

Assessment of Stabilities of Two Local Plant Dyes as Colorants for Petroleum Products (Petrol, Kerosene, and Diesel)

C.A. Nwadinigwe¹; O.M. Ilojeme¹; A.O. Nwadinigwe²; T.N. Alumona^{1*}; and K.G. Akpomie¹

¹Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka, Nigeria.

²Department of Plant Science and Biotechnology, University of Nigeria, Nsukka, Nigeria.

E-mail: theresa.alumona@unn.edu.ng*

ABSTRACT

Dyes from *Pterocarpusosun* Craib and *Lawsoniainermis* Linn. were extracted by cold maceration using ethanol and methanol, respectively. The extracted dyes were subsequently purified using chromatographic methods and characterized using ultra-violet (UV) visible and Fourier Transform Infrared Spectrophotometer (FTIR). The UV spectra of the dyes in petrol, kerosene, and diesel indicated presence of chromophores. The FTIR spectra of the dyes showed presence of phenolic O-H and C=C stretching of aromatic functional groups.

The color intensity of the dye from *Lawsoniainermis* measured with Lovibond Tintometer was remarkably stable in coloring petrol for a period of at least twenty-eight days but not kerosene or diesel while the color intensity of the dye from *Pterocarpusosun* was not stable. Thus, dye from *Lawsoniainermis* can be used as alternative colorants to synthetic dyes for petrol but not for kerosene or diesel. The dyes from *Pterocarpusosun* cannot be so used for any of the petroleum products because of their instability.

(Keywords: *Pterocarpusosun*, *Lawsoniainermis*, petroleum products, colorants, stability)

INTRODUCTION

In the present world of growing environmental consciousness, natural colorants have attracted the attention of researchers (Oparah, 2001; Osabohiem and Ukponwam, 2002). The alarming rate of high use of synthetic dyes which are prone to carcinogenicity, mutagenicity, greenhouse effect and high cost have provided an urgent quest for natural plant dyes in the petroleum industry (Bhuyan and Saikia, 2004; Kame *et al.*,

2005; Okolie 2006). Natural plant dyes have been discovered accidentally and their uses have become so much a part of man's customs that it is difficult to imagine modern world without dyes. The art of dyeing spread widely as civilization advanced (Krishnamurthy *et al.*, 2002).

With the increasing demand in petroleum industry and various sectors of the economy for dyes and pigments coupled with the high cost of synthetic dye importation, there is need to explore plant dyes. Their applications will improve the socio-economy and artistic development of any nation. Although many studies have been carried out using the extract from *P. osun* (Gill, 1992; Omotayo, 2000) and *L. inermis* (Chopra *et al.*, 1956; Petkewich, 2006; Habbal *et al.*, 2007; Chefty, 2008) as dyes for different purposes, no detailed report has been documented before now on their stability or suitability for colouring petroleum products.

The use of colorants for petroleum products cannot be avoided because it helps in quick, visual differentiation of petrol, kerosene, and diesel. It also helps in check-mating adulteration and identification of grade or quality of petroleum products (Rostad, 2010; Ezeokonkwo and Okoro, 2012).

Presently, the dyes used by Nigerian refineries are imported, coded and used without disclosing their exact chemical names and composition either to the refinery staff or to the public. The chemical nature of dyes in imported petroleum products are also shrouded in secrecy. These have necessitated the search for alternative sources of colorants for petroleum products for the oil industry using natural plant dyes from stem wood of *P. osun* and young leaves of *L. inermis*.

MATERIALS AND METHODS

Instrument and Materials

All the chemicals used were of analytical reagent grade product of Sigma Aldrich® (Germany). Electric Milling Machine made by Thomas Wiley Laboratory Mill Model 4 (USA), was used for milling the plant materials. Rotary Evaporator (BÜCHI ROTAVAPOR – R, Germany) was used to concentrate the filtrate. Column Chromatography (CC) was performed on silica gel (60-230 mesh, Merck, Germany) using a glass column (15 cm long x 1.5 cm i.d) with the bed of 100 cm height. Vacuum Liquid Chromatography (VLC) was performed on silica gel (230-400 mesh, Merck) using a glass column (30 cm long x 3.0 cm i.d). Freeze drying was performed using Freeze Drier Machine (YORCO, India). De-colorization of commercial petroleum products was performed with Edward High Vacuum Pump (England) using activated charcoal and fuller's earth. The UV-analysis was recorded using UV-2500PC Spectrophotometer (Japan). The Infrared analysis was recorded on FTIR-8400S (SHIMADZU, Japan). The color stability analysis was done using LovibondTintometer F Model (United Kingdom).

Plant Materials

The stem wood of *P. osun* and young leaves of *L. inermis* were collected from Eha-Alumona and Nsukka both in Nsukka L.G.A. in Enugu State, Nigeria. The plant materials were identified by a taxonomist in INTERCEED and the specimen was submitted through voucher No H – 1070 to the herbarium of the Institute and kept for future reference.

Extraction

The air-dried powdered stem wood of *P. osun* and young leaves of *L. inermis* (600 g, each) were soaked in 2.5 L of 96 % ethanol and methanol respectively and extracted by cold maceration at room temperature (29°C) for 48 h. The filtrates were concentrated *in vacuo* using rotary evaporator at reduced pressure (300 Psi) and temperature (40°C) to obtain the dry extracts.

Purification

Column Chromatographic Purification of *P. osun* Extract: 27.0 g of the extract was chromatographed on silica gel (60-230 mesh, 250 g) packed into a glass column (15 cm long x 1.5 cm, i.d) with the bed of 100 cm height [15]. The elution was done with ethanol (2.5 L) and the percentage yield calculated.

Vacuum Liquid Chromatographic Purification of *L. inermis* Extract: The methanol extract of *L. inermis* was purified using vacuum liquid chromatography (VLC). 35.0 g of the extract was purified by VLC using silica gel (230-400 mesh, 30 cm long x 3.0 cm i.d, 550 g) as the stationary phase and eluted with a gradient of ethyl acetate in ethanol (10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8, 1:9 and 0:10, each 500 cm³) to afford eleven sub fractions (LI₁-LI₁₁). LI₇ was freeze-dried and the percentage yield calculated.

De-Colorization of Commercial Petroleum Products: The de-colorization of the commercial petroleum products used was with activated charcoal and Fuller's Earth. Petrol, kerosene, and diesel (1L) each were decolorized using 50 g each of activated charcoal and Fuller's Earth on Edward High Vacuum Pump. The colorless petroleum products obtained were collected in 500 cm³ of Buckner flask and stored properly in sample bottles for analysis.

Characterization

Ultraviolet Spectroscopy (UV): The dyes (1.0 g,) each were separately dissolved in 3 cm³ each of petrol, kerosene and diesel in a sample bottle. They were used for the UV analysis for periods of twenty-eight days.

Infrared Spectroscopy (IR): The dyes (0.001 g) each were mixed with sodium chloride and potassium bromide respectively. Fourier Transform Infrared (FTIR) instrument, 8400S spectrophotometer was used to establish the functional groups present.

Table1: Physical Data of Dyes from *P. osun* and *L. inermis*.

Dyes	Solvents used for Extraction	Physical Color of Dyes	Melting Point (°C)	Yields (%)
<i>P. osun</i>	96% ethanol	Dark red	130-132	1.44
<i>L. inermis</i>	96% methanol	Orange- brown	190-191	1.50

Color Stability Analysis of the Dyes: The stability of the color of the dyes obtained was done using Lovibond Tintometer (F Model) according to ASTM D 1500 method (ASTM). The dyes (0.001 g, each) were separately dissolved in 2 cm³ each of petrol, kerosene and diesel in a sample bottle. They were used for the color intensity analysis for a period of twenty-eight days.

RESULTS AND DISCUSSION

Physical Properties

The physical properties of dyes extracted from *P.osun* and *L. inermis* using ethanol and methanol respectively, are shown in Table 1.

***P. osun* Wavelengths:** The maximum absorption wavelengths of *P. osun* dye in petroleum products (petrol, kerosene and diesel) for a period of twenty-eight days are shown in Figure 1.

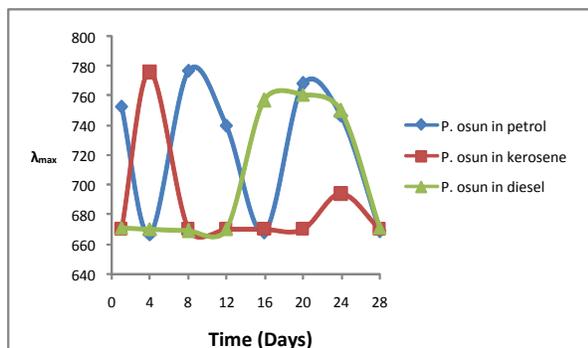


Figure 1: Variation of λ_{max} with time using petrol, kerosene and diesel colored with *P. osun* dye

***L. inermis* Wavelengths:** The maximum absorption wavelengths of *L. inermis* dye in petrol, kerosene and diesel for the same period are given in Figure 2.

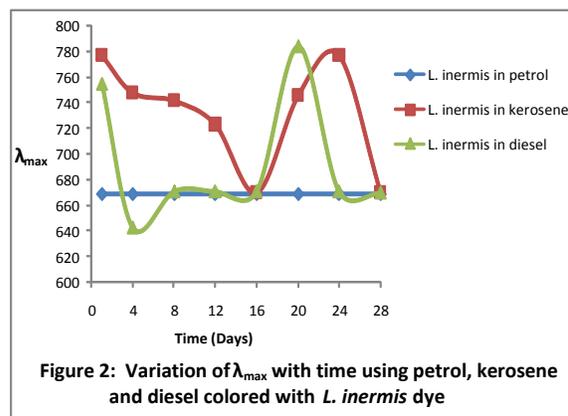


Figure 2: Variation of λ_{max} with time using petrol, kerosene and diesel colored with *L. inermis* dye

***P. osun* Color Intensity:** Figure 3 shows results of the color intensity of *P.osundye* in petrol, kerosene and diesel within the specified period of twenty-eight days.

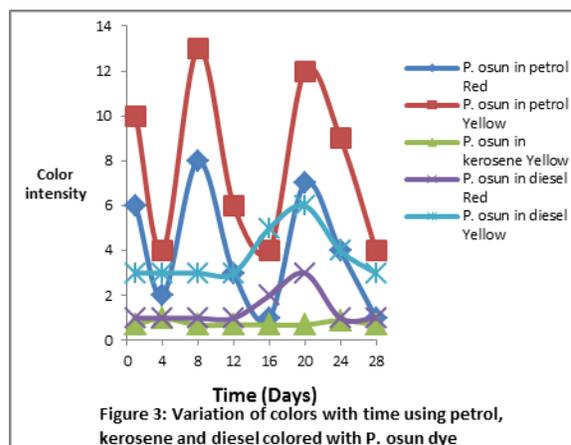


Figure 3: Variation of colors with time using petrol, kerosene and diesel colored with *P. osun* dye

***L. inermis* Color Intensity:** Figure 4 shows the color intensity results of *L. inermis* dye in petroleum products for the same period of time.

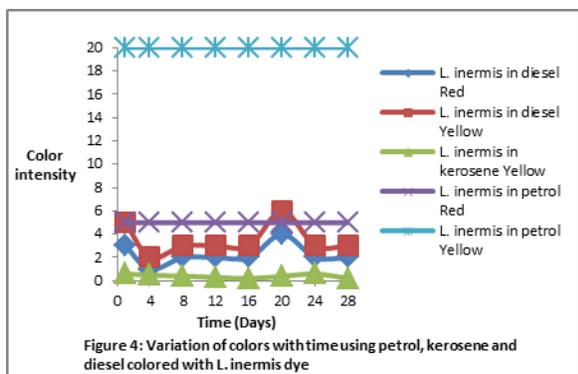


Figure 4: Variation of colors with time using petrol, kerosene and diesel colored with *L. inermis* dye

FTIR Spectra of the Plant Dyes: The spectra data in Figures 5 and 6 indicated the presence of hydroxyl groups (3435 cm^{-1} and 3380 cm^{-1}), absorption at 2935 cm^{-1} and 2930 cm^{-1} (CH_2 , CH_3 of aliphatic group), absorption at 2279 cm^{-1} and 2358 cm^{-1} ($\text{C}\equiv\text{C}$) and $\text{C}=\text{C}$ at $620\text{-}1441\text{ cm}^{-1}$ and $1627\text{-}1426\text{ cm}^{-1}$.

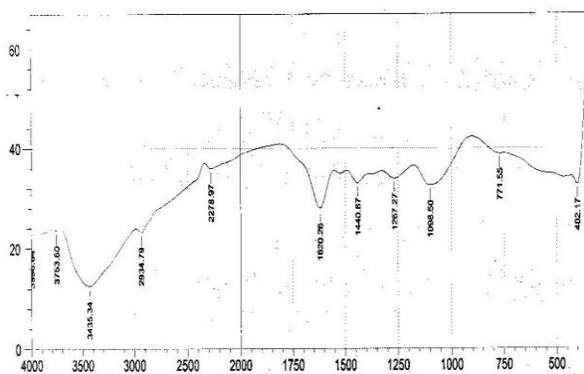


Figure 5: FTIR of *P. osun* Stem Wood Dye.

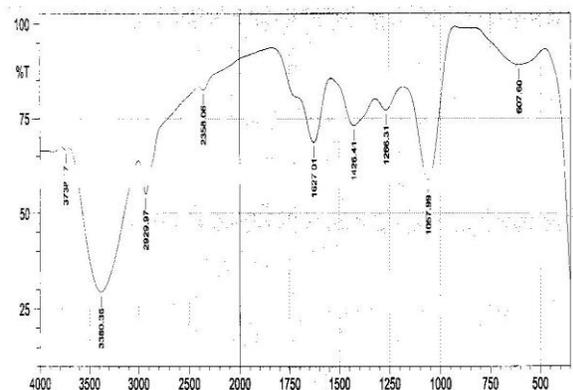


Figure 6: FTIR of *L. inermis* Leaf Dye.

Selection of the solvent used in the extraction, primarily depends on the availability of the solvent

as well as the solubility of the dye in the solvent. Ethanol and methanol were used for extraction of the dark red and orange brown color in the dyes.

Dyes, melted at high temperature and their percentage yields are low as shown in Table 1. Dyes from the stem wood of *P. osun* and *L. inermis* colored petrol or diesel (red and yellow). Its colored kerosene yellow as shown in Figures 3 and 4. The maximum absorption wavelengths and color intensity values of *P. osun* petrol, kerosene and diesel were unstable as shown in Figures 1 and 3. This was also the same when dye from *L. inermis* are added to kerosene and diesel but it is very stable in petrol as shown in Figures 2 and 4. It absorbed in petrol at 669 nm while color intensity was red and yellow (5 and 20). This was consistent throughout the period of twenty-eight days. FTIR carried out on the plants shows that phenolic and aromatic groups are the most important ones as shown in Figures 5 and 6.

DISCUSSION

Petroleum products are usually colored with synthetic dyes in order to enable people differentiate them from the others and for aesthetic purposes. Recently, interest in the use of natural dyes has been growing rapidly due to the result of stringent environmental standards imposed by many countries in response to toxic and allergic reactions associated with synthetic dyes (Kame *et al.*, 2005). Synthetic dyes are suspected to release harmful chemicals that are allergic, carcinogenic and detrimental to human health (Bhuyan and Saikia, 2004). With the worldwide concern favoring the use of eco-friendly and biodegradable materials, the use of natural dyes has once again gained interest (Padhy and Rathi, 1990; Garg *et al.*, 1991; Eom *et al.*, 2001).

In an earlier report (Ezeokonkwo and Okoro, 2012), the dye from the stem wood of *P. osun* extracted with ethanol was found to color petroleum products (gasoline, diesel, kerosene and wax), but the color intensity stabilities was not investigated and so were not reported. Dye from the leaves of *L. inermis* has also been studied by different phytochemical and pharmacological methods to show the characterizations of the leaves (Gagandeep *et al.*, 2010; Musa and Gasmelseed, 2012), but no work has been published on it with respect to

petroleum products. Based on the aforementioned, the stability of the dark red and orange brown dyes extracted from *P. osun* and *L. inermis* using ethanol and methanol, respectively, in petroleum products (petrol, kerosene, and diesel) was investigated for a period of twenty-eight days. The number of days was chosen as a rough estimate of the life of the petroleum products spanning production in the refinery, transportation and disposal by the filling station.

From results, *P. osun* dye wavelengths of maximum absorption and color intensity in petrol, kerosene, and diesel were not remarkably stable. Thus, the dye is unstable in petroleum products. Dye from *L. Inermis* showed that wavelengths of maximum absorption and color intensity in petrol were stable throughout the period of investigation (twenty-eight days) but were unstable in kerosene and diesel. In addition, it can be observed that the dyes colored petrol or diesel red and yellow while kerosene was yellow. This was inconsistent with previous report (Ezeokonkwo and Okoro, 2012), due to their inability to use an appropriate color instrument (Lovibond tintometer). Lovibond tintometer was used to determine red and yellow color in the leaves of *L. inermis* dye, which corresponds to earlier report (Musa and Gasmelseed, 2012).

FTIR of the two plants extract (*P. osun* and *L. inermis*) dyes showed the presence of phenolic O-H stretching at 3435 cm^{-1} and 3380 cm^{-1} . They also showed the presence of C=C of aromatic at $1620\text{--}1441\text{ cm}^{-1}$ and $1627\text{--}1426\text{ cm}^{-1}$ respectively as the functional groups present. This was entirely consistent with the values previously reported (Ezeokonkwo and Okoro, 2012; Musa and Gasmelseed, 2012).

CONCLUSION

The dye extracted from the young leaves of *L. inermis* can be used as alternative source of colorant for petrol in the oil industry. It cannot be used for the same purpose for kerosene or diesel because the color intensity of the dye was unstable. The dye extracted from the stem wood of *P. osun* can be used in coloring petrol, kerosene and diesel but the color intensity of the dye was not stable for long periods for commercial application.

REFERENCES

1. ASTM D. 2012. *1500 Standard Test Method for ASTM Color of Petroleum Product (ASTM Color Scale)*. ASTM International: West Conshohocken, PA.
2. Bhuyan, R. and C.N. Saikia. 2004. "Isolation of Color Compounds from Native Dye-Bearing Plants in North Eastern India". *Am. J. Pathol.* 164(5): 873–77.
3. Chefty, K.M. 2008. *Flowering Plants of Chittoor, 1st ed.*, Andhra Pradesh: New Delhi, India.132.
4. Chopra, R.N., S.L. Nayer, and I.C. Chopra. 1956. *Glossary of India Medicinal Plants*. CSIR Publications: New Delhi, India. 151.
5. Eom, S., D. Shin, and K. Yoon. 2001. "Improving the Dye Ability of Natural Colorants on Cotton by Cationization". *Ind. J. Fibre Text. Res.* 26(4):425-431.
6. Ezeokonkwo, M.A. and U.C. Okoro. 2012. "New Dyes for Petroleum Products". *J. Emerging Trends Eng. and Appl. Sci.* 3(1):8 -11.
7. Gagandeep, C., G. Sandeep, and P. Priyanka. 2010. "Lawsoniainermis Linnaeus: A Phytopharmacological Review". *Int. J. Pharm. Sci. and Drug Res.* 2(2):91-98.
8. Garg, A., S. Shenda, and K.C. Gupta. 1991. "Effect of Mordants on Color of Natural Dye Extracted from Tissue Flowers (*Butea mongosperma*)". *Colorage.* 38(2): 50-53.
9. Gill, L.S. 1992. *Ethanomedical uses of Plants in Nigeria*. Uniben Press, University of Benin: Benin City, Nigeria. 200-201.
10. Habbal, O.A., A.A. Al-Jabri, and A.G. El-Hag. 2007. "Antimicrobial Properties of Lawsoniainermis: A Review". *Aust. J. Med. Herb.* 19(3):114-125.
11. Kame, M.M., R.M. El-Shishtawy, B.M. Yussef, and H. Mashaly. 2005. "Ultrasonic Assisted Dyeing: III. Dyeing of Wool with lac as a Natural Dye", *Dyes Pigments.* 65:103-110.
12. Krishnamurthy, K.V., R. Sivia, and K.T. Senthil. 2002. "Natural Dye Yielding Plants of Shervaroy Hills of Eastern Ghats". In: *Proceedings of National Seminar on the Conservation of Eastern Ghats, Environ. Protec. Training and Res. Inst.:* Hyderabad, Pakistan. 151 – 153.
13. Musa, A.E and G.A. Gasmelseed. 2012. "Characterization of Lawsoniainermis as

- Vegetable Tanning Material". *J. Forest Prod. and Ind.* 1(2): 35-40.
14. Oparah, E.N. 2001. "The Return of Natural Dyes". *J. Chem. Soc. Nig.* 26(1):87- 90.
 15. Osabohiem, E. and D.O. Ukponwam. 2002. "Extraction of Natural Dyes from some Local Plants". *J. Chem. Soc. Nig.* 27(2):140 – 141.
 16. Okolie, N.J.C. 2006. "Investigation on the Staining of Parasites of Medical Important with Dyes". *Afri. J. Appl. Zool. and Environ. Biol.* 8:67 – 72.
 17. Omotayo, F.O. 2000. *Folk Medicinal Plants – A Thesis on Medical Ethnobotany*. University of Lagos: Lagos, Nigeria. 550.
 18. Padhy, R.N. and D. Rathi. 1990. "Effect of Mordants on Dyeing of Cotton with Vegetable Dyes". *Text Dyer Printer.* 23(25):27-28.
 19. Petkewich, R. 2006. "Dye Derived from Green Henna Leaves is used to Decorate the Body with Intricate Designs". *Chem. Eng., News.* 84:28.
 20. Rostad, C.E. 2010. "Analysis of Solvent Dyes in Refined Petroleum Products by Electrospray Ionization Mass Spectrometry". *Fuel.* 89(5):997–1005.

SUGGESTED CITATION

Nwadinigwe, C.A., O.M. Ilojeme, A.O. Nwadinigwe, T.N. Alumona, and K.G. Akpomie. 2017. "Assessment of Stabilities of Two Local Plant Dyes as Colorants for Petroleum Products (Petrol, Kerosene, and Diesel)". *Pacific Journal of Science and Technology.* 18(2):278-284.

 [Pacific Journal of Science and Technology](http://www.akamaiuniversity.us/PJST.htm)