

**INVESTIGATING RUBBER SEED OIL AS A POSSIBLE
SUBSTITUTE FOR LINSEED OIL IN PAINT PRODUCTION**

By

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(2006/24174EH)

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**A PROJECT SUBMITTED TO THE
DEPARTMENT OF CHEMICAL ENGINEERING,
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**IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF
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CERTIFICATION

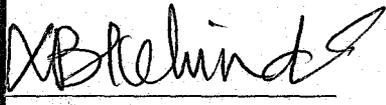
is to certify that this project report (thesis) entitled: "INVESTIGATION OF
BER SEED OIL AS A POSSIBLE SUBSTITUTE OF LINED OIL IN PAINT
DUCTION" by Chuku, Felicia Onyinyechi meets the requirements for the partial
ment of the award of Bachelor of Engineering (B. Eng) degree in Chemical
neering, Federal University of Technology, Minna.

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23/02/2012
Date

DEDICATION

I dedicate this book to the Almighty God for having sustained me generously all through years of study and to my parents who have been my backbone financially and morally.

ACKNOWLEDGEMENT

My gratitude to God who is the Alpha and Omega, the beginning and the end, for he has been with me right from the very beginning till the very end of my study, thank you Lord for your faithfulness. My special appreciation goes to my parents Rev. Dr. & Rev. Mrs. Godswill O. Chuku for their love, encouragement and their financial support. You have been the world best parents and this project would not have been a success without the both of you. To my understanding and loving siblings, I would never have come this far without you all. To Mr. Ossai Oputa, you have been a great inspiration to me. Also my thanks go to my ever-enduring supervisor Dr. D.O. Agbajelola; who helped me in choosing this topic which has broadened my knowledge, Mr. Maduka Ulu; who through his wealth of experience and knowledge provided useful information that made this project a success, the head of department of Chemical Engineering Dr. M.O. Edoga, Mr. Bulus, Engr. Abdullahi and all lecturers of the department for their support. Finally to all my friends, Miss. Okosun Edith and Mr. Ayodeji who has always been there for me and well wishers as well, God bless you all.

ABSTRACT

Rubber seeds used for this research were obtained in rubber research institute in Benin of Nigeria. The rubber seed oil was obtained by solvent extraction. The linseed oil was purchased commercially. The rubber seed oil obtained was investigated for physicochemical parameters and fatty acid composition. The result shows that for rubber seed oil: specific gravity (0.916), viscosity at 20 °C (43), pH (6.0). Others were free fatty acid (5.65 % oleic acid), acid value (11.3 mg/g), iodine value (147.20), saponification value (189.34 kg/g), and unsaponifiable matter (1.1 %). For linseed oil: specific gravity (0.927), refractive index (1.466), pH (5.6). Others were free fatty acid (3.82 % oleic acid), acid value (7.64 mg/g), iodine value (166.24), saponification value (160.72 kg/g) and unsaponifiable matter (0.5 %). The oil samples obtained are within acceptable standard. The yield of 41.87 % makes the commercialization of the seed in Nigeria possible and profitable. Also, the result of the analysis confirms rubber seed oil to be a semi- drying oil and of good quality and can find application in paint industry to replace imported linseed oil. The result of the gas chromatography analysis carried out shows that oleic acid is the most dominant constituent of the rubber seed oil examined with a value of 33.87 %.

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NOMENCLATURE

RSO – Rubber seed oil

ALA – alpha linolenic acid

NARICT – National research institute for chemical technology

linseed oil which is currently been imported, this will save foreign exchange for the country and thus enhance our goal of self reliant development.

Chapter Two

2.0 LITERATURE REVIEW

2.1 Botanical Source of Rubber Tree

The botanical or binomial name of rubber tree is *Hevea brasiliensis*. Rubber tree belongs to the family Euphorbiaceae and the most economically important member of the genus *Hevea*. The tree belongs to the sub family Crotonoidae and tribe Micrandreae. Its sub tribe is Heveinae.

2.2 History of Rubber Tree

Rubber is one of the most important products to come out of the rainforest. Though indigenous rainforest dwellers of South America have been using rubber for generations, it was not until 1839 that rubber had its first practical application in the industrial world. In that year, Charles Goodyear accidentally dropped rubber and sulphur on a hot stovetop causing it to char like leather yet remain plastic and elastic. Vulcanization, a refined version of this process, transformed the white sap from the bark of the *Hevea* tree into an essential product for the industrial age.

The Para rubber tree initially grew only in the Amazon rainforest. Increasing demand and discovery of the vulcanization procedure in 1839 led to the rubber boom in that region, enriching the cities of Belem and Manaus. The name of the tree is derived from Para, the second largest Brazilian state, whose capital is Belem.

The Brazilian rubber market was rushed by the rapid development of the more efficient rubber plantations of Southeast Asia. However, the prospects of developing plantations did not begin on a high note. Rubber seeds rich with oil and latex, could not survive the long Atlantic journey from Brazil.

The trees were used to obtain rubber by the Olmec people of Mesoamerica as early as 3600 years ago. The rubber was used, among other things, to make balls used in the Mesoamerican ballgame. There had been an attempt made in 1873 to grow rubber outside Brazil by Henry Wickham. After some effort, twelve seedlings were germinated at the royal botanic gardens, Kew. These were sent to India for cultivation but died. A second attempt was then made, some 7,000

seeds being smuggled to Kew in 1875, by Henry Wickham, at the service of the British Empire. About 4 % of these germinated and in 1876 about 2000 seedlings were sent, in wardian cases to Ceylon, and 22 sent to the botanic gardens in Singapore. Once established outside its native country, rubber was extensively propagated in the British colonies. Rubber trees were brought to the botanic gardens at Buitenzorg, Java in 1883. By 1898, a rubber plantation had been established in Malaya, and today most rubber tree plantations are in South and Southeast Asia and some also in the tropical West Africa (Encyclopedia Britannica, 2008).

The key findings from different publications on this research are thus stated below:

In India, Cant (1930) reported that oil is extracted from rubber seed by reducing them to powder in a crushing machine and then steam treating. The oil extracted at first smells of the solvent used but after treatment it is odorless and of bright color. He claimed that about 98.99 % of the oil present can be extracted by this process.

Work in India on rubber seed by Dow (1936) reported that rubber seed has an oil yield of 37.5 % of good oil and the characterization of the oil showed that rubber seed oil has physicochemical properties similar to those of linseed oil.

Hilditch *et al.*, (1951) showed the characteristics of rubber seed oil and the percentage of component fatty acids for six samples, two from Ceylon, two from Nigeria, one from Malaya and one from Siam. They concluded that with the exception of the Nigerian oil, which was more unsaturated than the rest, the rubber seed oil showed less variation in composition than candlenut oils which were also examined.

Work in Ceylon, Malaya and Japan have given generally similar results for the composition of the oil indicated its use as insecticides (CMRI, 1950) for alkyd resin manufacture (RRIM, 1975) and the production of artificial leather.

Some of the rubber seeds from which oil was to be extracted were analyzed for HCN content. The analysis for the undefatted cake was carried out by the alkaline picrate method of Gilchrest (1967) as modified by Ikediobi *et al.*, (1980). Also the effect of drying on the HCN contents of the rubber seed was investigated. Twenty gram samples of freshly decorticated kernels were used in four

replicates and dried overnight (15 hours) at the following temperatures; 105 °C, 80 °C, 60 °C, 40 °C and fresh seed (no drying). Thereafter, the samples were extracted with 0.1 M HCl and analyzed for HCN content.

Investigations were initiated with a paint industry in Malaysia (Anon, 1975) to use rubber seed oil for the manufacture of alkyd resins. The required oil meeting the specification of less than 0.3 % FFA, iodine value greater than 130 and percentage unsaponifiables of less than 1.5 was produced for the alkyd preparation. The use of the oil in 25/75 blend with linseed oil indicated promise for manufacturing alkyd resins. Also the rubber seed oil when appropriately treated could be used for the manufacture of adhesives, artificial leather, impregnating compositions for textiles and other materials.

Amantharaman and Carpenter (1969) analyzed the amino acid and composition of the oil seed, along with essential amino acid patterns for high quality protein that meets human requirements as established by the American Food and Nutrition Board (FNB). Some of these amino acids include lysine, ammonia, aspartic acid and glycine.

Ogun (1991) defined unsaturated fatty acids as those more difficult to isolate and study because of their instability. When two adjoining carbon atoms in the hydrogen chain of fatty acid each lacks hydrogen atom, the arrangement of an unsaturated fatty acid depresses the melting point and this decrease the hydrophobic character of the hydrogen chain. Because of the ability of unsaturated fatty acid to dry and act as drying agent (for example, linseed oil), they are of more value and importance than saturated fatty acids.

According to Loncin *et al.*, (1965) the solubility of water in rubber seed oil which increases in FFA content and rise in temperature was measured and shown against in neutral and virtually neutral oils. Water, which is dispersed, is very fine droplet rather than being in physical solution in oil does not directly affect the rate of hydrolysis. However, it is important to try to maintain the concentration of dissolved water if that is depleted for any reason. The action is autocatalytic in the sense that the rate of hydrolysis at any moment depends on the concentration of FFA present. Loncin then proposes that up to about 10 % FFA with the reaction having the form;

$$\frac{\delta a}{\delta t} = k \times a$$

2.1

Where: a = % FFA produced,

t = number of 10 days period

k = factor depending upon temperature and which at 60 °C is taken as 0.125.

The factor approximately doubles for each rise of 10 °C. The investigation by Loncin and others in the field is worth describing as they can be applied to large measures to other oils.

Uzu (1986) accounted for storage as a means of reducing the HCN content of rubber seed, since the seed contained some enzymes. He also stated that any treatment which inhibited FFA rise would also inhibit HCN production. Since according to him, toasting at 85 °C was shown or known to deactivate the enzymes and hence inhibit FFA production, the inhibition of HCN production was not surprising.

Adefarati (1980) stated that rubber seed oil is a semi-drying oil and has non yellowing properties which are characteristics of air drying oils. He analyzed that the yellowing and non yellowing properties were determined by the chemical composition of the oils. He said that oils with higher percentage of drying acids tended to show yellowing characteristics and exemplified this by linoleic acid which, he said, increased yellowing properties in oil. In this research, he attributed the differences observed that the differences in the characterization of the oil to the various methods of seed collection, oil extraction and purification as well as other treatments.

Fashina (1989) considered competitor from food sector as the greatest threat to the industrial use of rubber seed oil. He however, recognized that its use as cooking oil had not yet been approved.

Okaisabor (1980) explained that the oil which was sent to Nycil Nigeria limited was extracted mechanically by heating and pressing, a process which he said, charred the oil. The use of this method, he further explained, was because n-hexane which was usually employed in the solvent extraction process ran out of stock in the country at the time the oil was required. As a result of the chemical analysis, properties, and therefore, the range of products that can be made from

rubber seed oil, it is the most important item in the processing and analysis of seed. Recent analysis shows that rubber seed oil contains the following fatty acids:

Table 2.1: Fatty Composition of Rubber Seed Oil

Fatty acid	Nomenclature	Percent
Palmitic	C16:0	10.2
Stearic	C18:0	8.7%
Oleic	C18:1	24.6%
Linoleic	C18:2	39.6%
Linolenic	C18:3	13.2%

Source: Prashant *et al.*, (2008)

2.3 Linseed Oil

Linseed oil, also known as flax seed oil, is a clear to yellowish oil obtained from the dried ripe seeds of the flax plant (*Linum usitatissimum*, Linaceae). The oil is obtained by cold pressing, sometimes followed by solvent extraction. Linseed oil is a "drying oil", as it can polymerize into a solid form. Due to its polymer-forming properties, linseed oil is used on its own or blended with other oils, resins, and solvents as an impregnator and varnish in wood finishing, as a pigment binder in oil paints, as a plasticizer and hardener in putty and in the manufacture of linoleum. The use of linseed oil has declined over the past several decades with the increased use of synthetic alkyd resins, which are functionally similar but resist yellowing. It is edible oil but, because of its strong flavor and odor, is only a minor constituent of human nutrition in the U.S., although it is marketed as a nutritional supplement. In parts of Europe, it is traditionally eaten with potatoes and quark (cheese). It is regarded as a delicacy due to its hearty taste, which spices the bland quark (Vereshagin *et al.*, 1965).

2.4 Chemical Aspects of Linseed Oil

Linseed oil is a triglyceride, like other fats. Linseed oil is distinctive in terms of fatty acid constituents of the triglyceride, which contain an unusually large amount of α -linolenic acid, which has a distinctive reaction toward oxygen in air. Specifically, the constituent fatty acids in a typical linseed oil are of the following types:

- The triply unsaturated α -linolenic acid (51.9-55.2 %),
- The saturated acids palmitic acid (about 7 %) and stearic acid (3.4-4.6 %),
- The monounsaturated oleic acid (18.5-22.6 %)
- The doubly unsaturated linoleic acid (14.2-17 %).

Having a high content of di and triunsaturated esters, linseed oil is particularly susceptible to polymerization reactions upon exposure to oxygen in air. This polymerization, which is called "drying," results in the rigidity of the material. The drying process can be so exothermic as to pose a fire hazard under certain circumstances. To prevent premature drying, linseed oil-based products (oil paints, putty) should be stored in air-tight containers (Vereshagin et al., 1965).

2.5 Uses of Linseed Oil

Most applications of linseed oil exploit its drying properties, i.e. the initial material is liquid or at least pliable and the aged material is rigid but not brittle. The water-repelling (hydrophobic) nature of the resulting hydrocarbon-based material is advantageous.

2.5.1 Paint binder

Linseed oil is a common carrier used in oil paint. It can also be used as a painting medium, making oil paints more fluid, transparent and glossy. It is available in varieties such as cold pressed, alkali refined, sun bleached, sun thickened, and polymerized (stand oil). The introduction of linseed oil was a significant advance in the technology of oil painting.

2.5.2 Putty

Traditional glazing putty, consisting of a paste of chalk powder and linseed oil, is a sealant for glass windows that hardens within a few weeks of application and can then be painted over. The utility of putty is owed to the drying properties of linseed oil (Bently, 1997).

2.5.3 Wood finish

When used as a wood finish, linseed oil dries slowly and shrinks little upon hardening. Linseed oil does not cover the surface as varnish does, but soaks into the (visible and microscopic) pores, leaving a shiny but not glossy surface that shows off the grain of the wood. A linseed oil finish is easily repaired, but it provides no significant barrier against scratching. Only wax finishes are less protective. Liquid water will penetrate a linseed oil finish in mere minutes and water vapour bypasses it almost completely. Garden furniture treated with linseed oil may develop mildew. Oiled wood may be yellowish and is likely to darken with age. Linseed oil is a traditional finish for gun stocks. A very fine finish may require months to obtain. Several coats of linseed oil are the traditional protective coating for the raw willow wood of cricket bats. Linseed oil is also often used by billiards or pool cue-makers for cue shafts, as a lubricant/protectant for wooden recorders, and used in place of epoxy to seal modern wooden surfboards. Additionally, a luthier may use linseed oil when reconditioning a guitar, mandolin, or other stringed instrument's fret board; lemon-scented mineral oil is commonly used for cleaning, then a light amount of linseed oil (or other drying oil) is applied to protect it from grime that might otherwise result in accelerated deterioration of the wood (Bently, 1997).

2.5.4 Linoleum

Linseed oil is used to bind wood dust, cork particles, and related materials in the manufacture of the floor covering linoleum. After its invention in 1860 by Frederick Walton, linoleum, or "lino" for short, was a common form of domestic and industrial floor covering from the 1870s until its virtual replacement by PVC floor coverings. Linoleum has given its name to the printmaking technique linocut, in which a relief design is cut into the smooth surface and then inked and used to print an image. The results are similar to those obtained by woodcut printing.

2.5.5 Cricket bats

Linseed oil is used to coat cricket bats so that the wood will retain some moisture. New cricket bats are coated with linseed oil and knocked to perfection so they last longer (Bently, 1997).

2.5.6 Nutritional supplement and food

Although flax seeds contain lignans, a class of phytoestrogens considered to have antioxidant and cancer-preventing properties, the extracted linseed oil does not contain the lignans found in flax seed, and therefore does not have the same antioxidant properties. Some brands of supplement have lignans added during production. Flax seed oil is easily oxidized, and rapidly becomes rancid, with an unpleasant odor, unless refrigerated. Even when kept under cool conditions, it has a shelf life of only a few weeks. Oil with an unpleasant or rancid odor should be discarded. Oxidation of flax seed oil is major commercial concern, and antioxidants may be added to prevent rancidity. At least the ALA in flaxseed oil is suitable for cooking, however, as it (and the lignans in flax seeds themselves) can withstand temperatures up to 350 °F for 2 hours. Food-grade flaxseed oil is cold-pressed, obtained without solvent extraction, and marketed as edible flaxseed oil. Fresh, refrigerated and unprocessed, linseed oil is used as a nutritional supplement and is a traditional European ethnic food, highly regarded for its hearty taste. It contains the highest level of the omega-3 fatty acid alpha linolenic acid (ALA) among vegetable oils. Regular flaxseed oil contains between 52 % and 63 % ALA (C18:3n-3). Plant breeders have developed flaxseed with both higher ALA (70 %) and very low ALA content (< 3 %) (Thompson et al., 2003).

Table 2.2: Fatty Acid Content of Various Oils and Fats (in percentage)

Fatty acid content	Linseed oil	Soybean	Cotton
Palmitic acid	6.5	8.3	22.9
Stearic acid	4.5	5.4	5.4
Oleic acid	20.9	24.9	24.9
Linoleic acid	17.4	52.7	49.7
Alpha linolenic acid	50.6	7.9	-

Source: J.Lewkowitsch (chemical technology and analysis of oils, fats and waxes).

2.6 Drying Oil

A drying oil is oil that hardens to a tough, solid film after a period of exposure to air. The oil hardens through a chemical reaction in which the components crosslink by the action of oxygen (not through the evaporation of water or other solvents). Drying oils are a key component of oil paint and some varnishes. Some commonly used drying oils include linseed (flax seed) oil, Tung oil, poppy seed oil, perilla oil, and walnut oil. Their use has declined over the past several decades as they are replaced by alkyd resins and other binders. Oils that are susceptible to drying are also susceptible to becoming rancid autoxidation, the process by which fatty foods develop off-flavors.

2.6.1 Constitution of drying oils

Representative triglyceride found in a drying oil is shown in Figure 1.0. The triester is derived from three different unsaturated fatty acids, alpha-linoleic (top), linolenic (middle), and oleic acids (bottom). The order of drying rate is linolenic > linoleic > oleic acid, reflecting their degree of unsaturation (Vereshagin et al., 1965).

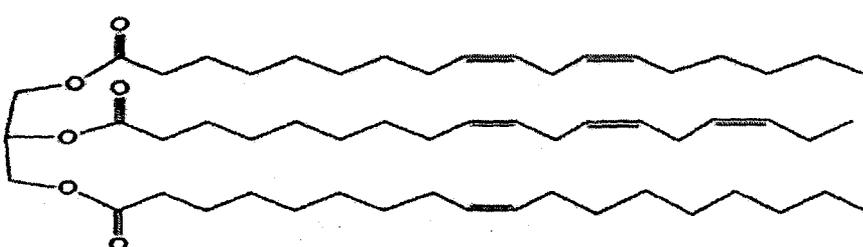


Figure 2.1: Structure of constituents of unsaturated fatty acid in drying oil.

The saturated and unsaturated fatty acid constitutions of drying oils are as shown below:

- Glycerol
- Palmitic acid (C16)
- Oleic acid (C18:1)
- Linolenic acid (C18:3)
- Triacylglycerol with C18:2- C18:2- C18:3 fatty acid moieties

Drying oils consist of glycerol triesters of fatty acids. These esters are characterized by high levels of polyunsaturated fatty acids, especially alpha-linolenic acid. One common measure to classify the "siccative" (drying) property of oils is based on the iodine number, which is an indicator of the number of double bonds in the oil. Oils with an iodine number greater than 140 are considered drying, those with an iodine number of 124-140 are semi-drying, and those with an iodine number of less than 125 are non-drying.

Table 2.3: Some Constant Values for Drying Oils

Oil	Specific gravity (25°C)	Iodine value	Saponification value	Acid value	Refractive index
Linseed	0.926-0.930	173-201	192-195	2.5	1.476-1.479
Soybean	0.920	135	190	3.0	1.478
Tung	0.915	170	192	0.2	1.517
Perilla	0.926	195	190	2.0	1.480

Sources: Gallagher (2008), J. Lewkowitsch (Chemical technology and analysis of oils and fats and waxes)

2.7 Paint

2.7.1 History of Paint

Cave paintings drawn with red or yellow ochre, hematite, manganese oxide, and charcoal may have been made by early Homo sapiens as long as 40,000 years ago. Ancient colored walls at Dendera, Egypt, which were exposed for years to the elements, still possess their brilliant color, as vivid as when they were painted about 2,000 years ago. The Egyptians mixed their colors with a gummy substance, and applied them separate from each other without any blending or mixture. They appeared to have used six colors: white, black, blue, red, yellow, and green. They first covered the area entirely with white then traced the design in black, leaving out the lights of the ground color. They used minimum for red, and generally for a dark tinge. Pliny mentions some

painted ceilings in his day in the town of Ardea, which had been done prior to the foundation of Rome. He expresses great surprise and admiration at their freshness, after the lapse of so many centuries. Paint was made with the yolk of eggs and therefore, the substance would harden and stick onto the surface it is applied to. Pigments were made from plants, sands, and different soil types (Berendsen, 1989).

2.8 Components of Paint

2.8.1 Pigments

Pigments are granular solids incorporated into the paint to contribute color, toughness, texture, give the paint some special properties or simply to reduce the cost of the paint. Alternatively, some paints contain dyes instead of or in combination with pigments. Pigments can be classified as either natural or synthetic types. Natural pigments include various clays, calcium carbonate, mica, silica, and talc. Synthetics would include engineered molecules, calcined clays, blanc fixe, precipitated calcium carbonate, and synthetic pyrogenic silica. Hiding pigments, in making paint opaque, also protect the substrate from the harmful effects of ultraviolet light. Hiding pigments include titanium dioxide, phthalo blue, red iron oxide, and many others (Berendsen, 1989).

2.8.2 Binder, vehicle, or resins

The binder, commonly referred to as the vehicle, is the actual film forming component of paint. It is the only component that must be present, components like solvent and additives are included optionally, depending on the desired properties of the cured film. The binder imparts adhesion, binds the pigments together, and strongly influences such properties as gloss potential, exterior durability, flexibility, and toughness. Binders include synthetic or natural resins such as oil, epoxy, cement, alkyds, acrylics, vinyl-acrylics, vinyl acetate/ethylene (VAE), polyurethanes, polyesters, melamine resins (Berendsen, 1989).

2.9 Application of Drying Oil in Paint

Drying oil is both the binder and the vehicle that are used in oil painting. Each particle of pigment must be thoroughly coated with oil to protect it from reacting chemically with other pigment

particle, to allow proper dispersion of pigment particles for luminosity and to provide a workable and durable paint film.

2.10 Extraction

2.10.1 Factors affecting the rate of extraction

2.10.1.1 Particle size

The smaller the size of the particle, the greater the interfacial area between the solid and the liquid, thus leading to a higher rate of transfer of material.

2.10.1.2 The solvent

This should be a good selective solvent and its viscosity should be sufficiently low for it to circulate freely. It should also be of high stability, low evaporation loss, low corrosion and low greasy residue.

2.10.1.3 The temperature

Solubility increases with temperature to give a higher rate of extraction. Further, the diffusion coefficient increases with rise in temperature and this will enhance the rate of extraction.

2.10.1.4 Handling of materials

Appropriate handling of the rubber seed will determine to a great extent the quality and yield of the oil produced.

2.10.1.5 Storage of rubber seeds

There are two dominant cost factors in storing commodities. First, there is the cost of physically storing the material; this includes warehousing, protection against special risks of damage and insurance. The second big factor is the interest payable with capital tied up in the stock. Management cost may easily be insignificant large variations in storage costs are to be expected according to the vulnerability of the seed to spoilage, the risk of pilferage and the relation of value of bulk. The location of the store and different point of the world introduces climatic conditions as

a factor. It becomes crucial importance to decide what is the maximum periods in particular conditions that the rubber seed may be held in store without the need to rotate the stock so as to preserve its condition and hence avoid loss of commercial value (Akinshipo, 2002).

2.10.1.6 Seed reduction

This facilitates the extraction of oil, but as the structure and degree of fineness of the seed meal directly influence the oil yield obtained, the method of reduction used, and the size of particle produced must be selected to suit the physical character of the particular seed and the process by which oil will be extracted. Grinding or rolling reduces the seed, in order to rupture a large proportion of the cellular membrane, and present thinner sections for the subsequent extraction operations (Akinshipo, 2002).

2.7 Industrial Application of Rubber Seed

Rubber seed oil resembles linseed oil in its physico-chemical properties. The suitability of various oils as drying oils for the manufacture of paint could be assessed based on the proportions of linoleic (diene acids) and linolenic (triene acids) acids present (Uzu et al., 1986). Available evidence indicates that oils containing triene acids (e.g. glycerol ethers) such as linseed, Tung, and perrila oils are yellowing oils, while oils containing diene acids such as rubber seeds, tobacco and soya oils are non-yellowing oils. Although both classes are drying oils, the non-yellowing oils have superior properties for manufacture of alkyd resins. A screening of the oils numerated above reveals that rubber seed, tobacco and conophor oils could be wholly or partially substituted for linseed and soybean oils as drying oils for manufacture of paint. Studies on practical utilization of rubber seed oil revealed that it has strong potential to substitute linseed oil in paint production. Generally, rubber seed oil was used in soap making. Gandhi et al (1990) reported that the rubber seed oil does not contain any unusual fatty acids and it was a rich source of essential fatty acids. The oil has found uses in soap, alkyd resin and lubricating oil industries (Uzu et al., 1986).

2.7.1 Rubber seed oil for paint manufacture

A drying oil suitable for replacement of linseed oil in paints should contain mixed fatty acids with not less than 70 % of polyethenoid (linolenic + linoleic) acids, of which linolenic acid should

form at least 50 % of the total fatty acids of the oil. Rubber seed oil has about 36 % of linoleic acid and 24 % of linolenic acid. A mixture of one part of rubber seed oil and three parts of linseed oil has been reported to give a film, which is equal or only slightly inferior to linseed oil itself. A mixture of one part of rubber seed oil and three parts of linseed oil would have 79 % of polyethenoid (linolenic + linoleic) acids of which linolenic acid is about 48 %. Thus a promising outlet for rubber seed oil is its use as a diluent or extender for linseed oil. The drying properties of rubber seed oil could be improved by treating with maleic anhydride. Since maleic anhydride has two carbonyl positions in α position in the double bond, it takes part in diene synthesis with conjugated compounds. Maleic anhydride also adds easily to compounds containing isolated double bonds at α methylene positions. The maleinisation of unsaturated oil is a very simple process. Refined rubber seed oil is mixed with 2 to 10 % of maleic anhydride and heated in a closed kettle for 2 hours at 230 °C. The progress of the reaction may be followed by extracting a sample with hot water and titrating to determine the unreacted maleic anhydride. Alternatively, the disappearance of all the maleic anhydride is indicated when a sample no longer gives a reddish yellow colour with dimethyl aniline. The product contains an anhydride group with latent acidic properties. In general, if the treated oil is to be used as a binder, this acidity is neutralized by reaction with an alcohol such as glycerol or pentaerythritol. It is estimated that 16 % of maleic anhydride produced is used in alkyd resins and in drying oil. The function of the binder in paint is to bind together the pigment particles and to hold them on to the surface. If the pigment is left out, the binder covers and protects the gloss. Binder in paint is a polymeric substance or a pre-polymer which polymerizes into a two dimensional polymeric net work at the surface after applications. Rubber seed oil is suitable as binder for paints. The binder is either dissolved in a solvent or dispersed in the form of emulsion in the liquid phase. The presence of the rubber seed oil gives to the synthetic polyesters obtained in this way, the property of "drying" in the air; that means they transform to an insoluble film as a result of polymerization processes in the unsaturated fatty acid chains. Hence, this oil can be used in the production of paint and lacquers. The outdoor durability, quick drying, inherent flexibility and water resistance of alkyd resins make them ideally suited for many surface coating applications such as high grade architectural enamels, primers and undercoats; interior and exterior enamels, marine paints, house paints; industrial finishes, baking

enamels, automotive finishes, plasticizers for nitrocellulose, high temperature baking white enamels in combination with urea formaldehyde resins and emulsion paints. Alkyds cannot be used successfully where resistance to alkali or other strong chemicals is required. Since alkyd resins are essentially esterification products, alkalis will cause saponification, with resultant disintegration of the film. The evaluation of alkyd resins in emulsion paints has been carried out by McLean (1954). He concluded that they yielded paints of superior adhesion and washability although there was some evidence that washability decreased with storage. The time for drying was longer than with synthetic resin emulsion paints, the brushes could not be cleaned with water since the emulsions broke and solvents had to be used and the whites were just off colour. The drying properties of rubber seed oil can be regarded as being intermediate between those of soybean and linseed oil (Gandhi et al., 1990).

Chapter Three

3.0 METHODOLOGY

3.1 Sample Collection

Rubber seed samples were obtained from Rubber Research Institute of Nigeria, Benin, Edo State, Nigeria. Linseed oil was obtained commercially from a market in Aba, Abia State.

3.2 Equipment and Material

3.2.1 Equipment

Table 3.1: List of Equipment

S/no	Equipment	Sources	Comment
1.	Oven	Waft lab	Gallenkamp
2.	Beaker	Waft lab	Glassware
3.	Conical flask	Waft lab	Glassware
4.	Pipette	Waft lab	Glassware
5.	Soxhlet extractor	Waft lab	Glassware
6.	Gas chromatography machine	NARICT lab	Gallenkamp
7.	Weighing machine	Waft lab	Ambassadors

3.2.2 Materials

Table 3.2: List of Materials

S/No	Materials	Sources	Comment
1.	Rubber seed	Rubber research Institute, Benin.	Raw material
2.	Linseed oil	Commercial market, Aba.	Raw material
3.	n-Hexane	Waft lab	Analytical grade chemical
4.	Sodium thiosulphate	Waft lab	Analytical grade chemical
5.	Sodium hydroxide	Waft lab	Analytical grade chemical
6.	Hydrochloric acid	Waft lab	Analytical grade chemical

3.3 Extraction and Experimental Process

3.3.1 Oil extraction process

In performing the extraction of oil from the seed under observation in this research, the rubber seed samples were prepared by cracking the outer seed kernel in order to remove the seed. The seeds were then dried under direct sunlight for about one week. After drying, the sample was milled into flour using a mechanical grinder. The flour sample was then stored in a clean dry polyethylene bag till its use.

5 g of the flour rubber seed sample were accurately weighed in a filter paper and placed in the center of the extractor. 200 ml of hexane was poured into a round bottom flask. The Soxhlet was heated at 60 °C. When the solvent was boiling the vapour rose through the vertical tube into the condenser at the top. The liquid condensate dripped into the filter paper thimble in the Centre which contained the solid sample to be extracted. The extract seeped through the pores of the thimble and filled the down into the round bottom flask. This was allowed to continue for 60

minutes. It was then removed from the tube, dried in the oven at 90 °C for fifteen minutes, cooled and weighed again to determine the amount of oil extracted. Further extraction was carried out at 60 minutes interval until the sample weight at further extraction and previous weight became equal. The weight of oil extracted was determined for each 60 minute interval for a total time of 7 hours. At the end of the extraction, the resulting mixture containing the oil was heated to recover the solvent from the oil. The oil sample was later filtered and heated (AOAC, 1990).

3.3.2 Determination of the percentage oil extracted

5 g of the sample (rubber seed) was placed in the thimble and about 200 ml of hexane was poured into the round bottom flask. The apparatus was heated at 60 °C and allowed for 6 hours for continuous extraction using Soxhlet apparatus. The experiment was repeated for different particle size of the sample. The percentage yield was then calculated as,

$$\text{Percentage yield} = \frac{\text{Total wt. of oil extracted}}{\text{wt. of sample(g)}} \times 100$$

3.1

3.4 Characterization of Rubber and Linseed Oil

3.4.1 Determination of acid value or free fatty acid

Acid value of an oil or fat is defined as the number of milligram potassium hydroxide required to neutralize the free acid in one gram of the sample. The acid value measures the extent to which the glycerides in the oil have been decomposed by lipase action.

Materials:

1. 1 % phenolphthalein in 25 % ethanol
 - a. 25 % = 25 ml of absolute ethanol diluted to 100 ml with distilled water
 - b. 1 % phenolphthalein = 1 g of phenolphthalein was dissolved in 25 % ethanol and filled up to 100 ml with 25 % ethanol.

2. 0.1 M NaOH (5.6 g NaOH in one litre of distilled water)
3. Neutral solvent: 25 ml diethyl ether plus 25 ml of 95 % ethanol and 1 ml of 1 % phenolphthalein solution neutralized with 0.1 M alkali (NaOH).

Procedure:

1. 3 g of the oil was mixed with 25 ml of the neutral solvent in a 250 ml conical flask
2. 4 drops of phenolphthalein was added to the mixture in the conical flask in (1) above.
3. The content in the conical flask was titrated against 0.1 M NaOH shaking constantly until a pink color which persists for fifteen seconds was obtained.

NB: If the volume of 0.1 M sodium hydroxide (NaOH) required for the titration is less than 2 ml, a more diluent titrant may be used or the sample size adjusted accordingly. The result may be expressed in terms of the volume of titrant used or in terms of the equivalent volume of 0.1 M sodium hydroxide (NaOH).

Calculation:

$$\text{Acid value (mg/KOH/g)} = \frac{\text{Titre value} \times 0.1 \text{ M KOH} \times 56.10}{\text{weight of sample (g)}} \quad 3.2$$

- Where: Titre Value (V) = ml of sodium hydroxide used
- 0.1 M = Molarity of the alkali used
- 56.10 = Milligram equivalent weight of the alkali
- W = Weight of sample used.

The FFA figure is usually calculated as oleic acid in which case the value = 2 × FFA.

3.4.2 Determination of Iodine Value

Iodine value measure the degree of unsaturation in oil. The glycerides of the unsaturated fatty acids present (more specifically as oleic acid series) with a definite amount of halogen and the iodine value is therefore a measure of the extent of unsaturation. The iodine value is mostly used

for identification of oil or to assign a particular group to the oil. The common method for determining Iodine value is Wijis' Method.

Preparation of Wijis' solution:

- i. 8 g of iodine trichloride was dissolved in 200 ml glacial acetic acid
- ii. 9 g of iodine was dissolved in 300 ml carbon tetrachloride
- iii. The two solutions in (i) and (ii) were mixed and diluted to 100 ml with glacial acetic acid.

Procedure:

- i. 0.25 ml of oil sample was measured and poured in a 250 ml dry glass-stoppered bottle (Iodine flask).
- ii. 10 ml of carbon tetrachloride was added to the oil and dissolved.
- iii. 20 ml of Wiji's solution was added to the mixture and the stopper which was previously moistened with potassium iodine solution inserted. The flask was then allowed to stand in the dark for 30 minutes.
- iv. 15 ml of potassium iodide solution (10 %) was added and mixed with 100 ml of water. The mixture or solution was then titrated with 0.1 M thiosulphate solution using starch as indicator just before the endpoint. (titration = a ml)
- v. A blank test was carried out at same time commencing with 10 ml of Carbon tetrachloride (Titration = b ml)

Calculation: The value of Iodine is determined from the expression:

$$\text{Iodine value} = \frac{(b-a) \times 1.269}{\text{wt. (g) of sample}}$$

3.3

Where; a = Titre value of sample

b = Titre value of the blank

Note: It is noted that if $(b - a)$ is greater than $b/2$, then the test must be repeated using a smaller amount of sample.

3.4.3 Determination of Saponification value

Saponification value of fat or oil or oil can be defined as the number of milligrams of potassium hydroxide required to neutralize the fatty acids resulting from the complete hydrolysis of 1 g of the sample. Saponification value actually does not give a better identification index when compared with iodine value. This value is useful for comparative study of the fatty acid chain length in oil or fat.

Procedure:

- i. 2 g of the oil was weighed into a conical flask and exactly 25 ml of alcoholic potassium hydroxide solution added.
- ii. A reflux condenser was attached and the flask heated in boiling water for one hour while shaken frequently.
- iii. 1 ml of phenolphthalein (1 %) solution was added and the hot excess alkali titrated with 0.5 M hydrochloric acid until the pink colour just disappears (Titration = a ml).
- iv. A blank test was carried out at the same time (Titration = b ml).

Note:

- i. Do not allow alcohol to dry up during saponification
- ii. Clarity and homogeneity of the test sample indicate complete saponification.

Calculation: The saponification value is determined by this expression:

$$\text{Saponification Value} = \frac{(b - a) \times 0.5 \times 56.10}{\text{wt. (g) of sample}} \times 100$$

3.4

Where: b = blank titre value

a = sample titre value

0.5 = molarity of HCl = Molarity of KOH

56.10 = Molecular Mass of KOH

3.4.4 Determination of unsaponifiable matter

This is defined as the material left behind in oil and fat which after saponification of the oil or fat by caustic alkali and extraction by suitable solvent remains non-volatile on drying at 80 °C. Most oils and fats of normal purity contain less than 2 % of unsaponifiable matter.

Procedure: To determine the unsaponifiable matter:

- i. After the titration of the saponification value, the neutralized liquid alkaline was prepared with 1 ml of aqueous 3 M potassium hydroxide solution.
- ii. The content in the conical flask (after titration) was then transferred to a separator and the flask, washed with water (50 ml less the volume of 0.5 M HCl acid used).
- iii. The solution was extracted while still warm 3 times with 50 ml of quantities of diethyl ether. The solution is each poured into another separator containing 20 ml of water.
- iv. The ether extract was washed twice with 20 ml of aqueous 0.5 M potassium hydroxide solution and twice with 20 ml quantity of water until the wash water was no longer alkaline to phenolphthalein.
- v. The ether extract was then poured into a pre-weighed flask and the solvent evaporated.
- vi. The residue was dried at 80 °C and then weighed to constant weight.

Calculation: The value of Unsaponifiable matter is calculated by the expression:

$$\text{Unsaponifiable matter} = \frac{(W_2 - W_1)}{W} \times 100$$

3.5

Where W_2 = weight of residue + beaker

W = weight of sample

W₁ = weight of beaker

3.4.5 Determination of pH Value

pH is a measure of the acidity or basicity of a solution. A solution with a pH less than 7.0 is said to be acidic and solutions with a pH greater than 7.0 are basic or alkaline. A solution with the pH value of 7.0 is said to be neutral.

Procedure:

- i. 10 % W/V suspension of the sample was prepared in distilled water.
- ii. It was then mixed thoroughly by stirring with a magnetic stirrer and the pH measured with a good pH meter.

3.4.6 Determination of Viscosity

This is simply the measure of the thickness of oil and its ability to flow at certain temperatures. Generally, thicker the oil, the higher its viscosity and vice versa.

Procedure: The viscosity of the oil was determined by:

- i. 10 ml of oil was dissolved in distilled water and then the mixture stirred for 2 hours at room temperature.
- ii. The viscosity was measured using Oswald type viscometer.

3.4.7 Determination of Specific gravity

Specific gravity determination is based on the ratio of the weight of a liquid or fluid to that of an equal volume of water.

Procedure:

- i. A pycnometer bottle was thoroughly washed with detergent, water and petroleum ether. It was then dried and weighed.
- ii. The bottle was filled with water and weighed.
- iii. After step (ii) above, the bottle was dried, filled with the oil sample and weighed.

Calculation: The specific gravity is determined by:

$$\text{Specific gravity} = \frac{\text{Weight of Xml of oil}}{\text{Weight of Xml of water}} \quad 3.6$$

3.4.8 Determination of refractive Index

The refractive index of a transparent medium is defined as the relationship of the vacuum velocity of light and the velocity of light within said medium. It can also be defined as the measure of the bending or refraction of a beam of light on entering a denser medium. It is used as a measure of the purity of oil.

Procedure:

- i. The Abbe's refractometer was reset with a light compensator (water at 20 °C).
- ii. The oil sample was smeared on the lower prism of the instrument and closed.
- iii. A light was then passed by means of the angled mirror and the reflected light appears in a form of a dark background.
- iv. By the use of the fine adjustment, the telescope tube was moved until the black shadow appears central in the cross wire indicator.
- v. The refractive index was read and then noted.

3.4.9 Determination of Smoke point

The smoke points of fatty materials are measures of its thermal stability. The smoke point is the temperature which smoking is first detected in a laboratory apparatus protected from drafts and provided with special illumination.

Procedure:

- i. 10 ml volume of the oil was poured into an evaporating dish.
- ii. A thermometer was then suspended at the Centre of the dish ensuring that the bulb just dips inside the oil without touching the bottom of the dish.
- iii. The temperature of the oil was gradually raised using an electric stove.
- iv. The temperature at which the oil sample gives off a thin bluish smoke continuously was noted as the smoke point.

3.4.10 Determination of peroxide value

Peroxide Value of oil is a measure of its content of oxygen. Fresh oils usually have peroxide values below 10 mEq/Kg. A rancid taste begins to show up when the peroxide value is between 20 and 40 mEq/Kg.

Preparation of reagent:

- i. Solvent mixture: 2 volume of glacial ethanoic acid was mixed with one volume of chloroform
- ii. 5 % KI solution
- iii. 1 % starch solution
- iv. 0.002 M $\text{Na}_2\text{S}_2\text{O}_3$

Procedure:

- i. 1 g of the oil sample was weighed into a clean dry boiling tube and 1 g of powdered potassium iodide and 20 ml of solvent mixture added.

- ii. The tube was placed in boiling water so that the liquid boils within 30 seconds and allowed to boil vigorously for not more than 30 seconds.
- iii. The contents in (ii) above were quickly poured into a flask containing 20 ml of potassium iodide solution (5 %).
- iv. The tube was washed out twice with 25 ml of water collecting into the conical flask each time.
- v. It was then titrated with 0.002 M Sodium thiosulphate solution using starch until the blue colour disappeared.
- vi. A blank test was performed at the same time.

Calculation: The peroxide value is calculated by this expression:

$$\text{Peroxide value} = \frac{T \times M \times 1000}{\text{weight of sample}} \quad 3.7$$

Where T= Titre value of sodium thiosulphate solution

M= Molarity of Na_2SO_3

3.4.11 Determination of Ester value

Ester is the number of mg of potassium hydroxide required to saponify the esters in 1.0 g of the substance. It is the difference of the saponification value and the acid value.

Calculation:

$$\text{Ester value} = \text{Saponification value} - \text{Acid value} \quad 3.8$$

3.5 Fatty Acid composition determination

Chromatographic system: The gas chromatograph is equipped with a flame ionization detector, maintained at a temperature of about 260 °C, a splitless injection system and a 0.53 mm 30 m

fused silica capillary column bonded with a 1.0 μm layer of phase G16. The chromatograph is programmed to maintain the column temperature at 70 $^{\circ}\text{C}$ for about 2 minute after injection, then to increase the temperature at the rate of 5 per minute to 240 $^{\circ}\text{C}$ and finally to maintain this temperature at the rate of 5 per minute to 240 $^{\circ}\text{C}$ and finally to maintain this temperature for 5 minutes. The injection port temperature is maintained at about 220 $^{\circ}\text{C}$. The carrier gas used is helium with a linear velocity of about 50 cm per second.

Procedure:

- i. 1 μl of the test solution was injected into the chromatograph.
- ii. The chromatographs were recorded and the fatty acid ester peaks in the chromatograph of the test solution identified by comparing the retention times of these peaks with those obtained in the chromatograph of the standard solution.
- iii. The peak areas for all the fatty acid ester peaks in the chromatograph obtained from the test solution were calculated.
- iv. The percentage of each fatty acid component in the test specimen was calculated.

Calculation: The fatty acid component percentage is determined by the expression;

$$\% \text{ fatty acid component} = 100 (A/B) \qquad 3.9$$

Where: A = area of the peak response obtained

B= sum of the peak areas of all of the peak

Chapter Four

4.0 RESULT AND DISCUSSION

4.1 Result

The results obtained in the extraction varying particle size and extraction time are shown below:

Table 4.1: Percentage Oil Yield of Rubber Seed with Particle Size Variation.

S/No.	Particle size (mm)	Weight of paper (g)	Weight of sample (g)	Amount of oil extracted (g)	Oil yield (%)
1.	1.16	0.953	5.00	2.089	41.78
2.	1.36	0.874	5.00	1.977	39.54
3.	2.36	0.874	5.00	1.794	35.88
4.	3.36	0.898	5.00	1.643	32.86

Table 4.2: Percentage Oil Yield of Rubber Seed with Time Variation.

S/No.	Time (min)	Weight of paper (g)	Weight of sample (g)	Weight of paper +sample afterextraction(g)	Oil yield (%)
1.	60.0	0.948	5.0	5.062	17.72
2.	120.0	0.898	5.0	4.684	24.28
3.	180.0	0.953	5.0	4.432	30.42
4.	240.0	0.874	5.0	4.170	34.08
5.	300.0	0.932	5.0	4.009	38.46
6.	360.0	0.874	5.0	3.897	39.54
7.	420.0	0.953	5.0	3.864	41.78

The result obtained from the characterization of rubber seed oil and linseed oil is shown in the table below:

Table 4.3: Experimental Result of Physicochemical Properties of Rubber and Linseed Oil

Parameter	Rubber seed oil	Linseed oil	Standard value drying oil
Colour	Dark brown	Light yellow	-
Viscosity (20°C)	43	28	24-29
Smoke point	92°C	87°C	-
Refractive index	1.470	1.466	1.476-1.480
Specific gravity	0.916	0.927	0.926-0.930
Iodine value	147.204	166.239	135-190
Peroxide value	13.4	4.2	-
Saponification value (Kg/g)	189.34	160.72	190-195
Unsaponifiable matter (%)	1.1	0.5	0-1.5
FFA (% Oleic acid)	5.65	3.82	-
Acid Value (Mg/g)	11.3	7.64	2.0-3.0
pH	6.0	5.6	-

Table 4.4a: Result of the GCMS Analysis

Peaks	Retention time (min)	Height of peaks (cm)	Half base (min)	Area of peak	Molecular weight	Molecular formula
1.	15.70	4.55	0.01	0.045	256	C ₁₆ H ₃₂ O ₂
2.	17.40	7.00	0.10	0.42	282	C ₁₈ H ₃₄ O ₂
3.	17.60	3.00	0.02	0.06	284	C ₁₈ H ₃₆ O ₂
4.	18.70	0.90	0.20	0.18	239	C ₃₅ H ₆₈ O ₅
5.	20.10	2.20	0.15	0.33	281	C ₁₈ H ₃₁ ClO
6.	20.30	1.00	0.20	0.20	297	C ₃₉ H ₇₆ O ₅

Table 4.4b: Result of Rubber Seed Oil Gas Chromatography Mass Spectrometry Analysis

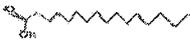
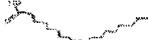
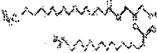
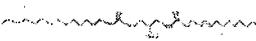
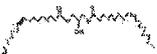
Peaks	Compound name	Iupac name	Molecular structure
1.	Palmitic acid	n- Hexadecanoic acid	
2.	Oleic acid	9-octadecanoic acid	
3.	Stearic acid	Octadecanoic acid	
4.	Glycerol-1,2-dipalmitate	Hexadecanoic acid	
5.	Linoleic acid	9,12- octadecadionic acid	
6.	2-hydroxy-1,3-propanediyl ester	Octadecanoic acid	

Table 4.5: Shows the Fatty Acid Percentage Composition in Rubber Seed Oil

Fatty acid constituent	Percentage composition (%)
Palmitic acid	3.63
Oleic acid	33.87
Stearic acid	4.84
Glycerol-1,2-dipalmitate	14.57
Linoleic acid	26.61
2-hydroxy-1,3-propanediyl ester	16.13
Σ Saturated fatty acid	8.47
Σ Unsaturated fatty acid	91.18

4.2 Discussion of Results

4.2.1 Extraction

In extracting the oil from rubber seed, particle size and extraction time was varied to determine the percentage yield of oil. The method of solvent extraction was used and hexane used as the solvent because of its high stability and its use leads to improved quality (Akinshipo, 2002).

Table 4.1 shows the effect of particle size on oil yield for the rubber seed sample. It is observed that the percentage yield of the sample decrease with increase in particle size. The highest oil yield for the sample was obtained at the smallest particle size of 1.16 mm while the lowest oil yield was obtained at the highest particle size of 3.36 mm. By decreasing the particle size from 3.36 > 2.36 > 1.36 > 1.16 mm, the oil yield percentage was increased from 32.86 < 35.88 < 39.54 < 41.78 % respectively for each different particle size.

The result in Table 4.1 shows that less oil is extracted from the larger particle compared to the smaller sized particles. This phenomenon could be attributed to the fact that smaller particles have larger amount of surface area as well as increased number of ruptured cells resulting in a high oil concentration at the particle surface area (Ebewele *et al.*, 2010). This shows that the amount of oil available for extraction is proportional to the surface area of the particle.

The results in Table 4.2 show the effect of time in the oil yield of rubber seed. As time is varied, the oil yield also varies. Therefore, as the time of extraction is increased, the oil yield of the sample increases. The rubber seed sample was left in the Soxhlet extractor for 7 hours and the weight of oil obtained taken at an interval of 60 minutes. The highest oil yield of 41.78 % obtained after 7 hours, while after 1 hour, the lowest oil yield of 17.72 % was obtained.

4.2.2 Physicochemical properties of Rubber seed oil and Linseed oil

The result in Table 4.3 shows the values of the physicochemical properties of rubber seed oil and linseed oil. Both physical and chemical characteristics of the oil under study were as good as those of commercial vegetable oil. The specific gravity of 1.470 obtained in this experiment for rubber seed oil is comparable with the specific gravity (1.466) of linseed oil and other vegetables

such as soyabean and sunflower reported in literatures (Goli et al.,2008). The pH value of 6.0 and 5.6 obtained for rubber seed and linseed oil respectively shows that both oils are acidic in nature. The iodine value of 147.204 is indicative of high contents of unsaturated fatty acids in the rubber seed oil and is comparable to that of linseed oil in Table 4.3. The iodine value is useful in predicting the drying property of oils and the high value of rubber seed oil suggests that it has drying property, a useful characteristic required in paint production. The acid value of 11.3 mg/g obtained for rubber seed oil is higher than the linseed oil experimental value of 7.64 mg/g. Oil of lower acid value decreases the drying rate of paint. The rubber seed oil acid value is higher than that of linseed oil. This can affect the rate of drying. Therefore, to reduce the rate of drying, the oil can be heated further to decrease the acid value. The saponification value obtained for linseed oil is lower than the standard of 190 -195 kg/g while that of rubberseed oil falls nearly the standard with a value of 189.34 kg/g. The high saponification value of both oils suggests their high potential for use in the production of soap and shampoos (Ku and Mun, 2007). Both oils showed a low level of unsaponifiable matter of 1.1 % and 0.5 % for rubber seed oil and linseed oil respectively. The peroxide value of 13.4 obtained for rubber seed oil compared to a value of 4.2 obtained for linseed oil. Peroxide value is used as an indicator of the level of deterioration of vegetable oils. Fresh oils have lower peroxide values and higher values indicate high level of rancidity (Dawodu, 2009). Peroxide value depends on a number of factors (Oluba et al., 2008) such as exposure to air, the method of extraction and type of fatty acid in the oil. The observed high peroxide value for rubber seed oil may be attributed to the heat during extraction as heat favors the oxidation of fatty acids. A high viscosity of 43 was obtained as a value for rubber seed oil compared to the lower value of 28 observed for linseed oil. The effect of the viscosity of oil in paint depends on the type of paint and the flexibility of the paint been produced. If the thickness of the oil is not favorable, a solvent can be added to decrease its resistance to flow.

4.2.3 Fatty acid composition of rubber seed oil

The above result in Table 4.4a shows the retention time at which each of the molecular weights were obtained. In the gas chromatography database, the compounds with the molecular weight were obtained with the molecular structures. Oleic acid with the retention time of 17.40 minutes

and peak height of 7.0 cm is shown to be the most dominant fatty acid in the oil. The result also shows that the rubber seed oil analyzed consists of saturated fatty acid (palmitic and stearic acid). The unsaturated acid in rubber seed oil obtained in the result is oleic acid, linoleic acid and glyceryl ester. The predominant fatty acid in the studied oil consist of monounsaturated (33.87 %) followed by linoleic acid (26.61 %) and saturated fatty acid (8.47 %). Monounsaturations of rubber seed oil are high (33.87 %). The major fatty acids in rubber seed oil were the oleic, linolenic, linoleic, palmitic acid and stearic fatty acid. Oleic acid showed the highest percentage composition of 33.87 %, followed by linoleic acid of 26.61 %. Rubber seed oil can be classified as oleic-linoleic oil.

Chapter Five

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Rubber seed is popular particularly in south east, Benin. The result of this investigation greatly reveals the potentials of rubber seed oil in the production of paint as a result of the properties obtained.

From the results obtained in the extraction of rubber seed oil, it can be safely concluded that the particle size and extraction time affects the amount of oil extracted. The higher the particle size, the lower the amount of oil extracted and vice versa. In the case of extraction time, as the extraction time increases, the weight of oil extracted increases and finally remains constant. Therefore, from the result, the extraction of rubber seed is best carried out with the optimum efficiency using a small particle size to allow the solvent (hexane) penetrate the wall of the seed easily.

From the results obtained in the characterization of the rubber seed oil, the result shows a great similarity to the results obtained in the characterization of linseed oil. The most important characteristic of oil in the production of paint is the Iodine value. From the characterization carried out, the following can be inferred:

- The iodine value of the rubber seed oil is comparably similar to the iodine value of linseed oil.
- The rubber seed oil has a high value of iodine value which means that it has a high degree of unsaturation making it useful in the production of paint as a result of its drying property.

The fatty acid composition analysis of the rubber seed oil showed that it has a high monounsaturated and polyunsaturated fatty acid. It also shows that the rubber seed oil is oleic-linoleic oil because it contains about 33.87 % oleic acid and 26.61 % linoleic acid.

Conclusively, with the result obtained in this investigation, the high yield of rubber seed oil (41.87 %) and its identification as oil of high unsaturated fatty acid of above 75 % which oleic acid is the most predominant constituent. It can be safely concluded that rubber seed oil can be used as a substitute for linseed oil in paint production.

5.2 Recommendation

Finally, because of the importance of this seed in industrial application in Nigeria, more research should be carried out on ways to improve rubber seed oil. Therefore, it is recommended that:

- Further research should be carried out to focus on ways to improve rubber seed oil.
- Development of rubber seed should be studied further in order to develop this local source of drying oil for its use in paint production and other industrial application.
- Rubber seed oil should be used to replace or substitute for edible oil in industrial application in order to reduce the high demand on edible oil.

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APPENDIX

Extraction of Oil Sample (Rubber Seed Oil)

A. Percentage Yield

$$\text{Percentage weight} = \frac{\text{Total wt. of oil extracted}}{\text{wt. of sample(g)}} \times 100$$

$$= \frac{2.089}{5.0} \times 100$$

$$= 41.78 \%$$

Characterization of Oil Samples

B. Saponification Value

$$\text{Saponification Value} = \frac{(b-a)}{\text{wt. (g) of sample}} \times 100$$

Where: a = Titre value of sample

b = Titre Value of blank titration

For rubber seed oil

$$a = 18.44$$

$$b = 29.90$$

Weight of sample = 2.0 g

$$\text{S.V.} = \frac{(29.90 - 18.44) \times 28.05}{2.0}$$

$$= 160.73$$

For linseed oil

$$a = 16.40$$

$$b = 29.90$$

Weight of sample = 2.0 g

$$\text{S.V.} = \frac{(29.90 - 16.40) \times 28.05}{2.0}$$

$$= 189.34$$

C. Iodine Value

$$\text{Iodine value} = \frac{(b-a) \times 1.269}{\text{wt. (g) of sample}}$$

Where: a = Titre value of sample

b = Titre value of blank titration

For rubber seed oil

Weight of sample = 0.1 g

a = 8.9 ml

b = 20.60 ml

$$\begin{aligned} \text{I.V.} &= \frac{(20.60 - 8.9) \times 1.269}{0.1} \\ &= 147.45 \end{aligned}$$

For linseed oil

Weight of sample = 0.1 g

a = 7.48 ml

b = 20.60 ml

$$\begin{aligned} \text{I.V.} &= \frac{(20.60 - 7.48) \times 1.269}{0.1} \\ &= 166.24 \end{aligned}$$

D. Free Fatty Acid (Acid Value)

$$\text{Acid Value} = \frac{T \times 0.1 \times 56.10}{\text{wt. (g) of sample used}}$$

Where: T = titre value (ml)

For linseed oil

Weight of sample = 3.0 g

Titre value of sample = 2.04 ml

$$\begin{aligned} \text{FFA} &= \frac{(2.04 \times 0.1 \times 56.1)}{3.0} \\ &= 3.82 \end{aligned}$$

$$\text{Acid value} = 2 \times 3.82$$

$$= 7.64$$

For rubber seed oil

$$\text{Weight of sample} = 3.0 \text{ g}$$

$$\text{Titre value of sample} = 3.02 \text{ ml}$$

$$\text{FFA} = \frac{(3.02 \times 0.1 \times 56.1)}{3.0}$$

$$= 5.65$$

$$\text{Acid value} = 2 \times 5.65$$

$$= 11.3$$

E. Unsaponifiable matter

$$\text{Unsaponifiable matter} = \frac{(W_2 - W_1)}{W} \times 100$$

Where W_2 = weight of residue + beaker

W = weight of sample

W_1 = weight of beaker

For linseed oil

$$W = 2.0 \text{ g}$$

$$W_1 = 23.11$$

$$W_2 = 23.12$$

$$\text{Unsaponifiable matter} = \frac{(23.12 - 23.11)}{2} \times 100$$

$$= 0.5 \%$$

For rubber seed oil

$$W = 2.0 \text{ g}$$

$$W_1 = 23.11$$

$$W_2 = 23.133$$

$$\text{Unsaponifiable matter} = \frac{(23.133 - 23.11)}{2.0} \times 100$$

$$= 1.1 \%$$

F. Specific Gravity

$$\text{Specific gravity} = \frac{\text{Weight of Xml of oil}}{\text{Weight of Xml of water}}$$

Where: Weight of empty bottle = W

Weight of bottle + water = W_1

Weight of bottle + oil = W_2

For linseed oil

$$W = 25.17$$

$$W_1 = 75.50$$

$$W_2 = 71.25$$

$$\text{Specific gravity} = \frac{71.25 - 25.17}{75.50 - 25.17}$$

$$= 0.9155$$

For rubber seed oil

$$W = 25.17$$

$$W_1 = 75.50$$

$$W_2 = 71.30$$

$$\text{Specific Gravity} = \frac{71.30 - 25.17}{75.50 - 25.17}$$

$$= 0.9165$$

G. Fatty Acid Composition

$$\% \text{ Component} = \frac{\text{area of peak}}{\text{total area of all peaks}}$$

Where total area = 1.035

For peak 1:

Area of peak 1 = 0.045 min

Total area = 1.035

Therefore,

$$\begin{aligned} \% \text{ Component} &= \frac{0.045}{1.235} \times 100 \\ &= 3.64 \% \end{aligned}$$