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Fatty acid composition of melon (*Colocynthis vulgaris* Shrad) seed oil and its application in synthesis and evaluation of alkyd resins

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Abstract: *The high cost and environmental problems associated with the use of petroleum - based monomers for synthesis of binders can be solved by the use of locally sourced vegetable oils as precursor for synthesis of binders. The polymers from the latter are biodegradable and cheaper than petroleum polymers. The GC-MS result revealed that melon seed oil contains octadec – 14, 17 – dienoic acid (56.86%) as the most abundant fatty acid. Four sets of alkyd samples formulated by varying the percentage of melon seed oil contents were synthesised according to the alcoholysis-polyesterification process. The effect of oil lengths and oil quality on properties such as the drying schedule, hardness, gloss, colour, and chemical resistance of the alkyds were evaluated. Short oil alkyd of crude and refined oil possessed the best hardness, drying time and resistant to 5% brine solution. These properties were comparable to those of the soya alkyd paints.*
Key words- *Alcoholysis, Alkyd resins, Biopolymers, Coatings, Melon seed oil*

I. Introduction

Vegetable oils are renewable resources and are mainly of plant origin. They are triglycerides and often have at least one unsaturated fatty acid in its chemical structure [1]. Most of the vegetable oils contain all straight – chain fatty acids with even number of carbon atoms ranging in size from 3 to 18 carbons [2]. The specific fatty acid composition of triglyceride oils varies with the species of the oil and its origin.

Melon (*Colocynthis vulgaris* Shrad) is cultivated in large quantity in the tropics in which the seed is used as thickener in soup. Melon seed oil contains a large amount of linoleic acid (C18:2) [3]. Melon seed contains a lot of oil, which can be extracted and used for industrial purposes. [3] reported the use of melon seeds for oil production, frying and cooking in some African and Middle East countries. The physicochemical characteristics of melon seed (*Citrullus colocynthis L.*) oil determined by [4] are given below specific gravity at 20^0C (0.914), colour (amber colour), refractive index at 20^0C (1.4733), acid value (1.00mgKOH/g), saponification value (188mgKOH/g), iodine value (119gI_2/100g), free fatty acid (as % oleic acid) (0.52), unsaponifiable matter (1.02%), ester number (187). The fatty acid profiles of *Citrullus colocynthis L.* seed oil determined by [4] shows unsaturated fatty acids content of 77.4% and saturated fatty acids of 22.6%. The predominant fatty acid was linoleic (18:2) acid (62.2%). Other fatty acids determined were lenolenic (18:3) acid (1.02%), oleic (18:1) acid (14.2%), stearic (18:0) acid (10.2%) and palmitic (16:0) acid (12.42%) respectively.

The fatty acid esters derived from the triglyceride vegetable oils are an attractive source of raw materials for polymer synthesis [5]. The use of tobacco seed, rubber seed, coconut seed, soybean, palm and castor oils as a precursor for synthesis of alkyd resins has been reported [6, 7, 8, 9, 2, 10, 11, 12 and 13]. Apart from its application as food, *Colocynthis vulgaris* Shrad can also be used in the synthesis of alkyd resins due to its high content of unsaturated fatty acids and less content of saturated fatty acids. The high degree of unsaturation and particular fatty acid composition of melon seed oil make it especially suitable for the synthesis of highly durable (non – yellowing) oil – modified alkyd resins that can be used in the production of white gloss paints. The properties of alkyd resins such as drying time, film hardness, gloss and adhesion largely depend upon the fatty acid composition of the modifying oil used; also, the percentage of modification by fatty acids greatly affects the said properties of the alkyd resins [2].

Alkyd resins have remained the foremost group of binders used in surface coatings due to their unique properties like colour and gloss retention, film flexibility and durability, and compatibility with other resin systems [11]. The developments of raw material feedstock for chemical industry from a biodegradable vegetable oil in recent times have been revitalized due to environmental hazards posed by non – biodegradable petroleum based feedstock. The use of alkyd resin from melon seed oil to produce alkyd gloss paint has not been reported elsewhere. However, the use of petroleum-based monomers in the manufacture of polymers is expected to decline in the coming years because of spiralling prices and the high rate of depletion of the stocks [14]. This has inspired the technologists all over the world to investigate renewable natural materials as an alternative source of monomers for the polymer industry and substitute for the petroleum – based monomers for the manufacture of polymers [14]. This research is aimed at widening the knowledge of fatty acid composition of melon seed oil, and evaluating its potential application in the synthesis of surface coating binder (alkyd resins) as well as studying the effect of refining of melon seed oil on the quality of surface coating products. This will help to reduce the cost of production of surface coating products in the tropics as well as reducing the dependence on crude oil as the major source of raw materials for the polymer industry to other naturally available agricultural products. It will also help to diversify the uses of this oil thereby increasing earnings for local farmers who depend on this crop as their source of livelihoods.

II. Experimental

2.1. Materials

Melon seeds were purchased at Akpan Andem market, Uyo. The seeds were dried, ground and the oils Soxhlet extracted with petroleum ether as the solvent. Technical grade phthalic anhydride, glycerol, xylene were obtained from commercial sources and used in the preparation of cottonseed seed oil alkyd resins without further purification. While technical grade titanium (IV) oxide, calcium trioxocarbonate (IV) and toluene were obtained from commercial sources and used in the preparation of alkyd gloss paints without further purification. In addition, soybean oil alkyd sample was bought from the open market to serve as control. Distilled water was use throughout the analytical procedure.

2.2. Extraction of oil

Melon seeds purchased from the open market were sieved to remove solid particles. The sample was dried at a temperature of 70^0C in a Gallenkamp hot air oven model OV 160 overnight to reduce moisture content. The dried melon seeds were milled with Corona traditional grain mill REF 121 (100µm mesh size). The oil was extracted using Soxhlet apparatus with petroleum ether as the solvent. The extracted oil was referred to as crude melon seed oil (CMESO).

2.3. Refining of oil

Crude melon seed oil was degummed and bleached according to the method described by [15]. 500g of CMESO was kept at 70^0C and treated with 0.5g 50% aqueous solution of citric acid. The mixture was stirred continuously for 10 minutes and then allowed to cool down to 25^0C. 8g of distilled water was added to the mixture with continuous stirring for 1 hour. The temperature of the mixture was raise to 60^0C within 20 minutes while stirring and then allowed to cool overnight. The oil was separated from the gum by centrifugation.

The degummed melon seed oil (403.292g) was bleached by stirring the oil under N_2 with 20.0g of Fuller's earth at 100^0C for 20 minutes. The oil was filtered out and dried over 15g of anhydrous sodium tetraoxosulphate (VI). This was later referred to as refined melon seed oil (REMESO). The crude and the refined melon seed oils were stored in a refrigerator prior to use.

2.4. Determination of fatty acid composition

The fatty acid composition of melon seed oil was determined by GC-MS analysis. GC – MS analysis was carried out on a GC Clarus 500 Perkin Elmer system comprising of a AOC-20i auto-sampler and gas chromatograph interfaced to a mass spectrometer (GC-MS) instrument employing the following conditions: column Elite-1 fused silica capillary column (30 x 0.25 mm ID x 1µM df, composed of 100% Dimethylpoly diloxane), operating in electron impact mode at 70eV; helium (99.999%) was used as carrier gas at a constant flow of 1 ml /min and an injection volume of 0.5 µI was employed (split ratio of 10:1) injector temperature 250 ºC; ion-source temperature 280ºC. The oven temperature was programmed from 110 ºC (isothermal for 2 min), with an increase of 10 ºC/min, to 200ºC, then 5ıC/min to 280ºC, ending with a 9min isothermal at 280ºC. Mass spectra were taken at 70 eV; a scan interval of 0.5 seconds and fragments from 40 to 450 Da. Total GC running time is 36min.

Interpretation on mass spectrum GC-MS was conducted using the database of National Institute Standard and Technology (NIST) Abuja, having more than 62,000 patterns. The spectrum of the unknown component was compared with the spectrum of the known components stored in the NIST library. The name, molecular weight and structure of the fatty acid components of melon seed oil were ascertained. Concentrations of the identified fatty acids were determined through area and height normalization.

2.5. Physicochemical properties

Crude (CMESO) and refined (REMESO) melon seed oil was analysed for its physicochemical properties viz: acid value, iodine value, saponification value, free fatty acid, specific gravity and colour using standard methods (ASTM D 1959 – 85; ASTM D1980 – 85).

2.6. Preparation of alkyd resins

Four grades of alkyd samples formulated to have oil content of 40% (short oil alkyd), 50% (medium oil alkyd) and 60% (long oil alkyd) were prepared with phthalic anhydride, glycerol, and refined and crude melon seed oil using a monoglyceride method according to the procedure described elsewhere [6, 2]. The alkyds were labelled as follows: REMESAR 1 (short oil alkyd resin of refined melon seed oil); CMESAR 2 (short oil alkyd resin of crude melon seed oil); CMESAR 3 (medium oil alkyd of crude melon seed oil) and CMESAR 4 (long oil alkyd resin of crude melon seed oil). The recipe used in the preparation of the alkyd samples is given in Table 1. Lead (II) oxide was use as the catalyst for the synthesis of all the alkyd samples. Determining the acid value of aliquots of the reactions mixture at 20min intervals monitored the extent of polyesterification. Each alkyd sample was processed to acid value below 10mgKOH/g.

2.7. Evaluation of melon seed oil alkyd resins

To evaluate the performance properties of melon seed oil alkyds resins, melon seed oil alkyd samples REMESAR 1, CMESAR 2, CMESAR 3 and CMESAR 4 were formulated into white gloss paint using the recipe in Table 2. Paint samples produced were of two sets, first sets were produce without lead octoate drier and the second sets were produce with lead, cobalt and calcium octoate driers. White gloss paint was also prepared with standard soybean oil alkyd resin using the recipe in Table 2 to serve as the standard, and the qualities of the alkyd paint samples were compared with those of the standard soybean oil alkyd paint. To ascertain the quality of the melon seed oil alkyd gloss paints, some parameters were determined. These include specific gravity, colour, gloss and solid content as well as drying time, hardness, and chemical resistance using the procedure described elsewhere [7, 2].

However, adhesion was determined using the following procedure: an applicator was used to evenly spread the paint sample on a smooth glass plate and a brush was used to apply the paint samples on the surface of plastered wall and wood and allowed to dry for 48hrs. Having certified that the samples were fully dried, the test panel (glass plate) was placed in a horizontal position such that when the thumb is placed on the film, the arm of the operator was in a vertical line from the wrist to the shoulder. The thumb was turned through an angle of 90^0 in the plane of the film with the thumb exerting maximum pressure. The adhesion of the film to the substrate was determined by checking any form of distortion on the film. The film was adjudged excellent when there was no distortion of the film and good when distortion of the film was observed. The adhesion of the film to substrate was adjudged poor when there was film removal.

III. Results And Discussion

3.1. Extraction and fatty acid composition of melon seed oil

Melon seed (C*olocynthis vulgaris* Shrad) extract was liquid at room temperature. This implies that it could be classified as oil. The percentage oil yield for melon seed oil was 43.49%. This compare favourably with other oil-bearing seeds such as palm kernel (40%), peanuts (49%), cottonseed (36%), and soybean (20%) [16] and tobacco seed oil (40%) [2].

The amount of melon seed oil recovered after degumming and bleaching were 403.292g and 373.162g corresponding to 80.65% and 92.53% yield respectively. The difference in percentage yield of the two processes above could have been because of the removal of phosphatides, proteinaceous compounds, resins and other impurities from the oil during degumming and bleaching.

Table 3 represent GC – MS result on fatty acid composition of melon seed oil (MESO). The total unsaturated and saturated fatty acids in melon seed oil were observed to be 70.45% and 29.56% respectively. Among unsaturated fatty acids, linoleic acid exists in two isomeric forms, octadec-14, 17-dienoic acid (56.86%) and octadec-9, 12-dienoic acid (11.18%) with the former being the most abundant unsaturated fatty acid. Oleic acid (2.41%) was the least abundant unsaturated fatty acid (Table 3). The most abundant saturated fatty acid was palmitic acid (14.44%), while the least abundant was eicosanoic acid (0.83%). The amounts of unsaturated and saturated fatty acids as reported in the present study are close to those reported by [4] (77.40% and 22.60% respectively). The slight difference in the amounts and types of fatty acids as shown in Table 3 may be due to different species of melon seed (*Colosynthis vulgaris* Shrad*)* used in this research or due to different environmental or geographical conditions.

3.2. Physicochemical properties of melon seed oil

The physicochemical properties of crude and refined melon seed oil (CMESO and REMESO) is given in Table 4. The colour of the crude and refined melon seed oil obtained from this research by solvent extraction was observed to be yellow and pale yellow respectively (Table 3), while the colour reported in the literature is amber colour [4]. The difference in colour may be attributed to the difference in the species of melon seed reported in the literature (*Citrullus colocynthis L.*), as well as the difference in geographical or environmental conditions. However, colour is a useful characteristic of oil and an important parameter commonly employed in quality grading of oils and their sales appeal [17], but it is not necessarily the major determinant of the potential end-use in industrial applications.

However, in the preparation of alkyd resin, consideration of the colour of the oil may be necessary because of possible interference with the colour of the coating produced from it. It is worth mentioning however, that the yellow and pale yellow colours of crude melon seed oil (CMESO) and refined melon seed oil (REMESO) can enhance their application in the formulation of white gloss coatings where bright colour is a necessity.

The specific gravity of crude melon seed oil (CMESO) (0.900), refined melon seed oil (REMESO) (0.921) (Table 4) were found to be comparable with those of known vegetable oils of commercial interest. [18] gave the specific gravity of the following commercial oils as follows: sunflower oil (0.916-0.923), soybean oil (0.917 – 0.924), linseed oil (0.925-0.932). The specific gravity of rubber seed oil was observed to be 0.919 [11], while [12] determined it as 0.926. [4] determined the specific gravity of melon seed oil to be 0.914.

The level of acidity is an important property of vegetable oils that is related to their use in alkyd preparation, as the level of acidity determines the quantity of excess polyol required to neutralize the acid. The higher the level of acidity of the vegetable oil, the higher the amounts of excess polyol required for the polycondensation reaction. As indicated by acid value and percentage free fatty acid in Table 4, the level of acidity of crude melon seed oil (CMESO), refined melon seed oil (REMESO) were observed to be low. This can enhance their use in alkyd preparation and other industrial applications. Also, the acid value of crude melon seed and refined melon seed oils of 3.647mgKOH/g and 1.122mgKOH/g respectively obtained in this study is slightly greater than 1.00mgKOH/g [4] reported in the literature for *Citrullus colocynthis L.*

One of the most dominant parameter affecting the fatty acid and oil properties is the degree of unsaturation. The iodine value gives an indication of the degree of unsaturation of the oils. Triglyceride oils are divided into three groups depending on their iodine values: drying, semi-drying and non-drying oils. The iodine value of a drying oil is higher than 130. This value is between 90 and 130 for semi-drying oils. If the iodine value is smaller than 90, oil is called non-drying oil [18].

The iodine value (93.906gI_2/100g) obtained for crude melon seed oil in this study shows that the level of unsaturation is fairly high, thus meeting the requirement of a semi-drying oil. Refining was found to increase the iodine value; hence, the iodine value of refined melon seed oil was 96.444gI_2/100g (Table 4). The increase in the iodine value of refined melon seed oil (REMESO) may be attributed to the removal of phosphatides, proteinaceous compounds, resins and other non-glyceride components from the oil during degumming and refining, thereby increasing the unsaturation per unit weight of the oil. [16] made similar observation in the study on production and refining of *Dacryodes edulis* “native pear” seeds oil. This result collaborates with the percentage unsaturated fatty acids earlier determined as 70.45%, making melon seed oil a preferred raw material for synthesis of binder which can be apply in the production air- drying alkyd coatings. [19] stated that drying oils owe their value as raw materials for decorative and protective coatings to their ability to polymerize or “dry” after they have been applied to a surface to form tough, adherent, impervious, and abrasion resistance films.

3.3. Preparation of melon seed oil alkyd resins

Alcoholysis method was used to prepare the alkyd resin samples. During the preparation of alkyd resins, the monoglyceride was the first product formed from the reaction of crude melon seed oil and refined melon seed oil with glycerol. The alcoholysis products of crude melon seed oil was observed to be misty or hazy while that formed from refined melon seed oil was very clear. This was attributed to the presence of impurities such as sterols and phosphatides in the crude oil. The relationship between the percentages of oil used in the alkyd formula and the time taken for alcoholysis show that alcoholysis increased with increase in oil length, [7] have reported similar observation.

Alcoholysis time for 60% crude melon seed oil alkyd sample (CMESAR 4), 50% crude melon seed oil alkyd sample (CMESAR 3), 40% crude melon seed oil alkyd sample (CMESAR 2) were 50mins, 40mins, and 35mins respectively. That of 40% refined melon seed oil alkyd sample (REMESAR 1) was the same as CMESAR 2. The increase in alcoholysis time with oil length for melon seed oil may be attributed to the ratio of the oil content to the quantity of glycerol used in the alcoholysis process. Alcoholysis is a redistribution of fractions of molecules between the glycerol and the triglyceride. Generally, the complete formation of monoglyceride is difficult to attain, as it is known that reaction mixtures always contain glycerol, mono-, di- and triglycerides [20, 7].

All the alkyd samples were of good colouration (brown - yellow) and compared favourably with the colour of standard soybean oil alkyds. This indicates the influence of the triglyceride oils on the colour of the finished alkyd samples as melon seed oil used in the preparation of these alkyd samples was yellow. It is, also assumed that the atmospheric oxygen that might have passed into the reaction flask when one of the inlets was opened to charge in raw materials may have influenced the colour of these alkyd resins. Specific gravity values ranged from 0.945 for CMESAR 2, 1.048 for CMESAR 3 and 1.089 for CMESAR 4. The trend above shows that the specific gravity values of melon seed oil alkyds increased with increased oil length. Similar observation of increased specific gravity with oil content during the studies on molecular weight determination of rubber seed oil alkyds have been reported [12]. Refining of melon seed oil was found to increase the specific gravity of alkyd resin such that the specific gravity of REMESAR 1 was 1.037 compared to CMESAR 2 of 0.945.

The acid values of the finished alkyds were relatively low making them preferred binder for paint production, since higher acid value of binders would contribute to corrosion. The acid values of melon seed oil alkyd samples decreases with increased oil length (Figure 1). Similar trend of results was obtained in a previous study involving soybean oil [8]. This observation may be because the polybasic acid content (phthalic anhydride) decreases as the oil length increases.

The saponification values of melon seed oil alkyds resins was also within acceptable limits [21] and tend to increase with oil content of the alkyds. The saponification values of the alkyd resins varies from 273.488mgKOH/g for REMESAR 1, 244.035mgKOH/g for CMESAR 2, 249.645mgKOH/g for CMESAR 3 and 256.006mgKOH/g for CMESAR 4 and were found to be higher than those of crude melon seed oil (CMESO) and refined melon seed oil (REMESO) as they are essentially polyesters. [9] also observed the higher saponification values of finished alkyd compared to the corresponding triglyceride oil in the study on production and characterization of castor oil-modified alkyd resins. Similar observation was made by [10] during the study on enhancing the quality of alkyd resins using methyl esters of rubber seed oil.

Further observed was an increased iodine value of the alkyds with oil length of the resins (Figure 2). This indicates that the level of unsaturation increases as the quantity of the oil used in the resins increased.

The percentage solid content of the finished alkyds also increased with oil length with the highest of 89.861% (Figure 3) occurring for CMESAR 4. This implies that 60% oil length alkyds will be suitable in making high solid content paints with lower amount of volatile organic compounds (VOC). CMESAR 2 will be suitable for making paints with very hard, resistant film that dry faster but will require large amount of volatile organic compounds. However, 40% oil length alkyd (CMESAR 2) was very viscous at the end of production and required more solvent for thinning so that it could flow, hence, its low percentage of non - volatile organic components. CMESAR 3 will be suitable for production of gloss paints that will dry faster, possess hard, resistant film and require fewer amounts of volatile organic components.

However, refining of crude melon seed oil was found to improve the quality of the finished alkyd sample, such that acid value of REMSAR 1 was less than CMESAR 2 (Figure 4), while the iodine value and non – volatile matter of REMESAR 1 were greater than that of CMESAR 2 (Figures 5 and 6). These differences could be due to quality enhancement of melon seed oil through degumming and refining of the crude oil. Hence, refining of melon seed oil will produce alkyd resin with low volatile organic compounds that can be use in the production of quality paints, which will dry faster and form hard, resistant film.

3.4. Evaluation of melon seed oil alkyd resins

The results on Table 5 shows the performance properties of melon seed oil alkyd paint samples. The Characteristics of the melon seed oil alkyd resin paints evaluated were colour, solid content, gloss, specific gravity and adhesion.

PREMESAR 1 and PCMESAR 2 – PCMESAR 4 are paint samples prepared from 40% refined melon seed oil alkyd sample (REMESAR 1), 40% crude melon seed oil alkyd sample (CMESAR 2), 50% crude melon seed oil alkyd sample (CMESAR 3) and 60% crude melon seed oil alkyd sample (CMESAR 4) respectively. It is evident from Table 5 that the colour of the paint samples compared favourably with the colour of the standard soybean oil alkyd paint (SAP). The colour of these paint samples may be due to the influence of the colour of the binders used in the paint production, which was brown - yellow. This observation on colour implies that melon seed oil alkyds resins can be used in the formulation of white coatings, where bright colour is a necessity.

The gloss property of melon seed oil alkyd resins paint increases with increased oil length of the alkyds. Those of 40% refined melon seed oil alkyd and 50% crude melon seed oil alkyd as well as 60% crude melon seed oil were comparable with the gloss of standard soybean oil alkyd paint. The gloss of 40% crude melon seed oil alkyd paint samples PCMESAR 2 was lower than that of refined melon seed oil alkyd paint sample of the same oil length. This implies that improvement on the properties of the oil through refining also improves the gloss characteristics of the coating samples. The solid content (%) as well as specific gravity were also observed to increased with increase in oil length of the alkyds. With the exception of paint sample PCMESAR 2; all the paint samples have a higher solid content than the standard soybean oil alkyd paint of 65.01%. The solid content of these paint samples were influenced by the solid content of the corresponding alkyd resins used in their preparation (see Figures 3 and 6). The differences in the solid content of the paint samples could be attributed to the fact that alkyd samples of 40% and 50% oil length were thinned on manufacture to about 95 and 88% respectively. A comparison of the specific gravities of the paints with those of the resins show that the specific gravities of the paints is a function of the resin type and depends on the degree of cross- linkage. The differences noticed between the specific gravities of the paint samples and those of the corresponding alkyd resins could be due to the contributions by other components of the paint samples. The specific gravity of paint sample PREMESAR 1 has the same value as that of standard soybean oil alkyd paint of 1.14, while those of sample PCMESAR 3 of 1.16, and PCMESAR 4 of 1.15 were slightly greater than that of standard soybean oil alkyd paint. Generally, the specific gravities of the prepared paint samples were within the range of the standard alkyd sample.

Adhesion is another property of the coating that is very important. Adhesion of paint sample to the substrate is dependent on the binder used, i.e., the oil length of the alkyd resins [8]. The short and medium oil alkyd resin paint samples PREMESAR 1, PCMESAR 2 and PCMESAR 3 showed excellent adhesion to the substrate (glass plate). This is in consonance with the gelled and sticky nature of the alkyd samples used for their preparation. This may be due to the high degree of cross – linkage. Adhesion of the above-mentioned paint samples to glass plate compared favourably with the standard alkyd paint. On the other hand, adhesion of the paint samples on other surfaces– wood and plastered wall were observed to be excellent. Hence, the adhesions of the paint samples on different surfaces were observed to follow the pattern: wood > plastered wall > glass plate. The increased adhesion of the paint samples on wood and plastered wall may be due to similarities in functional groups (-OH, -COOH and -COO-) present on both surfaces.

The quality of the resin is transferred directly to the finished products (gloss paints). Hence, short and medium oil alkyd samples of melon seed oil can be a better substitute for commercial alkyd used as binder in paint formulation.

Drying schedule was another important property of the alkyd samples evaluated. To ascertain the importance of lead drier (bottom drier) in drying schedule of the paint samples, two sets of paint samples were prepared with the alkyd samples – first set without lead drier and second set with lead drier, and their drying property compared. Tables 6 and 7 show the drying schedules of the solvent-borne alkyd paint samples of melon seed oil prepared without lead drier in terms of the times of set-to-touch and dry-through tested outdoors and indoor respectively.

However, from the results obtained in Table 6 it appears that the alkyd resin affects the drying property on a basis different from what is normally expected. Drying property is inherent of the resin used and this is dependent on the degree of unsaturation of the oil used. The set-to-touch time and dry-through time for the paint samples increased with oil length. This may be attributed to the degree of cross- linkage, which is highest for the short oil and reduces towards the long oil resins when subjected to the same manufacturing conditions. It is evident from Tables 6 and 7 that the drying times for both indoor and outdoor samples are dependent on the percentage oil content of the alkyds, sunlight and temperature of drying as well as volume of oxygen. The outdoor samples dry faster than the indoor samples. This may be due to increased volume of oxygen outdoors as well as high temperature outdoors as drying is basically auto-oxidation process. Drying is believed to occur through the process of auto – oxidation, which involves the adsorption of oxygen at the double bond of the unsaturated fatty acids [7].

It was also noticed that the difference in the set-to-touch time and dry-through time for both outdoor and indoor samples of the standard alkyd paint and the short oil alkyd paint sample PCMESAR 2 was not altogether significant. The drying time of paint sample REMESAR 1 also compares with that of the standard alkyd paint sample. The drying time (dry-through time) obtained in this research for the melon seed oil alkyd samples are greater than those reported by [8] for soybean oil-based alkyd resins paint. This difference may be due to the non-inclusion of lead drier in the production of these paint samples, while lead drier was an essential ingredient in the samples from soybean oil-based alkyd paints prepared by [8].

Incorporation of lead octoate in the second phase of melon seed oil alkyds gloss paints production brings about a significant influence in the drying property of the paint samples. Dry – through time of all the samples were reduce drastically such that the results obtained compares favourably with those reported by [8]. This implies that lead drier plays a vital role in the drying properties of the paint samples. The result obtained when lead drier was incorporated into the paint formulation is shown in Tables 8 and 9.

Table 10 shows the chemical resistance of the melon seed oil alkyds paints to different solvent media. All the alkyd samples seem to be highly resistant to 5% sodium chloride solution (brine) while they are poorly resistant to alkali. The poor resistance to alkali may be explained on the basis that alkyd resins which is the major ingredient in the paint samples are essentially composed of ester linkage that are susceptible to alkaline hydrolysis [22]. The refined melon seed oil alkyd sample paint PREMESAR 1 was virtually unaffected by water and acid. This implies refining of melon seed oil improves its resistance to water and acid. Similar observation was made during the studies on quality enhancement of alkyd resins using methyl esters of rubber seed oil [10]. Samples PCMESAR 2 and PCMESAR 3 showed almost the same resistance to the different solvent media, except alkali, despite the difference in the oil length. The standard alkyd paint gave the best resistance to the different solvent media. Generally, the alkyds compares favourably with the standard alkyd paint sample in terms of resistance to distilled water, brine and acid.

The hardness of the dry paint films (scratch and gouge) was determined by the pencil hardness test. Table 11 shows the results of the pencil hardness test on the dry film paint samples of melon seed oil alkyds resins. The scratch/gouge pencil hardness was 4H/5H, 4H/5H, 3H/4H, and 3H/4H for paint samples PREMESAR 1 and PCMESAR 2 – PCMESAR 4 respectively. The hardness trend shows that hardness decreases with increase in oil length of the melon seed oil alkyds used in the paint formulations. Samples PCMESAR 3 and PCMESAR 4, which have the least hardness, were prepared from 50% and 60% crude melon seed oil alkyd resins respectively. Samples PREMESAR 1 and PCMESAR 2 whose hardness compared favourably with that of the standard were prepared from 40% refined melon seed oil alkyd and 40% crude melon seed oil alkyd resin respectively. The result on Table 11 showed that hardness is influenced by drying time of the paint film, such that the faster the drying of alkyd paint samples the harder the film.

IV. Conclusion

The preparations of alkyd resins using crude and refined melon seed oil have been described. The alkyd resins obtained have been formulated into coatings for different surfaces.

This study shows that melon seed oil is a suitable starting material for the production of alkyd resins suitable for use in surface coating formulations for different surfaces. It has been shown from this study that some quality parameters of the manufactured alkyd resins and their surface coating products (paints) are comparable with those of standard soybean oil alkyd resins paint. It was also observed that the drying property of melon seed oil alkyd gloss paint is influenced by lead octoate (bottom drier). The drying time of the paint films were prolonged in the absence of lead drier and faster when lead drier was incorporated into paint formulation.

This study has helped to expand the raw material base of surface coating industries in the tropics as well as providing new avenues for the applications of melon seed oil. It has also helped to diversify the uses for which this oil is put into thereby increasing earnings for local farmers who depend on this crop as their source of livelihoods. This study has also strengthened indigenous capacity and provides opportunity for the acquisition of skill, which can be used in the development of value-added products from vegetable oil. The results obtained in this study have also provided information for our chemical industries data bank on fatty acid composition of melon seed oil, melon seed oil alkyd resins and its application in paint formulation.

Table 1
Formulations of solvent- borne alkyd resins

Ingredients	REMESAR 1	CMESAR 2	CMESAR 3	CMESAR 4
Refined melon seed oil (g)	60.00	-	-	-
Crude melon seed oil (g)	-	60.00	75.00	90.00
Phthalic anhydride (PA)	59.40	59.40	53.07	39.66
Glycerol (GA) (g)	30.60	30.60	21.92	20.34
PbO (g)	0.08	0.08	0.03	0.03
Oil length (%)	40.00	40.00	50.00	60.00
Total components (g)	150.08	150.08	150.02	150.03

Table 2
Formulation for long, medium and short oil alkyd paints using melon seed oil and standard soya alkyds and octoate driers

Ingredients	**Long oil alkyd paint formula (g)**	**Medium oil alkyd paint formula (g)**	**Short oil alkyd paint formula (g)**	**Standard soya alkyd paint formula (g)**
White spirit	16.50	16.50	16.50	16.50
Melon seed oil /standard soya alkyds	50.22	50.22	50.22	50.22
Calcium drier	0.60	0.60	0.45	0.80
Cobalt drier	0.65	0.50	0.58	0.50
Lead drier	1.50	0.80	1.16	2.70
Titanium (IV) oxide	16.55	16.55	16.55	16.55
Calcium carbonate	6.00	6.00	6.00	6.00
Formalin	2.03	2.03	2.03	2.03

Table 3
Fatty acid composition of melon seed oil

Fatty acid	No. of carbon	Weight (%)
Hexadecanoic acid (Palmitic acid)	16	14.44
Octadecanoic acid (stearic acid)	18	14.29
Eicosanoic acid	20	0.83
Octadec-9-enoic acid (Oleic acid)	18	2.41
Octadec-14,17-dienoic acid (Linoleic acid)	18	56.86
Octadec-9,12-dienoic acid (Linoleic acid)	18	11.18

[a] Total unsaturated fatty acids = 70.45%; total saturated fatty acids = 29.56%

Table 4
Some physicochemical properties of melon seed oil

Properties	Result		Literature
	Crude melon seed oil	Refined melon seed oil	[4]
Colour	Yellow	Pale yellow	Amber
Specific gravity (at 28^0C)	0.900	0.921	0.914
Acid value (mgKOH/g)	3.647	1.122	1.00
Free fatty acid (% oleic acid)	1.833	0.564	0.52
Saponification value (mgKOH/g)	231.413	224.400	188
Iodine value (gI_2/100g)	93.906	96.444	119

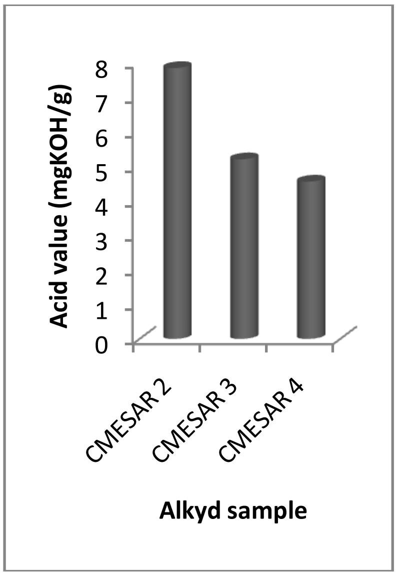

Figure 1: Acid value of crude melon seed oil alkyd resins

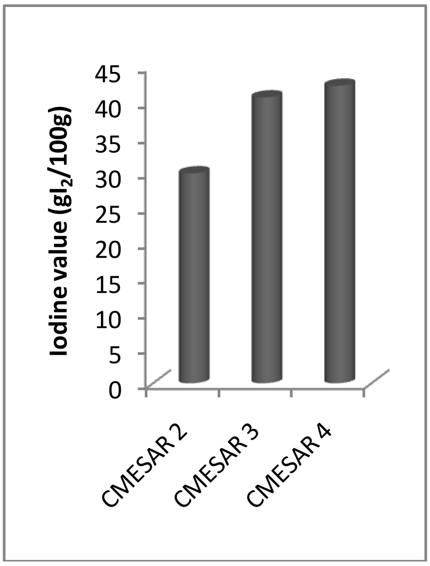

Figure 2: Iodine value of crude melon seed oil alkyd resins

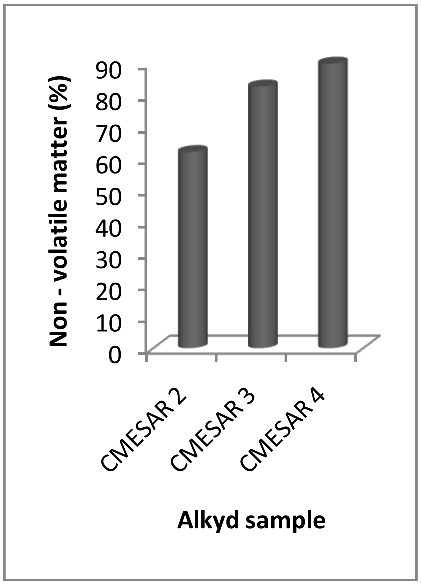

Figure 3: Non – volatile matter of crude melon seed oil alkyd resins

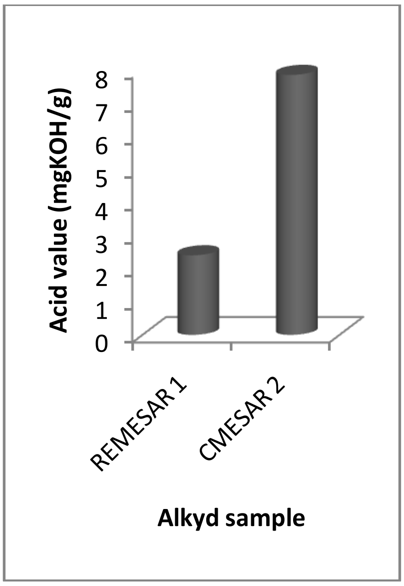

Figure 4: Acid value of refined and crude melon seed oil alkyd resins

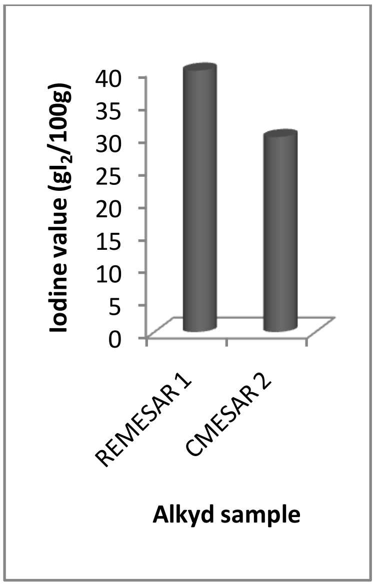

Figure 5: Iodine value of refined and crude melon seed oil alkyd resins

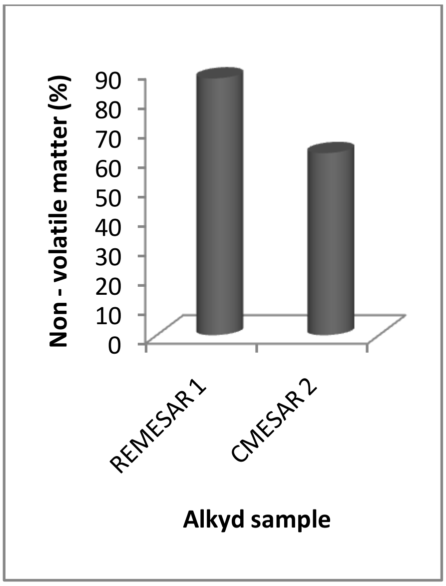

Figure 6: Non – volatile matter of refined and crude melon seed oil alkyd resins

Table 5
Performance properties of melon seed oil alkyd resins

Sample	Colour	Solid content (%)	Specific gravity	Adhesion	Gloss (60^0)
PREMESAR 1	Warm white	76.23	1.14	Excellent	60.3
PCMESAR 2	Warm white	63.52	1.11	Excellent	57.7
PCMESAR 3	Off – white	71.44	1.16	Excellent	61.8
PCMESAR 4	Off – white	78.05	1.15	Good	63.4
Standard soya alkyd paint (SAP)	Brilliant white	65.03	1.14	Excellent	64.7

Table 6
Outdoor drying schedule of melon seed oil alkyd paint and standard soya alkyd paint samples formulated without lead drier (outdoor temperature = 33^0C).

Paint sample	Set – to – touch time (min)	Dry – through time (min)
PREMESAR 1	15	780
PCMESAR 2	9	660
PCMESAR 3	23	1260
PCMESAR 4	32	1442
Standard soya alkyd paint (SAP)	8	660

[b] Sample PREMESAR 1– 40% refined melon seed oil phthalic alkyd resin paint. Sample PCMESAR 2– 40% crude melon seed oil phthalic alkyd resin paint. Sample PCMESAR 3– 50% crude melon seed oil phthalic alkyd resin paint. Sample PCMESAR 4– 60% crude melon seed oil phthalic alkyd resin paint.

Table 7
Indoor drying schedule of melon seed oil alkyd paint and standard soya alkyd paint samples formulated without lead octoate drier (indoor temperature = 28^0C).

Paint sample	Set – to – touch time (min)	Dry – through time (min)
PREMESAR 1	20	900
PCMESAR 2	13	810
PCMESAR 3	31	1440
PCMESAR 4	40	1800
Standard soya alkyd paint (SAP)	12	750

[b] Sample PREMESAR 1– 40% refined melon seed oil phthalic alkyd resin paint. Sample PCMESAR 2– 40% crude melon seed oil phthalic alkyd resin paint. Sample PCMESAR 3– 50% crude melon seed oil phthalic alkyd resin paint. Sample PCMESAR 4– 60% crude melon seed oil phthalic alkyd resin paint.

Table 8
Outdoor drying schedule of melon seed oil alkyd paint and standard soya alkyd paint samples formulated with lead octoate drier (outdoor temperature = 33^0C).

Paint sample	Set – to – touch time (min)	Dry – through time (min)
PREMESAR 1	12	420
PCMESAR 2	8	390
PCMESAR 3	15	510
PCMESAR 4	24	580
Standard soya alkyd paint (SAP)	6	360

[b] Sample PREMESAR 1– 40% refined melon seed oil phthalic alkyd resin paint. Sample PCMESAR 2– 40% crude melon seed oil phthalic alkyd resin paint. Sample PCMESAR 3– 50% crude melon seed oil phthalic alkyd resin paint. Sample PCMESAR 4– 60% crude melon seed oil phthalic alkyd resin paint.

Table 9
Indoor drying schedule of melon seed oil alkyd paint and standard soya alkyd paint samples formulated with lead octoate drier (indoor temperature = 28^0C).

Paint sample	Set – to – touch time (min)	Dry – through time (min)
PREMESAR 1	17	465
PCMESAR 2	11	420
PCMESAR 3	26	540
PCMESAR 4	32	635
Standard soya alkyd paint (SAP)	10	420

[b] Sample PREMESAR 1– 40% refined melon seed oil phthalic alkyd resin paint. Sample PCMESAR 2– 40% crude melon seed oil phthalic alkyd resin paint. Sample PCMESAR 3– 50% crude melon seed oil phthalic alkyd resin paint. Sample PCMESAR 4– 60% crude melon seed oil phthalic alkyd resin paint.

Table 10
Chemical resistance of melon seed oil – modified alkyd resin paint samples.

Paint sample	Solvent media			
	Distilled water	NaCl (5% solution)	H_2SO_4 (0.1 moldm^{-3})	KOH (0.1 moldm^{-3})
PREMESAR 1	n	n	n	r
PCMESAR 2	w	n	w	b
PCMESAR 3	w	n	w	r
PCMESAR 4	w	n	w	r
Standard soya alkyd paint (SAP)	n	n	n	w

No effect = n, whitening = w, shrinkage of film = s, blistering of film = b, removal of film = r

Table 11
Pencil hardness of melon seed oil alkyd paint samples

Paint sample	Pencil hardness	
	Scratch	Gouge
PREMESAR 1	4H	5H
PCMESAR 2	4H	5H
PCMESAR 3	3H	4H
DCMESAR 4	3H	4H
Standard soya alkyd paint (SAP)	5H	6H

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