KEY POINTS

- This article describes the development of hair dyes with 100% vegetable-derived colorants.
- Testing showed good semi-permanent hair color efficacy without the use of synthetic colorants, alkalizers and peroxide or other oxidizers.

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Vegan Roots

Siddha-inspired Botanical Extracts as Colorants for Hair Dyes*

**Editor's note: This paper is excerpted from a thesis presented in 2020 by Francesca Schumann for her master's degree in cosmetic science at the University of Pavia, Italy.*

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Dissatisfaction with the color of one's hair, since the earliest of times, has led men and women to seek solutions to change it. The first records of hair coloring date back to Ancient Egypt and to traditions of the contemporary period in China and the Indian subcontinent. Ancient civilizations derived coloring substances from what nature had to offer: berries, fruits, leaves, flowers, roots and barks—as well as various minerals and biological sources.[1]

Today, women and an ever-increasing number of men are hair color-obsessed for several reasons, including fighting the signs of aging/gray coverage, the desire for change or to fully express their personality. Approximately 80% of women color their hair beginning in their thirties;[2] men do typically from their fifties, although not to the same extent.[3]

The dominant technology to manufacture today's hair colors was developed at the end of the 19th century[4] and is based on precursors and couplers that undergo oxidation—i.e., oxygen is supplied by developers containing diluted hydrogen peroxide; and colorants that

Results suggest the tested extracts are effective as natural colorants in semi-permanent hair dyes at a use level of 0.2%.

The global market for hair coloring surpassed US $29 billion in 2019 and is expected to increase at a CAGR > 8% to reach $40 billion by 2023.

Source: Statista

impart the desired shade to hair in 30-40 min. This process has remained largely unchanged today.

Dyes of natural origin also exist and contain botanicals with coloring properties; henna is perhaps the most well-known. These align with today's consumer values for natural and sustainable products. Notably, some traditional oxidation dyes are marketed for botanical, natural or herbal additives but this can be misleading, as it conveys the idea that the product contains only botanicals. In fact, many times these components are added at percentages irrelevant to a product's color effects.

In response, the present article describes the development of a 100% vegetable-derived hair colorant for use in dyes without: synthetic colorants; alkalizers such as ammonia or other amines; and peroxide or other oxidizers. Further requirements included mildness to hair and the absence of adverse effects, e.g., allergic reactions in consumers or professional hairdressers.

The approach taken was based on the Siddha tradition of natural medicine and well-being; a holistic system indigenous to the Tamil Nadu people in southern India and elsewhere.[5, 6] This system can be traced back to at least 4,000 B.C. through textual and archaeological evidence, but also in the culture of ancient civilizations that existed in the same area, pre-dating much of recorded history. To Siddhars, all therapies were derived from vegetable or mineral sources. They also were among the first peoples to adapt their diets to achieve a balance between physical and psychic well-being.[7]

Table 1. Dark Blonde Formulations B and C

Ingredient	Formula B (% w/w)	Formula C (% w/w)
Laureth-4	28.0	0.0
Sodium Cocoyl Glutamate	0.0	20.0
Polyglyceryl-10 Laurate (and) Water (*Aqua*) (and) Citric Acid	8.0	0.0
Cetearyl Alcohol	0.8	0.8
Elaeis Guineensis Palm Oil	2.0	2.0
Lonicera Caprifolium (Italian Honeysuckle) Flower Extract (and) *Lonicera Japonica* (Honeysuckle) Flower Extract (and) Isopentyldiol	2.5	2.5
Helianthus Annuus (Sunflower) Seed Wax (and) Sodium Polyacrylate	0.0	20.0
Eclipta Prostrata Extract	0.2	0.2
Benzyl Alcohol (and) Dehydroacetic Acid (and) Water (*Aqua*)	1.0	1.0
Water (*Aqua*), de-ionized	57.5	53.5

For the present work, as noted, semi-permanent dye formulas containing wholly natural colorants were created. These were tested for physicochemical properties, stability, carrier performance, color performance and other effects on hair, as described here.

Materials and Methods

Botanicals tested: A range of botanicals was chosen from vast geographical areas including: Tibet-South, Sikkim, The Republic of India, Myanmar, Sri Lanka, Bangladesh, Maldives, Mauritius, Madagascar, Vietnam, Laos, Cambodia, Indonesia, Malaysia, Philippines and other ASEAN countries. The specific extracts tested for tinctorial properties included: *Aloe barbadensis*, *Coccinia indica* (ivy gourd), *Curcuma longa* (turmeric), *Eclipta prostrata* (false daisy), *Corallina officinalis* (coral weed), *Melia azadirachta* (neem), *Moringa oleifera* (horse radish), *Ocimum basilicum* (basil) and *Solanum melongena* (eggplant).

These extracts are provided in commercially available powder (oil or water soluble) or solution (in hydrophilic media and in oils)[a] form. The tests described hereafter refer to only the *Eclipta prostrata* extract[b], as it was the best option for the current work, which focused on obtaining natural tones such as light brown, dark blonde, golden blonde, etc. Other shades were under development when this study ended; these formulations are not included.

Colorants manufacturing process: The coloring extracts used for this study were obtained through a manufacturing process with minimal modifications to the original method (specific details undisclosed). Traditionally, the natural high molecular weight waxes from Siddha botanical sources are incorporated with a variety of substrates, e.g., minerals or freshwater-sourced pearls. The materials are buried together in earthenware containers underground and heated by the sun, geothermically or by fire using a critical (high) temperature (the *Puddam* or *Surya Patham* process). The result is a calx of mineral (or oxide), pearl or marine shell finely coated with the colorant waxes.

Test Formulations

As noted, several hair color formulas were developed based on different emulsifiers, from anionic to cationic and nonionic, to ascertain the stability and color delivery performance of each formula. Emulsions were prepared by separately heating the oil and water phases, adding the oil to the water phase and homogenizing. The extract (colorant) was dispersed in a part of the water (5%) and added at the end of the process.

Different carrier ingredients also were tested to determine those most suited to improve color solubility and to obtain a perfect color release. Furthermore, this work sought to obtain data on the most suitable pH and to determine the interval of values where the extracts maintained their dyeing properties. All formulas were developed at pH levels of 4.0, 5.0, 7.0 and 9.0; those ranging between 4.0-5.0 showed the best coloring effects, as will be shown. For the sake of brevity, only the best-performing formulas, which were based on powdered water-soluble (PWS) colorants, are discussed here.

Anionic surfactant system: Formula A was based on a blend of glyceryl stearate, cetearyl alcohol, stearic acid and sodium lauroyl glutamate[c].

[a] *Campo Siddha Medico-Botanical Extracts (INCIs: Vary) and*
[b] *Campo Siddha Karushalai (INCI:* Eclipta prostrata *extract) are products of Campo Research.*
[c] *Protelan ENS, Zschimmer & Schwarz*

This formula showed good performance for color delivery but it proved unstable during stability testing. For this reason, it is not reported here; further improvements were made after the conclusion of the thesis work.

In formula C (see **Table 1**), an acyl-glutamate was used as the main emulsifier, and sodium cocoyl glutamate[d] and cetearyl alcohol as the consistency factor. Also, a viscosity enhancer[e] was added.

Nonionic surfactant system: In formula B (see **Table 1**), two different emulsifiers were used: laureth-4[f] and polyglyceryl-10 laurate[g] (50% solution) as co-emulsifier and solubilizer.

[d] *Protelan AGL 95 C, Zschimmer & Schwarz*
[e] *Jeesperse CPW-S (INCI:* Helianthus Annuus *(Sunflower)* Seed Wax *(and)* Sodium Polyacrylate*), Jeen International*
[f] *Mulsifan CPA RSPO-MB, Zschimmer & Schwarz*
[g] *Dermofeel G10 LW 70 (INCI: Polyglyceryl-10 Laurate (and)* Water (Aqua) *(and) Citric Acid), Evonik*

Cationic surfactant system: Cationic emulsifiers were excluded during pre-formulation due to poor performance for color delivery.

In all formulations, a booster/solubility enhancer[h] also was used. Its amphiphilic character was found to help the color molecules penetrate the hair's outer layer (cuticle).

Natural Origin Index: Considering the present work aimed to develop a natural hair dye, the Natural Origin Index was calculated for the test formulas according to ISO 16128-2:2017. Formula B rated > 70%; Formula C was > 80%.

Physicochemical Parameters

Viscosity, pH, stability: Standard parameters for the two formulations, including viscosity, pH and stability, were measured after one day, one week, one month and three months. Results are reported in **Tables 2** and **3**.

Emulsion photo-stability—irradiation plus spectrophotometer: Further assessments of the light/heat-fastness of emulsions also were made instrumentally. For irradiation, a xenon arc chamber[j] was used to reproduce the damage caused by full spectrum sunlight. This can reproduce, in a few days or weeks, the damage that occurs over months or years outdoors. This approach is compliant with the provisions set by ISO 16474-2:2013.

For this test, each sample was split into two test groups; one cuvette protected by aluminum foil and the other unprotected. This approach ensures the protected samples can only

Table 2. Physicochemical Properties of Formula B

	1 day	1 week	1 month	3 months
pH	5.1/23°C	5.1 /23°C	5.0/22°C	5.0/23°C
Viscosity	9200-9900 mPa.s	9000-9800 mPa.s	8900-9700 mPa.s	8800-9600 mPa.s
Centrifugation stability test 3000 rpm x 15 min: Pass				
Organoleptic properties (RT)				
	ok	ok	ok	ok
Organoleptic properties (oven, 40°C)				
	ok	ok	ok	ok
Organoleptic properties (refrigerator, 4°C)				
	ok	ok	ok	ok

Table 3. Physicochemical Properties of Formula C

	1 day	1 week	1 month	3 months
pH	4.95/23°C	4.92/23°C	4.91/22°C	4.91/23°C
Viscosity	9,000-12,000 mPa.s	8,900-11,600 mPa.s	8,800-11,400 mPa.s	8,800-11,300 mPa.s
Centrifugation stability test 3000 rpm x 15 min: Pass				
Organoleptic properties (RT)				
	ok	ok	ok	ok
Organoleptic properties (oven, 40°C)				
	ok	ok	ok	ok
Organoleptic properties (refrigerator, 4°C)				
	ok	ok	ok	ok

[h] *Campo Bio IPD (INCI:* Lonicera Caprifolium *(Italian Honeysuckle) Flower Extract (and)* Lonicera Japonica *(Honeysuckle) Flower Extract (and) Isopentyldiol), Campo Research*

The best-performing formulas were in the pH range of 4.0 to 5.0, and different emulsifiers greatly affected the color results.

be altered by heat, not by light. The exposure time for samples was 12 hr.

The same samples were tested for changes in color by spectrophotometer[k], indicative of long-term stability to light, both before and after irradiation. Illuminant D65 and a 10-degree field of view were used.

ΔE was calculated according to the following formula:

$$\Delta E^*_{ab} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2}$$

where ΔL^* is the variation between brightness before and after photostability, Δa^* is the variation of red color change before and after photostability, and Δb^* is the variation of yellow color change before and after photostability. Results are reported in **Table 4**.

[j] *Xenon Test Chamber Q-SUN Xe-1 Chamber, Q-LAB*
[k] *Shimadzu UV-2600 Spectrophotometer with single monochromator*

Formulations B and C were stable to light and therefore submitted to further testing.

Hair Dyeing Protocol

To test the efficacy of the natural colorant in a dye formula, strands of natural Caucasian

Table 4. Photo- and Thermostability of Test Formulas

	ΔE unprotected product	ΔE aluminum-protected product
Formula B	0.42	1.50
Formula C	0.31	0.49

Note: ΔE must be ≤ 3 for emulsions to be considered light- and thermostable hair (60%+ gray) were procured. The application was performed to simulate in-use conditions: an alkaline shampoo (pH ~8.0) was applied to hair strands, left on for 2-3 min, rinsed and towel-dried. Both formulas B and C were applied to the strands with a flat brush and left on the hair for 50 min. Once the application time was over, the strands were rinsed until the water ran clear, then dried using a hairdryer.

Hair Structure and Color Penetration

A Filament Surface Tester (FST) was used to assess hair structure modifications and color penetration into the dyed hair fibers. This technology[8] is used for the quantitative evaluation of hair characteristics such as color and gloss. The device uses a light beam with specific wavelengths to illuminate the sample, both in vivo and ex vivo, and acquire digital images (see **Figures 1a-b**). Specific parameters are processed through dedicated software by the correlation of the different images and RGB readings. RGB values were converted into L^*, a^*, b^* values to calculate the ΔE.

Figure 1. In vitro (a) and ex vivo (b) FST test

Table 5. FST Data for Formulas B and C

	L*	a*	b*	ΔE T0-T1
Formula B				
T0_B	42.0	19.0	34.0	na
T1_B (after treatment)	38.0	21.0	35.0	4.9
T2_B (after 3 washes)	39.0	21.0	37.0	4.7
T3_B (after 6 washes)	38.0	20.0	34.0	4.1
Formula C				
T0_C	41.0	18.0	34.0	na
T1_C (after treatment)	37.0	24.0	34.0	7.2
T2_C (after 3 washes)	38.0	21.0	35.0	4.3
T3_C (after 6 washes)	39.0	21.0	34.0	3.6

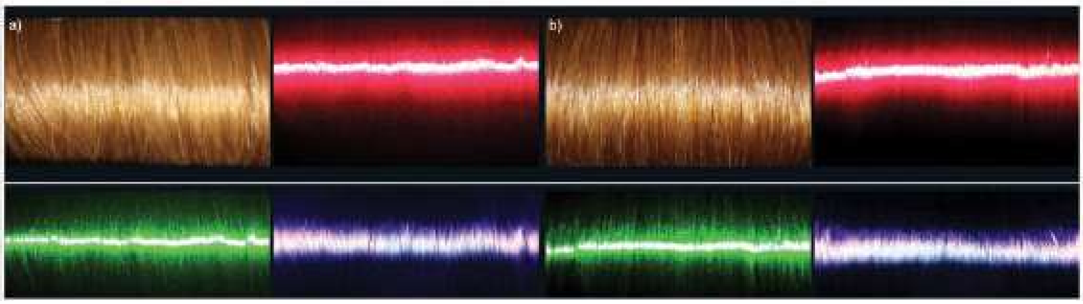


Figure 2. FST image at T1 after application (a) and at T3 (b) after application and six washings

The measurement protocol entailed comparing the results of the tested hair with those of natural untreated blonde human hair (positive reference) and with hair chemically treated with strong reducing agents (negative reference) at different intervals: T0; after application (T1); after 3 washings (T2); and after 6 washings (T3). **Figure 2** shows a comparison of digital images collected using the FST device.

FST analysis: Formulas B and C were compared, assuming ΔE > 2 as significantly different. From all readings where ΔE > 2, results indicated both formulas were effective as per their coloring effect (gray coverage) for up to six washings, as shown in **Table 5** and **Figure 3**.

Data collected using the FST tester allowed for the evaluation of different hair properties, namely hair gloss (= intensity of reflected light) and color fastness to washings for each formulation, taking into consideration the specific areas of the test strands illuminated; i.e., aggregate pixel clusters close to the hair roots, tips, etc.

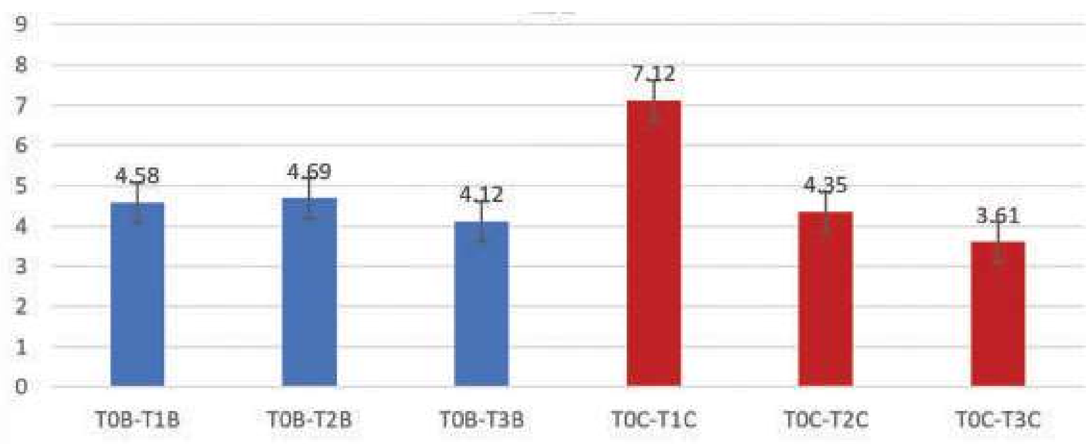
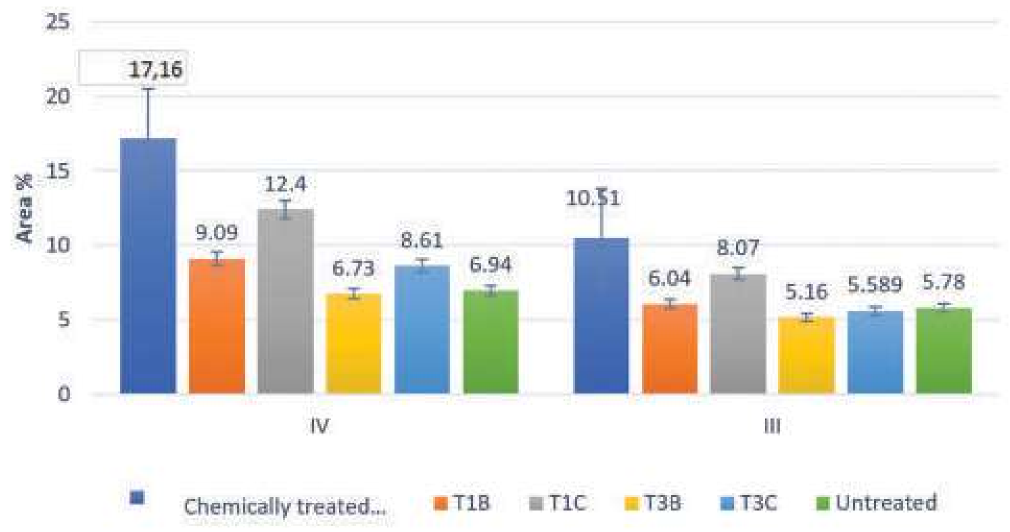


Figure 3. ΔE values over time for Formula B (blue bars) and Formula A (red bars)



Positive reference = untreated hair; negative reference = chemically treated hair; T1-B and C = hair treated with formulas B and C after 3 washings; T3-B and C = hair treated with formulas B and C after 6 washings

Figure 4. Surface area reflection % (damage) measured in cluster areas IV and III

Figure 4 shows the values for Formulations B and C compared with the positive reference (untreated hair) and negative reference (chemically treated hair).

Upon illumination by the FST device, the larger the surface area of light reflection in hair, the greater the structural damage, as this reflection indicates texture is less compact. In other words, the size of the surface area reflection is inversely proportional to values such as gloss and color fastness (i.e., the smaller the surface area, the greater the gloss and color fastness).

Untreated hair presented narrow bands of reflection (approx. 6%), while chemically treated hair showed a larger area of reflection (17% and 10.5% for cluster areas IV and III, respectively). From these results, Formula B at T3 (T3B) represented the formulation closest to the positive reference—i.e., natural untreated blonde hair showing no structural damages (see **Figure 4**)—yielding the smallest area of surface reflection, which extrapolates to higher gloss and color fastness.

Application Results

Figure 5a-c shows the reference natural, untreated Caucasian hair (> 60% gray) before application, and after the application (1 hr) of formulations B and C, respectively. Since the visual difference is not easily perceptible, differences have been ascertained through instrumental data (ΔE) taken from **Table 5**. The color delivery was different due to the different emulsifier used.

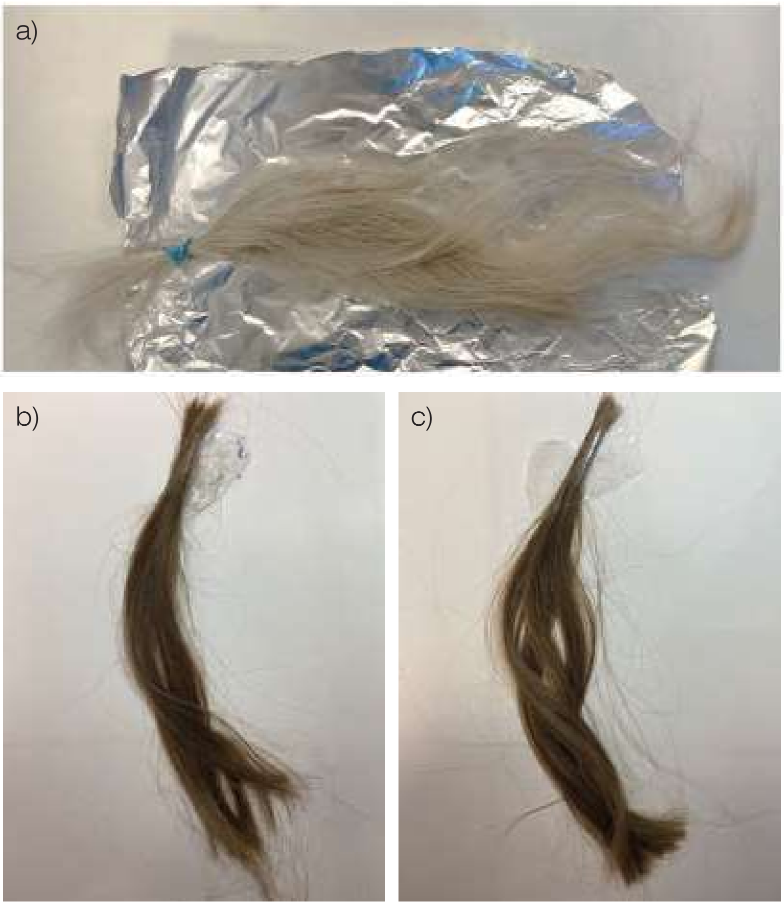


Figure 5. Example swatches of untreated (a) and treated hair; Formula B (b) matched color expectations while Formula C (c) was lighter than expected

Conclusions

The present article describes the development of a 100% vegetable-derived hair colorant for use in semi-permanent hair dyes without synthetic colorants, alkalizers (such as ammonia or other amines) and peroxide or other oxidizers. Multiple hair dye formulas were developed using botanically derived colorants[a], two of which are shown here, and tested for physicochemical parameters and effects on hair structure and color. The results suggest the tested extracts are effective as natural colorants in semi-permanent hair dyes at a use level of 0.2%.

The best-performing formulas were acidic—in the pH range of 4.0 to 5.0. Higher pH levels resulted in both poor color uptake and color fastness. Notably, the use of different emulsifiers also greatly affected the resulting color on hair. The most suitable systems for color uptake were nonionic and anionic while the cationic formula was easily washed away without color uptake.

Cconsidering the safe toxicological profile of the extracts, the pH and the lack of alkalizers and oxidizers, the test formulas could represent an alternative for consumers with known sensitivity to oxidation dyes.

Finally, through FST testing and L^*, a^*, b^* measurements, the formulation based on nonionic surfactants and an amphiphilic carrier show good color fastness after six washings, maintaining gray coverage and improving hair gloss. FST results also indicated no damage occurred after the application of both test formulas; hair structure was more compact compared with the chemically treated negative reference, in turn producing higher gloss.

The present work therefore demonstrates the potential for developing hair dyes based on truly natural colorants to meet the demands of today's consumers. In addition, considering the safe toxicological profile of the extracts, as well as the other ingredients; the pH; and the lack of alkalizers and oxidizers, the test formulas presumably represent an alternative for consumers with known sensitivity to oxidation dyes, which can easily turn into allergic reactions.

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