Comparative Fastness Assessment Performance of Cellulosic Fibers Dyed Using Natural Colorants

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ABSTRACT: Two natural dyes of plant origin, namely, bixin and curcumin, were extracted, purified, and used as color additives in two fibrous constructions of floor carpet and cotton fabric by the "exhaust dyeing" technique. The fastness properties of these dyes, both to light and to washing normally encountered in storage, and the use of these products were assessed comparatively to evaluate the stability of the dyestuffs as color additives in these industrial products. Curcumin was found to have higher average fastness ratings—4.0 to light and 3.0 to alkaline wash—over its bixin counterpart. This observation was explained by the higher stability of curcumin to those agencies arising from its structure. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 752–755, 2000

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INTRODUCTION

The use of dyes and pigments of vegetable and mineral origins was first reported in the Bible, when Noah was instructed to coat his ark inside and out with pitch—an organic pigment.[1] Ever since, man has discovered ways of exploiting the coloring matters of nature to his own advantage, with applications ranging from the painting of culturally relevant events on walls of buildings (environmental embellishment) to their use as cosmetics in facial treatments and lipsticks (personal adornment). Other more important areas of use include the dyeing of various household articles, ranging from items of clothing to leather and carpet.

Although the emergence of synthetic coal-tar dyes in the latter part of the 19th century led to a considerable decline in the exploitation for use of these natural coloring molecules, mostly because of both the technical and commercial merits of the newly discovered set of dyes and pigments, dyes and pigments of plant origin are still used today in applications where substitutes are still difficult to find. For instance, in food coloring and medicinal and cosmetic preparations where strict adherence to certain legislative conditions is required, dyes and pigments from natural sources are considered generally acceptable because they are clinically safer than their synthetic analogs both in handling and use. Some other specialty colors, mostly those of logwood and henna, still continue to fulfill unique roles in hair and leather coloring. Except for the use of some natural dyes for specialty applications, most countries have stopped their use.[2] This situation however, is not entirely the same for less developed nations where the cost of importing dyes for home countries is prohibitive and the technology for utilizing petrochemicals in synthesising these essential raw materials is at a very low ebb. Consequently, for such countries a sizeable amount of dyes and pigments in use mostly for cottage industries comes from nature's reserve. In recent years a number of such dye-yielding plants has been screened, and their uses for imparting fast and substantive colors to textiles, leather, and other materials are being systematically investigated. Two such dyes, bixin and curcumin, were developed for use in this work on two cellulosic fibrous constructions (cotton fabric and reed carpet). Both the light and wash fastness properties of the dyed materials were subsequently assessed to evaluate the substantivity of the dyes on these industrial products.[3]

EXPERIMENTAL

Extraction of Dyes

Bixin and curcumin are the coloring molecules found in the plants *Bixa orellana* and *Curcuma longa* (a family of the perennial herb *Zingiber officinale*), respectively. Bixa orellana seeds were harvested, cleaned, and subsequently processed for moisture, oil, and dye contents. Extraction was carried out in a soxhlet. Prior to the extraction, the seeds were dried in an oven at 110°C for 3 h to remove moisture. Thereafter about 20 g of the seeds were packed into a sintered-glass extraction thimble contained in the soxhlet extractor and washed with *N*-hexane for 6 h to remove oil that might prevent the dyestuff from crystallizing out from the extracting liquor. Subsequently, the seeds were extracted using chloroform and ethyl acetate prepared in a mixture ratio of 3 : 2 (v/v). The extraction process was carried out until the extractant liquid was virtually colorless, indicating no further transfer of dyestuff into the mother liquor. The extracting solvent was later recovered by distilling off the solvent, while the crude dye was separated out for drying in the oven at 105°C for 3 h for further purification prior to use.

The procedure adopted for the extraction of curcumin from ginger was similar to that described above for bixin except that methanol was used as the extractant.

Dye Purification

Dye purification was achieved by first recrystallizing the crude dyes. Bixin was separated out from the crude by recrystallizing it in hot ethanol, while curcumin was recrystallized from dry ether. The recrystallized dyes were then fractionated by column chromatography over alumina in a glass column, using solvents varying in their polarities. The fractions collected were spotted on TLC (thin-layer chromatography) in a chloroform–acetone mixture (90 : 10 v/v) for 10 min, and spots were detected with sulfuric–nitric acid reagents and bromocresol green. Single spots obtained on TLC for the dyes confirmed their purities.

Dyeing of the Products

Both cotton fabric (scoured and bleached, supplied courtesy of Nichemtex textile industry, Lagos, Nigeria) and reed fibers obtained from the plant *Thaumatococcus danielli*, commonly used for carpet constructions, were dyed by the "exhaust dyeing" technique. Dyeing was done without mordants. Two separate dye baths were prepared, each containing the same amount, 1 g, of the pure dyestuff dispersed in 1000 cm^3 of 96% ethanol contained in a 2-L culture flask equipped with a thermometer and a stirrer. One bath was used for the dyeing of the cotton fabric, while the other was used for the reed fiber. Two grams each of both the fabric and the reed were introduced to the dye bath at a dyeing temperature (T_d) of 80°C, and dyeing was carried out continuously for 16 h to allow for saturation of both products with the dyestuffs. A high, uniform stirring speed was maintained throughout the period of dyeing to ensure that dyestuffs were in a dispersed state. After dyeing, the specimens were removed and washed in water and dried in a vacuum oven.

Determination of Fastness Properties

Fastness tests to light were carried out on the two dyed fibers to provide a comparative basis for assessing the stability of the two dyes to UV (ultraviolet) radiation. The fastness to alkaline wash could only be carried out on the cotton fibers because the ISO (International Standard Organization) method employed[4] could not be used on the reed fibers.

Fastness to Light

Fibers (both cotton and reed) dyed according to the procedure already described were exposed to an artificial source of light to induce fading, using the Shirley Institute's light fastness tester SDL 237. The method used was that described by the International Standard Organization.[4] After testings, samples were assessed on the standard eight-point Gray scale. Ten specimens were used for the test, and the mean value of the results obtained was taken as the fastness rating for the stability of the dyed fiber to light.

Fastness Rating to Alkaline Wash

Since the cotton was dyed in the form of fabric, the fastness-to-washing test No. 3, specifically designed for cellulosic fabrics, was used.[4] Fabric specimens measuring 10 cm × 4 cm each were placed in turn between one piece each of undyed cotton and wool fabrics measuring 5 cm × 4 cm and stitched around, leaving a portion of the specimen uncovered. A beaker containing 100 mL solution of 0.5 g of a nonionic surfactant, Matexil DN (ICI), was heated to a boil. The fabric in this case was allowed to remain in the solution at this temperature for 30 min, with occasionally stirring. The specimen was later rinsed in cold running water, the stitch line removed along two sides, and the specimens hung out to dry. After drying, the change in color of the dyed specimens was assessed, both in terms of alteration of shade of the uncovered portion of the dyed fabric and in the degree of staining of the undyed portion against the standard five-point Gray scale. As in the case of fastness to light, 10 specimens were assessed, and the mean value for the 10 specimens was taken as the stability of the dyed fabric to washing.

Table I Fastness to Light of Cellulosic Fibrous Constructions Dyed Using Bixin and Curcumin Dyes

	Bixin		Curcumin	
Serial No.	Cotton	Reed	Cotton	Reed
1	4	4	5	4
2	3	3	4	3
3	3	2	5	3
4	4	3	5	3
5	4	3	4	4
6	4	4	4	3
7	4	3	5	4
8	5	4	4	4
9	4	4	4	4
10	3	4	4	4
Mean value	3.8	3.2	4.4	4.0

RESULTS AND DISCUSSION

A cardinal requirement for a dye or pigment meant for use as a color additive, used mostly in textile fibers, is fastness (or stability) to a number of agencies; this requirement tends to militate against other desired properties, both for storage and use, thus limiting their serviceability. These agents principally include UV radiation, water, gas fumes, dry heat (in the case of sublimable colorants), and so forth. In this study the stabilities of both dyes to UV radiation and alkaline wash were tested on dyed fibers.

The rating results for fastness to light of both cotton fabric and reed fibers dyed with both dyes are shown in Table I, while fastness to washing of these dyes on cotton fabric only is shown in Table II.

From the results presented above, the following trends are clearly discernible.

1. For the fastness-to-light rating, the average mean fastness (on an eight-point scale) is comparatively higher for cotton dyed material than the reed fibers for each dye class.
2. The mean fastness-to-light rating for curcumin dye is higher than that of bixin when used on the same cellulosic material.

These observations can be interpreted in terms of both the relative substantivities of the two dyes to the substrates used as well as the stabilities of the dyestuffs themselves to ultraviolet rays. Since a higher stability (fastness) value is recorded with cotton dyed materials in both cases, a preliminary inference can be drawn that the dyestuffs are both more substantive to and have/exhibit more affinity to cotton fabric than the reed plant. This can be either a result of the stronger force of attraction between the dyes and the cotton fabric and or of higher uptake of the dyes in cotton. It should be noted, however, that since both substrates are cellulosics, similar forces of attraction are expected to be in force between the two substrates and the dyes. The more acceptable explanation therefore rests on a differential level of dye uptakes by the fibers. In a previous study carried out using similar dye obtained from the plant *Pterocarpus erinaceous*, it was shown[5] that the cotton fabric used had a crystallinity value of about 42.30% while that of the reed fiber was about 56.40%. Since the reed fiber is more crystalline than its cotton counterpart, it permits a lower level of dye absorption compared to the less crystalline cotton. Indeed, a higher level of dye uptake was obtained for cotton fibers either with or without mordant than for reed fibers using dyestuff from the African rosewood plant (*P. erinaceous*).[5] Another significant factor controlling the fastness ratings of the two dyes on the substrates is the relative stability structurally of the dyes themselves to ultraviolet rays. Generally, dyestuffs with open-chain structures, though conjugated, are less stable to light energy than those having conjugated benzenoid or fused macrocyclic structures. The structures of the two dyes, as shown in previous works,[6] indicated bixin as an

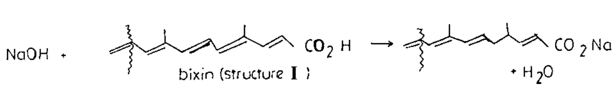
Table II Fastness to Washing of Cotton Fabric Using Bixin and Curcumin Dyes

	Bixin		Curcumin	
Serial No.	Degree of Staining	Alteration of Shade	Degree of Staining	Alteration of Shade
1	2	2	3	3
2	2	2	3	3
3	3	2	3	2
4	3	2	3	3
5	2	3	3	4
6	2	3	3	3
7	3	2	3	2
8	3	3	2	3
9	2	2	3	3
10	2	2	2	3
Mean value	2.4	2.0	2.8	2.9

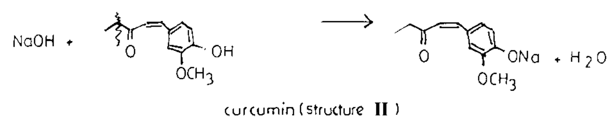
extended open-chain conjugated system (structure **I**) while curcumin is a more stabilized structure, having two benzenoid rings at its two terminals, which exert considerable resonance stability on the dye structure in addition to that obtained from the conjugated system (structure **II**).

It can be inferred from this observation that the higher stability shown to light energy by curcumin over bixin is therefore a result of this increased stability to ultraviolet radiation arising from its conjugated benzenoid structure.

The results obtained for the fastness ratings of the two dyestuffs to alkaline wash, both in terms of degree of staining and alteration of shade, are just about average considering that this property was assessed on a scale of 5. As is the case with fastness to light, however, slightly higher values were obtained for curcumin dye compared to bixin, again showing that curcumin is more stable to alkaline wash than bixin, probably a result of the chemistry of the reaction of the dyes with the washing liquor. Bixin has been shown to react well with alkali, as 5% caustic soda (NaOH) converts it to a soluble sodium salt, a process that can be reversed by treatment with a mineral acid (HCl, H_2SO_4, etc.).[7] Similarly, curcumin is readily converted to its soluble salt in the presence of alkali. Eqs. (1) and (2) explain these reactions:



(1)



(2)

The loss in shade resulting from the alkaline washing of the dyed fabric can be attributed to the removal of the dyestuffs from the dyed fabric as a result of their convertion to soluble products and salts of the dyes and consequently a lowering of the fastness rating to washing observed.

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