A REVIEW OF OIL INSULATING FLUIDS AND RECENT DEVELOPMENT ON NATURAL ESTERS

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ABSTRACT
The significant use of petroleum-based product has hitherto been justified by its wide availability, good properties, good combination with cellulose and low-cost. However, with environmental issues now becoming extremely fundamental, the need for a product with a high fire point temperature and high biodegradability has become imperative. The discovery of natural ester fluids based on renewably sourced plants and vegetable oils have paved ways for the new insulating fluids for use in transformers and power equipments. The efficacy attributed to the various types of vegetation-based insulating fluids in many industrial situations have made them an indispensable ingredients of industrialization globally and development that has characterized the past century. This review presents a comparison of the fundamental thermal, insulating and coolant properties of mineral oil, synthetic esters and natural esters.

1. INTRODUCTION

The availability of vegetable oil and natural ester fluids derived from renewable sources have provided new insulating fluids for use with transformers and other power equipment. The poor biodegradation rates observable for the insulating fluids currently in use, has paved the way for the various methods of bioremediation currently being researched with the isolation of various microbe species with the ability to use up mineral oils as a carbon and energy source. Therefore, in the face of increasing demand for the use of environmentally friendly products in the industry, various institutions have been working to develop the use of vegetable oils in transformers and to extend its use to high voltage power transformers and reactors (Lea, 2005; Bertrand & Hoang, 2004).

The consumer and industrial interest in the development of eco-friendly materials have captured such environmentally benign agricultural resources as feedstock of the polymer industry. Polymers are obtained from renewable resources such as starch, protein, cellulose, wool, fibres and vegetable oils. They find innumerable industrial applications in lubricants, adhesives, biodegradable packing materials, printing inks, paints and coating. Vegetable oils are non-toxic, non–depletable domestically abundant, non-volatile and above all biodegradable resources. These abundant resources are capable of competing with fossil fuel derived petroleum based products, besides their other industrial applications, (Lu & Larock, 2009; Xia & Larock, 2010; Salimon, Salih & Yousif, 2012).

Plants and vegetable oils were used as the primary constituents in paint and coating even during the days of cave painting. Today, due to several environmental and health hazards cropping up from fossil fuel derived products, and fear of depletion of petroleum resources, material scientists and technologists have reverted to the extensive utilization of naturally abundant resources (Manawwar, Deewan, & Sharif, 2014).

In a liquid-filled transformer, the insulating fluids play significant roles by providing both the electrical insulation in combination with a solid such as cellulose and the means of transferring the thermal losses to the cooling system (Murphy & Weber, 2006). The insulating fluid can also provide important and easily obtainable information for use in diagnosing the condition of a transformer. To make the change from mineral oil to a natural ester, vegetable oil is an interesting challenge to address (Martin, Khan, Dai & Wang, 2006).

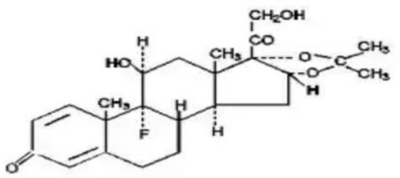
This paper begins with a correlation of the properties of insulating oils; mineral oil and ester oils. This is followed by a presentation of the technical and manufacturing issues theoretically connected to the use of natural esters. The paper concludes with a discussion on temperature rise tests carried out on transformers filled with either mineral oil or vegetable oil.

2. CORRELATION OF CHARACTERISTICS OF TRANSFORMER OILS

Transformers can be filled with three basic types of insulating fluids:

i. Mineral oils
ii. Synthetic esters or
iii. Natural esters

Mineral oil is a hydrocarbon mixture produced from the distillation of crude oil. Because of its wide availability, useful properties and low cost, mineral oil is the insulating liquid most commonly used in the transformer industry. Mineral oil is transparent and colorless made up of different types of hydrocarbons such as; straight chain alkanes, branched alkanes, and cyclic paraffins (Gary & Hardwek, 2001).

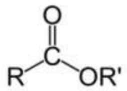


$C_{24}H_{31}FO_6$, MW 434.50

The two types of mineral oil mostly used as insulating oil for transformers are Paraffinic oil and Naphthenic oil. Paraffinic oil is derived from crude oil containing substantial quantities of naturally occurring n-paraffins. It has a relatively high pour point and may require the inclusion of additives to reduce the pour point. Naphthenic oil, on the other hand, is derived from crude oil containing a very low level (or none) of naturally occurring n-paraffins. It has a low pour point and requires no additives to reduce the pour point. Naphthenic oil provides better viscosity characteristics and longer life expectancy. Naphthenic oil has more polar characteristics than paraffinic oil. Transformer oils contain inhibitors which delay the oxidation of oil. These inhibitors might be natural, as occur in uninhibited mineral oils, or synthetic and added, as in inhibited oils (Gray, 2013).

2.1 Esters

The term ‘Ester’ comes from the chemical linkage which is formed from the reaction of an alcohol and a fatty acid.

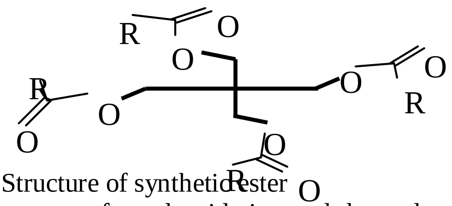


Structure of an Ester

Where O represents oxygen, C represents carbon, R and R’ represent carbon chains, which may be the same or different. The single line represents a single bond, and a double line represents a double bond. The C=O double bonds behave differently from the C=C double bonds found in the chains of natural esters. The ester linkage occurs in both natural and synthetic esters, but does not occur in mineral or silicone oils.

2.2 Synthetic ester fluid

Synthetic esters are derived from chemicals. They are usually the product of a polyol (a molecule with more than one alcohol functional group) with synthetic or natural carboxylic acids to give structures where several acid groups (usually 2, 3 or 4) are bonded to a central polyol structure, such as those made from the tetra-alcohol pentaerythritol $C_5H_{12}O_4$. Importantly, the acids used are usually saturated (no C-C double bonds) in the chain, giving the synthetic esters a very stable chemical structure.

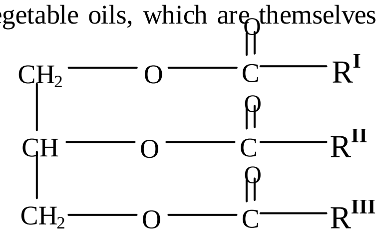


Structure of synthetic ester

Synthetic esters offer the advantage of good oxidation and thermal stability as well as good biodegradability. Thus synthetic esters are particularly appreciated in applications where fire resistance is important and spillage/environmental concerns are critical. New synthetic esters are produced in accordance with IEC 61099 and an in-service maintenance guide that is published as in IEC 61203 (Darwin, Perrier & Folliot, 2007).

2.3 Natural ester fluids

Natural esters are produced from vegetable oils, which are themselves manufactured from renewable (sustainable) plant crops.



Structure of natural ester

The structure of the natural esters is based on a glycerol backbone, to which 3 naturally occurring fatty acid groups are bonded. Again, these fatty acids may be the same or different. Plants produce these esters as part of their natural growth cycle. They are stored in the seeds, and can provide a valuable high calorific foodstuff when harvested. Natural esters offer the advantage of high fire point as well as good biodegradability, but all types of natural esters suffer from not being as oxidation stable as other types of insulating liquids (Rycroft, 2014).

2.4 Comparison of Viscosities

The viscosity of a fluid is one of the key parameters in determining the cooling capability of the fluid from the perspective of designing transformers. The following graphs show both the logarithmic and linear plot of viscosity versus temperature for the commonly used transformer fluids.

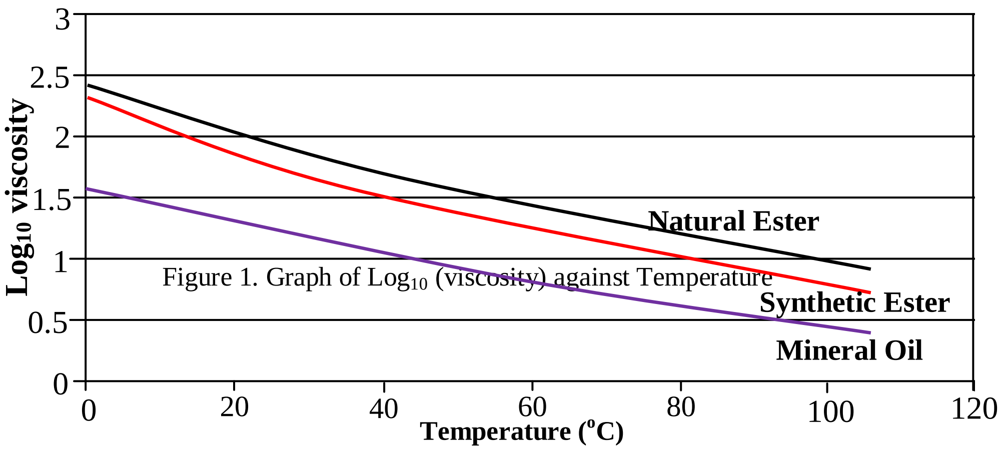


Figure 1. Graph of Log_{10} (viscosity) against Temperature

Note. From The Use of Natural Ester in Fluids in Transformers by Darwin, A., Perrier, C., & Folliot, P. (2007), MATPOST 07.

From the graph above, it can be seen that except the low viscosity silicone fluid, all the rest of above mentioned alternative fluids are more viscous than mineral oil over a wide temperature range; however the differences diminish with increasing temperature. Viscosity of fluids represents resistance to flow; since an insulating liquid also acts as the thermal coolant, a higher viscosity may slow the flow of fluid in the winding ducts, and increase the operating temperature of a transformer. The flow rate at nominal ratings is important as at temperatures of > 80^{o}C, cellulose degradation becomes an issue (Darwin, Perrier, & Folliot, 2007).

2.5 Comparison of moisture tolerance

Water is a very polar molecule and polar molecules tend to be most strongly attracted to other polar molecules. In this context the term 'polar' refers to regions of a substance which have different attractions, like the poles of a magnet. Mineral oil is not polar. The ester linkages present in both natural and synthetic esters make these fluids 'polar', and like tiny magnets, these linkages are able to attract water molecules in a way that mineral oil cannot.

2.6 Solubility of water in fluids

The water solubility of transformer fluids at room temperature is the total amount of moisture content which the fluid can hold without free water being deposited.

Table 1: Solubility of water in fluids

	Ester linkages	Approximate water saturation 23°C (ppm)
Mineral oil	0	55
Synthetic ester	4	2600
Natural ester	3	1100

Note. From Vegetable oil as insulating fluid for transformers by Rycroft, M. 2014, Energize, p. 39.

The solubility of water in all these fluids increases with temperature. The more polar esters are able to absorb more water across the temperature range 29, 30.

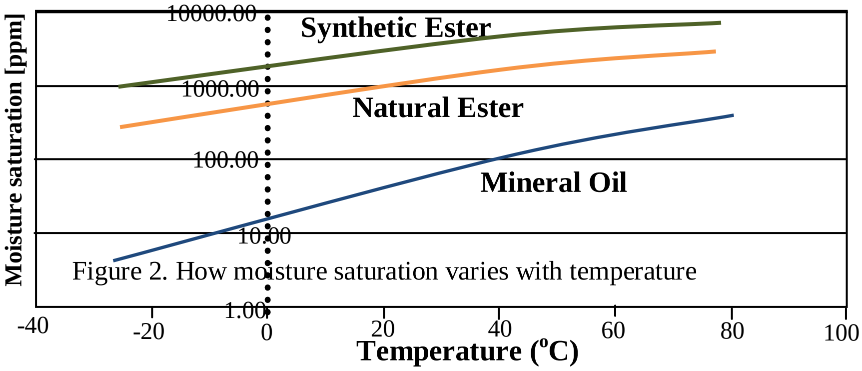


Figure 2. How moisture saturation varies with temperature

Note. From Understanding Water in Transformer Systems. by Lance, L. 2002. Neta World Report.

As well as representing the water content of dielectric fluids by absolute ppm values of dissolved water, it is also useful to represent the water content by relative percentage of water saturation. The relative water saturation, W_{rel} of a fluid at a specific temperature is given as a percentage by; $W_{rel} = \frac{W_{abs}}{W_{sat}} \times 100$. Where W_{abs} is the water content measured in ppm and W_{sat} is the water saturation limit at the temperature (Lance, 2002).

2.7 Biodegradability

The term 'biodegradability' reflects the extent which the fluid is metabolised by naturally occurring microbes in soil or water courses, in the event of a spillage or leak. Clearly it is an advantage if spilt fluids can quickly disappear naturally without the need to instigate expensive clean up measures.

To be classified as *readily biodegradable* a substance must satisfy both of the following criteria:

- 60% biodegradation must occur within 10 days of exceeding 10% degradation
- At least 60% degradation must occur by day 28 of the test (Situ, 2016)

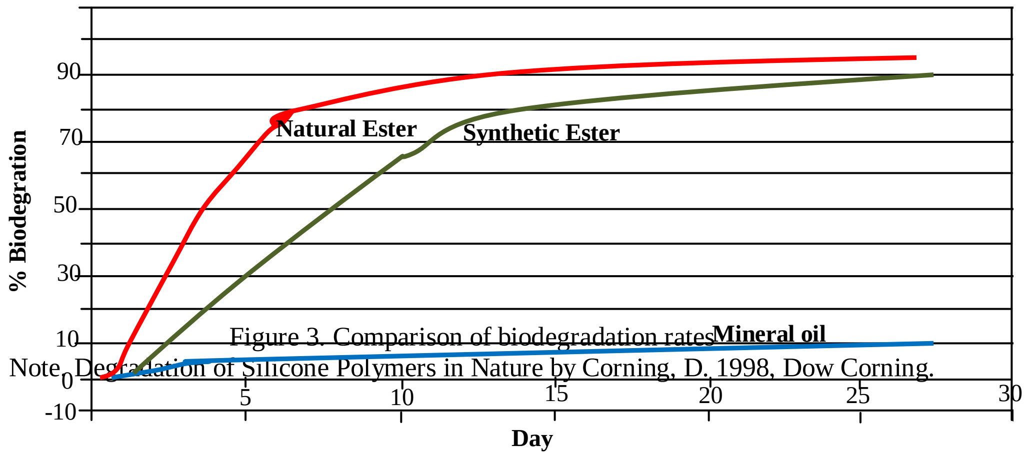


Figure 3. Comparison of biodegradation rates

Note. Degradation of Silicone Polymers in Nature by Corning, D. 1998, Dow Corning.

2.8 Comparison of Oxidation stability of alternative fluids

The oxidation stability of alternative fluids for transformers is a key concern to end users. The relative stabilities of fluid to oxidation are as follows:

Synthetic ester: Synthetic esters based on saturated acids and pentaerythritol oxidise only very slowly, at temperatures > 125°C, and darken as they do. Oxidation of synthetic esters does not produce sludge, but organic acids are produced.

Mineral oil: Mineral oil begins to volatilize and oxidize at temperatures above 105°C. Oxidation results in the formation of many degradation products, which include organic acids and sludge. These by-products may cause problems in a transformer by reducing the dielectric properties of the insulation and by corroding metals (Qian, Fu, & Zong, 2013).

Natural esters: Natural esters are the most susceptible to oxidation of the alternative fluids. In simple terms natural esters are susceptible to oxidation because of their chemical structure. They have a structure based upon a glycerol backbone to which is attached 3 fatty acid groups.

3. OPERATIONAL MECHANISM OF AN ANTI-OXIDANT

The word anti-oxidant is used in a general sense to refer to any type of chemical agent which inhibits or manifest attack by oxygen or ozone (Scott, 1965). As applied to insulating fluids, anti-oxidant are compounds which interrupt the oxidation process by preferentially reacting with the fast radical to form a stable radial which does not quickly react with oxygen (Eastman chemical company, 2007).

4. THERMAL STABILITY OF INSULATING OILS

According to Booser, (1984),"Thermal stability when used in reference to lubricating oils may be defined as the resistance posed by the lubricant to either molecular breakdown, or some form of re-arrangement at elevated temperatures in the absence of oxygen." It is a well observed fact that all oils will start to decompose even in the absence of oxygen when they are heated above a certain temperature. When heated mineral oils break down to yield basically methane, ethene and ethylene (Stachowiak & Bachelor, 2005).. The improvement of the thermal stability of mineral oils is achieved right from the refining process. It is known that Organonitrogen molecules are largely responsible for poor color and stability of base oils (Emmanuel & Mudiakeoghene, 2009). Therefore, the finishing process undertaken during refining must necessarily involve operations which are effective for removing organonitrogen molecules.

Thermal stability may not be improved via the means of additives, rather, usually additive used with lubricant base stocks have lower thermal stability than the base stocks themselves (Stachowiak and Bachelor, 2005) thermal stability is also dependent on the length of usage (Emmanuel & Mudiakeoghene, 2009). Synthetic and natural ester oils, in general exhibit better thermal stability than mineral oils (Stockwiak and Batchelor, 2005).

5. HEAT TRANSFER

Insulating fluids in transformer must ensure the transfer of heat. This function is realized both by thermal conductivity and convection. The convection represents all of the properties which lead to the heat transfer by fluid displacement (viscosity, specific heat, thermal expansion, co-efficient), whereas the conduction is realized within the fluid, because Kinematic viscosity is the most influential parameter for the heat transfer.

Table 2 - Thermal properties of insulating fluids

Properties	Mineral Oil	Synthetic Ester	Natural Ester
Viscosity at 40°C (mm^2/S)	9	30	42
Viscosity at 100°C (mm^2/S)	2.50	5.25	9.00
Density Viscosity at 25°C (kg/m^2)	0.88	0.97	0.91
Specific Heat at 25°C (J/kgK)	1860	1880	1963
Thermal Conductivity at 25°C (W/mk)	0.126	0.144	0.170
Thermal Expansion Coefficient (1/°C)	0.00075	0.00075	0.00068

Note. From measurement of selected thermal properties of insulating liquids used in the high voltagepower transformers by Dombek, G. & Nadolny, Z. 2011, Computer Applications in Electrical Engineering, p. 191

5.1 Comparison of Fire Safety Point

The classification of insulating liquids is based upon Fire Point & Net Calorific Value according to the standard IEC 61100.

Table 3: Fire classification of fluids

Class	Fire point	Class	Fire point
O	≤300°C	1	≥ 42MJ/kg
K	>300°C	2	≤ 42MJ/kg and ≥ 32MJ/kg
L	No measurable Fire Point	3	32MJ/kg

Note. From Vegetable oil as insulating fluid for transformers by Rycroft, M. 2014, Energize, p. 38. According to Roycroft (2014), from a fire safety aspect, the advantages of using the less flammable K class fluids are:

- Less costs for installation and maintenance safety equipment: "for electrotechnical equipment installed in areas of particular fire hazard (e.g. Buildings), less stringent measures are required in the case of less flammable liquids" IEC 60695-1-40 7.1
- No fire risk in event of major electrical fault; "even if spray ignites the resulting pool of liquid rapidly ceases to burn" IEC 60695-1-40 7.1
- Low density, non toxic smoke

Silicone fluids and both natural and synthetic esters can offer a high degree of fire safety, due to their low fire susceptibility.

Table 4 - Fire properties of fluids

Type	Flash point	Fire point	Class
Mineral oil	160-170	170-180	O
Synthetic ester	>250	>300	K3
Natural ester	>300	>350	K2

Note. From Vegetable oil as insulating fluid for transformers by Rycroft, M. 2014, Energize, p. 38.

In addition to the breakdown voltage (BDV) and the heat transfer characteristic, insulating fluids must have a good ageing stability. Oxygen which is present in the oil can also be ingested from the environment and constitutes one of the more influential factors; ageing the oil by oxidation. Temperature acts as catalyst as well as some metals such as copper. The ageing stability of oil, therefore, is even more important if the transformer is free breathing (Darwin, Perrier, & Folliot, 2007). Sulphur compounds are present in mineral oils and as natural inhibitors, but some synthetic inhibitors DBPC can be added to reduce the ageing process (Darwin, Perrier, & Folliot, (2007).

6. AUTO OXIDATION AND OXIDATIVE STABILITY IN VEGETABLE OILS

The main shortfall on the application of vegetable oils for industrial uses is in their natural forms, they lack sufficient oxidation stability. Oxidative stability of oil is a measure of the length of time taken for oxidative deterioration to occur (Ferrari, Oliviera, & Scabin, 2004).

On a general level, the rates of reactions in auto-oxidation schemes are dependent on the hydrocarbon structure, heteroatom speciation, oxygen concentration and temperature (Ferrari, Olivveira, & Scabin, 2004).

Oxidative rancidity in oils occurs when heat, metal or other catalysts cause unsaturated oil molecules to convert to free radicals. These free radicals can be easily oxidized to yield hydro peroxides as well as organic compounds such as aldehydes, ketones or acids which will give rise to the unwanted odors and flavors character of rancid (Eastman chemical company, 2001). Auto oxidation reactions are seen to progress more rapidly in oils that contain predominantly unsaturated fat molecules. Auto oxidation refers to a complex set of reaction which results in the incorporation of oxygen in lipid structures.

7. TECHNICAL AND MANUFACTURING ISSUES FOR POWER TRANSFORMERS

The insulating fluids oil-immersed transformers and reactors rely heavily on the oil to provide part of the insulation structure as well as allow the thermal losses to be cooled. Then, if these insulating fluids are to be changed, it is mandatory to authenticate its use with respect to both design and manufacture.

Dielectric issues:- The natural ester has a relative permittivity that is closer to the solid insulation used in oil-immersed transformers and reactors (such as paper and press board). This has several effects on the dielectric design (Darwin, Perrier, & Folliot, 2007).

The capacitances of the insulation structure change, causing different voltage distribution under transient condition such as impulse application (lightening strike). This change was not found to be significant. The distribution of voltage stress within the insulation structure also changes, such that for a given voltage distribution the voltage stress in the fluids was less for the natural ester than the mineral oil. This in no small measure allowed higher level withstand for certain electrode as well as insulation configuration (Darwin, Perrier, & Folliot, 2007).

As a matter of fact, much work was carried out to investigate the comparative voltage tolerance of the different fluids under various tests and service voltage condition such as power frequency and impulse application. This enabled the design of the windings and insulation structures to be carried out with full confidence. The ester-filled transformer and shunt reactor both successfully passed all their dielectric tests (Darwin, Perrier, & Folliot, 2007).

Thermal issues:- The esters have higher viscosity than mineral oil for the same temperature. This reduces the fluid flow rate for a give dynamic head causing a higher temperature difference between top and bottom of the cooling device in distribution size transformers (Girgis, Bernesjo, & Frimpong, 2010). This is significant for natural cooled transformers. Another important issue was the characteristic of a natural ester to “gel” with the exposure to air (especially if hot). Although this effect was not instantaneous and was found not to have a deleterious effect on the dielectric withstand capability. If the “gel” reduces the size of oil ducts, then the cooling could be put at risk. Therefore, for this reason, the “breathing” system of the transformer and reactors was effectively of a sealed type, using a nitrile rubber bag to isolate the ester from the atmosphere during operation (Darwin, Perrier, & Folliot, 2007).

- ⇨ Ester are similar to mineral oils with respect to the dielectric strength.
- ⇨ Ester oils are seen to be more viscous than mineral oils for a given temperature and are thus less efficient for the transfer of heat by convection. Different types of vegetable oil have different levels of viscosity effect.
- ⇨ Ester oils are less stable with respect to oxidation than mineral oil. However, depending on the type and the presence or lack of inhibitor, the oxidation behavior of vegetable oils can be very different.

8. CONCLUSION

Natural esters are more viscous than mineral oil or synthetic esters. This implies that at low temperatures they serve as poor coolant. This may result in the overheating of the components. However, at sufficiently high temperatures, the resistance to flow of the natural esters is greatly reduced. Since the operation of most machineries is accompanied by the release of heat, natural esters may therefore, be the coolant of choice where great heat is involved. This thus leaves a window for researches into additives that can cause a reduction of the viscosity of natural esters at low temperature without compromising their thermal, lubricating and insulating properties.

Because natural esters have poor oxidation staability, they require isolated environment (such as sealed transformers) for enhanced lifespan. Once in a sealed environment they can exhibit better dielectric properties than mineral oil or synthetic esters. However, further investigation is needed to find better oxidation inhibitors which could enable the natural esters to function optimally even in environments that are not sealed.

The review also showed that natural esters hold the highest amount of moisture content without water being deposited. This is followed by synthetic esters and then mineral oil. Furthermore, natural esters are the most biodegradable of all the insulating oils. Mineral oil based insulating fluids, although very dominant in industrialization have been fingered as the major source of both atmospheric and environmental pollution and degradation due to their unsustainable, contaminating and non-biodegradable nature. Hence, their continued patronages are currently described as indefensible. Increased environmental awareness has placed the blame for the continued release of harmful-non biodegradable components into the atmosphere on mineral oils. This is so because the compounds are not only toxic, they are also quite expensive to remedy. Thus the quest for an environmentally friendly alternative in the form of oils based primarily on plants and vegetable oils. The prospect is both fascinating an overdue and holds a lot of promise for Nigeria and the world at large.

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