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Eco-friendly UV Blocking Finishes Extracted from *Amaranthus viridis* and *Solanum nigrum*

Okolju prijazni apreturi iz izvlečkov Amaranthus viridis in Solanum nigrum za zaščito pred UV žarki

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Abstract

This research work deals with a qualitative analysis of extracts from *Amaranthus viridis* and *Solanum nigrum* plants as eco-friendly ultraviolet (UV) blocking finishes. The presence of flavonoid and phenolic contents in the plant extracts and the influence of concentrations towards UV blocking was studied. The plant extracts were obtained through solvent (aqueous and methanolic) extraction and coated onto cotton fabrics with the pad-dry-cure method. UV-visible and CIELAB spectroscopy analysis were carried out for the quantitative measurement of UV blocking and sequential analysis. The results show that loading of selected extracts on the fabric samples results in a significant enhancement in UV blocking. The treated fabrics show exceptional UV blocking in both UV-A and UV-B region, where the highest anti-UV values were obtained when the fabrics were treated with methanolic extracts. Furthermore, a considerable influence on CIELAB coordinates was found inordinate for methanolic extracts treated fabric compared to aqueous extracts.
Keywords: *Amaranthus viridis*, *Solanum nigrum*, medicinal plants, UV blocking, natural finishes

Izvleček

Ta raziskava obravnava kvalitativno analizo izvlečkov iz rastlin Amaranthus viridis in Solanum nigrum kot okolju prijazne ultravijolične (UV) zaščitne apreture. Proučevana je bila prisotnost flavonoidnih in fenolnih snovi v rastlinskih izvlečkih ter vpliv koncentracije na UV zaščito. Z izvlečki, pridobljenimi z ekstrakcijami rastlin v topilih (v vodi in metanolu), so bile impregnirane bombažne tkanine. Na podlagi spektroskopskih meritev UV-vis in CIELAB je bila kvantitativno ocenjena UV zaščita in izdelana analiza. Rezultati kažejo, da prisotnost izbranih izvlečkov na vzorcih tkanin znatno izboljša UV zaščito. Obdelane tkanine imajo izjemno UV zaščito v obeh območjih, UV-A in UV-B, najvišje vrednosti UV zaščite pa so bile dobljene na tkanini, obdelani z metanolnimi izvlečki. Poleg tega je bila ugotovljena znatna razlika v CIELAB koordinatah med tkaninami, obdelanimi z metanolnimi izvlečki, v primerjavi s tkaninami, obdelanimi z vodnimi izvlečki.
Ključne besede: Amaranthus viridis, Solanum nigrum, zdravilne rastline, UV zaščita, naravne apreture

1 Introduction

UV radiations (UVR) that contain electromagnetic radiations can damage human skin and may result in chronic and non-chronic diseases [1]. Research shows that 90% of non-melanoma skin cancer is a consequence of the exposure to UV radiation. UVA can penetrate deeply into the skin and can damage

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the cells of DNA. An overdose of UVB radiations induces skin cancer, sun-burning, and cataracts, which have more serious effects than UVA [2]. The erythemal spectral effectiveness of UV radiation increases by 1000 times as the wavelength changes from UVA (315 nm) to UVB (300 nm) [3]. Wearing clothes is one of the protections recommended by physicians and medical experts to reduce or block the negative effects of UV radiation to human skin [4, 5].

Textiles can be used to provide protection to a product or wearer from UV radiation. To do so effectively, the textile requires the ability to resist UV transmission through the constituent fibres or the penetration of radiation through the fabric interstices. This means that the fibres themselves should be UV resistant and the fabric structure should have good breathability, yet low optical transparency.

Many physical and chemical factors are interrelated with the effectiveness of UV blocking [5, 6]. Various aspects are allied with the relative amount of radiation that is reflected, absorbed and transmitted through the fibre. They can include the type and selection of the fibre, smoothness of the fibre surface, surface area, presence of dyes and finishing, an incorporation of UV absorber [7]. To increase UV blocking, UV resistant particles can be applied as a finishing treatment. Often, such fabric finishes are a part of the dyeing process or an additional stage after the dyeing. They provide lustre and microscopic surface texture to reduce the UV penetration by reflecting, absorbing and/or scattering the radiation. Since last decades, different kinds of organic and metal oxide-based UV absorbers have been introduced to render the UV blocking property of textiles. Among them, titanium dioxide and zinc oxide-based finishing agents are widespread due to their effects on the UV blocking property [8]. Zinc oxide is always used with titanium dioxide in sunscreens because of its high refractive index [9]. However, the metal-based finishes tend to be non-biodegradable and they represent a threat during interaction with nature. The protection from UV radiations using plant-based natural finishing agents on textile materials is thus a potential solution with great benefits. UV protection has been imparted to fabrics using different types of extracts obtained from natural sources. These extracts are found mostly in ratanjot (*Onosma echioides*), annatto (*Bixa orellana*), manjistha (*Rubia cordifolia*), banana peel (*Musa, cv. Cavendish*) [10] and babool (Acacia Arabica) plants [11]. Silk and wool fabrics have been made to protect from UV radiations by having applied on them the extracts from neem and eucalyptus [12, 13]. Although several natural dyes have been studied with respect to UV protection and antibacterial properties [14], limited work has been reported on medicinal plant extracts for UV protection properties.

In this study, two medicinal plant extracts were tested as finishes for UV blocking. It was reported that flavonoids and phenolics present in Ray plants could shelter the plants from UV radiations [15]. However, with a thorough review of literature based on our best capabilities, we came to the conclusion that a UV blocking finish by using *Amaranthus viridis* and *Solanum nigrum* plant extracts is a nobel and sustainable approach.

2 Experimental

2.1 Materials

The cotton fabric used in this experiment was purchased from Guangdong overflow of textile co., Ltd (China). The average weight of the fabric was 200 g per square meter (GSM), thread density was 78 ends per inch (EPI) and 60 picks per inch (PPI), warp and weft count were 28 Ne. The mean ultraviolet protection factor (UPF) of the bleached fabric was 8.7. All the reagents used in this experiment were purchased from Sinopharm chemical reagent co., Ltd (China) of analytical grade and used as received without further purification. The water used throughout the experiment was purified using a Milli-Q Plus-185 water purification system (Millipore, Bedford, MA) with the resistivity higher than 18 MΩ cm.

2.2 Methods

Preparation of extracts

The plant leaves were collected and dried naturally at room temperature and powdered using an electric grinder. The powdered materials (100 g/l) were stirred with 95% methanol for 48 h at room temperature, blended with a continuous magnetic force stirrer as explained by Russo et al [16]. The aqueous extracts were prepared by wringing the dried plant powders (50 g/l) in distilled water for 30 mins, followed by heating at 95 °C for 40 min and vacuum extraction using standard filter paper. The extracts were filtered and concentrated to remove the solvents at 75 °C for 4 h and freeze-dried as the report in Nostro et al [17].

Determination of flavonoid and phenolic content
A diluted solution of plant extracts containing flavonoids was mixed with a requisite amount of 5% (w/w) $NaNO_2$ and 30% (v/v) ethanol for 5 min, and then a few drops of 10% $AlCl_3$ were added and mixed all together. A few minutes later, 5 ml of NaOH (1M) was added. The solution was then diluted to 25 ml with 30% (v/v) ethanol. After standing for 10 min, the absorbance of the solution was measured at 430 nm using a UV-visible spectrophotometer. The results were expressed in (quercetin/mg)/(dry-weight/g) by comparison with the quercetin standard curve, which was made under the same condition. On the other hand, the total phenolic content was determined using Folin-Ciocalteu reagents with the analytical grade gallic acid as the standard. Typically, 1 ml of extract or standard solution (0–500 mg/l) was added to deionized water (10 mL) and Folin-Ciocalteu phenol reagents (1.0 ml). After 5 minutes, 20% $NaCO_3$ (2.0 mL) was added to the mixture. After being kept in total darkness for 1 h, the absorbance was measured at 750 nm using a UV-visible spectrophotometer. The amounts of total phenolic contents were calculated using the gallic acid calibration curve. The results were expressed as gallic acid equivalents (GAE)g/g of dry plant matter as described in Kolasec et al and Gasemzadeh et al [18, 19].

Application of plant extracts on cotton fabric
Plant extracts were applied on a bleached cotton fabric by dispersing them in distilled water, followed by padding and drying on a laboratory scale padder and stenter machines according to the design of experiments explained by Huang et al (2010) and Wang et al (2006) [20, 21]. It was decided to treat the sample cotton fabric at different concentrations of extracts (1 g/l, 2 g/l, 4 g/l and 8 g/l). The padding pressure for all samples was 3.0 bars with 70% pick-up. The drying temperature of aqueous extracted finishes was 90 °C and 25 °C for methanolic extracted finishes.

Characterizations
The UV blocking of treated cotton fabrics and other UV-visible spectroscopic measurements were taken by using an Ultraviolet Transmittance Analyzer (HD902C, Nantong Hongda Experiment Instruments Co., Ltd, China) with integrating sphere according to corresponding standard methods. The ultraviolet protection factor (UPF) was computed as the ratio of ultraviolet radiation (UV-R) irradiance at the detector with no test sample to the UV-R irradiance at the detector with a test sample present as shown in equation 1 [22]:

$$UPF = \frac{\sum_{280\ nm}^{400\ nm} E_\lambda \times S_\lambda \times \Delta\lambda}{\sum_{280\ nm}^{400\ nm} E_\lambda \times S_\lambda \times T_\lambda \times \Delta\lambda} \quad (1)$$

The percentage of blocking in the UV-A and UV-B region was determined with equations 2 and 3:

$$UVA\ blocking = \frac{\sum_{315\ nm}^{400\ nm} \times T \times \Delta\lambda}{\sum_{315\ nm}^{400\ nm} \times T \times \Delta\lambda} \quad (2)$$

$$UVB\ blocking = \frac{\sum_{280\ nm}^{315\ nm} \times T \times \Delta\lambda}{\sum_{280\ nm}^{315\ nm} \times \Delta\lambda} \quad (3)$$

Where E_λ is relative erythemal spectral effectiveness, S_λ is solar spectral irradiance, T_λ is average spectral transmittance of the test sample, $\Delta\lambda$ is measured wavelength interval (nm) and T is average spectral transmission of the specimen.
The CIE whiteness values of samples were determined according to the AATCC 110-2005 methods by using Macbeth Color Eye 7000A (Gretag Macbeth Company, USA).

3 Results and discussion

3.1 Total flavonoid and phenolic contents in plant extracts

The quantity of the overall flavonoid and phenolic content present in extracts of plants is shown in Figure 1. The results indicate that the total flavonoid (mg QE/g) and phenolic (mg GAE/g) contents of *AV* aqueous extracts were 47 mg QE/g and 15 mg GAE/g, and of methanolic extracts 72 mg QE/g and 36 mg GAE/g, respectively. A similar scenario was noticed at *SN* extracts. The overall amount of flavonoid and phenolic content present in *AV* was higher than at *SN*. The analysis perceived that the flavonoid and phenolic contents were higher in methanolic extracts for both plants as contrasted to aqueous extracts. This may result from the fact that, water is not as effective as methanol in extracting flavonoid or phenolic contents from these two plants, despite the inclusive yield of the powder extracted from the plants being higher in water compared to that in methanol.

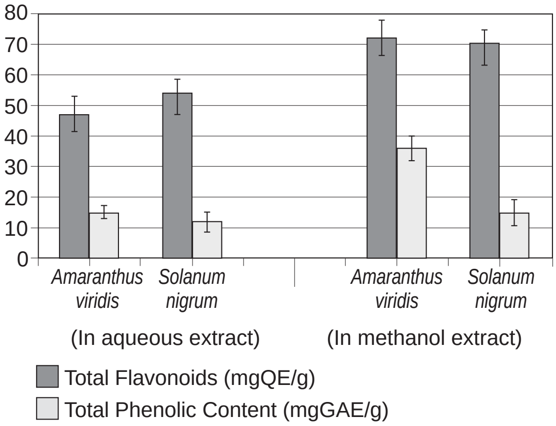

Figure 1: Total flavonoid and phenolic content present in extracts from Amaranthus viridis and Solanum nigrum

This may be explained by the improved solubility of flavonoid and phenolic contents in methanol and that of other plant contents in the aqueous solution. Such behaviour of both extracts results from the methanolic system containing more flavonoid and phenolic contents and other conjugated systems as compared to the aqueous system. So, the more is the system conjugated, the better is the UV protection (UPF) rating of a material.

3.2 UV blocking property of treated cotton fabric

The influence of extracts and their concentration on UPF is shown in Figure 2. The results show that the cotton fabric treated with both plant extracts maintained UV blocking capabilities. By comparing, contrasting and analysing the UPF value of untreated and treated fabric, it was seen that the UPF value increased with the increased concentration of the applied extract.

In the case of aqueous extracts of *AV,* the recorded UPF values were 10.6, 12.2, 18.8 and 36.2 against the concentration of extracts of 1, 2, 4 and 8 g/l respectively, which specifies that an increase in UPF can be achieved with an increase in concentration. For methanolic extracts, the UPF rating is significantly influenced by the concentration of extracts. In a typical run, the UPF values were 58.8, 125.2, 270.6 and 464.1 against the concentration of extracts of 1, 2, 4 and 8 g/l. A similar phenomenon was observed for *SN*. The highest UPF, i.e. 231, was found for 8 g/l of methanolic extracts of *SN*. Comparing the UPF rating between *AV* and *SN*, it can be seen that in the case of an aqueous extraction, there is no significant variation, whereas in the case of a methanolic extraction, *AV* gave the highest rating of 464.1 at 8 g/l, which is even more extraordinary than the highest yield of *SN*, i.e. 231. The fabric finished with both plant extracts rendered higher UVB than UVA protection (Figures 3 and 4).

The latter is also the main requirement of any UVR blocker, as UVB radiations cause greater erythemal damage and hence bear greater weight in calculating UPF. Comparing the UVA and UVB blocking of *AV* and *SN,* no significant difference was noticed between them, apart from the fact that *AV* showed much lower UVA blocking, i.e. 54.8%, at 1 g/l compared to *SN*. It became obvious that the fabrics treated with the methanolic extract show

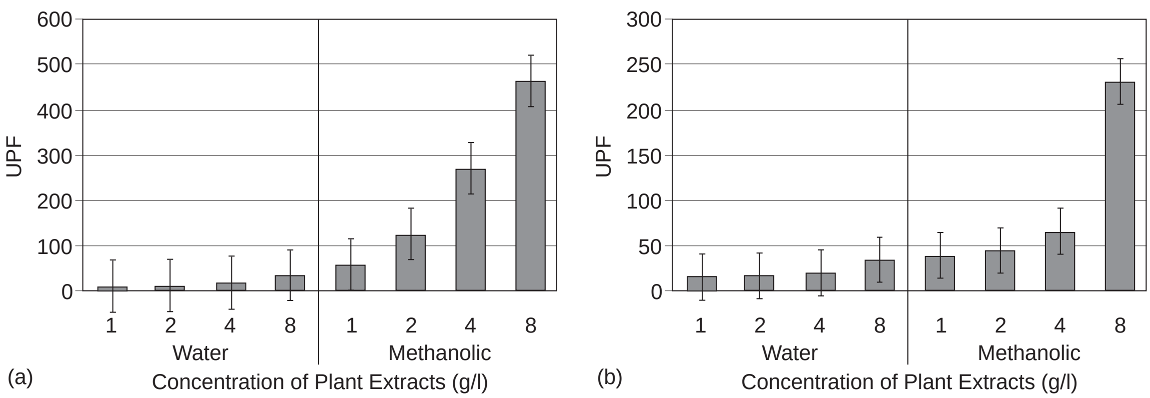

Figure 2: Mean ultraviolet protection factor (UPF) of cotton fabric treated with Amaranthus viridis (a) and Solanum nigrum (b) extracts

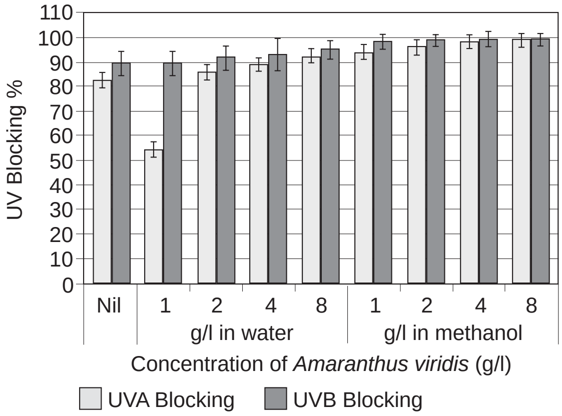

Figure 3: Blocking of UV radiations in UVA and UVB regions by different concentrations of Amaranthus viridis

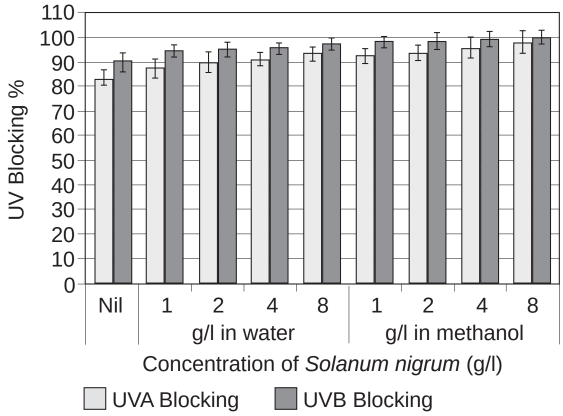

Figure 4: Blocking of UV radiations in UVA and UVB regions by different concentrations of Solanum nigrum

better results than the samples treated with the aqueous extract. The UV blocking properties of extracts could be attributed to the presence of total flavonoid and phenolic contents present in the methanolic extract. The UV blocking properties are better in the methanolic extract than in the aqueous extract, as the system responsible for a higher UPF rating is more conjugated in the methanolic extract.

3.3 CIELAB analysis of treated fabrics

The decrease in CIELAB analysis can be seen in Table 1.

CIELAB spectroscopic analysis of treated fabric has been compared and contrasted with untreated fabric. The L*, a*, and b* of the untreated fabric was measured 86,0.4, and 0.68, respectively. The CIELAB analysis indicates the presence of colouring

Table 1: CIELAB spectroscopic analysis of treated cotton fabric

Treatment	Extraction method	Conc. [g/l]	ΔL	Δa	Δb
Raw fabric	–		86	0.4	0.68
Treated with extracts of *Amaranthus viridis*	Aqueous	1	0.00	–0.14	1.09
		2	0.01	–0.15	1.83
		4	–0.136	–0.17	3.62
		8	–2.47	–0.11	5.49
	Methanolic	1	–2.24	–0.74	5.95
		2	–5.70	–2.55	11.34
		4	–6.44	–3.69	14.45
		8	–9.37	–4.14	18.75
Treated with extracts of *Solanum nigrum*	Aqueous	1	0.23	–0.34	1.67
		2	–0.35	–0.63	3.58
		4	–0.40	–0.73	3.82
		8	–2.00	–1.03	7.41
	Methanolic	1	–1.21	–1.07	4.77
		2	–1.69	–0.65	5.78
		4	–2.78	–1.70	9.57
		8	–4.42	–2.35	13.31

materials with the increased concentration. Methanolic extracts, when compared with aqueous extracts, were found to cause a higher influence in colour coordinates, which may be attributed to higher contents of flavonoids and phenolics, and subsequent UV blocking. The Δa and Δb coordinates of CIELAB were also influenced by different concentrations of extracts, thus reducing the brightness. However, Figures 3 and 4 show that both plants extract are able to impart superior UV blocking in the UV-A and UV-B region, which was proved by the UPF analysis. With a 4 g/l concentration of *SN* plant extracts, UPF increased from 8.7 to 19.9 (UPF rating 15–20 is considered as "good" according to the "Australian Radiation Protection and Nuclear Safety Agency" [5, 6]).

The increase in UPF mainly results from the components in extracts, which were successfully deposited on the cotton fabric. However, methanolic extracts, when applied on fabric samples, rendered exceptional UPF. The values close to 60 were achieved by using only 1 g/l of methanolic extracts; hence, concentrations much lower than that can be used. The methanolic extracts of *AV* showed excellent UPF.

At a minimum concentration of 2 g/l, the methanolic extracts of *SN* provided UPF of about 40, which is above the minimum UPF value considered "very good" UV protection by textile clothing. As methanolic extracts influence the CIELAB coordinates, this method can provide a sustainable solution, and the concentration of the plant extracts can be increased to obtain a much higher UPF. The use of fluorescent brightening agents may also be made in the combination with plant extracts to further optimize UPF as well as fabric whiteness [23]. The fastness of the applied finishes was measured for household laundry wash and it was noticed that the UPF values decreased adversely, which is a great drawback of natural finishes (Figure 5). Further experiments and analysis are needed to introduce sustainable fastness of the finishes.

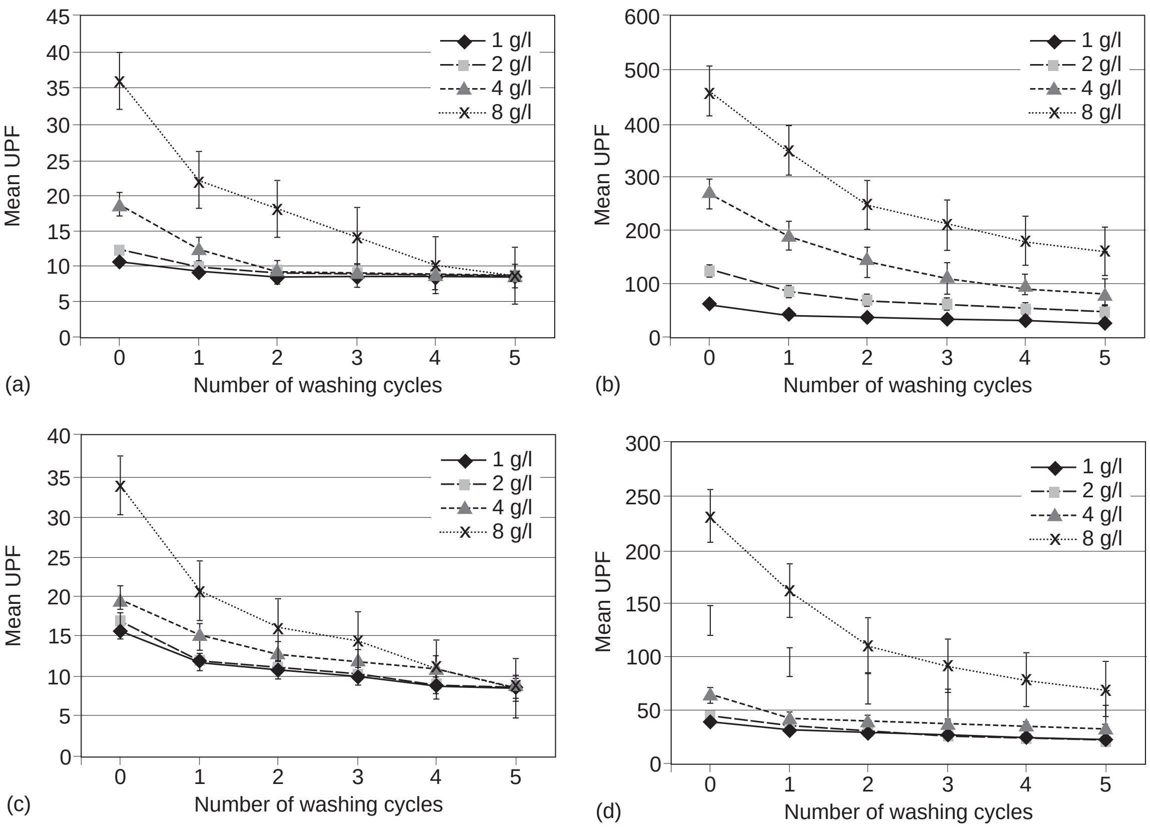

Figure 5: Fastness of applied finishes after household laundry wash treated with water (a) and methanolic (b) extracts of Amaranthus viridis, and water (c) and methanolic (d) extracts of Solanum nigrum

4 Conclusion

This work investigated and analysed a comparative performance of UV blocking of a cotton fabric treated with different natural finishes. Aqueous and methanolic extracts of two medicinal plants were applied on prepared bleached fabrics. About 99% of UVA and UVB rays were blocked. Methanolic extracts demonstrated better UV blocking property than aqueous extracts, causing a higher shade change in fabric color at the same time. This research is worthwhile for the preparation of a cost-effective and environmentally friendly material to formulate the UV blocking properties of textiles. Further research on the durability factor of extracted finishes and shade variation of the treated textile material is required to ensure a sustainable commercial application.

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