Journal of Emerging Trends in Engineering and Applied Sciences (JETEAS) 3 (1): 8-11
 (ISSN: 2141-7016)
jeteas.scholarlinkresearch.org

New Dyes for Petroleum Products

M. A. Ezeokonkwo and U. C. Okoro

Department of Pure & Industrial Chemistry,
University of Nigeria, Nsukka

Corresponding Author: M. A. Ezeokonkwo

Abstract

Petroleum products are usually coloured with dyes, which can be natural or synthetic. In Nigeria, a number of plants serve as a source of dyes. Among these are Rothmenia hispidia, Pterocarpus osun and Terminalia superba. In the present work, the seeds of Rothmenia hispidia were extracted with water using cold maceration method, while the stem wood of Pterocarpus osun and Terminalia superba were extracted with ethanol. The extracts of Rothmenia hispidia were isolated by sedimentation whereas those of Pterocarpus osun and Terminalia superba were isolated by simple distillation. Petroleum products (gasoline, diesel, kerosene and wax) were coloured with the aqueous extract of Rothmenia hispidia and ethanol extracts of Pterocarpus osun and Terminalia superba. The dyes gave the products beautiful colours ranging from yellow through orange to red. Consequently, application of these dyes in petroleum products will serve for aesthetic purposes, identification of different petroleum fractions as well as trademark. The UV-Visible and Infrared Spectroscopy of the dyes were also determined

Keywords: rothmania hispidia, pterocarpus osun, terminalia superba, petroleum products, aesthetic, trade mark

INTRODUCTION

Dyes are coloured substances that impart more or less permanent colour to other materials. They are generally soluble substances, although some are soluble only during application (McGraw-Hill, 1983). Dyes are used to colour gasoline and lubricating oils in order to improve the appearance, as well as for identification of grade, type of use or merely as a trademark of the manufacturer. Solvent dyes used to colour refined petroleum products is to be able to differentiate between gasoline, diesel, and jet fuels (Rostad, 2010). Petroleum dyes helps in identification of fuel adulteration. It also helps to create differentiation in various petroleum products such as leaded and unleaded, high and low octane gasoline, high and low sulphur diesel and aviation fuels attributes (Meghmanidyes, 2011). Other reasons for dyeing fuel, such as for aviation, supports the fuelling process itself, to ensure that the right type of fuel is used in the correct aircraft - as the consequences of getting this wrong can be disastrous (Petroleum Logistics, 2010).

Other petroleum products such as waxes, shoes polishes and candle wax are also coloured. Solubility as well as hue and fastness are the major determinant factors for dyes used in these petroleum products. Other uses of dyes include in the colouring of textiles, paper, wood, leather, inks, food items and metals. Other areas of use include photographic paper, as indicator in chemical analysis and biological stain (Hampel and Hawley, 1973) and as point leak detection (Uniglow liquid dye distributed by United Colour).

Nature provides varieties of dyes. Natural dyes are those dyes derived from animal or plant sources without chemical processing. The production and use of natural dyes from plant and animal sources have increased rapidly in the recent times despite the large-scale use of synthetic dyestuffs (D'auria, Gilchrist and Johnstone, 1973). With the extensive testing of all synthetic products for carcinogenicity and mutagenicity, the food and drug industries have turned to natural products as the source of their colouring matter (Kirk-Othmer, 1979 and Lubs, 1972). In addition, the colouring of textiles, wood, leather and other related items with dyes from plants is receiving increasing attention (Oparah, 2001). Moreover, a number of companies are presently producing natural dyes in commercial quantity. These include such companies as Milan de la Rabbia, which produces weld, chlorophyll, logwood and cochineal dyes; Allegro Natural dyes in USA, which produces a group of natural dyes known as Ecolor; and Livos Pflanzenchemic Forschungs and Entwickungs Gmblt, in Germany, which developed and marketed kits of colours based on local plant dyes (Hill, 1997). The recent increase in the use of natural dyes has been attributed to a number of factors which include health friendliness in the environment, harmonising natural shade and possibly, just the novelty (Hill, 1997).

In Nigeria, a number of plants serve as a source of dyes. These include Morinds lucida, Vitax gradifola, Baphia nitida, Daniella oliveri, Guinea cornhusk, Cola nitida (Akpuaka, 1992) and Turmeric (Akpuaka, Ezenwoye and Okerulu, 2001) to mention but few. Despite the enormous work that have been done on dyes from plant sources, no known report on the use of these dyes for colouring of petroleum products exist in the literature. With the increasing demand in petroleum industry for dyes and pigments coupled with the high cost of importation of synthetic dyes, there is need to explore locally available sources of colouring matters. The present work aims at extraction, isolation and application of dyes from Rothmenia hispidia, Pterocarpus osun and Terminalia superba on some petroleum products. These plants are in abundance in Nigeria and some other African countries. Considering the large quantity of Rothmenia hispidia seeds, Pterocarpus osun and Terminalia superba stem woods that are wasted every year due to lack of proper storage facilities, which arises mainly due to their limited usage, the conversion of these seeds and stem woods to dyes for petroleum products has become necessary. This will not only go a long way in reducing the wastage but also will reduce the amount of foreign exchange expanded on the importation of petroleum dyes and encourage the growth and utilization of Rothmenia hispidia seeds, Pterocarpus osun stem wood and Terminalia superba stem wood.

Rothmenia hispidia is one the tropical plants mostly found in Southern part of Nigeria as well as other African countries such as Guinea and Democratic Republic of Congo. It exists as a shrub or tree of about 11m height. The dye occurs as colourless substance in the plant, and is contained in the fruits. On extraction, the colourless substance transforms into dark-blue dye by air oxidation. Water was used in the extraction of the Rothmenia hispidia dye because the colourless substance is soluble in it and water is readily available. In Nigeria, the leaf sap and fruit juice are used to draw black designs on the body and to blacken tattoos; mixed with palm oil, they are applied on the skin against fungal infections (Jansen and Cardon, 2005).

Pterocarpus osun, mostly found in tropical vegetations exists as a tree of about 30 m height and 2.5 m girth with a spreading crown and the wood marketed as African padauk (Jansen and Cardon, 2005).The principal colouring matter is contained in the wood and develops in a felled tree over a long period. Ethanol was used in the extraction because of it availability. Pterocarpus osun in its crude form is applied locally in the Eastern part of Nigeria as a medication for treatment of chicken pox in children.
Terminalia superba is one of the trees used extensively in Nigeria as timber. It grows to about 50 m high and 5 m girth. The colouring matter is contained in the wood. The bark also yields yellow to reddish brown dyes and black dyes if mordanted with iron-rich salts (Jansen and Cardon, 2005). Ethanol was used in the extraction because of it availability.

EXPERIMENTAL

Plant Materials

Whole fruits of Rothmania hispidia, stem woods of Pterocarpus osun and Terminalia superba were collected at Ibeagwa and Orba in Nsukka, Enugu State, Nigeria, and were identified at the herbarium, Botany Department of the University of Nigeria, Nsukka.

Extraction and Isolation of Dyes

550 g of seeds of matured Rothmania hispidia fruits were pulverized in a grinding mill and steeped in 110 ml distilled water for 72 hours in an air-tight container. At the end of this period, the steeped seeds were agitated and filtered using buckner funnel. The residue was discarded while the light yellow filtrate was stirred vigorously with a magnetic stirrer for hours until a dark blue solution was obtained. The solution was allowed to stand at room temperature for 2 weeks after which the dark blue dye precipitated out and form sediment at the bottom of the containing vessel. The supernatant liquid was decanted and the dye allowed to dry at room temperature.

To extract the dye from Pterocarpus osun, 300 g of the stem wood was ground and steeped in 1.2 litres of ethanol (96 %) for 72 hours. At the end of the period, the steeped wood was agitated and filtered using buckner funnel. The residue was discarded while the filtrate was concentrated by simple distillation to about one-third the original volume. The dye was precipitated by adding 1.2 litres of distilled water to the concentrate. The precipitate was collected by filtration and purified by recrystallization from a mixture of 96 % ethanol and distilled water (3:1) and activated charcoal. A dark-red solid obtained was dried at room temperature.

The dye from Terminalia superba was obtained by first grinding 400 g of the stem wood and steeping it in 2.6 litres of 96 % ethanol for 72 hours. The steeped wood was agitated at the end of this period and filtered with a buckner funnel. The residue was discarded while the orange-red filtrate was concentrated by simple distillation. The remaining ethanol was removed using a rotary evaporator to obtain an orange-red solid which was purified by recrystllization from 90 % ethanol and 0.5 g charcoal.
Application of the dyes on petroleum products:
Gasoline, diesel and kerosene. About 0.2 g of each of the dyes was separately added to 5 ml of gasoline, 5 ml of diesel and 5 ml of kerosene in 100 ml beakers. Pterocarpus osun dye coloured gasoline yellow, diesel purple and kerosene red while Rothmania superba and Terminalia osun dyes did not colour the petroleum fractions at all.

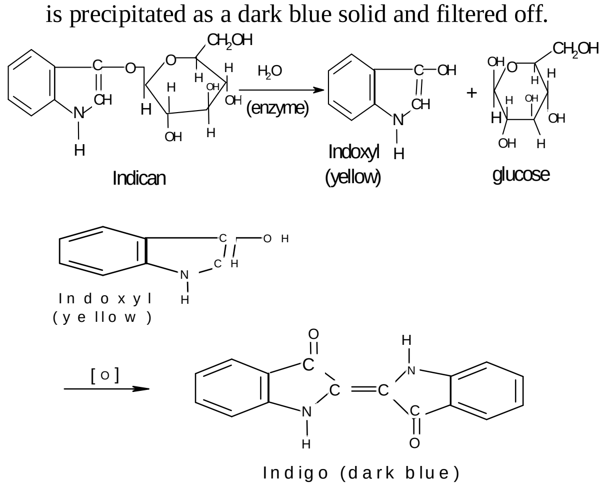
Candle wax

Three sets of white candle wax, each weighing 33.0 g were melted separately in three clean beakers. They were heated to a temperature of about 70^{o}C and 0.5 g each of the dyes was added to one of the melted wax. The entire mixture was stirred vigorously and poured into a candle mould through which a wick had been passed. This was allowed to remain in the mould for abut 10 minutes during which it solidifies. On solidification, it was put into cold water and from one end of the mould the candle was removed.

Spectroscopic Analysis
The ultraviolet and visible spectra were run using ethanol on a Unico – Uv2102 PC spectrophotometer. Infrared spectra were obtained on a magna – IR system 750 spectrophotometer using KBr disc.

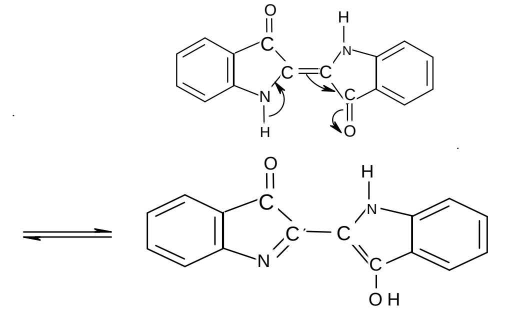
RESULTS AND DISCUSSION

Table 1 shows the physical properties of the dyes. 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. The *Rothmania hispidia* plant as have already been said, does not contain the dark blue dye but rather a colourless liquid which changes to light yellow on steeping in water and subsequently to the dark blue dye on oxidation by air. This is exactly the process of obtaining indigo dye from *Indigofera tinctoria* (D'auria, Gilchrist and Johnstone, 1973). Although the structure of the dye is yet to be elucidated it is believed that the colourless liquid is indican - a glucoside of indoxyl, which is hydrolyzed by the enzyme present in the plant material, to indoxyl during fermentation process. The indoxyl when oxidized by atmospheric oxygen gives indigo, which is precipitated as a dark blue solid and filtered off.



Scheme 1: Typical process of forming indigo dye

The ultraviolet spectrum of the dye showed absorption maxima at 294 and 324 nm, which could be due to multiple conjugations in the compound. It also showed a maximum absorption in the visible region at 595 nm as against 602 nm in the literature for indigo. The difference could be due to possible tautomerism in the dye **(Scheme 2)**. The unavailability of a suitable solvent made it impossible to examine the infrared spectrum of the dye.



Scheme 2

Table 1: Physical data of the dyes

Dye	Solvent used for extraction	Physical colour of dye	Mp (%)	Yield (%)
Rothmania hispidea Dye	Water	Dark blue	> 300	0.873
Pterocarpus osun Dye	96 % ethanol	Dark red	130 – 132	10.430
Terminalia superba Dye	96 % ethanol	Orange red	100 – 102	1.500

In the extraction of the dye from *pterocarpus osun,* water was not used because the dye is insoluble in water. However, the dye is extremely soluble in ethanol and therefore ethanol was used to obtain a high yield. Nevertheless, because of its high solubility in ethanol, it was difficult for the dye to precipitate out from the solution without a "precipitating" solvent. Hence, to precipitate the dye requires the addition of water to the concentrated solution. The amount of water added to avoid precipitating impurities is when the ratio of water to the concentrate is 3:1. The dye showed absorption band in the utraviolet region at 226 nm, which is consistent with the substituted benzene ring and shows the presence of a conjugated system. The absorption band observed at 474 and 506 nm are in agreement with the dark red colour of the dye. The infrared absorption band observed at 3400cm-^{1} shows the presence of OH (hydrogen bonded) in phenols. It can also be due to N-H (stretching) in primary aromatic amines which is hydrogen bonded. The band at 1350 -1280 cm-^{1} is attributable to C –N (stretching) in primary amines. Also observed was the absorption band of C – O (stretching) in phenols.

The dye from *Teminalia superba* is insoluble in water but soluble in a number of organic solvents such as ethanol, methanol and acetic acid. Extraction with ethanol was due to its availability. The solubility of the dye in ethanol was such that it was able to precipitate after concentration without any ''precipitating'' solvent. The absorption band in the ultraviolet region observed at 344 nm suggests the presence of a long conjugated system. The observed absorption in the visible region at 478 nm is consistence with the orange colour of the dye. The band in the infrared region at 3380 cm^{-1} is due to O-H in phenols which is hydrogen bonded. The bands at 1440 and 1310 cm^{-1} could also be due to $-NO_2$ vibrations in aromatic nitro compounds.

Application of Dyes on Petroleum Products

A number of petroleum products can be coloured with dye, for identification and aesthetic purposes. These include gasoline, diesel, and kerosene, lubricating oil and candle wax. However, not all dyes can colour these products. Table 2 shows the results obtained by applying the dyes on the petroleum products. In colouring candle wax, gasoline, diesel and kerosene with the dyes isolated, it was found that all the dyes colored candle wax beautiful colours as follows: *Rothmania hispidia* gave dark-blue coloration, *Pterocarpus osun* gave red coloration while *Terminlia superba* coloured the candle wax orange. The petroleum fractions were not colored at all by both *Rothmania hispidia* and *Terminalia superba*. This is due to the inability of the dyes to dissolve in the petroleum fractions. *Pterocarpus osun* dye coloured gasoline yellow, diesel purple and kerosene red.

Table 2: Results obtained by application of the dyes on petroleum products

Dye Applied	**Petroleum products**			
	Gasoline	Diesel	Kerosene	Wax
Rothmania hispidia dye	-	-	-	Dark-blue
Pterocarpus osun dye	Yellow	Purple	Red	Red
Terminalia superba dye	-	-	-	Orange

CONCLUSION

Dyes extracted from *Rothmania hispidia*, *Pterocarpus osun* and *Terminalia osun* are potential dyes for colouring and identification of different petroleum products sold in the market since they give each of the products beautiful and distinct colours. Individual manufacturers can also use these dyes as trademark to differentiate their petroleum products from those of other manufacturers. They can also be used in preparing test kits for the detection of adulterated petroleum products.

REFERENCES

Akpuaka, M. A. 1992. Book of Abstract, Chemistry Soc. of Nig., Enugu Chapter, 6th Annual Conference, pp. 13-19.

Akpuaka, M. A; Ezenwoye, O. M and Okerulu, I. O. 2001, Sourcing a Yellow Dye from Turmeric (Curculonga) – A locally available rhizome, J. Chem. Soc. Nig., 26 (1), 11-13.

D'auria, J. M; Gilchrist, H. B and J.J. Johnstone, J. J. 1973. Chemistry and the Environment, 1st ed., W. B. Saunders company, Philadelphia, p. 103.

Hampel, C. A and Hawley, G. G. 1973. The Encyclopedia of Chemistry, 3rd ed., Van Nostrand Reinhold Company, New York, p. 31.

Hill, D. J. 1997. Rev. Prog. Coloration, 27, pp. 8-19.

Jansen, P. C and Cardon, D. 2005 Plant Resuorses of Tropical Africa 3: Dyes and Tannins, PROTA Foundation/ Backhuys Publishers?CTA Wageningen, Nitherlands, pp. 132-165.

Kirk-Othmer. 1979. Encyclopedia of Chemical Technology, vol. 8, 3rd ed., John Wiley and Sons, Inc., New York, p. 302.

Lubs, H. A. 1972. The Chemistry of Synthetic Dyes and Pigments, Robert, E. Kroyer Publishing Co, New York, p. 520.

McGraw-Hill Encyclopedia of Chemistry. 1983. 1st ed., McGraw-Hill, Inc., New York, p. 276.

Meghmani Dyes and Intermediates Ltd.; Petroleum dyes,http://www.meghmanidyes.com/products/dyes/petroleum_dyes.html Accessed November 2011

Oparah, E. N. 2001. The Return of Natural Dyes. J. Chem. Soc. Nig., 26 (1) 87-90.

Petroleum Logistics Ltd.; Diesel and petrol dye. http://www.petroleumlogistics.com/petroleum.html; Accessed December, 2011.

Rostad, C. E. 2010. Analysis of solvent dyes in refined petroleum products by electrospray ionization mass spectrometry, Fuel, Volume 89, Issue 5, pp. 997-1005.

United Color Ltd.; Petroleum, http://www.unitedcolor.com/petroleum.html. Accessed December, 2011