COMPARATIVE STUDY ON THE PERFORMANCE CHARACTERISTICS OF RUBBER SEED OIL ALKYD RESIN AND COMMERCIAL RESIN

BY

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B.SC. (HONS.) CHEMISTRY

DEPARTMENT OF CHEMISTRY

FACULTY OF PHYSICAL SCIENCES

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JULY, 2021

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CERTIFICATION

We the undersigned certify that this project work was carried out by **IFINEDO, Prosper Oluchukwu,** in the Department of Chemistry, Faculty of Physical Science, University of Benin in partial fulfillment of the requirement of the degree of Bachelor of Science (B.Sc.) in Chemistry.

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Head of Department

DEDICATION

I dedicate this work to God Almighty who has kept me through the process of carrying out this research work and also keeping me through my stay in School and also to my lovely parents Mr. and Mrs. IFINEDO for their never ending love, support and prayers to me. I LOVE YOU MUM AND DAD.

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I would like to express my profound gratitude to the Lord Almighty who has kept me thus far and given me the strength to complete my undergraduate program.

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My profound gratitude and respect to my loving and sweet parent Mr and Mrs. IFINEDO for their sacrifice and struggle they went through, understanding, loving, and financially supporting me during the course of my studying in the UNIVERSITY OF BENIN and also my wonderful siblings, Joy, Favour, Goodness and Dominion and my baby brother, Emmanuel for their love and support.

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Lastly, to class 2020 of the Department of Chemistry, thank u all, I will miss you all. To the members of ECWA Student Ministry and Omega Fire Ministries Ugbowo branch. Thank you so much.

ABSTRACT

Alkyd resins are products of poly condensation reaction between polybasic acid and polyhydric alcohol modified with fatty acid or drying oil. Oil modified alkyd resins are used as binders in surface coatings. It is estimated that alkyd resins contribute about 70% to the conventional binders used in surface coatings today. Rubber seed oil is a renewable raw material. Rubber seeds were collected from Rubber Research Institute of Nigeria (RRIN), Iyanomo, Benin city and its oil was extracted by soxhlet extraction process. The oil obtained was used in the preparation and synthesis of alkyd resin. Monoglycerides were obtained from alcoholysis process where RSO was reacted with glycerol at very high temperature in presence of a catalyst. The resulting mixture was then reacted with phthalic anhydride of which xylene was introduced in the reaction acting as an azeotropic solvent in order to obtain the water of condensation. Rubber seed oil (RSO) and rubber seed oil alkyd resin (RSOAR) were characterized by the determination of physico-chemical properties. The values for RSO and RSOAR were found to be; Specific gravity 0.906 and 0.940, Density 0.903 and 0.937 (kg/m^3), Acid value 11.42 and 7.54 (mg KOH/g), Peroxide value 1.85 and 1.49 (meq/kg), Iodine value 130.36 and 83.23 ($gI_2/100g$), Saponification value 186.88 and 210.62 (mgKOH/g) respectively. The performance characteristics of RSO was studied in terms of set to touch, surface dry and dry through and resistance to chemicals and compared with commercial resin. The results revealed that alkyd resin formulated by RSO dried faster than that of commercial resin and also had high resistance to water, salt and sulphuric acid solutions.

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LIST OF ABBREVIATION

SV	Saponification value
IV	Iodine value
AV	Acid value
FFA	Free Fatty Acid
SG	Specific gravity
RSO	Rubber Seed Oil
RSOAR	Rubber Seed Oil Alkyd Resin
CPAR	Commercially Prepared Alkyd Resin

CHAPTER ONE

INTRODUCTION

1.0 INTRODUCTION

An industrial resin is a synthetic polymer which has adhesive, film-forming or useful reactive properties (Malti, 1978; Sibban, 2009). Many of such polymers, which include unsaturated polyester resins, emulsion polymers, amino resins for surface coatings, polyurethane resins, polyamide-epichlorohydrin resins, formaldehyde resins, and alkyd resins, are made commercially. Unsaturated polyester resins are formed from the reaction of a diol (a molecule containing several hydroxyl groups) and an unsaturated diprotic acid. The resulting polyester chains are dissolved in a reactive solvent which crosslink to form a hard and strong resin used in making the hulls of boats and synthetic marble. .Emulsion polymers are emulsions of monomers in water. As the water evaporates, the monomers polymerise to form a thermosetting film. These are widely used as adhesives (e.g. poly(vinyl alcohol)) and in water-based paints. Amino resins for surface coatings are formed when molecules containing amino groups are reacted with formaldehyde. Their primary use is as a cross linking agent and as such they are used in paints in conjunction with other polymers such as alkyds. Polyurethane resins result from the reaction of a polyalcohol and an organic di isocyanate. They can be used as surface coatings, to make furniture and footwear and in foam form, for packaging.

In a study done by (Saunders, 1973, 1988; Malti, 1978; Sibban, 2009), it was reported that Polyamide-epichlorohydrin resins are formed in two steps. The first step involves a reaction between polyfunctional amine and a diprotic acid to form a polyaminoamide resin. This is then crosslinked with an epichlorohydrin monomer. The resultant resin is used to coat paper fibres, increasing the strength of the wet paper from less than 2% to around 30% of its dry strength. Formaldehyde resins are made by reacting formaldehyde with any of a variety of substances such as urea and phenol. The reagents are mixed to form a thermosetting crosslinked polymer used in reconstituted wood (e.g. plywood) and timber adhesives.

An alkyd is polyester modified by the addition of fatty acids and other components. It is derived from polyols and a dicarboxylic acid or carboxylic acid anhydride. The term alkyd is a modification of the original name "alcid", reflecting the fact that they are derived from alcohol and organic acids (Jones, 2007). (Malti, 1978), defined an alkyd as the reaction product of an oil or fatty acid, polyol and polyacid such that the inclusion of the fatty acid confers a tendency to form flexible coating.

(Ikhuoria *et al.*, 2004), descried alkyd resins as product gotten from the poly condensation reaction between poly-basic acids and poly-hydric alcohols modified with fatty acid or drying oils. Oil modified alkyd resins constitute a major group of resins used as binders in surface coating. It is estimated that alkyd resins contribute about 70% to the conventional binders used in surface coating today. The popularity of the alkyd resins as a vehicle for coatings is largely due to other gloss retention, resistance to abrasion etc. Impacted on them through modification with drying oils. (Ikhouria *et al.,* 2004).

Alkyd resins are used in many solvent-based paint systems and are a type of polyester made from polyols, acids and vegetable oils. They are the dominant resin or "binder" in most commercial "oil-based" coatings. The original alkyds were compounds of glycerol and phthalic acid sold under the name Glyptal. The reaction can be represented in Figure 1.1 as follows:

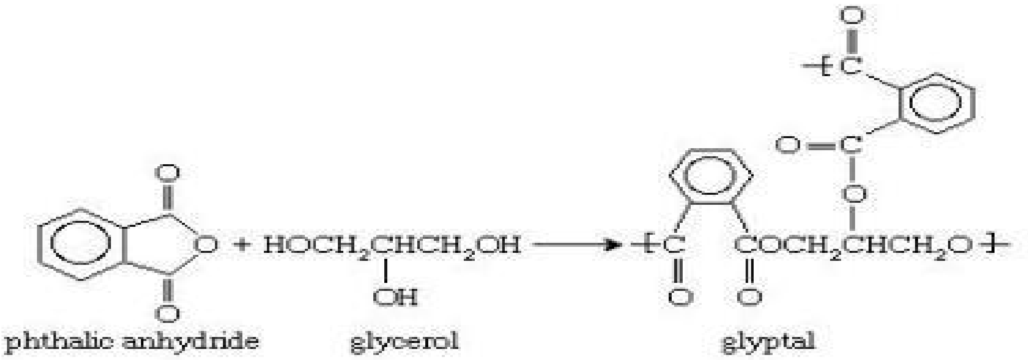

Figure 1.1: Synthesis of glyptal (Malti, 1978)

In the surface coating industries, oil-modified polyesters or alkyds dominates as the most widely used solventborne binder (Bognar *et al.,* 1991). (Anthawale *et al.,* 2000), in his study describes these low molecular weight esters which are products of polycondensation reaction of polyol, diacid, and mono-acid (oils or fats) as very flexible and versatile and are been found to be com-patible with other polymer systems. Also, attempt on waterborne alkyd, which is as a result of current trends in the industry to meet up with environmental regulation and government legislature has been successful according to several report (Aigbodion *et al.,* 2003a, 2003b; Makarewick, 1996).

According to (Mukhtar *et al.,* 2007), alkyd resins have acquired a good reputation because of their economy, availability of raw materials and ease of application. They are to a greater extent biologically degradable polymers because of the oil and glycerol parts and they are eco-friendly compared to petroleum based polymers that constitutes environmental pollution and degradation. (Ogunniyi and Odetoye, 2008), said there are other unique properties of alkyd resins that make it an indispensible raw material in surface coating industry and they include: gloss and gloss retention, film flexibility and durability, good adhesion and ease of application under variable environmental conditions.

In the early stage of the surface coating industry, vegetable oils used consisted entirely of those oils with pronounced drying ability like the linseed oil. (Aigbodion *et al.,* 2001). Vegetable oils have freshly achieved a lot of benefit due to the fact that, they are renewable resources and have high ecological benefits. Vegetable oils such as castor oil, linseed oil, soybean oil, rapeseed, olive, cotton seed and rubber seed are used in chemical industries for the manufacturing of coatings, surfactants, soaps, cosmetic products, lubricants, and paints (Aigbodion *et al.,* 2001; Can, 2002 and Ramamurthi, 1998).These oils were seldom used in their natural form as they could not fulfill the standard requirement for film properties like resistance to chemical and abrasion. Vegetable oils used as modifiers of alkyd resin for the purpose of imparting certain properties, such as ability to air-dry, film hardness and durability, gloss and gloss retention, etc., include linseed oil, soybean oil, castor oil and tall oil (Aigbodion *et al.,* 2001). These drying oils, which are regarded as standards in the surface coating industry, are still largely import.

In a study done by (Ikhuoria *et al.,* 2004), it was reported that drying oils are available locally, and have remained untapped. Oils mostly employed for the alkyd resins synthesis are linseed, rubber seed, soybean, castor and tall oil. These oils are largely imported to Nigeria for the formulation of coating of metals cans use in the packaging of beverages, drugs, food etc.

Rubber seed is obtained in high yield as a big product of hevea brazilleensis cultivated primarily for its latex. (Ikhuoria *et al.,* 2004), reported that Rubber is abundant in Nigeria and is found to contain 47% oil. However, research has shown it to be a rich source of oil that is comparable in quantity to the drying oils commonly used for surface coating. Although rubber seed is rich in nutrient, it also contains cyanogen glyossides which will release prussic acid in the presence of enzymes or in stighty acids conditions.

Rubber seed oil (RSO), on the other hand, have shown strong potential in the manufacturing of alkyd resins for the use as a binder in surface coating, polymer processing and diesel fuel substitute and/or extender (Aigbodion *et al.*, 2001). It is also of commercial importance, it is a semi-drying oil (i.e a thin layer of the oil is almost incapable of drying into a hard and durable film no matter how long exposed). It is used in the manufacture of soap for the production of linoleum and alkyd resins in medicine as antimalarial oil and in engineering as core binder for practice preparation. (Https://www.google.com/url?gzhttps://en.m.wikepedia.org/wike/rubber-seed-oil).

In the continued effort aimed at developing RSO as an industrial raw material, several studies have carried out such as a study on the effect of heat treatment on the characteristic of RSO by A. I. Aigbodion in 2001 and the enhancement of the quantity of alkyd resins using methyl esters of the rubber seed oil by E.U.Ikhuoria in 2004. Particularly to it's drying ability, as compared to the incorporation of the oil into polyester to yield the alkyd (Aigbodion *et al.*, 2001).

1.1.1 BACKGROUND OF PROBLEMS

The cost of using petroleum based monomers in the manufacturing of surface coating are increasing by the day, beside there is a potential danger of the depletion of the stock (petroleum) (Asiagwu *et al.,* 2008). (Mahatta, 1996; Aigbodion *et al.,* 2004) in their research reported that the scarcity of petroleum products coupled with exhaustible petroleum reserve and fluctuation in their prices have caused uncertainty in the future availability and supply of petroleum products as the major source of raw materials for both domestic and industrial uses and as such there has been tremendous increase in the demand for alkyd resin production for use in the Nigerian surface coating industry due to the rapid growth of the economy.

(parton, 1962; Ikhuoria *et al.,* 2007), in their research reported that the development of alkyd resins is that of the translation of chemistry of polyesters to a wide variety of useful industrial product and this development has taken place largely during the last 35 years and has resulted in new and improved coating compositions, adhesive, plastics and textile fibre and as such they have enjoyed a consistent annual growth of with current production running well over one-half billion pounds. Today, alkyd resins surpass all other synthetic coating resins used as binders in the paint industries (Ikhuoria *et al.,*2007).

In a study done by (Ikhuoria *et al.,* 2010), it was reported that despite the advantages of alkyd such as good adhesion, film flexibility, colour, gloss, broader temperature range application, etc, there are some draw-backs, for instance, its susceptibility to alkali as a result of the splitting of the ester linkages by hydrolysis, this reaction is very typical of esters, low mechanical strength and hardness and fair thermal stability (E.F. assanvo *et al.,* 2015). Due to these drawbacks many significant efforts have been made to increase the production of alkyd resins and also improve its quality.

1.1.2 STATEMENT OF PROBLEMS

The properties of the alkyd resin are determined by the amount and the composition of the fatty acid and oil blend used. (Aigbodion *et al.,* 2001), in his study reported that the type of oil used as the modifier is responsible to a large extent for the properties of the alkyd resin.

Vegetable oils used as modifiers of alkyd resin for the purpose of imparting certain properties, such as ability to air-dry, film hardness and durability, gloss and gloss retention, etc., include linseed oil, soybean oil, castor oil and tall oil (Killeffer, 1938;Ikhuoria *et al.,* 2004;Aigbodion *et al.,* 2001). These drying oils, which are regarded as standards in the surface coating industry, are still largely imported.

In the preparation of oil-modified alkyds, particularly rubber seed oil alkyds, there is relatively little or no information about the type of catalyst used. However some authors in their study enlisted different kinds of catalyst used in the synthesis of alkyd. For instance (Ikhuoria *et al.,* 2004), in her study entitled “enhancing the quality of rubber seed oil alkyd resins using methyl ester”used lead oxide (PbO) as catalyst, also in a study done by (Aigbodion *et al.*, 2003) entitled “Rubber Seed Oil Modified with Maleic Anhydride and Fumaric Acid and Their Alkyd Resins as Binders in Water-Reducible Coatings” the catalyst used was lead (II) oxide. However there are other examples of catalyst that can be used in synthesis of alkyd resin such as lithium hydroxide (LiOH), Calcium oxide (CaO), Zinc oxide (ZnO) etc.

Hence this research is aimed at comparing the performance characteristics of RSO prepared using lithium hydroxide (LiOH) as catalyst with commercially prepared resin.

1.1.3 JUSTIFICATION / RELEVANCE OF THE RESEACRHWORK

The development of alkyd resins is that of the translation of chemistry of polyesters to a wide variety of useful industrial products (Ikhuoria *et al.*, 2007). This development has taken place largely during the last 35 years and has resulted in new and improved coating compositions, adhesive, plastics and textile fiber (Parton, 1962; Ikhuoria *et al.*, 2007) and thus there has been renewed interest in the search and development of renewable resources that would serve as valuable alternative to petroleum products in production of alkyd resin (Enujiugba and Ayodele, 2003).

(Chakrabarty, 1981; William and Charles, 1984) reported that despite the apparent popularity of petroleum products as raw materials in different areas of application, fats and oils are being greatly favored for use in surface coatings, soaps, cosmetics, pharmaceuticals, lubricants, surfactants and polymer processing. Their wide acceptance in these fields of applications is attributable to their being renewable resources and biodegradable, hence environment friendly. Today, alkyds resins surpass all other synthetic coating resins used as binders in the paint industries.

(Patel *et al.,* 2007) also reported that this development has given rise to a number of investigations on the quality and applications of vast number of African seed oils and thus creating a competitive environment for coating industry thereby providing the drive and motivation to develop coatings that utilizes less expensive materials.

Rubber used oil (RSO) on the hand, have shown strong potential in the manufacturing of alkyd resins for the use of binders in surface coatings (Aigbodion *et al.,* 2001). it has also been reported to be suitable for both alkyd and water-borne alkyd resin(Okieimen *et al.,* 2002; Ikhuoria *et al.,* 2005) along with other potentials such as epoxidation of the oil, production of metal soaps and biodiesel etc (Okieimen and Eboaye, 1992; Ikhuoria *et al.,* 2002).

1.1.4 SCOPE OF WORK

This research work is limited to the extraction of rubber seed oil (RSO) from rubber seed, characterization of rubber seed oil, preparation of alkyd resin using catalyst such as Lithium Hydroxide (LiOH), physico-chemical characteristics (characterization) of alkyd resin such as color, specific gravity, refractive index, acid value, free fatty acid, saponification value, iodine value and non-volatile matter according to ASTM standard methods and comparing its performance characteristics to that of commercial resins.

1.1.5 AIMS AND OBJECTIVES

The main objective of this study is to synthesize and characterize rubber seed oil (RSO) alkyd resin and compare its performance characteristics to that of commercial resin.

To achieve the above stated aim; **the following objectives** were ensured:

1. Collection of rubber seeds from rubber plantation.
2. Extraction of oil from the rubber seeds collected.
3. Preparation of alkyd resin.
4. Physic-chemical characterization of alkyd resin according to ASTM and AOAC methods.
5. Performance characterization of RSOAR and comparing with commercial resin.

1.2 LITERATURE AND REVIEW

Alkyd resins are products of poly-condensation reaction between polybasic acid and polyhydric alcohol modified with fatty acid or drying oil. Oil modified alkyd resins constitute a major group of resins used as binders in surface coatings. It is estimated that alkyd resins contribute about 70% to the conventional binders used in surface coatings today (Bajpai and Seth, 2000; Ikhuoria *et al.,* 2004). It is reported that the popularity of alkyd resins as vehicle for coatings is largely due to their unique properties such as film hardness, durability gloss, gloss retention and resistance to abrasion impacted on them through modification with drying oils (Aigbodion, 1991; Ikhuoria *et al.,* 2004).

The oils that are mostly employed for alkyd resin synthesis are linseed, soybean, castor and tall oils (Kildiran *et al.,* 1996; Majumder *et al.,* 1999; Oguniyi and Njikang, 2000b; Ikhuoria *et al.,* 2004). According to (Adefarati, 1986; Ikhuoria *et al.,* 2004), these oils are largely imported to Nigeria for the formulation of coatings for metal cans used in packing of beverages, drugs and food. However, there are locally available drying oils that have remained untapped. These include rubber seed oil, walnut oil and tobacco oil (Ikhuoria *et al.,* 2004).

The industrial value of vegetable oil generally depends on its constituent fatty acids and the ease with which it can be modified or combined with other chemicals (Pryde and Rothfus, 1989). Several physical and chemical modifications of the oils to enhance their initial quality have been evolved over the years (Solomon, 1977). Examples of such modification techniques include acrylation (Akintayo and Adebowale, 2004), catalytic and thermo-catalytic polymerization (Trumbo *et al.,* 2001), inter-esterification (Athawale and Joshi, 2001), phosphorrylation and expoxidation (Zhong *et al.,* 2001). Chemical transformation of vegetable oil to fatty acid alkyl esters called trans-esterification or alcoholysis is one of the methods of modifying the quality of vegetable oils.

Raw vegetable oils are composed of glycerol, esters of fatty acids and various amounts of solubilised impurities such as pigments, vitamins, sterols and phospholipids, which may compromise the quality of the finished alkyd resins. However, esters of the vegetable oils would preclude some of these undesirable effects.

1.3 CLASSIFICATION OF ALKYD RESIN

According to (Panda, 2002), alkyd resin can be classified on the basis of their oil length and their kind of monobasic fatty acid present in the alkyd. On the basis of oil length, alkyd resins are typically sold in three classes, these are: long, medium and short. These terms however represent the relative fraction of drying oil component in the resin.

- **Long Oil Alkyds:** These alkyds contain a high percentage of drying oil content (75% and above) and are generally sold as medium duty coating for the consumer market.
- **Medium Oil Alkyds:** This type of alkyd has less percentage of drying oil content (50-65%) and has a high percentage of large molecular weight polyester backbone. They dry slower and are employed as high gloss coating sand wood finished.
- **Short Oil Alkyds:** These alkyds have low percentage of dying oil content (40-45%) in relation to the base polyester polymer or backbone chain. These coating will not air dry or harden unless heated. Short oil alkyds are employed as banking enamels for finished metal. Oil length is an important factor that affects the properties of the final products.

On the other hand, there are three types of alkyd resins based on the kind of monobasic fatty acid in the alkyd, drying alkyds; semi-drying alkyds and non-drying alkyds.

I. **Drying (Oxidizing) Alkyds:** In drying alkyds, the monobasic fatty acids contains unsaturation in sufficient quantity to cause a thin film of the alkyd to polymerize in the presence of oxygen at room temperature to give a coherent; soild film (Sibban, 2009).
   Examples of vegetable oil used in synthesis of drying alkyds are Tung and linseed oils which contain large amount of linolenic and linoleic acid.
II. **Semi-Drying Alkyds:** The semi-drying alkyds have moderate levels of unsaturation in the monobasic fatty acid and the drying process is slow when a thin film of the alkyd is exposed to the atmosphere (oxygen). Oils that are used for this purpose are soya bean and cotton seed oils among others.
III. **Non-Drying (Non-Oxidizing) Alkyds:** The amount of unsaturation in the monobasic fatty acid is so low that little or no polymerization occurs with oxygen. The oils that fall into this category are castor and coconut oils.

According to (Micciche, 2005), these oil contain considerable amounts of saturated acid residues such as stearic acid and palmitic acid. All types are typically produced from dicarboxylic acids or anhydrides, such as phthalic anhydride or maleic anhydride, and polyols, such as trimethylolpropane, glycerine, or pentaerythritol.

1.4 SYNTHESIS OF ALKYD RESIN

According to (Panda, 2000), there are various synthetic procedures involved in the production of alkyd resin, with each having certain variables. Alkyd resins are prepared by the poly-condensation reaction of polyols and polyacids until predetermined values of viscosity, acid value or theoretical water loss are obtained. Alkyd resin can be made directly from oils or by free fatty acids.

According to (Panda, 2000), the properties of formulated alky resin depend on the chemical composition and also their preparation process. Alkyd resins are produced in two processes;

- Fatty acid process
- Alcoholysis/mono-glyceride process

1.4.1 SYNTHESIS OF ALKYD FROM FATTY ACID PROCESS

According to (Sibban, 2009), fatty acid process produces higher quality and higher performance alkyds such that the composition of the resulting resin can be more precisely controlled. In this process, an acid anhydride, a polyol and an unsaturated fatty acid are combined and cooked together until the product has achieved a predetermined level of viscosity. Penta alkyds are made via this process.

1.4.2 SYNTHESIS OF ALKYDS FROM ALCOHOLYSIS PROCESS (GLYCERIDE PROCESS)

In this process, raw vegetable oil high in unsaturated component, is combined with additional polyol and heated to cause trans-esterification of the triglycerides into a monoglyceride. This can be illustrated in equation of reaction shown below (Figure 1.2)

To this mixture, acid anhydride is added to build the molecular weight of the resin into roughly the same product as in the fatty acid process. More economical alkyd resins are however produced in this process.

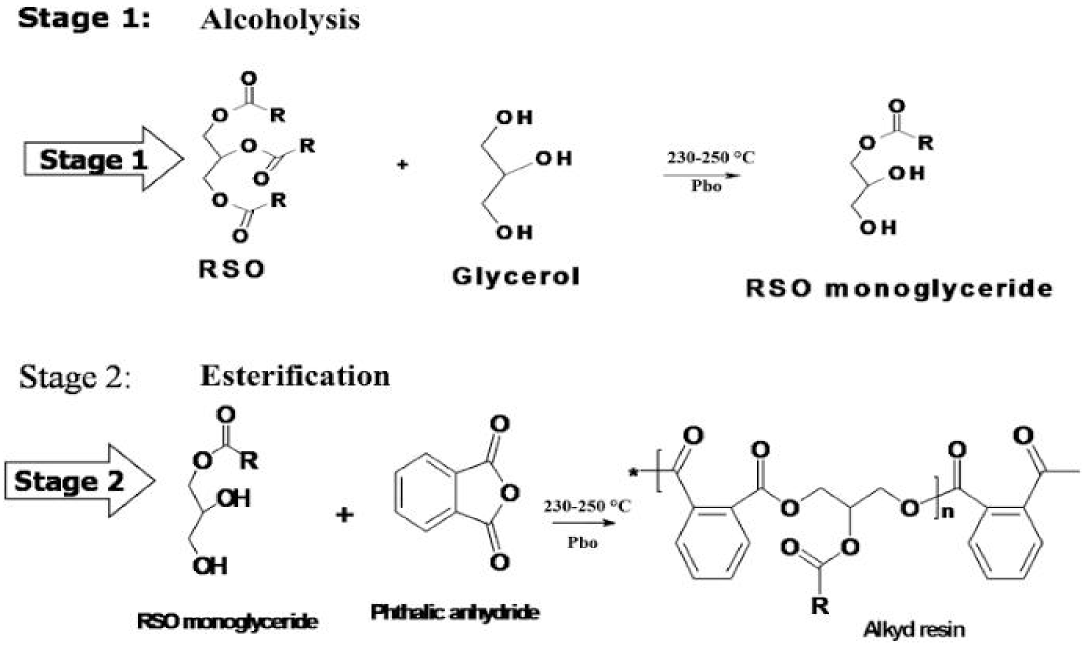

Figure 1.2: Synthesis of alkyd resin via alcoholysis process.

However, the alcoholysis process, also known as the glyceride process, produces a more randomly oriented structure. To remove the water produced as a by-product and to increase the reaction rate, surplus phthalic anhydride was added as shown in fig 1.2. Water was thus removed with the unreacted acid by heating the bulk to a temperature needed to do this. It meant that the reaction was not as controllable as would be desired. A new process was introduced, in which xylene was added to produce an azeotrope with the water. This gave greater control at a lower temperature and this also produces resins at a lower viscosity, useful in making high solids paints. This process was known as the AZO process. In both cases the resulting product is a polyester resin to which pendant drying oil groups are attached. At the conclusion of both processes the resin is purified, diluted in solvent and sold to paint and varnish makers (Sibban, 2009).

1.5 ESTIMATING THE PROGRESS OF A REACTION

A critical aspect of alkyd synthesis is deciding when the reaction is completed. The progress of reaction is monitored by periodically checking of acid number and viscosity, while the disappearance of carboxylic acid is followed by titration and the increase in the molecular weight is followed by viscosity. (Biemans *et al.*, 2014).

According to (Biemans *et al.,* 2014), many variables tend to affect the acid number and viscosity of alkyds. For instance, the ratio of reactants; the greater the ratio of hydroxyl groups to carboxylic acid groups, the faster the acid groups are reduced to a low level. The degree of completion of the reaction is an important factor controlling the viscosity, as well as acid number. It is usually desirable to have a low acid number.

The composition of the fatty acids and oils are also major factor affecting the viscosity. Some volatilization of polyol, phthalic anhydride and fatty acids out of reactor which will occur depending on the design of the reactor, the rate of reflux of the azeotroping solvent, the rate of inert gas flow and the reaction temperature are other variables. The amount and ratio of these losses affect the viscosity and acid number. In other words, side reactions can affect the viscosity-acid number relationship. Glycerol and other polyols form ethers to some degree during the reaction (under high temperature).

When these reactions occur, the mole ratio of dibasic acid to polyol increases and the number of hydroxyl groups decreases. Therefore, at the same acid number the molecular weight will be higher (Biemans *et al.,* 2014).

1.6 APPLICATIONS OF ALKYD RESIN

According to (Panda, 2000), Alkyd resins are widely used in paint and coating industry due to their versatility and performances on metal substrates. Alkyd based coatings are well-known for fast drying, good anticorrosion, high gloss and the ease of application even over poorly treated surfaces. They are commonly used in the printing industry as components for offset printing inks. Alkyds are also used in storing enamels where they are cross-linked with amino resins.

One of the important attributes of alkyd resins is their good compatibility with many other coating polymers. Alkyd resins are important ingredients in many synthetic paints, varnishes and enamels and also find application as thermosetting plastics that can be molded (source: file:///C:/Users/hp%20820/Pictures/FB/alkyd-resins-technology)

However, the principal applications are furniture and architectural coatings, product finishes, special-purpose coatings and automotive refinishing primers. Alkyd resins are manufactured from the condensation reaction between oil or polyols, acids, and alcohol. They are typically used as binders for coatings and printing inks.

(source: file:///C:/Users/hp%20820/Pictures/FB/alkyd-resins-technology)

1.7 THE RUBBER TREE

The rubber tree (hevea brasilliensis), also known as the Para rubber belongs to the family Euphorbiaceae. It is the most economically important member of the genus hevea originated from Amazon region of brazil in South America (Onoji *et al.,* 2016a; Rashed *et al.,* 2015; kittigowittana *et al.,* 2013).

According to (venkatachalam *et al.,* 2013), it was reported that hevea exhibits morphological variability, along with ten species, namely; H. brasilliensis, H. benthamiana, H. camorun, H. guianensis, H. microphylla, H. nitida, H. pauciflora, H. rigidifolia, H. camargoana, and H. spruceana identified that range from large forest trees to shrubs with latex in their parts.(Aravind *et al.,* 2015; Atabani *et al.,* 2013), in their study reported that Hevea brasiliensis produces about 99% of the world's natural rubber.

In a study done by (Onoji *et al.,* 2016a; Eka *et al.,* 2010), it was stated that Rubber tree has 6-9 years of gestation period before tapping for latex, though the seeds are available between 4-6 years. A recent statistical analysis put the global harvested areas of rubber trees plantations at 11,096,400 ha (FAOSTAT, 2014), thus eliminating competition for land space with vegetable crops (Zhu *et al.,* 2014).

Rubber trees have been reported by (Takase *et al.,* 2015; Ashraful *et al.,* 2014; Kumar & Sharma, 2011) to grow to a height of 34 to 40 m in the wild. (Ashraful *et al.,* 2014; Omo-Ikerodah *et al.,* 2009) also reported that It requires warm humid climate with temperatures ranging from 20 to 35°C, a fairly-distributed rainfall of about 1800 to 2000 mm throughout the year and its growth is most rapid at altitudes below 200m (Reshad *et al.,* 2015).

1.8 RUBBER SEED AND RUBBER SEED OIL

Rubber seeds were analysed by (Eka *et al.,* 2010) to determine its potential use as proteins, fats, carbohydrates and amino acids as food supplements for livestock. It was however reported that well processed rubber seed oil could be used as food claiming that good storage and heat treatment can reduce the levels of poisonous hydrogen cyanide present in the seed.

Rubber seed oil on the other hand, is oil extracted from the seeds of rubber trees. In the latex manufacturing process, rubber seeds are not historically collated and commercialized. Recent analysis shows that rubber seed oil contained the following fatty acids;

Palmitic acid (C16:0) – 10.2%

Stearic acid (C 18:0) – 8.7%

Oleic acid (C 18:1) – 24.6%

Linoleic acid (C 18:2) – 39.6%

Linoleic acid (C 18:3) – 16.3% (Ikhuoria *et al.,* 2010)

Although rubber seed is rich in its nutrients, it also contains cyanogenic glycocides which will release slightly acids conditions. Oil from the rubber seed is also of commercial importance the useful properties of the rubber seed oil make it similar to well-known linseed and soybean oil. Rubber seed oil is also used in the paint industry as semi-drying oil, in the manufacturing of soap, for the production of linoleum and Alkyd resin.

Source: https://en.wikipedia.org/wiki/Rubber_seed_oil)

1.9 EXTRACTION OF OIL

Rubber seed oil can be extracted via the following methods:

a. Soxhlet extraction (solvent extraction)

b. Mechanical pressing (extraction)

c. Traditional extraction method

A. Soxhlet Extraction

Soxhlet extraction which is known as solvent extraction refers to the preferential dissolution of oil by contacting oil seeds with a liquid solvent (Mohd-Setapar *et al.,* 2014). Solvent extraction is much related to soxhlet extraction most of this type of extraction is done in the soxhlet extractor which was invented by Franz von soxhlet.

According to (Mohd-setapar *et al.,* 2014), the choice of solvent used is based on solvent extraction capacity, effects of solvent in oil properties, process safety, solvent volatity and stability, and economic considerations. This is because most of the common solvent used, high paraffin petroleum fraction such as pentane, hexane, heptane and octane are flammable, and thus studies have been developed to use chlorinated hydrocarbons, alcohols, water etc.

Soxhlet extraction is carried out in the laboratory using a fat extractor (soxhlet extractor). The fat extractor uses the solvent reflux and siphon principle to continuously extract the soled matter by pure soled matter by pure solvent, which saves the solvent extraction efficiency and high efficiency. The solid material is ground prior to extraction to increase the area of soled liquid contact. The solid material is then place in a filter paper holder and placed in an extractor. The bottom end of the extractor is connected to a round bottom flask containing a solvent and is connected to a reflux condenser. The bottom flask is heated to boil the solvent, the vapor rises through the branch pipe of the extractor, is condensed and drops into the extractor, and the solvent is contracted with the solid for extraction. When the solvent liquid level in the extractor reaches the highest point of the siphon tube, the solvent containing the extract is siphoned back to the flask, thus extracting the portion of the material. The leaching solvent in the round bottom flask then continues to evaporate, condense, leaching, reflux, and so on, so that the solid material is continuously extracted as a pure leaching solvent, and the extracted material is concentrated in the flask. The liquid-solid extraction uses the solvent to have a large solubility to the desired component in the solid mixture, and the solubility to the impurities is small to achieve the purpose of extraction and separation. (source:https://www.hawachextractionthimble.com/the-basic-principle-of-soxhlet-extraction/).

B Mechanical Extraction

The main applications of mechanical expression are in the extraction of oils and juices. Expression is often combined with size reduction to maximize the yield of product. Components are extracted from plant parts either for direct use or for use in subsequent processing such as refining. In oil-bearing seeds, the oil is found inside cells in small droplets (10–80 µm) in diameter (Fellows, 1998).

However, a single type of equipment is not suited to all oilseeds owing to variation in oil content, moisture content, porosity and solidity of the material, applied pressure, heating temperature, heating duration, particle size and shape, storage and handling practices, and the proportions of hulls in different oilseeds are factors influencing yield and quality of vegetable oil expressed (Weiss, 2000).

Mechanical extraction of the oil is accomplished by exerting sufficient force on confined seed. Under this condition pressure is high enough to rupture the cells and force oil from the seed to "escape." Extraction is accomplished by compressing the material in a container that has small perforations, either round or slotted, that allow the liquid component to leave. This operation may be done in either a batch process or a continuous process.

Batch Process vs. Continuous Process

A batch process involves extracting the oil from one batch of seeds completely, before cleaning out the container and starting over. In this operation, the seeds are placed into a container with a moveable surface, most often the top. Then hydraulic pressure is applied to this moveable surface, which compresses the material, forcing the liquid component of the material to escape, usually through a perforated section in the bottom. In some cases, screw pressure was used instead of hydraulic pressure, as this was inexpensive and could be worked by people or animals.

An advantage of a batch operation is that after maximum pressure is reached, it can be maintained for a short period of time, permitting the last bit of oil to flow through the medium and out the escape perforations. The disadvantage is that the container has to be completely cleaned out before the process can be started again. With a continuous process, the seeds are continuously fed into the machine. As long as the machine is on, it continues to press oil out of the seeds.

In the past, the batch process was more common, whereas today in the United States, almost all facilities use a continuous process. However, in some parts of the world, the batch process is still used. Source: https://farm-energy.extension.org/mechanical-extraction-processing-technology-for-biodiesel/

C. Traditional Extraction of Oil

Traditionally, the commonest way of oil extraction is the water flotation process; oilseeds are thermally treated, crushed and milled into slurry (paste). With the aid of simple domestic utensils, oil is extracted by hand kneading. Water is added to the slurry and the mixture stirred and kneaded by hand until the oil separates to the top and sides of the utensils being used for the kneading. Water plays a vital role in hydrolyzing the paste, which displaces oil from hydrophilic surfaces in the slurry (Aremu *et al.,* 2015).

Under the traditional method, there are two ways of extracting oil; wet and water assisted extractions. This method is used, however, on a small scale, as it is labour-intensive, slow and tedious in operation compared to other methods but is assumed to produce high oil quality. In the wet extraction method, water is used in relatively large amounts to suspend the oilseeds such that the extracted oil floats on the top of the suspended oilseeds (Aremu *et al.,* 2015).

Hot water flotation method of edible oil extraction is traditionally used in the rural areas of many developing countries. The water-assisted method involves the addition of small quantities of water to the slurry before the oil is extracted by manual kneading. The slurry is suspended in boiling water and boiled for at least 30 min with liberated oil floating on the surface. Further quantities of water are added after boiling to replace the lost water that occurred during evaporation, and to facilitate the floatation of the oil to the surface. The oil is carefully scooped from the surface of the water and boiled (Aremo *et al.,* 2015).

1.10 PHYSICO CHEMICAL CHARCATERISTICS OF RUBBER SEED OIL

1.10.1 DENSITY/SPECIFIC GRAVITY

The density of a homogenous substance is its mass per unit volume. Its specific gravity is the ratio of the mass of an equal volume of water. Specific gravity is a dimensionless gravity. At a given temperature triglycerides are considerably denser in the solid state than in the liquid state. Weight of fatty acid present in oils and level of unsaturation are factors that affect their density.

Density increases in weight, while it decreases in unsaturation. Under normal room temperature fats and oil have lower densities than water. The comparison of the weight of one unit of oil to one unit volume of water at specified conditions of temperature is termed as the specific gravity of the oil.

1.10.2 VISCOSITY

This is the measurement of the intermolecular friction and resistance to motion of the oil when caused to flow under the influence of force (Sherwin, 1979). Due to the long chain structure of their triglyceride molecules, oils decreases slightly with increase in their decrease in unsaturation, and oils containing fatty acid of low molecular weight fatty acid. However, viscosity also increases with polymerization of oil.

1.10.3 ACID VALUE

In chemistry, **acid value** or (neutralization number or acid number or acidity) is the mass of potassium hydroxide (KOH), in milligrams that is required to neutralize one gram of oil or fat. The acid number is a measure of the amount of carboxylic acid group present in a chemical compound, such as fatty acid, or mixture in a compound. It is also an indication of the condition of the seed from which the oil is extracted and in the refining to which it has been subjected.

The acid number is used to quantify the amount of acid present, for example in a biodiesel. It is the quantity of the base, expressed in milligrams of potassium hydroxide, which is required to neutralize the acidic constituents in 1g of a sample.

There are standard methods used in the determination of acid number, such as ASTM D974 and DIN 51558(for mineral oils, biodiesel), or specifically for biodiesel using the European standard EN 14104 and ASTM D664 are both widely utilized worldwide acid number (mg KOH/g oil) for biodiesel should be lower than 0.5 mgKOH/g in both EN 14214 and ASTM D6751 standard fuels.

Acid value can thus be calculated using the formula:

$$Acid\,Value = \frac{[5.61 \times V \times N]}{W}$$

The molarity concentration of the titrant (N) is calculated us the formula:

$$Molarity(N) = \frac{1000 \times W_{KHP}}{204.3 \times V_{eq}}$$

Where:

V =Average titre

W= Weight (in gram) of the oil used

$W_{KHP} =$ Amount of KHP used in standardization of KOH

$V_{eq=}$ Average titre from standardization of KOH

1.10.4 FREE FATTY ACID

The percentage free fatty acid is calculated as the percentage by the weight of fatty acid used of specified molecular weight, normally, oleic acid of molecular weight 282g. In a number of cases an average molecular weight, more appropriate to the nature of the fat is used.

The free fatty acid is calculated by the conversion of the acid value to the percentage free fatty acid, using the relationship:

%FFA (oleic) = 0.503 × Acid value

Acid value = 1.99× %ffa (as oleic acid)

1.10.5 IODINE VALUE

The iodine value (or iodine adsorption value or iodine number or iodine index) is the number of iodine in grams required to saturate the double bonds in 100g of an oil under condition of test. It can also be said to be the mass of iodine that is consumed by 100g of a chemical substance.

On application, it is a measure of the level of unsaturation (i.e. the amount of unsaturation present in a fatty acid). This unsaturation is in the form of double bonds which reacts with the iodine compounds such that the higher the iodine value the more unsaturated fatty acid bonds is present in a fat. The iodine value can be used as a basis in the classification of oils and fats into drying, semi-drying and non-drying oils- an invaluable information about the ability of an oil to form a soild film on exposure to air. It can also serve as a satisfactory quality control specification of fats and oils. In the hydrogenation process of fats and oils, it is a helpful test in the determination of the ability of an oil to harden.

On application, the iodine value of an oil can be determined using the relationship:

$$Iodine\ value = \frac{12.69[V_{blank} - V]}{W}$$

Where:

V_{blank}= volume (ml) of thiosulphate solution used in blank

V= volume (ml) of thiosulphate solution used in the test

W= weight(g) of sample used

1.10.6 PEROXIDE VALUE

The peroxide value of an oil or fat is the amount of peroxide oxygen per 1kg (kilogram) of fat or oil. Traditionally this was expressed in units of milliequivalents, although upon using SI units, the appropriate option would be millimoles per kilogram.

The peroxide value of an oil or fat is used as a measurement of the extent to which rancidity reactions have occurred during storage. Other methods are available but peroxide value is the most widely used.

The double bonds found in fats and oils play a role in auto-oxidation. Oils with high degree of unsaturation are most suspectible to auto-oxidation. The best test for autoxidation (oxidative rancidity) is the determination of the peroxide value this is because peroxide are intermediates in auto-oxidation reaction.

The peroxide value of an oil can be calculated using the equation:

$$Peroxide\ value(PV) = \frac{1000 \times (V_1 - V_2) \times N}{W}$$

Where:

W= Weight of sample

$V_1 =$ Volume (ml) of thiosulphate used

$V_2 =$ Volume (ml) of thiosulphate used in blank

N= Normality of thiosulphate ($Na_2S_2O_3$)

1.10.7 SAPONIFACTION VALUE

The saponification value denotes the number of milligrams of potassium hydroxide required to saponify (neutralize the free fatty acids, and the fatty acids combined as the glycerides) 1 gram of oil or fat. Saponifcation value is related to the mean molecular weight of water-insoluble fatty acid by the expression:

MEAN MOLECULAR WEIGHT= $^{56108}/_{SV\ OF\ FATTY\ ACIDS}$

The value is useful for certain calculations in the use of oils, such as in the manufacture of alkyd resins. Saponification value is not changed significantly by polymerization but increases rapidly with oxidation. A saponification value higher than normal indicates the presence of oxidized or brown oils or else modification with chemicals such as maleic or fumaric acids.

On application, saponification value can be calculated using the formula:

$$saponification\ value = \frac{56.1 \times [V_1 - V_2]}{W}$$

Where,

N= Normality of HCl acid used

V_1= volume of HCl used in blank

V_2= Volume of HCl used in the test

W= weight of oil sample used in the test

CHAPTER TWO

2.0 MATERIALS AND METHODS

2.1 MATERIALS USED

2.1.1. COLLECTION OF RUBBER SEEDS

Dried rubber seeds were collected from Rubber Research Institute of Nigeria, Iyanomo, Benin city.

2.1.2 APPARATUS

The following apparatus/equipments were used in the course of this study. These apparatus/ equipment are outlined as follows:

1. Industrial blender
2. Electronic weighing balance
3. Dessicators
4. Soxhlet extractor timble
5. Reflux condenser
6. Three mouth adaptor
7. Hot plate
8. oven
9. Magnet stirrer
10. Retort stand
11. Rotator evaporator
12. Beakers
13. Measuring cylinders
14. Burette

15. Stoppers
16. Watch glass
17. Stirrers
18. Pipette
19. Heating mantle
20. Conical flask
21. Volumetric flask
22. 250ml quick-fit conical flask
23. Alkyd reactor
24. Oil bath
25. Petri dish
26. Dean and stark
27. Thermometer
28. Stop watch
29. Water bath / water circulator

2.1.3. REAGENTS USED

1. N-Hexane
2. Acetone
3. Glacial Acetic Acid
4. Distilled Water
5. Carbon Tetrachloride
6. Sulphuric Acid
7. Sodium Thiosulphate
8. Sodium carbonate
9. Sodium Chloride Solution
10. Wijs Solution
11. Starch Solution
12. Phenolphthalein indicator
13. Potassium Hydroxide
14. Ethanol
15. Potassium Iodide
16. Chloroform
17. Diethyl Ether
18. Phthalic Anhydride
19. Glycerol
20. Xylene
21. Lead Oxide (As Catalyst)

22. Lithium Hydroxide

23.Potassium Hydrogen Phthalate

24.Kerosene

25.Methanol

2.2 METHODOLOGY

2.2.1 STANDARD OPERATING PROCEDURE (SOP)

All methods and procedure used in this study were as strictly according to ASTM (American Standard Test Method) and AOAC (Association of Official Analytical Chemists) with little alterations.

2.2.2 EXTRACTION OF RUBBER SEED OIL (RSO)

Dried rubber seeds were cracked, crushed and sundried for about seven days and then subjected to temperatures of about 40°c-50°c for an hour and thirty minutes in the oven. These seeds were grinded using an industrial machine of which the converted into powdered form and then stored for further study.

The oil from the rubber seeds was extracted using soxhlet extraction process. The extraction process was carried out using analytical grade N-hexane of boiling range 64-70°C (Esuoso and Odetokun, 1995). The extraction process for a batch of rubber seed took place for eight hours. The resulting mixture gotten from the soxhlet apparatus (rubber seed oil and hexane) was then taken to the rotatory evaporator where the hexane was separated leaving the concentrated oil sample for analysis and the extracted oil was quantified gravimetrically.

2.3 PHYSICO-CHEMICAL PROPERTIES OF RUBBER SEED OIL

2.3.1 Determination of physical characterization of rubber seed oil

The color of the oil sample was determined by observation using color sensation of the human eyes. The specific gravity (SG) was determined using picometer.

2.3.2 Determination of oil yield

The percentage oil yield of the seed oil extracted was determined be weighing the dried grinded rubber seed powder and the concentrated oil extracted and calculated using the formula shown below:

$$percentage\ yield\left(\%\frac{w}{w}\right) = \frac{weight\ of\ concentrated\ oil}{weight\ of\ dried\ seed\ powder} \times 100 \qquad (2.1)$$

2.3.3 Determination of density

The density of the rubber seed oil was determined by the method described below.

Procedure:

(a) The mass of the empty density bottle was measured using an electronic balance and recorded as M_1

(b) The density bottle was filled with oil sample and weighed using the electronic balance and was recorded as M_2

(c) The volume of the oil sample in the density bottle was measured and recorded as V in cm3

(d) The density of the oil was then calculated using the formula:

$$Density\left(\frac{g}{cm^3}\right) = \frac{[M_2 - M_1]}{V} \qquad (2.2)$$

2.3.4 Determination of specific gravity

The specific gravity of rubber seed oil sample was determined by the method described below:

A density bottle was rinsed with distilled water and left to dry. The empty density bottle was weighed and recorded as $W_{1.}$. The density bottle was then filled with distilled water and weighed on the electronic balance and recorded as W_2. The difference of the was recorded and divided with density of water (standard). The specific gravity was the calculated using the formula:

$$Specific\ Gravity = \frac{W_2 - W_1}{Density\ of\ water\ (standard)} \qquad (2.3)$$

2.3.5 Determination of Acid Value

The acid value was determined by titrating in alcoholic solution with aqueous solution of KOH, the result is expressed in mg/KOH/g. The method (ASTM, 1994) was used in the determination of acid value.

Reagents:

(a) Ethanol

(b) Phenolphthalein indicator

(c) 0.1N KOH

(d) Diethyl ether

(e) Distilled water

Procedure:

0.5g of RSO was weighed accurately into 250ml conical flask. 25ml of equimolar mixtures of diethyl ether and ethanol was added into the flask and swirled properly until all mixtures blend together. Three drops of phenolphthalein was added and was titrated against 0.1N KOH until a pink coloration is observed. The reading on the burette is the read and recorded.

Acid value is calculated as follows:

$$Acid\,Value = \frac{[5.61 \times V \times N]}{W} \qquad (2.4)$$

The molarity concentration of the titrant (N) is calculated us the formula:

$$Molarity(N) = \frac{1000 \times W_{KHP}}{204.3 \times V_{eq}} \qquad (2.5)$$

Where:

V =average titre

W= weight(in gram) of the oil used

W_{KHP} = amount of KHP used in standardization of KOH

$V_{eq=}$ average titre from standardization of KOH

2.3.6 Determination of Iodine Value

Iodine value is used to determine the amount of unsaturation present in the oil sample. In the determination of iodine value, the method of ASTM (1979) was used.

Reagents:

(a) Carbon tetrachloride (CCl4)

(b) Wijs reagent

(c) 0.1N sodium thiosulphate ($Na_2S_2O_3$)

(d) Glacial acetic acid and chloroform (2:1 mixture)

(e) 10% potassium iodide solution

(f) Freshly prepared starch solution(1g of starch in 100ml of water)

(g) Potassium iodate

(h) Potassium iodide solution

Procedure:

0.5g of RSO was weighed into a conical flask, 15ml of CCl4, 20ml wijs reagent and 15ml 10% KI was added into the conical and swirled thoroughly to allow the mixtures blend properly. The resulting mixture was then allowed to stand for 1hr while it was kept in a dark place. After 1hr, 10ml of distilled water was then added to the mixture and was then titrated against 0.1N $Na_2S_2O_3$ solution using Starch as an indicator. A blank experiment was also carried out with the same procedure without using the sample.

The iodine was then calculated using the formula:

$$Iodine\ value = \frac{12.69[V_{blank} - V]}{W} \tag{2.6}$$

Where:

V_{blank}= volume (ml) of thiosulphate solution used in blank

V= volume (ml) of thiosulphate solution used in the test

W= weight(g) of sample used

2.3.6.1 Standardization of 0.1N and 0.02N thiosulphate ($Na_2S_2O_3$) solution

0.25g of pure dry potassium iodate into two conical flasks. Each of the potassium iodate was dissolved into 25ml boiled out distilled water. 2g of KI (potassium iodide) and 5ml of 1M H_2SO_4 was added and titrated with 0.1 and 0.02M thiosulphate solution with constant swirling until a yellow coloration is observed. 1ml of starch was added and titrated until it turned colorless.

2.3.7 Determination of Peroxide Value

For the determination of peroxide value (PV), 2g of each oil sample was weighed into a 200ml conical flask, then 25ml of 2:1 glacial acetic acid: chloroform solvent was added. This was followed by addition of 10ml of saturated KI and the mixture left in the dark for 1 hour. Next, 25ml of distilled water was added and the mixture titrated with 0.02N thiosulphate solution using 1ml starch as indicator. A blank determination was similarly carried out without using the sample. This above procedure was carried out according to (Pagout and Hautfenne, 1987).

The peroxide value was then calculated using the formula:

$$Peroxide\ value(PV) = \frac{1000 \times (V_1 - V_2) \times N}{W} \qquad (2.7)$$

Where:

W= Weight of sample

$V_1 =$ Volume (ml) of thiosulphate used

$V_2 =$ Volume (ml) of thiosulphate used in blank

N= Normality of thiosulphate ($Na_2S_2O_3$)

2.3.8 Determination of Saponification Number

In this method each of the oil sample was completely saponified by heating with an excess of alcoholic potassium hydroxide (KOH), the excess remaining being estimated by direct titration with standard acid. The method (ASTM,1979) was used in the determination of saponification value.

Reagents used:

(a) 0.5N ethanolic KOH

(b) 0.5N aqueous HCl

(c) Phenolphthalein indicator

Procedure:

(a) 1g of each sample was weighed directly into a flask using an electronic weighing balance.

(b) 12.5ml 0.5N ehanolic KOH solution was added using a burette.

(c) The flask was then was fitted with an air condenser tube and heated to boiling temperature in steam bath and allow to cool at room temperature.

(d) After slightly cooling the solution, 1ml of phenolphthalein solution was then added.

(e) It was then titrated using 0.5N HCl until it turned pink and the burette reading was recorded.

(f) A blank experiment was carried out using the same procedure without the sample.

The saponification value was then calculated using the formula:

$$saponification\ value = \frac{56.1 \times [V_1 - V_2]}{W} \tag{2.8}$$

Where,

N= Normality of HCl acid used

V_1= volume of HCl used in blank

V_2= Volume of HCl used in the test

W= weight of oil sample used in the test

2.4 PREPARATION OF ALKYD RESIN

Table 2.1

Recipe for the formulation of alkyd resin with Rubber Seed Oil

INGREDIENTS	**ALKYD**
RUBBER SEED OIL(g)	678.80g
GLYCEROL (g)	317.52g
PHTHALIC ANHYDRIDE(g)	450g
LITHIUM HYDROXIDE (LiOH) (g)	3.00g
METHANOL (g)	34.85g
XYLENE (g)	68.80g
OIL LENGTH (%)	50

The alkyd resin was prepared with rubber seed oil, having oil length 50%, glycerol, and phthalic anhydride according to the recipe shown in the table 2.1. The reaction was carried out in an 2litre five-necked alkyd reactor made of two flask connected to an oil bath (filled with silicon oil) fitted with a mechanical stirrer, reflux condenser, thermometer, dean and stark, and nitrogen gas inlet to create an inert atmosphere in the alkyd reactor. Lithium hydroxide (LiOH) was used as catalyst, while xylene was used as the cooking solvent in the reaction which involved two stages:

The first stage is called the **ALCOHOLYSIS STAGE**, in this stage; the rubber seed oil, glycerol, and lithium hydroxide were poured into the reaction flask. The mixture was heated in the reaction flask which was fitted with a motorized stirrer, thermometer and condenser. The reaction temperature was raised and maintained at a temperature 230°C for about 3 hours under nitrogen gas. This process was said to be completed when the mixture was tested for its solubility in methanol (1:3 mixture). The mixture was then allowed to cool to 120°C. this process tends to mark the first stage of the alcoholysis process.

The second process is called the **TRANSESTERIFICATION STAGE**, in this stage; the glyceride mixtures, phthalic anhydride and xylene were poured into the alkyd reactor. The reactor was then fitted with a dean-stark apparatus carrying a water-cooled condenser. The reaction as carried out in an inert atmosphere created by the bubbling of nitrogen gas into the reactor with the temperature still maintained at 230°C. The reflux was drained into the dean-stark apparatus, in which xylene was separated from water released during the condensation reaction also called the water of condensation and was returned to the reactor through the over flowing point. The progress of the reaction was monitored by the determination of the acid value of aliquots of the reaction such that a decrease in the acid value (less than 9) indicates the reaction was completed. A sample of the alkyd was collected and characterized.

2.5 PHYSICO-CHEMICAL CHARACTERIZATION OF ALKYD RESIN SAMPLE

The physico-chemical properties of the alkyd sample (color, specific gravity, density, acid value, iodine value, saponification value and peroxide value) were analysed using AOAC and ASTM standard methods.

2.6 PERFORMANCE CHARACTERISTICS OF ALKYD RESIN SAMPLE

The performance characteristics of the seed oil alkyd films were determined in terms of drying process and chemical resistance using different solvent media such as acid, alkali and water using standard methods as reported in the previous studies (Ikhuoria *et al.,2004;* Ikhuoria *et al., 2010;* Atta *et al.,* 2013; Ikyenge *et al.,* 2015).

2.6.1 DETERMINATION OF DRYING PROCESS TEST

The solutions of the alkyd in xylene together with the drying agents (cobalt naphthalate and lead naphthalate) were applied on a clear glass panel and dried at room temperature to study the film performance property. The drying process was monitored in terms of the time of set-to- touch, surface-dry and dry-through. The tests were carried out under similar conditions with commercial resin and the results were compared.

2.6.2 DETERMINATION OF CHEMICAL RESISTANCE TEST

The test panel was assessed for their resistance to different service media by immersion method for 2 hours at 50°C. The service media were used distilled water, 0.1M NaCl solution, 0.1M KOH solution and 0.1M H_2SO_4 solution.

2.6.2.1 WATER RESISTANCE TEST

A set of the alkyd sample (RSOAR and commercial resin) were immersed in distilled water in a 250ml beaker. It was allowed to stand for 24hours after which they were determined to detect film removal, blistering and wrinkling.

2.6.2.2 ACID RESISTANCE TEST

A set of the alkyd sample (RSOAR and commercial resin) were immersed in 0.1M H_2SO_4 (Tetraoxosulphate (vi)acid)solution in a 250ml beaker. It was allowed to stand for 24hours after which they were determined to detect film removal, blistering and wrinkling.

2.6.2.3 ALKALI RESISTANCE TEST

A set of the alkyd sample (RSOAR and commercial resin) were immersed in 0.1M KOH (potassium hydroxide) solution in a 250ml beaker. It was allowed to stand for 24hours after which they were determined to detect film removal, blistering and wrinkling.

2.6.2.4 SALT SOLUTION RESISTANCE

A set of the alkyd sample (RSOAR and commercial resin) were immersed in 0.1M salt solution in a 250ml beaker. It was allowed to stand for 24hours after which they were determined to detect film removal, blistering and wrinkling.

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

The rubber seed oil (RSO) and the rubber seed oil alkyd resin (RSOAR) were characterized with parameters stated in the table below: the following results were achieved.

3.1 DATA REPRESENTATION AND ANALYSIS

TABLE 3.1: PHYSICO-CHEMICAL CHARACTERISTICS OF RUBBER SEED OIL (RSO)

PROPERTIES	**RUBBER SEED OIL (RSO)**
COLOR	**GOLDEN YELLOW**
SPECIFIC GRAVITY @ 28°C	**0.906**
DENSITY (kg/m^3)	**0.930**
ACID VALUE (mg KOH/g)	**11.42**
IODINE VALUE (gI_2/100g)	**130. 36**
PEROXIDE VALUE (meq/kg)	**1.85**
SAPONIFICATION VALUE (mgKOH/g)	**186.88**

The color of rubber seed oil (RSO) was found to be golden yellow which is different from other colors reported by some authors for instance a brownish yellow coloration was reported by Maliki *et al.,* 2020; dark brown coloration reported by (Asuquo *et al.,* 2012; Abdulkadir *et al.,* 2014; Ebewele *et al.,* 2010) and golden yellow (Pearson, 1976). The properties of the rubber seed oil can be attributed to factors such as its crude color, the extraction procedures and the color of the oil after extraction process. However, it was reported by (Asuquo *et al.,* 2012; Maliki *et al.,* 2020) that degumming process and decolourisation can significantly improve the appearance of oil. Rubber seed oil was also observed to have an unpleasant odor; this physical appearance of the oil tends to make it desirable as edible oil.

The specific gravity value 0.903 obtained for RSO was found to fall below the range of values (0.923 ± 0.10) documented by Asuquo *et al.,* 2012; Ebewele *et al.,* 2010; and Kaur et al., 2016 for RSO. These values are comparable to the specific gravities of other edible vegetable oils (Negash*, et al.,* 2019) and within the 0.919-0.925 levels advised by FAO/WHO. The high specific gravity obtained for RSO could be attributed to the presence of high content of linoleic acid (Maliki *et al.,* 2020).

Acid value is a measure of the amount of free fatty acids present in the fat and oils. It give an indication of the deterioration, rancidity, or edibility of the oil. High acid values imply that the oil will require an excess polyol for its condensation reaction (Maliki *et al.,* 2020). The acid value obtained for RSO in this study was 11.42mg KOH/g. This value was found to be higher than the 1.68mg KOH/g reported by (Asuquo *et al.,* 2012) but lower than those obtained from (Maliki *et al.,* 2020) and (Abdulkadir *et al.,* 2014) and (Ebewele *et al.,* 2010) whose values were reported 32.0, 34.0 and 37.96 mg KOH/g respectively. High acid value may be due to hydrolytic reaction during processing or due to enzymatic action in the RSO (Maliki *et al.,* 2020). The acid value of RSO suggests that it cannot be used in any edible applications.

The iodine value is a measure of the degree of unsaturation of oils. It is an identity characteristics of seed oils making it an excellent raw materials for soaps and cosmetics industries (Hamilton, 1999). High iodine value is attributed to high unsaturation. It is the amount of iodine in grams that will saturate 100 grams of oil or fat. Iodine value is also a measure of the drying property of the oil. It is used as a basis for the classification of fats and oils into drying oils (iodine value higher than 150gI_2/100g), semi-drying and non-drying oils (iodine value of the range 100-

150gI_2/100g) as reported by (Aremu *et al.,* 2015; Asuquo *et al.,* 2012). The iodine value was observed to be 130.36 gI_2/100g, indicating that there is higher unsaturation present in the oil. The high iodine value of RSO also suggest that the oil can be classified as a semi-drying oils as reported by (Aremu *et al.,* 2015; Asuquo *et al.,* 2012) and can thus be used in the production of alkyd resin and other formulation such as liquid soap and shoe polish as reported by (Malkiti and Ifijen.,2020).

Peroxide value (PV) is the common indicator of lipid oxidation. The peroxide value gives an indication of the quality and stability of the oil. It is used to determine the extent to which an oil can go rancid as a result of storage, heating or oxidation (Malkiti and Ifijen, 2020). The peroxide value of RSO was found to be 1.85meq/kg and was found to be lower than values reported by (Malkiti and Ifijen, 2020) whose value was found to be 14.30 meq/kg. High values of peroxide value indicate high levels of oxidative rancidity of the oils and also suggest low levels of anti-oxidants. It is however reported that the maximum peroxide value level as stipulated by WHO/FAO (1994) is 10 meq/kg of the oils (Onoji *et al.,* 2016). The value obtained for RSO tends to fall within the range as stipulated by WHO/FAO (1994) and thus on this basis can be considered as an edible oil. On the hand the odour and acid value of rubber seed oil still makes it undesireable as edible oil.

The saponification value gives an indication of the molecular weight of the fatty acid contained in the oil. (Aremu *et al.,2015*) defined saponification value as a measure of oxidation during storage, and also indicates deterioration of oils. It also gives an indication of the purity status of the oil or whether the oil is adulterated (Akubugwo and Ugbogu, 2007). High saponification values suggest that the oil has little impurities. In this study the saponification value obtained was found to be 187.17 mg KOH/g which is high and when compared with values reported in (Malkiti and Ifijen,2020) for RSO (185.333 ±3.51 mg KOH/g oil) falls within the range but lower than 193.61 mg KOH/g and 226.02 mg KOH/g oil reported by (Asuquo *et al.,* 2012) and (Ebewele *et al.,* 2010) in similar studies for RSO. High saponification values obtained indicates that the oils could be used for soap making.

TABLE 3.2 PHYSICO-CHEMICAL PROPERTIES OF RUBBER SEED OIL ALKYD RESIN (RSOAR)

PROPERTIES	**RUBBER SEED OIL ALKYD RESIN (RSOAR)**
COLOR	DARK BROWN
SPECIFIC GRAVITY @ 28°C	**0.940**
DENSITY (kg/m^3)	**0.937**
ACID VALUE (mg KOH/g)	**7.54**
IODINE VALUE (gI$_2$/100g)	**83.23**
PEROXIDE VALUE (meq/kg)	**1.49**
SAPONIFICATION VALUE (mgKOH/g)	**210.62**

From the table 3.2 above; the color of the alkyd was observed to be dark brown. This brownish coloration shows typical characteristics properties of alkyds reported by other studies on alkyd resin by (Athawale *et al.,* 2000; Dutta *et al.,* 2004; Ikhuoria and Aigbodion, 2005). The acid value was found to be 7.54 mg KOH/g and when compared to values reported in (Ikhuoria *et al.,2004*) whose values were ranged 0.74-14.45 mg KOH/g and (Ikhuoria *et al.,2010*) whose value was reported ranging from 11.89-12.18 mg KOH/g it was found to be lower compared to the values reported. However, a decrease in the acid value indicates the completion of alcoholysis stage during the formulation of alkyd. The saponification value of the alkyd was found to be higher than the rubber seed oil extracted as they are essentially polyesters. This implies that upon esterifiaction, the saponification value is increased with percent glycerol and phthalic anhydride modification with rubber seed oil. The iodine value of the alkyd resin was also found to be lower than RSO when compared. This decrease in the iodine value could be as result of the dimerized polymerization reactions at the reactive double bonds of the unsaturation of the oils during alkyd synthesis.

TABLE 3.3: PERFORMCE CHARACTERISTICS (DRYING TEST) OF RUBBER SEED OIL ALKYD RESIN (RSOAR) COMPARED WITH COMMERCIALLY PREPARED RESIN (CPAR)

CHARACTERISTICS	**(RSOAR)** **Time (minutes)**	**COMMERCIAL RESIN** **Time (minutes)**
SET-TO-TOUCH	**831.00**	**950.00**
SURFACE DRY	**360.00**	**720.00**
DRY THROUGH	**540.00**	**720.00**

The performance characteristics carried out on Rubber Seed Oil Alkyd Resin(RSOAR) and commercial resins was found that the RSOAR was set to touch at 831 minutes(13hrs and 51minutes) after it was coated on a slide. Surface dry (tac-free)was observed on the surface of the slide where the alkyd was applied after 360.00minutes(19hrs and 51minutes) after set to touch. The surface the alkyd was coated with was observed to dry through after 540minutes (28hrs and 51minutes), showing complete drying. Upon comparism with commercial resin it was observed that the commercially prepared resin took quite some time before it showed complete drying.

Based on the result obtained, it can thus be inferred that alkyd resin formulated with rubber seed oil could be used in air-drying coatings.

TABLE 3.4 CHEMICAL RESISTANCE OF THE RUBBER SEED OIL ALKYD RESIN (RSOAR) AND COMMERCIAL RESIN

ALKYD SAMPLE	DISTILLED WATER	0.1M NaCl	0.1M KOH	0.1M H_2SO_4
RSOAR	**A**	**A**	**D**	**A**
COMMERCIAL RESIN	**A**	**A**	**D**	**A**

A= No visible change

B= slight whitening of film

C= wrinkled film

D= Disappearance of film

Table 3.4 shows that the performance characteristics of alkyd resins improved with the treatment of the rubber seed oil with Phthalic anhydride during the synthesis of the alkyd. The result also revealed that the alkyd resin were not affected by the NaCl solution, dilute sulphuric acid (H_2SO_4) and water. However, both resins were found to have poor resistance to KOH solution and can thus be deduced that this alkyd have potential applications for which resistance to alkali is not the main requirements.

3.2 CONCLUSION

Results got from this assessment shows that oil and oil prepared alkyd resin synthesized from rubber seeds showed extraordinary execution credits regardless, when differentiated and financially made pitch.

The high chemical resistance exhibited by this resin is an indication that it has great potential for various industrial applications such as formulation of coatings like lacquer for metal cans used in food packaging, beverages and drugs.

This implies that the recently referenced seed oil will expect unbelievable part in various applications, for instance, chemical creation and meaning of surface coatings. Pondering the current practices in Nigeria where imported oils, for instance, linseed oils resin, build up the specific resin used in the covering and its related undertakings, subbing these with rubber seed oil alkyd from our locally sourced oil is apparently a positive turn of events.

3.3 RECOMMENDATIONS

It is my greatest desire that further evaluations be done on the course of action of paints and stains with their properties utilizing the passed on alkyd resin. Likewise further evaluations ought to be facilitated on the impact of various type of catalyst utilized in the arrangement of alkyd resin and that is ought to be driven utilizing different seeds of locally tapped oils. Regardless of the above thoughts, the active compounds, with their exact structures, present in the alkyd gum ought to be likewise seen utilizing the mix of NMR, IR, GC-Mass spectroscopy. It is also my yearning that further evaluations be done on the development of alkyd resin from other locally open vegetable oils to adulate the investigated ones for more indisputable accessibility of crude materials.

3.4 CONTRIBUTIONS TO KNOWLEDGE

Vegetable fats and oils are widely applicable as raw materials in the chemical industry (Asiagwu *et al.,* 2008). (Meier *et al.,* 2011) reported that this wide acceptance of vegetable oils is attributable to its sustainability, biodegradability and environmental friendliness which are becoming more significant considerations in recent times due to the pressing environmental challenges of climate change and global warming. This recent shift towards the green products has consequently triggered the demand for more oils needed to expand the present supplies in the oleochemical industry. The valuable information obtained from this research has shown that rubber seed oil, although been classified as non-edible oil is a very good source of industrial oil and can also be applied in the oleochemical industry and specifically for the production of alkyd resin, giving valuable information about its physico-chemical properties and chemical composition.

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APPENDIX

Determination of Specific Gravity

Mass of density bottle (picometer) = 22.013g

Mass of Rubber Seed Oil + density bottle = 44.304g

Mass of distilled water + density bottle = 46.623g

Let X = [mass of distilled water + density bottle] – [mass of density bottle]

= 46.623g – 22.031g

= 24.61g

Let Y = [Mass of Rubber Seed Oil + density bottle]- [mass of density bottle]

= 44.304g – 22.013g

= 22.291g

Specific Gravity = $\frac{Y}{X}$

$= \frac{22.291}{24.610} = 0.9057$

Determination of Density

DENSITY = SG× density of water

= 0.9057 × 0.997

= 0.9030 kg/m^3

Determination of Acid Value

T_1	T_2
13.30	26.70
0.00	13.30
13.30	13.40

Average titre = $\frac{13.30+13.40}{2} = \frac{26.70}{2}$ = 13.35cm^3

Standardization of KHP (Potassiumhydrogenphthalate)

T_1	T_2
4.30	8.00
0.00	4.30
4.30	3.70

Average titre = $\frac{4.30+3.70}{2} = \frac{8.00}{2}$ = 4.00cm^3

KHP + KOH ---------> $K_2P + H_2O$

1 **1**

Using the formula

$\frac{C_1 \times V_1}{C_2 \times V_2} = \frac{n_1}{n_2}$ where C_1 = Concentration of KHP

Where C_2 = Concentration of KOH

Where V_1 = average titre

V_2 = volume of KHP used

$C_1 = \frac{no.of\ moles}{volume\ (dm^3)}$

No. of moles $= \frac{Reacting\ mass}{Molar\ mass}$

Given that molar mass of KHP is 204.22

100ml converted to dm^3 equals $0.1dm^3$

No. of moles $= \frac{0.25}{204.22} = 1.22 \times 10^{-3}$moles

Thus, $C_1 = \frac{1.22 \times 10^{-3}}{0.1} = 0.0122\ mol\ dm^{-3}$

$\frac{C_1 \times V_1}{C_2 \times V_2} = \frac{n_1}{n_2}$

Making C_2 subject of formula

$C_2 = \frac{1.22 \times 10^{-3} \times 100}{4.00} = 0.305 mol\ dm^{-3}$

Acid value $= \frac{13.35 \times 0.305 \times 56.1}{2} = 11.42$ mg KOH/g

Determination of Iodine value

T_1	T_2
12.80	31.50
0.10	12.80
$\underline{12.70}$	$\underline{18.70}$

Average titre = $\frac{12.70+18.70}{2}$ = 15.70cm^3

Titre values obtained for blank

T_1	T_2
44.70	45.60
0.20	0.10
$\underline{44.50}$	$\underline{45.50}$

Average titre = $\frac{44.50+45.50}{2}$ = 45.00cm^3

Standardization of 0.1M thiosulphate solution

T_1	T_2
5.70	12.80
0.00	5.70
5.70	7.10

Average titre = $\frac{5.70+7.10}{2}$ = 6.40cm^3

Na_2SO_4 reacts with KIO_3 In a 6:1 manner

Thus, using the equation,

$\frac{C_1 \times V_1}{C_2 \times V_2} = \frac{n_1}{n_2}$ where C_1 = Concentration of Na_2SO_4 solution

Where C_2 = Concentration of KIO_3

Where V_1 = volume of thiosulphate used

V_2 = volume of KIO_3 used

Calculation for the concentration of KIO_3

$C_1 = \frac{no.of\ moles}{volume\ (dm^3)}$

No. of moles $= \frac{Reacting\ mass}{Molar\ mass}$

$= \frac{0.02}{214} = 9.35 \times 10^{-5}$ moles

$C_1 = \frac{9.35\times10^{-5}}{0.025} = 3.74 \times 10^{-3} mol\ dm^{-3}$

$C_2 = \frac{3.74\times10^{-3}\times100\times6}{6.40\times1} = 0.35\ mol\ dm^{-3}$

Iodine value $= \frac{[45.00-15.70]\times12.69\times0.35}{1} = 130.36gI_2/100g$

Determination of Peroxide value

T_1	T_2
0.80	1.80
0.00	0.80
0.80	1.00

Average titre = $\frac{0.80+1.00}{2}$ =0.90cm^3

Titre values obtained from blank

T_1	T_2
2.70	3.50
2.00	2.70

<u>0.70</u>	<u>0.80</u>

Average titre = $\frac{0.80+0.70}{2}$ =0.75cm^3

Titre values obtained for standardization of 0.02M thiosulphate solution

T_1	T_2
20.10	45.40
0.00	20.10
20.10	25.30

Average titre = $\frac{20.10+25.30}{2}$ =22.70cm^3

Given that the concentration of KIO_3 is $3.74 \times 10^{-3} mol\ dm^{-3}$ as calculated above;

Thus, the concentration for the standardization of 0.02M thiosulphate solution is equal to

$$C_2 = \frac{3.74\times10^{-3}\times25\times6}{22.70\times1} = 0.0247\ mol\ dm^{-3}$$

$$\text{Peroxide value} = \frac{[0.90-0.75]\times100\times0.0247}{2} = 1.85 meq/kg$$

Determination of Saponification Value

T_1	T_2
15.60	36.70
0.00	15.60
15.60	21.10

Average titre = $\frac{15.60+21.10}{2}$ =18.35cm^3

Titre values obtained for blank

T_1
45.00
0.00
45.00

Titre values obtained for standardization of 0.5M HCl

T_1	T_2
13.00	16.90

11.30	15.40
1.70	1.50

Average titre = $\frac{1.70+1.50}{2}$ =1.60cm^3

Saponification Value = $\frac{56.1\times(45.00-18.35)\times0.5}{2} = 373.77$mgKOH/g

Since saponification value is defined by the amount of KOH that can saponify 1g of fat, thus; the saponification value for 1g of fat can be calculated as:

Saponification Value = $\frac{373.77}{2} = 186.88$mgKOH/g