

Chromating of Wool Fibers Dyed with Madder Colorants, Luteolin Colorant and Iron Surface Treatment with a Residual Chromating Bath

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Abstract The chromating of madder colorants (*Rubia tinctorum*) and luteolin colorant from dyer's weed (*Reseda luteola*) used in wool dyeing allows for a high degree of washing and rubbing fastness. The chromating process was optimized and verified by calculating the fixation rate of natural dyes and the reduced chrome. Chrome-dyes achieved a higher fixation rate than those without chromating dyes (61.8% versus 16.0% for madder colorants and 30.1% versus 11.0% for a luteolin colorant). The residual chromating bath was used to passivate the iron surface to avoid chrome rejection in the environment. The passivation was efficient, and the chrome was used almost completely on the metal surface. The chromating dyeing achieved a rigid fixation, as confirmed by washing-fastness test 105C6A01.

Keywords Wool, Dyeing, Dyer's weed, *Reseda luteola*, *Rubia tinctorum*, Chromating, Metal passivation, Washing fastness

1. Introduction

Mordant dyes have chelating sites that form stable coordination complexes with metal ions from metal salts (mordants). The dye-mordant reaction or chelation requires the presence of salt-forming groups, such as hydroxy or nitroso groups, and the presence of oxygen or nitrogen-containing groups, such as carbonyl, carboxyl, and azo groups, so that a lone-pair electron can be donated to the chromium atom [1]. The dyes used in this study contained oxygen and hydroxy groups in the anthraquinone chemical structure (in dye extracted from the madder plant (*Rubia tinctorum*)) and in the luteolin chemical structure (in dye extracted from the *Reseda luteola* plant) (Figures 1 and 2).

Dyes can form chelates with different mordants, thus allowing for the development of various shades with superior wash fastness. Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) or potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) are commonly used mordants for wool because of the presence of reducing thiol groups [2, 3].

Because of their low cost and ease of application, the mordanting of wool with sodium or potassium dichromate is

widely used. This technique provides full bright shades with fairly good fastness properties, particularly improved washing- and light-fastness. The shade brightness can be improved by organic-acid addition, such as formic, oxalic or tartaric acid [1, 4].

Potassium dichromate and stannous chloride are brightening mordants. Complexes can be formed by first applying the mordant and then dyeing (pre-mordanting process), by simultaneous application of the dye and the mordant (meta-mordanting process), or by post-treatment of the dyed material with the mordant (post-mordanting process) [5]. The post-treatment process is most efficient and has a high degree of uniformity, because it can avoid the formation of dye-mordant complexes in the dye bath that occurs with simultaneous application. Also, the post-treatment can prevent the non-uniform absorption and fixation that occurs when the dye-mordant complexes are formed by pre-mordanting. Despite the high fixation rate and bright shade achieved by the chromating of dyes, the residual chromating bath poses an important ecological problem. Hexavalent chrome is toxic and carcinogenic. Trivalent chrome is considered less toxic than hexavalent chrome because it has not yet been shown to cause cancer in humans, but it may be proven in the future to be carcinogenic.

Chromate conversion coating prevents metal oxidation (rusting) by passivating the metal substrate and preventing corrosion of the metal surface by oxygen in air. Chromate conversion coating is used on metals, such as aluminum and

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zinc, and to a lesser extent copper, cadmium, silver, tin, and other metals and their alloys [6-9]. The major concern with the use of chromate conversion coating is its toxicity. Therefore, metal passivation with hexavalent chrome has been replaced with the more ecological trivalent chrome, which is reinforced with organo-metal or chromate-phosphate complexes [10-15].

The aim of this research was to study the possibility of reusing the residual chromating bath in the surface passivation of iron metal. The first aim was to increase the

wash and light fastness when dyeing with madder colorants (*R. tinctorum*) and luteolin from dyer's weed (*R. luteola*). This was assessed by calculating the exhaustion and fixation dye rates. The second aim was to avoid the toxic effect when discharging the residual chromating bath to the environment. Chromating passivation was assessed on the basis of color changes when the chrome reduction reaction was achieved from hexavalent chrome VI ($K_2Cr_2O_7$, green) to trivalent chrome III ($Cr(OH)_3$, yellow) (Figure 3).

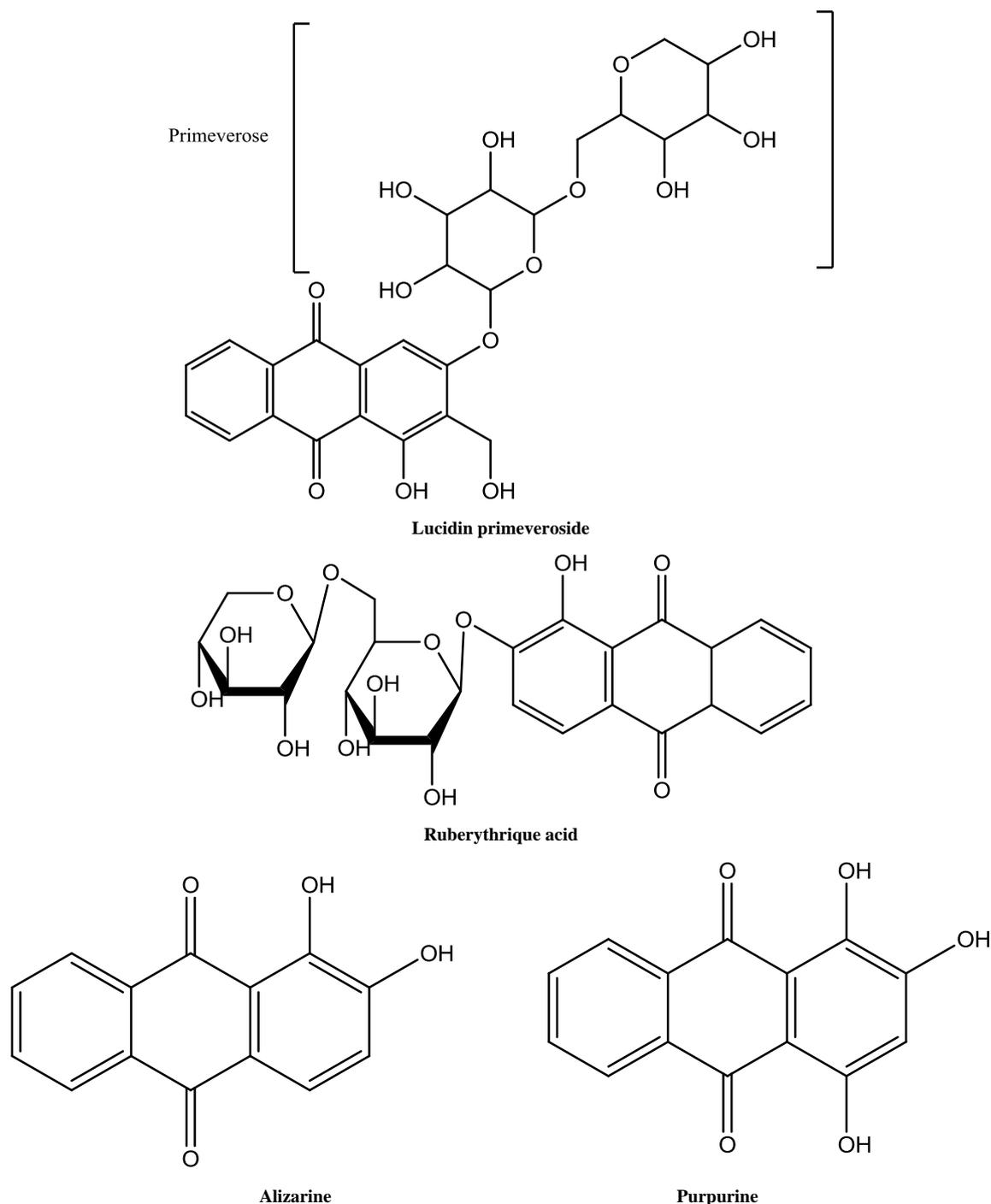


Figure 1. Chemical structures of principal madder colorants

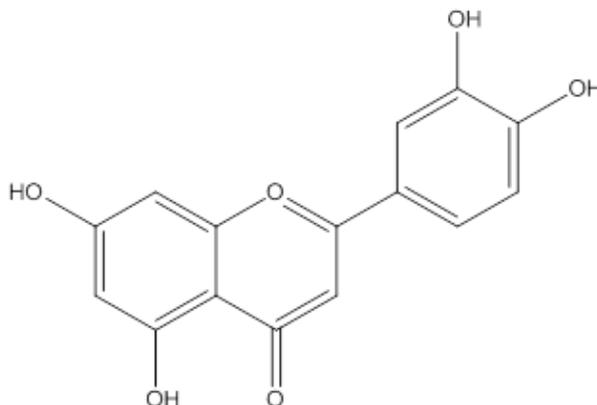


Figure 2. Chemical structure of Luteolin (dye's weed)

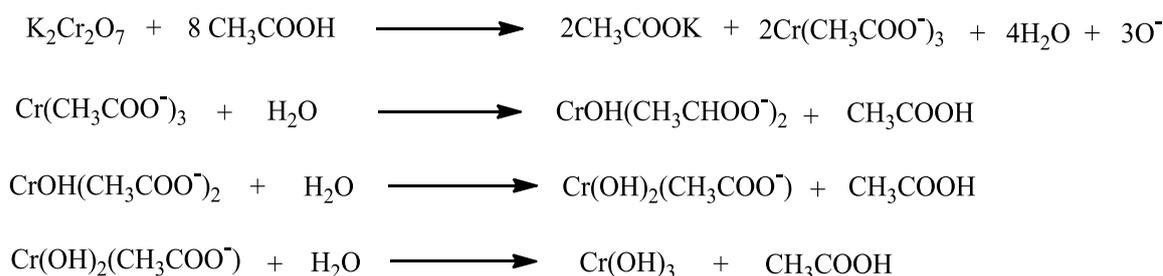


Figure 3. Reduction reaction of chrome (transformation from the hexavalent chrome VI to the trivalent chrome III)

2. Experimental

2.1. Materials and Method

2.1.1. Wool Fiber Features

Wool fiber was from Boujaâd in Morocco. White fleece was compacted and homogenized into a medium-weight fleece of 1.5–3 kg, and the fiber fineness was 50–60 on the Bradford scale [16, 17].

2.1.2. Metal Plaques

The metal plaques were zinc with dimensions of 60 mm × 40 mm × 4 mm, which were fixed in the anode of the electrolyzer and iron with dimensions of 60 mm × 40 mm × 2 mm, which was fixed at the cathode.

2.1.3. Natural Dye

The madder colorants (mainly ruberythric acid, lucidin primeveroside, alizarine, and purpurine (Figure 1) [18, 19], and luteolin dye (the main colorant in plants, Figure 2) [20–22] were extracted from the *R. tinctorum* plant and *R. luteola*, respectively. These plants grow in the southeast and central regions of Morocco [23]. The extraction method was based on the boiling of a dried and powdered root of the *R. tinctorum* plant and of the dried stem and leaves of *R. luteola*.

2.1.4. Chemicals

The acidic reagents acetic acid (CH₃COOH), hydroxide

chloride (HCl), nitric acid (HNO₃), and the mordant reagent of potassium dichromate (K₂Cr₂O₇) were of analytical grade and were from Sigma Aldrich (Casablanca, Morocco).

2.1.5. Spectrophotometry

An ultraviolet–visible Thermo Evolution 300 spectrophotometer was used with a spectral bandwidth from 0.2 to 4 nm and double-beam technology, able to operate either offline or under the control of a personal computer, and with a photodiode detector or photomultiplier.

2.1.6. Electrolyzer

A Combi 5 electrolyzer was coupled electrically to a generator to receive electrical power from 0 to 10 V.

2.1.7. Ph Meter

A Henne AD1000 pH meter was used as a multimeter to measure pH, oxidation–reduction potential, and temperature of dye bath and dye extraction.

2.1.8. Bath

A 250-mL flask was used in dyeing and dye extraction. Heating was performed with a thermostat hotplate (Scilogex MS-H280-Pro).

2.1.9. Filter

The filter was a metallic sieve (1–5-mm diameter).

2.2. Spectral Analysis

2.2.1. Spectrophotometer Calibration

Spectrophotometer calibration was achieved using a standard solution that was prepared according to the mass of wool yarn and the concentration of every ingredient that was added to the dye or chromating baths.

2.2.2. Measurement of Dye Exhaustion and Fixation Rate

We removed 1 mL of solution from each dye bath for measurement. Each sample was diluted to 10 mL using the prepared standard solutions. The absorbance measurements are provided in Tables 1 and 2. The absorbance values were measured at 400 nm.

2.3. Dyeing Process with Madder Colorants and Luteolin Dye

2.3.1. Preparation of Madder Dye Bath

Madder plant samples (10 g) were macerated in 100 mL distilled water at 95°C for 30 min and filtered using a metallic sieve.

2.3.2. Preparation of Luteolin Dye Bath

R. tinctorum plant samples (14 g) were macerated in 100 mL distilled water at 95°C for 30 min and filtered using a metallic sieve.

2.3.3. Dyeing in the Madder Colorant Dye Bath

Wool yarn (2 g) was soaked and wrung before being placed in the dye bath. The dyeing conditions of the dye bath were madder colorants (50 mL) at pH 6.5, at 95°C for 20 min, 30 min or 45 min with a liquid ratio of 1/50, according to the dyeing cycle illustrated in Figure 4.

2.3.4. Post Chromating of the Madder-dyed Sample

Potassium bichromate (1.5 g) and acetic acid (15 mL) at pH 3 or pH 4 were added to the dye bath after the dyed yarn had been removed, and the temperature was decreased to 60°C. A reduction reaction proceeded at this temperature for 30 min or 45 min, as shown in Figure 4.

The dyed yarn wool was returned to the chromed dye bath, the temperature was increased to 95°C, and treatment continued for 25 min (Figure 4).

2.3.5. Dyeing in the Luteolin Dye Bath

Wool yarn (2 g) was soaked and wrung before being placed in the dye bath. The dyeing conditions of the dye bath were luteolin (50 mL) in the dye bath and pH 6.5 at 95°C for 30 min with a liquid ratio of 1/50 (Figure 4).

2.3.6. Post Chromating of the Luteolin Dyed Sample

Potassium bichromate (0.7 g) and acetic acid (5 mL) at pH 4 were added to the dye bath after the dyed yarn had been removed. A reduction reaction proceeded at 60°C for 30 min.

The dyed yarn wool was returned to the chromed dye bath, the temperature was increased to 95°C, and the wool was treated for 25 min (Figure 4).

2.3.7. Hot and Cold Rinse

Rinsing of the samples (dyed with madder colorants and luteolin dye) was conducted at the end of the dyeing process to remove dyes from the fiber and inter-surfaces and to neutralize the acidic medium. Hot rinsing was carried out at 60°C for 15 min with a liquid ratio of 1/50. The cold rinse was conducted in a similar manner, except that it was undertaken at ambient temperature.

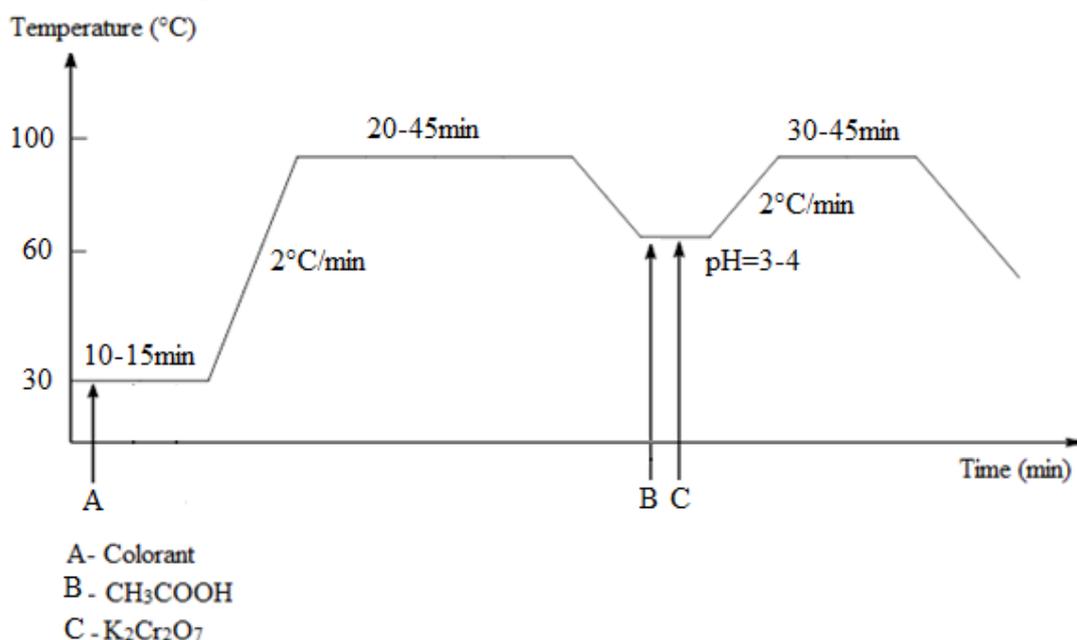


Figure 4. Dyeing cycle of madder colorants and luteolin colorant

2.3.8. Drying

Samples were dried in a sterile environment at 60°C and 80°C.

2.3.9. Washing Fastness

The washing fastness was determined at 40°C over 30 min according to ISO 105-C6: A1S [24].

2.4. Surface Preparation of the Iron Metal

Stripping of the iron sample was achieved using hydrochloric acid (HCl 50%), rinsing with distilled water, zincating in a 400-mL zinc bath by passing a direct current at 8 V for 15 min at room temperature, rinsing, passivating with a residual chromating dye bath (with a higher fixation rate of madder colorants and luteolin colorant) using nitric-acid addition (HNO₃, 5%) at pH 1, and rinsing with hot water at 80°C.

3. Results and Discussion

3.1. Exhaustion Rate of Madder Colorants, Luteolin and Chrome in Dyes Bath

The absorbance values of the initial and final dye bath are presented in Table 1.

Under all dyeing conditions, the exhaustion rates of the madder colorants and luteolin colorant were lower than the chrome adsorption in the chromating of wool. The dye-chrome complexes that formed inside the fiber absorbed additional chrome. The residual colorants in the dye bath formed a dye complex with a higher affinity for wool fibers, because of their cationic nature when applied to wool [2].

The uptake of chrome at pH 3 was higher than that at pH 4. This result can be explained by the higher transformation of chrome VI to chrome III in a more acidic medium.

Optimum fiber dyeing with madder colorants and luteolin colorant was achieved at 95°C after 45 min.

The optimum conditions for the chromating of dyed fibers with madder colorants and luteolin colorant were 60°C, after 45 min and 30 min at pH 3 and pH 4, respectively.

3.2. Fixation Rate of Madder Colorants, Luteolin Colorant and Chrome in Dye Baths

The absorbance values of the residual hot- and cold-rinse baths of the dyed samples are presented in Table 2.

Almost no chrome dyes were removed from the dyed sample during the soaping phase of the dyeing process; therefore, we concluded that total fixation was achieved. The high dye fixation was attributed to the complex formation between dyes and chrome inside the fiber, which enabled the chromium atom to chelate with the fiber through coordinate bonds. Dyes that were removed from the dyed sample without chrome during the soaping phase indicated a lower fixation rate.

3.3. Metal Surface Passivation with Residual Chromating Dye Bath

The residual chromating dye bath was conserved for reuse during passivation of the iron surface. We selected the residual chromating dye bath that had achieved a higher fixation rate of madder colorants (61.8%). The passivation process described above led to a total absorption of chrome III on the metal surface, as demonstrated by the colour change from green to yellow in the passivation bath and on the metal surface. A complete transformation of hexavalent chrome VI to trivalent chrome III was achieved. Therefore, the residual chromating dye bath allowed the use of toxic chromium VI to be avoided.

Table 1. Exhaustion rate of madder colorants, luteolin colorant and chrome in dyes bath

	Conditions			Initial dye bath	Final dye bath	Exhaustion rate * $\frac{(Abs_i - Abs_f)}{Abs_i} * 100$
	pH	T°C	T(min)			
madder colorants absorbance without chrome	6.5	95	20	0.237	0.150	32.0
	6.5	95	45	0.405	0.198	51.0
	6.5	95	30	0.316	0.180	43.0
luteolin colorant absorbance without chrome	6.5	95	30	0.281	0.177	37.0
chrome absorbance on dyed wool with madder colorants	3	60	30	0.396	0.188	52.0
	3	60	45	0.413	0.157	61.8
	4	60	45	0.327	0.183	44.0
chrome absorbance on dyed wool with luteolin colorant	4	60	30	0.236	0.165	32.0

*Abs_i : initial dye bath absorbance; Abs_f : final dye bath absorbance.

Table 2. Fixation rates of madder colorants, luteolin colorant and chrome in dye baths

	Conditions			Residual hot rinse bath	Residual cold rinse bath	Fixation rate ((Absi-Absf-Abshr-Abscr)/Absi)*100
	pH	T°C	T(min)			
madder colorants absorbance without chrome	6.5	60	20	0.050	0.0156	09.0
	6.5	60	30	0.084	0.058	16.0
	6.5	60	30	0.062	0.033	13.0
luteolin colorant absorbance without chrome	6.5	60	30	0.058	0.015	11.0
chrome absorbance on dyed wool with madder colorants	3	95	25	0.00	0.00	52.0
	3	95	60	0.00	0.00	61.8
	4	95	60	0.00	0.00	44.0
chrome absorbance on dyed wool with luteolin colorant	4	95	30	0.00	0.00	32.0

*Abshr : residual hot rinse bath absorbance; Abscr : residual cold rinse bath absorbance.

3.4. Washing Fastness

Measurements for the two rinsed samples are presented in Table 3.

Table 3. Washing fastness of chrome-madder colorants and chrome-luteolin dye

Samples	Washing fastness (assessing staining)						Washing fastness (assessing change in color)
	WO	PAC	PES	PA	CO	CA	
dyeing in chromed madder colorants	5	5	5	5	5	5	4-5
dyeing chromed luteolin	5	5	5	5	5	5	4-5

The values from these experiments confirmed the solid fixation of dyes, as described previously.

An excellent washing fastness was achieved for the chrome-dyes from madder and chrome-luteolin.

Chrome-dyes that contain hydroxyl group(s) near their chromophore enable metals, such as chromium atoms, form a complex because of chelation through coordinate bonds. In fact, complex formation increases the size of the dye molecules and hence their washing fastness.

4. Conclusions

This study confirmed the greater color fastness of the organometallic complex and its efficacy in the reuse of a residual chromating dye bath on metal surface passivation. Chromate-conversion coating technology has been used for decades, but hexavalent chrome is toxic and carcinogenic. Because the residual chromating dye bath was able to be reused for metal-passivation treatment, the resulting effluent

was free from chrome and could be disposed of safely in the environment.

Chromium salts act as an efficient mordant, promoting dye-metal complex formation to improve fastness, and they enhance acid-dye uptake because of its cationic nature when applied to wool before and after dyeing. However, the mordant affects the electron distribution and density within the dye, and the colour of the dyed fabric tends to change. This behaviour must be considered for shade establishment.

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