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Influence of Polybasic Acid Type on the Physicochemical and Viscosity Properties of Cottonseed Oil Alkyd Resins

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ABSTRACT

Three medium oil alkyd resins (50% oil length) were synthesized with cottonseed oil using different polybasic acids [phthalic anhydride (I), maleic anhydride (II) and succinic acid (III)] according to the alcoholysis process. Dilute solution viscosity measurements were carried out on the alkyd resins in acetone and in toluene. The effect of polybasic acid type on dilute solution viscosity characteristics of the alkyd samples were investigated by determining the following parameters: viscosity number (η_{rv})*, intrinsic viscosity* [η] *and Huggins constant* (K_H)*. Also, the effect of polybasic acid type on properties such as colour, solid content, specific gravity, adhesion, drying time, chemical resistance and hardness was evaluated by formulating the alkyds into white gloss paints. (III) and (I) respectively had the lowest and highest* (η_{rv}) *in both acetone and toluene, while that of (II) was intermediate. The* [η] *values of the alkyd samples in acetone were found to vary in the order: (I) > (II) > (III) in acetone and (II) > (I) > (III) in toluene. Generally, the* [η] *values were found to be larger in acetone than in toluene. The* K_H *of the alkyd resins on the other hand, were found to be larger in toluene than in acetone. The phthalic and maleic anhydrides alkyd paint samples possessed the best hardness and drying time, while succinic acid alkyd resins produce coatings with very soft film. All the alkyd paint samples were highly resistant to 5% NaCl(aq) and poorly resistant to 0.1 moldm*$^{-3}$ *KOH. Succinic acid alkyd paint sample was poorly resistant to distilled water. Also, standard soybean alkyd resin was used separately to formulate white gloss paints and the properties of phthalic and maleic anhydrides alkyds were found to be comparable with the standard alkyd samples.*

KEYWORDS: *Alcoholysis, Alkyd resins, cottonseed oil, Phthalic anhydride, Viscosity*

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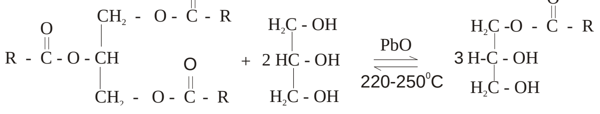
1. INTRODUCTION

The chemistry and application of alkyd resins have attracted the interest of many chemists from both academia and industry as can be seen from the huge number of papers and patents covering this field. The term alkyd is a variant of "alcid" meaning the product of an alcohol and acid [1]. It was first used in 1929 to define the reaction products of polyhydric alcohols and polybasic acids or polyesters.Alkyd resin is one of the oldest polymers prepared from triglyceride oils by the esterification of polyhydroxy alcohols with polybasic acids. Typical equations for the reaction between triglyceride oil, polyhydroxy alcohol and polybasic acid leading to the formation of alkyd resin are shown below [2].



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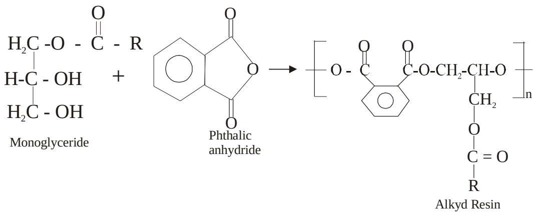

(2)

Alkyd resin is a product of polyesterification reaction of unsaturated oils like soybean, linseed oils and the likes with diacids and polyhydroxy alcohol. There have been several other attempts to define alkyd resins over the years. One of such definitions is that of Bobalek *et al.* [3], which define alkyd resins as the reaction product of polyhydric alcohol and poly – functional acids modified by fatty acid or their triglyceride. Igwe and Ogbobe [4] and [5] describe it as polyesters modified with unsaturated fatty acids. Aigbodion and Pillai [6] define it as products of condensation between polyol, usually having an average functionality equal to or greater than 3 and a polybasic acid, usually dibasic acid or its anhydride modified with monofunctional acids, most commonly C_{18} fatty acid or triglyceride. Alkyd resins as products of polycondensation reaction between polybasic acids and polyhdric alcohol modified with fatty acid or drying oil is the definition given by [7]

Alkyd resins constitute a very high proportion of conventional binders used in the coating industry. It has become an indispensable raw material used for the production of industrial and household finishes [8]. Alkyd resins have acquired a good reputation because of their economy, availability of raw materials and ease of application [1, 2]. Additionally, they are to a greater extent biologically degradable polymer because of the oil and glycerol parts, and they are eco – friendly compared to petroleum – based polymers that constitute environmental pollution and degradation. Other unique properties of alkyd resins that make it an indispensable raw material in surface coating industry include: gloss and gloss retention, film flexibility and durability, good adhesion, and ease of application under variable environmental conditions [6, 8, 9]. They are also compatible with other film formers such as acrylic resins to form alkyd hybrid systems that combine the technical benefits of both resins than when used alone.

Acids with more than one replaceable hydrogen atoms are called polybasic acids. Polyfunctional acids used in alkyd resins preparation include phthalic anhydride (PA), glutaric anhydride, (GA), Maleic anhydride (MA), and succinic anhydride (SAN) [2, 10]. Other polybasic acids are sebacic, isophthalic, and fumaric acids [11]. Most alkyd chemists and technologists prefer PA to other polybasic acids; this may be due to the relatively low melting point (the pure compound melts at 131°C) of this product, which falls below the reaction temperature of 230 – 250°C for alkyd resin production. This implies, the crystals of PA will melt and dissolve readily in the reaction mixture within the reaction temperature, thereby reducing the reaction time. It also improves solubility of the resin, and increases hardness and resistance to water. In large – scale manufacturing, molten PA is used, which reduces packaging, shipping and handling costs.The next most widely used acid is isophthalic acid. Esters of isophthalic acid are more resistant to hydrolysis than that of PA in the pH range of 4 – 8, the important range of exterior durability. On the other hand, under alkaline conditions, esters of PA are more resistant to hydrolysis than isophthalic esters. However, the use of isophthalic acid in alkyd resin production poses a problem of longer reaction time and higher temperature because of its high melting point of 330°C, which is above the reaction temperature of 230 – 250°C. Isophthalic acid is also too costly, though it produces a better-performing product than phthalic anhydride. Fumaric acid also produces resin with higher impact resistance, but is more expensive [11].Kangas and Jones [12] and Kangas and Jones [13] stated that the longer time at higher temperature leads to greater extent of side reactions of the polyol component. Thus, when substituting isophthalic acid for phthalic anhydride, a lower mole ratio of isophthalic acid to polyol must be used in order to obtain an alkyd of similar viscosity.On the other hand, measurements of solution viscosity are usually made by comparing the efflux time (t) required for a solution of the sample to flow through a capillary tube with the corresponding efflux time (t_o) of the pure solvent. There are practical considerations for studying solution behaviour of polymers like alkyd resins since their practical significance is only achieved in their solution in suitable solvent system [14]. Apart from being the medium of dispersion for resins, solvent should be able to evaporate at a desirable rate to leave the alkyd film.

It is therefore of great scientific and economic interest to evaluate the potentials of other polybasic acids like maleic anhydride (MA) and succinic acid (SA) in the production of alkyd resins. This may help provide an alternative polybasic acid for alkyd synthesis. This research is therefore aimed at evaluating the performance, as well as the viscosity properties of medium oil alkyd resins prepared from phthalic anhydride, maleic anhydride and succinic acid.

II. EXPERIMENTAL

2.1 Materials

Cottonseed oil was purchased at Sabongari market, Kano and used in alkyd synthesis without further purification. Technical grade polybasic acids- phthalic anhydride (BDH, England), maleic anhydride (BDH, England) and succinic acid (BDH, England), glycerol and xylene were obtained from commercial sources and used in the preparation of alkyd resins without further purification. Analytical grade acetone (BDH, England) and toluene (BDH, England) used in the determination of solution viscosity of the synthesised solvent-borne alkyd resins were also obtained from a commercial source. While technical grade titanium (IV) oxide and calcium trioxocarbonate (IV) were obtained from commercial sources and used in the preparation of alkyd gloss paints without further purification.

2.2 Preparation of the Alkyds

Three alkyd samples each of 50% oil length were prepared with glycerol (GL), cottonseed oil (COSO), phthalic anhydride (PA) (I), maleic anhydride (MA) (II) and succinic acid (SA) (III) employing the alcoholysis process according to the procedure described elsewhere [15]. The recipe used is shown in Table 1. Xylene was used as the azeotropic solvent. Each alkyd was processed to acid value below 10 mgKOH/g.

2.3 Viscosity Measurements

Viscosity measurements were carried out using solution of the alkyd resins in acetone and toluene following the procedure described elsewhere [16]. Solutions of the alkyd samples were prepared by dissolving weighed amount of alkyd sample to give a solution of concentration of approximately 2.5 g/100cm^3. This was filtered to remove any suspended particle to give the stock solution. The exact concentration of this stock solution was obtained by measuring 5 cm^3 of the solution into a watch glass and the solvent evaporated by drying at 100^{0}C and cooled in a desiccator. The non-volatile content was weighed and the actual concentration of the alkyd in 100 cm^3 of the stock solution was calculated. Viscosity of the solution was determined using Ostwald viscometer at different concentration of the samples. The efflux time of the solution was measured for each concentration. Four dilutions were made as follows: 2.5, 2.0, 1.5 and 1.0 g/100cm^3. Efflux time of the pure solvents, acetone and toluene were determined under the same conditions.

2.4 Viscosity Ratio and Viscosity Number

The viscosity ratio, η_r, which is the ratio of the viscosity of the alkyd solution to the viscosity of the pure solvent and equivalent to the ratio of their efflux times, is given in equation (3).

$$\eta_r = \eta/\eta_o = t/t_o \qquad (3)$$

Where, t, is the efflux time of the alkyd solution and, t_o, is the efflux time of the pure solvent. Specific viscosity, η_{sp}, is given in equation (4),

$$\eta_{sp} = \eta_r - 1 = t/t_o - 1 = \frac{t - t_o}{t_o} \qquad (4)$$

The viscosity number commonly called reduced viscosity is given in equation (5)

$$\eta_{rv} = \frac{\eta_{sp}}{c} \qquad (5)$$

where, c, is the concentration (g/100cm^3). The limiting viscosity number (intrinsic viscosity), [η], which is equal to η_{rv} is given by equation (6).

$$[\eta] = \frac{\eta_{sp}}{c} \qquad (6)$$

Plot of η_{sp}/c versus concentration extrapolated to zero concentration gives an intercept equal to [η] according to the Huggins' relationship, given by equation (7),

$$\eta_{sp}/c = [\eta] + K_H [\eta]^2 c \qquad (7)$$

where K_H is Huggin's constant.

2.5 Infrared Spectroscopy (IR)

FTIR spectra of the alkyd samples were obtained using FTIR – 8400S Fourier Transform Infrared spectrophotometer. The samples were smeared on ZnSe prism and the scanning method was adopted to determine the functional groups in the alkyd samples.

2.6 Physicochemical Properties and Performance Evaluation of the Finished Alkyds

The following standard tests methods were used to determine the physicochemical properties of the finished alkyds such as acid value, saponification value, iodine value and non – volatile matter (ASTM D 2689 – 73), specific gravity and colour [17]. The finished alkyds were formulated into alkyd gloss paints and the following performance characteristics were evaluated using standard tests methods: chemical resistance of the dry films (ASTM D 1647 – 89), drying schedule (ASTM D 1640 – 83) and film hardness (ASTM D 3363 – 74). Other performance characteristics evaluated using the method described by [1, 17] were specific gravity, adhesion and non- volatile matter. In addition, standard soybean oil alkyd resin was used to prepare alkyd gloss paint to serve as the standard. The recipe for the formulation of the alkyd gloss paint is shown in Table 2.

III. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Cottonseed Oil Alkyd Resins Prepared from Different Polybasic Acids

In order to study the effect of other polybasic acids on the physicochemical properties of alkyd resins as binder in surface coatings, three alkyd samples of the same oil length (50%) were prepared using phthalic anhydride (PA) (I), maleic anhydride (MA) (II) and succinic acid (SA) (III), glycerol and cottonseed oil. All the alkyd samples were of good colouration,

though it is assumed that the colour of the alkyds may have been influenced by atmospheric oxygen, as one of the inlets of the reactor was kept opened at regular intervals in order to charge in raw materials. The acid value increases from sample (I) (5.086 mgKOH/g), sample (II) (8.818 mgKOH/g) to sample (III) (9.407 mgKOH/g) (Fig. 1 and Table 3). The three alkyd samples produced from phthalic anhydride, maleic anhydride and succinic acid respectively had relatively low acid values, which are an advantage, since higher values would contribute to corrosion. The variation in the acid values of the samples may be attributed to variation in the acid values of the anhydride type used in the alkyd production. Aydin *et al.* [10] gave the acid value of maleic anhydride as 1144.2 mgKOH/g, phthalic anhydride as 757.5 mgKOH/g and that of succinic anhydride as 1121.1 mgKOH/g.

The saponification values were also within acceptable limits [18, 19] with the highest value of 357.638 mgKOH/g obtained for sample (II). The next in the trend was 283.305 mgKOH/g obtained for sample (III) and the least was 253.853 mgKOH/g obtained for sample (I). Generally, the saponification values of these alkyd samples were found to be higher than that of cottonseed oil, which fall within the range of 189 – 198 mgKOH/g [20] as they are essentially polyesters. The iodine value of alkyd sample (III) (30.146 $gI_2/100g$) was the lowest and that of sample (I) of 39.339 $gI_2/100g$ was the highest, while that of sample (II) (35.725 $gI_2/100g$) was intermediate, (Fig. 2 and Table 3). This implies the degree of unsaturation is highest in phthalic anhydride alkyd sample (I), followed by maleic anhydride alkyd sample (II) and lowest in succinic acid alkyd sample (III). Alkyd samples (I) and (II) will produce paints with good drying properties; while alkyd sample (III) will produce paint with prolonged drying time.

The percentage solid content of alkyd sample (III) was higher than that of samples (I) and (II) (Fig. 3). This implies that succinic acid alkyd sample will be suitable in making high solid content paint. It is also evident from Table 3 that the specific gravity of these samples was almost the same, with that of sample (III) being slightly higher than those of samples (I) and (II). Phthalic anhydride and maleic anhydride alkyd samples will also produce paint with high solid content considering their percentage solid content. It can be inferred that apart from the nature and quality of the triglyceride oil used in alkyd synthesis, the type of polybasic acid used can also influence the physicochemical properties of the alkyd resins. On economic consideration, it can be deduced that maleic anhydride can substitute phthalic anhydride in alkyd synthesis without compromising those properties (acid value, iodine value and non – volatile matter) that will lead to quality product.

3.2.FTIR Analysis of Cottonseed Oil Alkyd Samples Prepared from Different Polybasic Acid

FTIR – 8400S Fourier Transform Infrared spectrophotometer was used to detect the chemical structure of ester links present from the polycondensation reaction between polybasic acids and glycerol modified with cottonseed oil. The functional groups present are similar to those obtained elsewhere [21]. The FTIR spectra of the three samples were similar. Straight chain alkane (- CH -) for alkyd sample (I) was detected at 1372 cm^{-1}, 1454 cm^{-1} and 2858 cm^{-1} with correlation intensities of 7.686 (strong), 42.922 (very strong) and 18.249 (very strong) and correlation area of 3.019, 12.523 and 6.102 respectively. Carbonyl group (C=O) was detected at 1746 cm^{-1} with correlation intensities of 0.529 (weak) and correlation area of -44.277 (Figure 4). C=C-H group was detected for alkyd sample (I) at a band of 981 cm^{-1} with correlation intensity of 9.844 (strong) and correlation area of 2.572. Carbonyl group (C = O) for maleic anhydride alkyd sample (II) was detected at the band of 1726 cm^{-1} with a correlation intensity/area of 0.032 (weak)/0.002, while that of succinic acid alkyd sample (III) was detected at 1747 cm^{-1} with a correlation intensity/area of 0.029 (weak)/ 0.263 (Figs. 5 and 6). Straight chain alkane (-CH-) for sample (II) was detected at the following bands 1453 cm^{-1} and 2921 cm^{-1} with correlation intensities/correlation areas of 13.734 (very strong)/3.929 and 0.832 (weak)/0.607 respectively. That of alkyd sample (III) was detected at the following bands 723 cm^{-1}, 1370 cm^{-1}, 1457 cm^{-1} and 2855 cm^{-1} with the following correlation intensities/correlation areas of 16.885 (very strong)/5.447, 0.154 (weak)/0.890, 1.428 (weak)/-0.088 and 16.164 (very strong)/6.291 respectively.

Comparing the correlation intensities and correlation areas of carbonyl group (C=O) for cottonseed oil alkyd samples (I), (II) and (III), the following order for correlation intensity was observed – phthalic alkyd sample (I) > maleic anhydride alkyd sample (II) > succinic acid alkyd sample (III). On the other hand, correlation areas varies as follows – succinic acid alkyd sample (III) > maleic anhydride (II) > phthalic anhydride alkyd sample (I). Generally, the presence of – OH groups in the chemical structure of all the alkyd samples studied indicates the impossibility in obtaining complete formation of monoglyceride during the alcoholysis of the triglyceride oils with glycerol, as well as incorporation of excess glycerol into the alkyd chains. Ogunniyi and Odetoye [8], Ogunniyi [22] and Stoye [23] stated that the complete formation of monoglyceride is difficult to attain, as it is known that reaction mixtures always contain glycerol, mono-, di- and triglycerides. Also, the presence of residual carboxylic groups (– COOH) and other polar groups in the chemical structure of all the alkyd samples suggest that the alkyd samples will have excellent adhesion to substrate, as well as excellent flexibility. Certain polar groups in a film such as carboxylic groups (– COOH) are very active promoters of adhesion, due to their attraction to the substrate, or by their influence in improving the wetting properties [21]. Good initial wetting of a surface by a coating and the maintenance of wetting during the process of film formation are essential for good film adhesion. From Figures 4 – 6, it is observed that correlation intensities for O – H (stretch) for carboxylic acid for alkyd samples I – III varies from 9.707 (sample I), 3.072 (sample II) and 0.068 (sample III). This may suggest that phthalic anhydride alkyd sample will produce coatings with the best adhesive property, followed by maleic anhydride alkyd sample, while succinic acid alkyd sample will produce coatings with poor adhesive property.

3.3 Solution Viscosity Properties of Cottonseed Oil Alkyd Resins Prepared from Different Polybasic Acids

Solution viscosity properties of cottonseed oil alkyd resins prepared from different polybasic acids were determined in toluene and acetone, while the η_{rv} of the alkyds were plotted against concentration according to the Huggins relationship given by equation (7). Values of the [η] and K_H were also determined from the plots through regression analysis of the linear plot. Linear functions were observed between η_{rv} and concentration in acetone and toluene (Figs. 7 and 8) for the alkyd samples prepared from different polybasic acids. This implies that polyesters (alkyd resins) prepared by alcoholysis process are linear polymers irrespective of the type of polybasic acid used. It is evident from Figs. 7 and 8 that alkyd sample III has the lowest η_{rv} in both solvents (acetone and toluene), while alkyd sample I has the highest value in both solvents and that of alkyd sample II was intermediate. The above observation could be explained based on the anhydride type used in the preparation of each alkyd sample. Sample (I) was prepared with phthalic anhydride, which contain benzene ring that gives a rigid structure, so the samples prepared from phthalic anhydride resist flowing more than other samples. Sample (II) was prepared with maleic anhydride that contains double bond in its structure. There is a possibility of thermal polymerization with maleic anhydride, which could bring about increased viscosity. Aydin *et al.* [10] made similar observation in the study of the effects of anhydride type and amount on viscosity and film properties of sunflower oil alkyd resin. Sample (III) was prepared with succinic acid, which has aliphatic carbon chain in its structure, this type of structure causes low viscosity.

It is observed from Fig. 9 that the [η] values of the three alkyd samples are larger in acetone than in toluene. Also noticed in Fig. 9 is the variation of [η] in acetone in the order: sample (I) > sample (II) > sample (III) and in toluene as sample (II) > sample (I) > sample (III). This difference was attributed to the variation in composition of the alkyd samples, since they were prepared from different polybasic acids (phthalic anhydride, maleic anhydride and succinic acid) with different structures, which also influenced the polymer backbone. It has been observed that [η] value depends on the size and shape of the polymer molecule under investigation [24]. The larger intrinsic viscosity values obtained in acetone could be attributed to the possibility of polymer entanglement at increased concentration of the solvent and possibility of the formation of hydrogen bonding in the acid-base interaction, which could promote molecular extension.

It has been established that intrinsic viscosity is affected by solvent- polymer interaction [25]. The better the solvent, the greater the extent of solvent associated with a polymer molecule, the more the coil expands and hence, the higher the intrinsic viscosity. These results seem to show that acetone is a better solvent than toluene for cottonseed oil alkyd resins prepared from different polybasic acids.Also from Fig. 10, values of K_H increases from sample (I) (0.832) to sample (II) (1.321) and finally sample (III) (45.369) in acetone. This pattern was not observed in toluene, but K_H values are larger in toluene than in acetone with that of sample (III) being the largest in both solvents. This implies that polybasic acid type, among other factors, to some extent affects the Huggin's constant.

Therefore, this research has led to the discovery of another factor, which affects the Huggin's constant, and it is one of the significant contributions of this work to knowledge in polymer science and technology. Other factors, which influence Huggin's constant, K_H, include the molecular weight, molecular weight distribution, degree of branching in the molecule, molecular shape and configuration, and polarity [25].However, the increased K_H values for the alkyds in toluene than in acetone, further verifies that acetone is a better solvent for the alkyd samples, since K_H values are larger in a solvent in which the polymer is less soluble and lower in a solvent in which it is highly soluble. This collaborate our earlier observations that acetone is a better solvent for the alkyd resins.

3.4 Evaluation of Performance Characteristics of Cottonseed Alkyd Resin Paints

The alkyd samples (I) – (III) were formulated into white gloss paints following the recipe in Table 2 and properties such as colour, solid content, specific gravity and adhesion were determined. The drying time, chemical resistance in different solvent media and pencil hardness (scratch and gouge) of the paint samples were also tested. Standard soybean oil alkyd resin was also used to produce paint sample following the recipe in Table 2 to serve as the standard. The colour of the three alkyd paint samples varies from off – white (sample PS_I) to warm white (samples PS_{II} and PS_{III}). This indicates that polybasic acid type also exert some influence on the colour characteristics of the final coating products as the alkyds used for the production of these paint samples were prepared from different polybasic acids and cottonseed oil. The colour of the alkyd resins, which varies from brown to light brown (Table 3) is also transferred to these paint samples. The colour of the alkyd gloss paint samples compared favourably with the colour of the standard alkyd paint sample.

The solid content increased from sample PS_I with 76.90%, followed by sample PS_{II} of 77.93% and finally sample PS_{III} of 80.00%. This implies that succinic acid alkyd paint sample has the highest solid content. The solid content of the three paint samples are higher than that of the standard. It was also observed that the solid content of the corresponding alkyds (see Table 3) increases from phthalic alkyd sample to succinic acid alkyd sample. On the contrary, specific gravity was observed to increase from sample PS_{III} (1.12) to PS_I (1.18). A comparison of the specific gravities of the paint samples with those of the corresponding alkyd resins in Table 3 show that specific gravity 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 (Table 4) and those of the corresponding alkyd sample in Table 3 could be attributed to the contribution by other components of the paint samples.

Adhesion of paint sample on substrate according to [17] is dependent on the binder used, that is, the oil length of the alkyd resins. In this case, the binders were of the same oil length (50% cottonseed oil) but different polybasic acids. It is evident from Table 4 that paint samples prepared from phthalic anhydride (PS_I) and maleic anhydride (PS_{II}) have better adhesion to the substrate (glass plate) than the paint sample prepared from succinic acid (PS_{III}). The variation in adhesion may be attributed to the difference in the structures of the polybasic acids used in each case. On the other hand, adhesion of the paint samples on other substrates – wood and plastered wall was observed to be better than the adhesion of the samples to glass plate. The increase adhesion of these paint samples on wood and plastered wall compared to glass plate may be due to similarities in functional groups present on both surfaces, that is, the wood, plastered wall and the paint samples. The FTIR analysis reveals the presence of polar groups such as -COO-, -OH in the chemical structure of these alkyd samples used in the preparation of these paint samples. These polar groups usually enhance adhesion of the surface coating products on the surface of the substrate.The drying schedule of the white gloss alkyd paint samples formulated from cottonseed oil alkyd resins prepared from different polybasic acids were examined in terms of the times of set-to-touch and dry-through for both indoor and outdoors. This is a very important consideration in coating formulation, as some coated surface may need to dry so that they can be put into service immediately after the coating has been supplied. Tables 5 and 6 show the drying schedule of alkyd gloss paints monitored both outdoors and indoors. It is evident from Tables 5 and 6 that set-to-touch time as well as dry-through time of the paint samples depends on the amount of sunshine and temperature of drying, volume of oxygen as well as the nature of the polybasic acid used in the alkyd formulation. The set-to-touch and dry-through times for indoor samples were greater than that of outdoor samples.

This may be attributed to increase volume of air (oxygen) outdoors compared to indoor since drying is an auto–oxidation process. The set-to-touch and dry-through times for outdoor samples were found to be 14 mins and 490 mins for phthalic anhydride alkyd resin paint sample $PS_{I,}$ 17 mins and 515 mins for maleic anhydride alkyd resin paint sample PS_{II}, and 28 mins and 660 mins for succinic acid alkyd paint sample PS_{III}. On the other hand, the set –to touch time and dry – through time for indoor samples were found to be 25 mins and 565 mins for paint sample PS_I, 27 mins and 665 mins for paint sample PS_{II}, and 33 mins and 780 mins for paint sample PS_{III}. This trend is of the order: $PS_I > PS_{II} > PS_{III}$. This trend is in agreement with the level of unsaturation as indicated by the iodine value of the corresponding alkyds in Table 3. The higher the level of unsaturation, the faster is the drying time [25]. Another factor that can contribute to these differences in drying time of the three alkyd paint samples could be the structure of the polybasic acid used in the alkyd resins preparation. Phthalic anhydride has a benzene ring in its structure, which contains conjugated bonds that can enhance auto-oxidation process. Maleic anhydride has a double bond in its aliphatic structure, which also enhances auto-oxidation. Succinic acid has aliphatic carbon chain in its structure, without any double bond to facilitate auto-oxidation.

This contributes to its prolonged drying time compared to sample PS_I and PS_{II}. 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] and that of the polybasic acid. However, from these results, it can be inferred that phthalic alkyd and maleic alkyd samples can be very useful for formulation of coatings for both interior and exterior decorations with good drying properties, while succinic acid alkyd cannot be used for the same purpose because it produced coatings with prolonged drying time. Table 7 shows the chemical resistance of cottonseed oil alkyds paints prepared from different polybasic acids to different solvent media. All the alkyd samples were highly resistant to 5% sodium chloride solution (brine) and acid, while they were 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 [14]. The phthalic alkyd and maleic alkyd paint samples PS_I and PS_{II} respectively, were highly resistant to distilled water, while the succinic acid alkyd paint sample PS_{III} was poorly resistant to distilled water. This difference may be due to the soft nature of PS_{III} film.

Table 8 shows the hardness test results (scratch/gouge) carried out on the paint film prepared from 50% cottonseed oil alkyd resins from different polybasic acids. The scratch/gouge hardness test for paint samples PS_I, PS_{II} and PS_{III} respectively are as follows 4H/5H, 3H/4H and 2H/3H respectively. It is evident from the above results that hardness of the films varies from $PS_I > PS_{II} > PS_{III}$. This implies that paint film prepared from alkyd sample (I) (50% cottonseed oil phthalic alkyd sample) produces the hardest film that compared with the standard followed by alkyd sample (II) (50% cottonseed oil maleic anhydride sample), while alkyd sample (III) (50% cottonseed oil succinic acid alkyd sample) produces coatings with soft film. This may be due to the nature of the structure of these polybasic acids as earlier explained during drying property of these paint films. This observation shows that polybasic acid type exerts an influence on the hardness property of the coatings. Hence, from the physicochemical properties studied so far, maleic anhydride can be used in place of phthalic anhydride in the production of solvent – borne alkyd resins with physicochemical properties similar to those of the standard soybean oil alkyd resins.

Table 1
Formulation for the Alkyds

Ingredients (g)	Alkyd Samples		
	I	II	III
Cottonseed Oil (COSO)	75.00	75.00	75.00
Glycerol (GL)	21.92	21.92	21.92
Phthalic Anhydride (PA)	53.08	-	-
Maleic Anhydride (MA)	-	53.07	-
Succinic Anhydride (SA)	-	-	53.07
PbO	0.03	0.03	0.03

Table 2
Formulation for medium oil alkyd paints using cottonseed oil alkyds and octoate driers

Ingredients	Medium Oil Alkyd Paint Formula (g)
White spirit	16.50

Cottonseed oil alkyds/standard soybean oil alkyd	50.22
Calcium drier	0.60
Cobalt drier	0.50
Lead drier	0.80
Titanium (IV) Oxide	16.55
Calcium carbonate	6.00
Formalin	2.03
Total	**92.71**

Table 3
Physicochemical properties of cottonseed oil alkyd resins Prepared from different polybasic acid

Properties	**Alkyd Samples**		
	(I)	**(II)**	**(III)**
Colour	Brown	Light brown	Light brown
Specific gravity (at 30^{0}C)	1.025	1.011	1.002
Acid value (mgKOH/g)	5.086	8.818	9.407
Saponification value (mgKOH/g)	253.853	357.638	283.305
Iodine value (Wijs) (gI_2/100g)	39.339	35.725	30.146
Non – volatile matter (%)	72.960	85.420	90.800
Volatile Organic components (%)	27.040	14.590	2.200

[a] Sample (I) – 50% cottonseed oil phthalic alkyd resin; Sample (II) – 50% cottonseed oil maleic alkyd resin; Sample (III) – 50% cottonseed oil succinic acid alkyd resin.

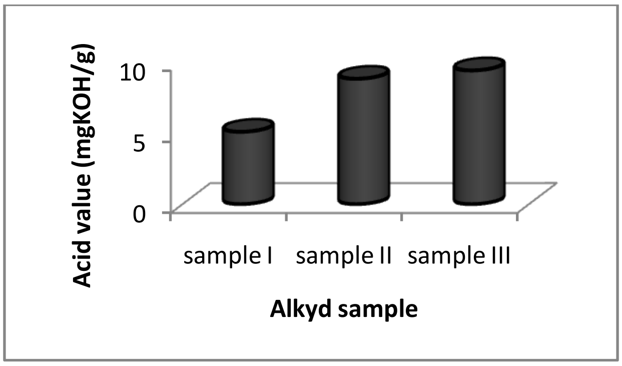

Figure 1: Chart of acid value of cottonseed oil alkyd sample I, II and III prepared from different polybasic acids.

[a] Sample (I) – 50% cottonseed oil phthalic alkyd resin; Sample (II) – 50% cottonseed oil maleic alkyd resin; Sample (III) – 50% cottonseed oil succinic acid alkyd resin.

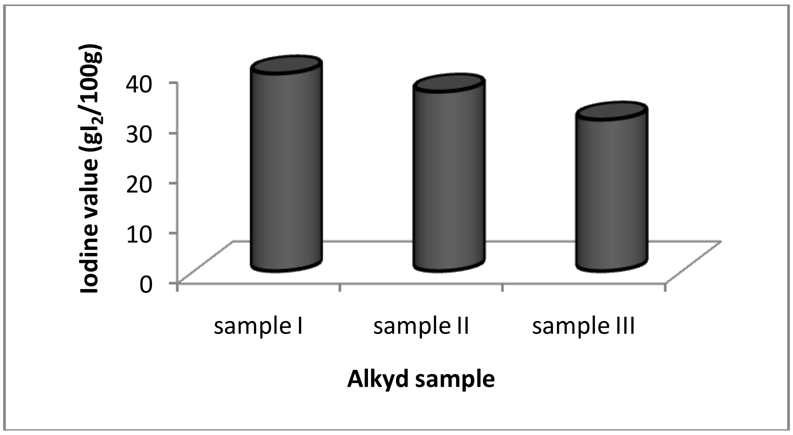

Figure 2: Chart of iodine value of cottonseed oil alkyd sample I, II and III prepared from different polybasic acids.

[a] Sample (I) – 50% cottonseed oil phthalic alkyd resin; Sample (II) – 50% cottonseed oil maleic alkyd resin; Sample (III) – 50% cottonseed oil succinic acid alkyd resin.

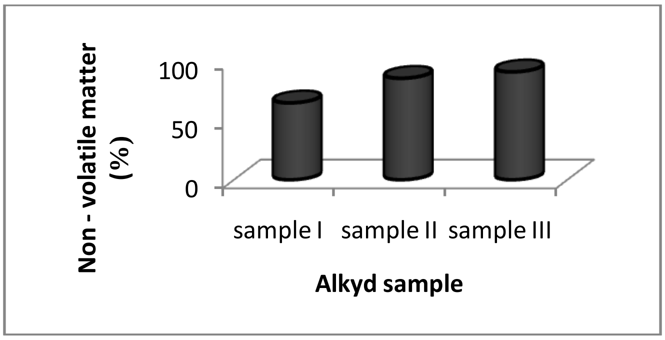

Figure 3: Chart of non – volatile matter of cottonseed oil alkyd sample I, II and III prepared from different polybasic acids.

[a] Sample (I) – 50% cottonseed oil phthalic alkyd resin; Sample (II) – 50% cottonseed oil maleic alkyd resin; Sample (III) – 50% cottonseed oil succinic acid alkyd resin.

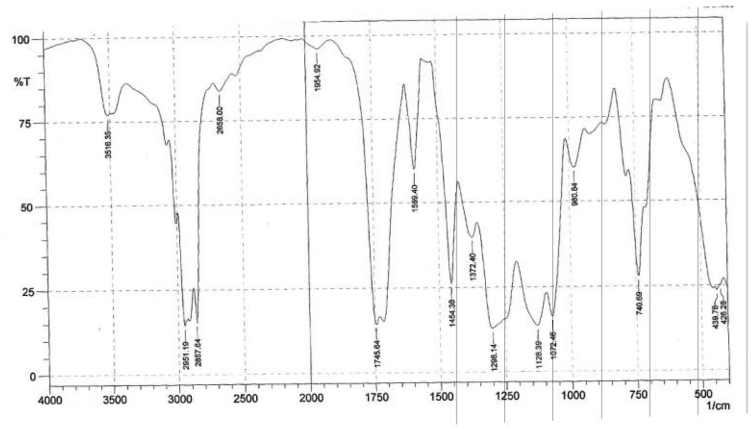

Figure 4: FTIR spectrum of 50% cottonseed oil phthalic alkyd sample (I)

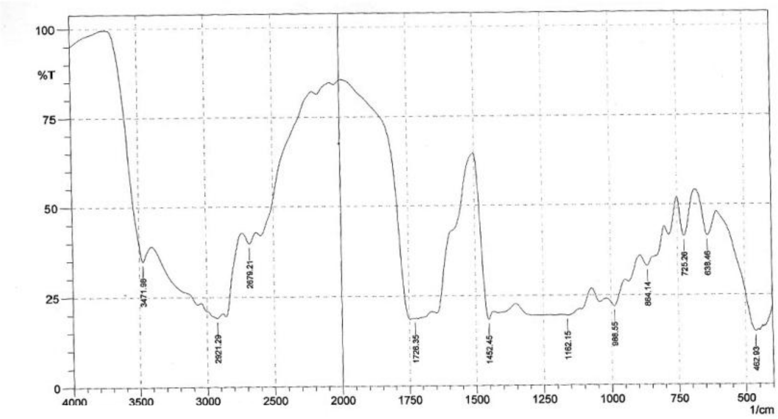

Figure 5: FTIR spectrum of 50% cottonseed oil maleic anhydride alkyd sample (II)

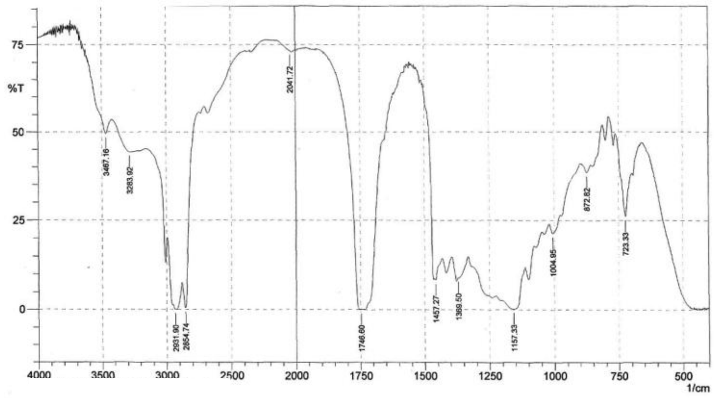

Figure 6: FTIR spectrum of 50% cottonseed oil succinic acid alkyd sample (III)

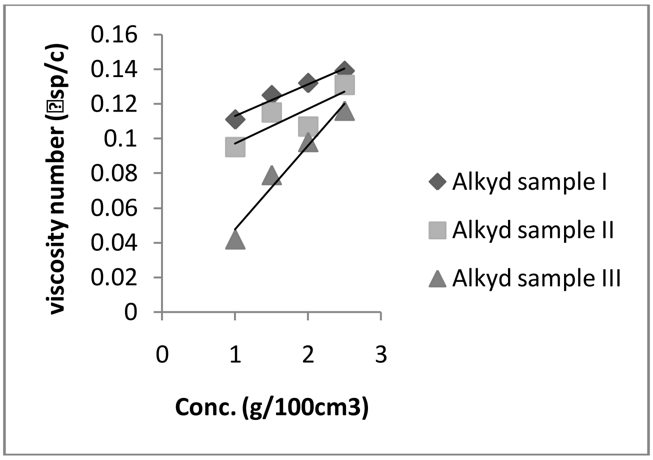

Figure 7: Plot of viscosity number of cottonseed oil alkyd sample I, II and III against concentration in acetone.

[a] Sample (I) – 50% cottonseed oil phthalic alkyd resin; Sample (II) – 50% cottonseed oil maleic alkyd resin; Sample (III) –50% cottonseed oil succinic acid alkyd resin.

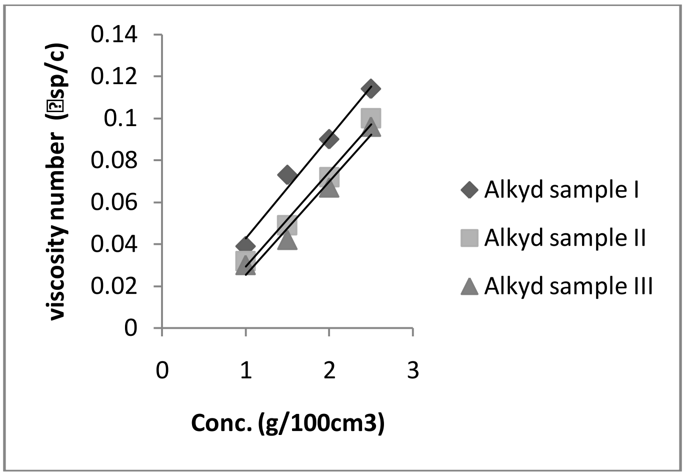

Figure 8: Plot of viscosity number of cottonseed oil alkyd sample I, II and III against concentration in toluene.

[a] Sample (I) – 50% cottonseed oil phthalic alkyd resin; Sample (II) – 50% cottonseed oil maleic alkyd resin; Sample (III) – 50% cottonseed oil succinic acid alkyd resin.

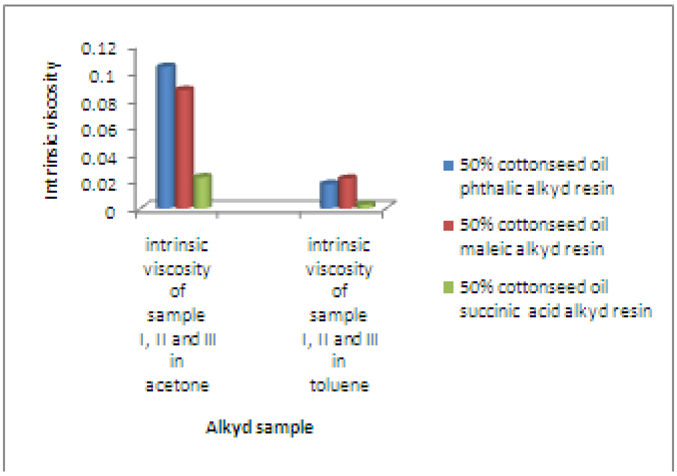

Figure 9: Chart of intrinsic viscosity values of cottonseed oil alkyd samples I, II and III prepared from different polybasic acids in acetone and toluene.

[a] Sample (I) – 50% cottonseed oil phthalic alkyd resin; Sample (II) – 50% cottonseed oil maleic alkyd resin; Sample (III) – 50% cottonseed oil succinic acid alkyd resin.

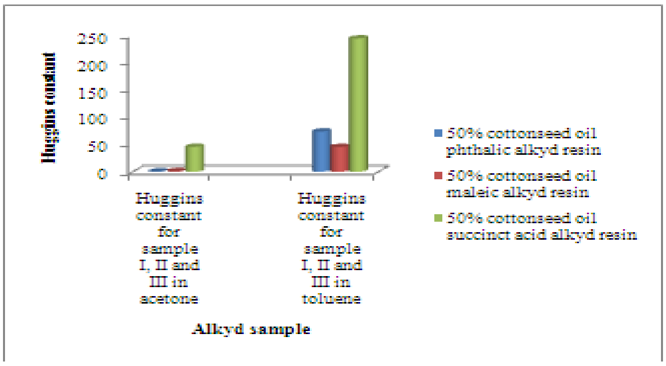

Figure 10: Chart of Huggins constant of cottonseed oil alkyd samples I, II and III in acetone and toluene.

[a] Sample (I) – 50% cottonseed oil phthalic alkyd resin; Sample (II) – 50% cottonseed oil maleic alkyd resin; Sample (III) – 50% cottonseed oil succinic acid alkyd resin.

Table 4
Performance properties of cottonseed oil alkyd resin paint samples formulated with octoate driers.

Paint sample	Colour	Solid content (%)	Specific gravity	Adhesion
PSI	Off-white	76.90	1.18	Excellent
PSII	Warm white	77.93	1.16	Excellent
PSIII	Warm white	80.00	1.12	Good
Standard alkyd paint (SAP)	Brilliant white	65.01	1.14	Excellent

b Sample PS1 – 50% cottonseed oil phthalic alkyd resin paint; Sample PSII – 50% cottonseed oil maleic alkyd resin paint; Sample PSIII – 50% cottonseed oil succinic acid alkyd resin paint.

Table 5
Outdoor drying schedule of cottonseed oil alkyd paint and standard soybean oil alkyd paint samples formulated with octoate driers (outdoor temperature = 330C).

Paint sample	Set-to-touch time (min)	Dry-through time (min)
PSI	14	490
PSII	17	515
PSIII	28	660
Standard alkyd paint (SAP)	6	360

b Sample PSI– 50% cottonseed oil phthalic alkyd resin paint; Sample PSII– 50% cottonseed oil maleic alkyd resin paint; Sample PSIII– 50% cottonseed oil succinic acid alkyd resin paint.

Table 6
Indoor drying schedule of cottonseed oil alkyd paint and standard soybean oil alkyd paint samples formulated with octoate driers (indoor temperature = 280C).

Paint sample	Set-to-touch time (min)	Dry-through time (min)
PSI	25	565
PSII	27	665
PSIII	33	780
Standard alkyd paint (SAP)	10	420

b Sample PSI– 50% cottonseed oil phthalic alkyd resin paint; Sample PSII– 50% cottonseed oil maleic alkyd resin paint; Sample PSIII– 50% cottonseed oil succinic acid alkyd resin paint.

Table 7
Chemical resistance of cottonseed oil-modified alkyd resin paint samples.

Paint sample	Chemical resistance			
	solvent media			
	Distilled water	NaCl (5% solution)	H2SO4 (0.1 moldm-3)	KOH (0.1 moldm-3)
PSI	n	n	n	r

PSII	n	n	n	r
PSIII	w	n	n	r
Standard alkyd paint (SAP)	n	n	n	w

No effect = n, whitening = w, shrinkage of film = s, blistering of film = b, removal of film = r
b Sample PSI– 50% cottonseed oil phthalic alkyd resin paint; Sample PSII– 50% cottonseed oil maleic alkyd resin paint; Sample PSIII– 50% cottonseed oil succinic acid alkyd resin paint.

Table 8
Pencil hardness of melon seed oil and cottonseed oil alkyd paint samples.

Paint Sample	Pencil hardness	
	Scratch	Gouge
PSI	4H	5H
PSII	3H	4H
PSIII	2H	3H
Standard alkyd paint (SAP)	5H	6H

b Sample PSI– 50% cottonseed oil phthalic alkyd resin paint; Sample PSII– 50% cottonseed oil maleic alkyd resin paint; Sample PSIII– 50% cottonseed oil succinic acid alkyd resin paint.

IV. CONCLUSION

Apart from the nature of the triglyceride oil used in alkyd resin synthesis, the type of polybasic acid used can also influence the physicochemical and viscosity properties of alkyd resins. The FTIR analysis of the alkyd samples show that phtthalic alkyd sample give the highest value of correlation intensity for C=O, followed by maleic alkyd sample and succinic acid alkyd sample give the least value. On the other hand, correlation area of C=O for the alkyd samples were observed to vary in reverse order of correlation intensities. Succinic acid produces alkyd resin with the least value of ηrv. The [η] values of the alkyd resins were larger in acetone than in toluene, KH values were larger in toluene than in acetone. Also, polybasic acid type has been discovered as one of the factors affecting KH. Phthalic and maleic anhydrides alkyd resin produces coatings whose properties were found to be comparable with that of standard soybean oil alkyd sample. The properties of succinic acid alkyd coating were very poor. Hence, on economic consideration, it can be deduced that maleic anhydride can substitute phthalic anhydride in alkyd synthesis without compromising those properties that will lead to quality product.

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