow convective cooling of the samples. The radiation intensity was uniform across the samples with a UV intensity of 182 μW cm^{-2} integrated from 290 nm to 400 nm and with a visible intensity of 1265 μW cm^{-2} integrated from 400 nm to 600 nm. The radiation had a spectral distribution which approximated that of solar radiation at the earth's surface. The temperature within the radiation chamber was 5 °C above ambient.

Irradiations were carried out for up to 2500 h with subsamples removed periodically and stored in the dark until tensile strength measurements were performed. The extent of phototendering was determined by measurement of the breaking strength using an Instron model 1122 tensile tester. Tests were carried out on fabric strips which were 10 cm in length by 12 threads wide and that had been conditioned overnight at 20 °C and 65% RH. Prior to irradiation the strips of fabric had a breaking load of 51 ± 2 N.

Wool pre-treatment involved immersion of the fabric for 10 min in warm water plus detergent, followed by thorough rinsing. The wool was then agitated gently with 0.1 mol l^{-1} hydrochloric acid for 5 min, followed by rinsing with deionised water until the washings were no longer acidic. Treatments with metal cations were carried out by immersing the wool samples in solutions of 5% ferric, cupric or stannic chlorides or aluminium sulphate adjusted to pH 4 with acetic acid for 30 min at 90 °C with gentle agitation. The samples were then thoroughly washed in cold water.

Dye treatments were carried out by placing the wool sample in the dye solution and boiling for 30 min, or until the sample did not absorb further dye. The dyed sample was removed from the dye bath, rinsed thoroughly with running water and was then air dried at ambient temperature.

3. Results

The effects on tensile strength of up to several thousand hours of irradiation with simulated solar radiation on undyed wool that has been treated with the metal ions ferric, aluminium or cupric ions at pH 4 relative to untreated wool are shown in Fig. 1. Wool that had been mordanted with metal ions and dyed with madder, weld (luteolin) or alizarin sulphonate exhibited substantial differences in the kinetics of light-induced changes in the tensile strength of wool fabric as shown in Figs. 2–4. When mordanted with ferric or stannic ions, dyed wool exhibited monotonic decreases in tensile strength and extensibility over periods of up to 2500 h of photolysis. When subjected to extended periods of photolysis, dyed wool that had been mordanted using cupric ions produced small increases or no change in the tensile strength. However, there were substantial losses of extensibility. Irra-

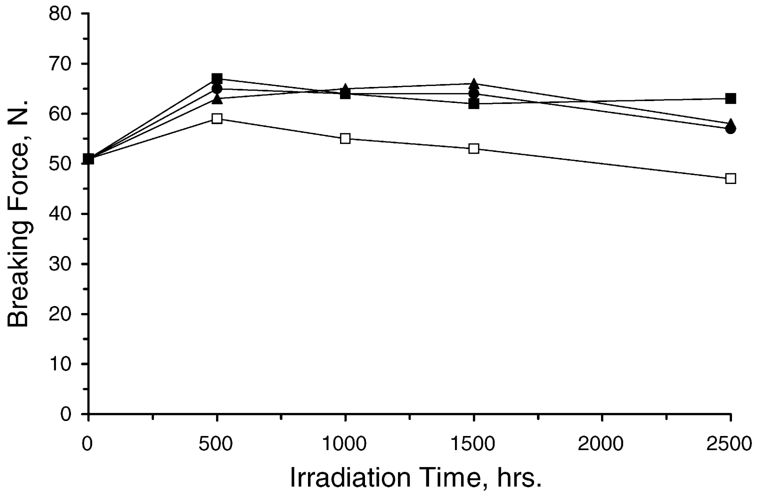

Fig. 1. The change in tensile strength, breaking force, of undyed fabric strips. Treated with aluminium ions, (■); cupric ions, (●); ferric ions, (▲); and untreated with metal ions, (□).

diation of fibres that had been dyed using aluminium ions as a mordanting agent produced a significant strengthening of the fabric relative to undyed wool or dyed wool mordanted with the other metal ions investigated. As is the case with undyed wool, the aluminium mordanted fabrics dyed with natural polyphenolics undergo a gradual reduction in extensibility with increasing doses of irradiation. However, this occurs at a considerably slower rate than the light-induced loss of extensibility observed for wool dyed with weld or madder and mordanted with cupric, ferric or stannic ions as shown in Fig. 5.

4. Discussion

Undyed wool displayed increases in the breaking load resulting from <1000 h of irradiation with simulated solar radiation and this behaviour has been shown previously to be associated with the photochemical formation of crosslinks in the keratin proteins. There is a concomitant reduction in fibre extensibility and elasticity that is attributed to disruption of the α-helical, tertiary polypeptide structure in irradiated wool [11,17]. After periods of irradiation with simulated solar radiation >1000 h, a loss of tensile strength becomes apparent. This has been explained in terms of cleavage of both the polypeptide microfibril chains and the crosslinking bonds between these chains and the matrix proteins of the fibre [18].

It has been reported previously that when the anthraquinonoid dye, alizarin, is applied as an acid dye without mordant metal ions it participates actively in the phototendering of the wool protein substrate [12]. Many anthraquinones are oxidising agents (i.e. hydrogen atom and/or electron acceptors) and their oxidising power is enhanced in their electronic excited states produced by absorption of light [19–21].

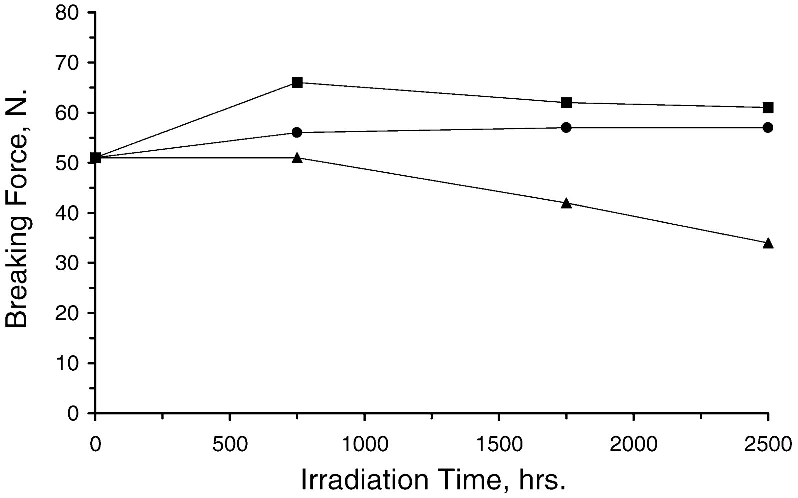

Fig. 2. The change in tensile strength, breaking force, of fabric strips dyed with weld and treated with aluminium ions, (■); cupric ions, (●); and ferric ions, (▲).

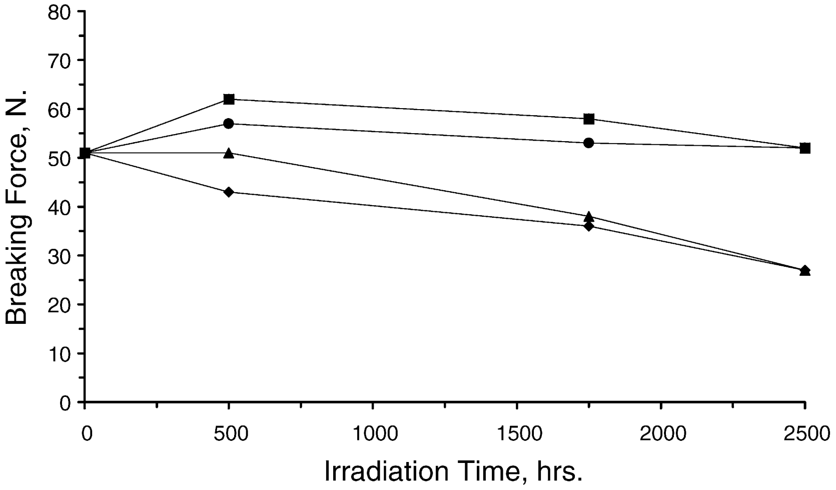

Fig. 3. The change in tensile strength, breaking force, of fabric strips dyed with madder and treated with aluminium ions, (■); cupric ions, (●); ferric ions, (▲); and stannic ions, (♦).

It is inferred from this that fragmentation and crosslinking of the microfibril polypeptide chains and matrix proteins are initiated by light-induced hydrogen atom or electron abstraction from wool polypeptides by the excited states of alizarin which contributes to the reported photoinduced changes in the tensile strength and extensibility of the dyed wool [12].

The metal ions, iron and copper, when applied to wool under acidic conditions without associated dye molecules, have also been reported to photosensitize chemical reactions that lead to the degradation of wool [22]. Under the less acid conditions used in this work, i.e. pH 4, and in the absence of liganded polyphenolics, the metal ions are bound to the protein as hydroxides/oxides formed by hydrolysis [15]. Primary photochemical decarboxylation reactions involving complexes formed between metal ions and free carboxylate groups of the substrate proteins lead to the formation of alkyl free radicals by rupture of α C–H bonds and C–C bonds with vicinal carboxyl groups of the microfibrils' polypeptide backbones [22–24]. Adjacent protein chains are held in close proximity to each other by bridges formed by liganding carboxyl groups from neighbouring chains to a single, common metal ion or multinuclear metal oxohydroxides. This is analogous to the interactions between polypeptide chains established in the metal ion tanning of collagen [25]. Such molecular configurations will facilitate coupling reactions between the free radical produced that covalently crosslink the chains and this can account, at least partly, for the observed increase in tensile strength with a concomitant loss of elasticity in irradiated wool treated with metal ions/hydroxides.

Upon dyeing, the hydroxide or oxohydroxides ligands of the hydrolysed metal ions are progressively displaced by polyphenolic ligands as exemplified by the first two of the displacement reactions [16].

$$\mathrm{M(OH)}_m + \mathrm{LH}_n \rightarrow \mathrm{M(OH)}_{m-1}\mathrm{LH}_{n-1} + \mathrm{H_2O}$$

$$\mathrm{M(OH)}_{m-1}\mathrm{LH}_{n-1} + \mathrm{LH}_n \rightarrow \mathrm{M(OH)}_{m-2}(\mathrm{LH}_{n-1})_2 + \mathrm{H_2O}$$

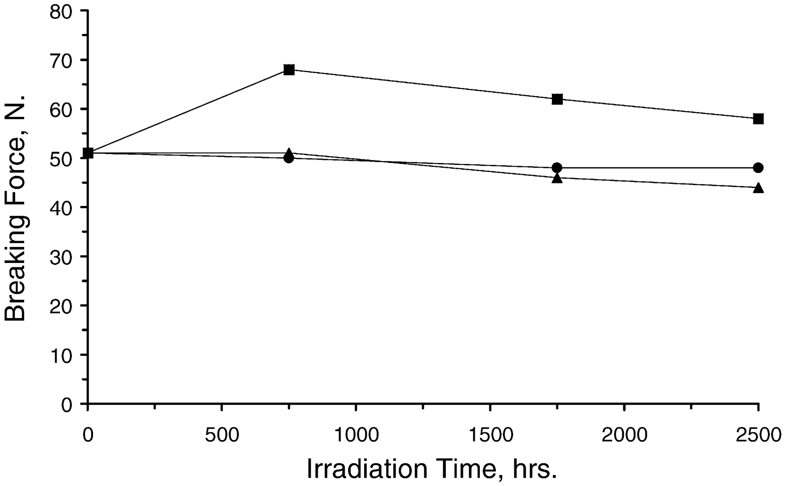

Fig. 4. The change in tensile strength, breaking force, of fabric strips dyed with alizarin sulphonate and treated with aluminium ions, (■); cupric ions, (●); and ferric ions, (▲).

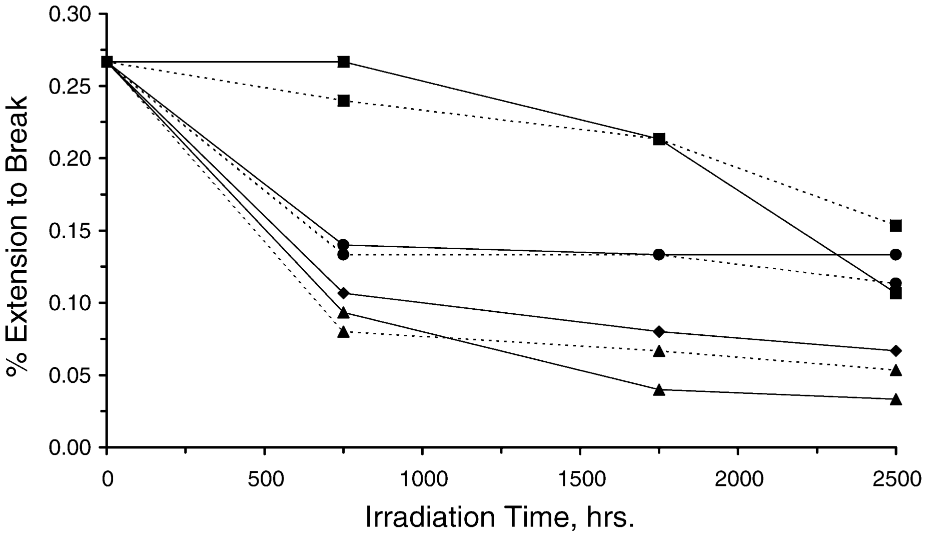

Fig. 5. The loss of extensibility of fabric strips. Dyed with madder and treated with aluminium ions, (■); cupric ions, (●); ferric ions, (▲); and stannic ions (♦). Dyed with weld and treated with aluminium ions, (■); cupric ions, (●); and ferric ions, (▲).

This removal of hydroxide ligands capable of complexing with free carboxyl groups of the polypeptide chains will be accompanied by a loss of the interlocking of neighbouring chains through a common metal ion [25]. As a result, the probability of crosslinking reactions mediated by free radicals will be reduced and bond scission reactions will dominate with a consequential loss of fibre tensile strength [11,17,18].

There is a substantial increase in the phototendering, i.e. loss of strength and extensibility, of dyed wool which are fixed to wool by ferric or stannic ions. This can be rationalized in terms of additional bond cleavage reactions initiated by free radicals produced by electron transfer, hydrogen atom transfer or decarboxylation reactions involving the excited states of the polyphenolic molecules and the associated ferric or stannic oxohydroxides. In appropriate cases, the photodegradation could be also affected by the abilities of some metal ions to alter the population of the reactive triplet states of the polyphenolics by relaxation of the spin selection rules responsible for suppressing transitions from singlet to triplet states [26]. These triplet states can either react with oxygen to produce damaging singlet oxygen or react directly with the polypeptide to abstract hydrogen atoms with the production of free radicals [19–21].Relatively minor changes to the tensile strength of wool dyed with madder or weld attend irradiation with simulated solar radiation when cupric ions are used as the mordant compared with stannic or ferric ions. This can be attributed to the high specific affinity of cupric ions for sulphur atoms in cysteine and cystine amino acid residues [8]. Copper ions that are bound to sulphur-containing amino acid residues are capable of photosensitizing sulphur radical production and some of these radicals will form S–S bond crosslinks between peptide strands and between the microfibrils and the surrounding amorphous protein matrix [8,17]. However, like the other metal ions that can assume multiple valence states, cupric ions that are complexed to the polyphenolic dyes photosensitize the cleavage of bonds with an attendant loss of fibre extensibility (Fig. 5).Although significant increases in tensile strength have been reported for irradiated wool dyed with alizarin sulphonate without metal ion mordants, i.e. applied as an acid dye to protonated protein residues, only small changes in light-induced fibre strength were observed when the dye was used in conjunction with multiple valence state metal ion mordants (Fig. 4). This result is consistent with the close interaction of the sulphonate anion with the bound metal ion that impedes photo-induced electron transfer reactions between the oxidisable alizarin phenolic nucleus and the metal ion, the products of which ultimately participate in bond cleavage reactions that compromise the strength of the fibres.

5. Conclusions

The metal ion-mordanted polyphenolic dyes, widely used since antiquity, are not passive UV-screening chromophores but they participate in UV and visible induced reactions with the substrate which culminate in modifications to the mechanical properties of the wool fibre. Free radicals generated by the primary photoreactions result in chain scissions and/or crosslinking within and between the keratin microfibrillar polypeptide backbones and the amorphous protein matrix in which the microfibrils are imbedded.

In contrast with the other metal ions that participate in redox reactions with polyphenolic dye molecules, the aluminium ion mordant exhibits different photoinduced changes in the mechanical properties of dyed fibres. Photolysis with simulated solar radiation produces an increase in the tensile strength of aluminium mordanted, dyed wool relative to undyed wool and substantially lesser reductions in extensibility than that encountered in dyed fabric that had been mordanted with other metal ions.

It is interesting to note that the most widely used mordant metal for dyeing with polyphenolics in antiquity was aluminium (alum). As well as the availability of this substance and the bright colour rendition it affords in association with this class of dyes, the findings of this work invite speculation that it may also have been favoured by ancient dyers who recognized the diminished phototendering of dyed fabrics that occurred in sunlight when aluminium ions were used as a mordanting agent instead of the other available metal salts.

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