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Synthesis and Characterization of Paint Driers from Jatropha Seed Oil

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Abstract

This work is concerned with the synthesis and characterization of paint driers from jatropha seed oil. TheJatropha curcas oil was extracted using soxhlet extraction process with n-hexane as the solvent. The physiochemical properties of the oil were determined using standard analytical methods and the oil was analyzed to have an iodine value, peroxide value, acid value, saponification value, moisture content, and specific gravity of 108 mg/g, 2.87 meq/g, 3.80 mgKOH/g, 187.99 mgKOH/g, 0.40%, and 0.89 respectively. The oil was used to prepare a soluble soap by cold process with potassium hydroxide. Afterwards, Cobalt and zinc driers were prepared by reacting its chlorides with the soluble soap in an aqueous medium. The driers were characterized to determine their color, texture, solubility in water and kerosene, and foaming characteristics. The efficiency of the driers were evaluated by first examining the driers combination that will yield the best drying time, and then studying the effect of increase in mass of driers in a fixed volume of paint. In both cases, the dust free time (DFT), dry for recoating time (DFRT) and dry hard time (DHT) of the paint-driers mixtures were evaluated. From the results obtained, it was observed that combining the driers gave a better drying time than when used individually and the optimum drier combination is 75% Co and 25% Zn. It was also deduced that the optimum concentration of the driers in a paint is 2% (wt/vol) which reduces the DFT, DFRT, and DHT of a purchased emulsion paint from 27, 37, and 130 minutes to 18, 28, and 90 minutes respectively. The paint driers produced can be applied in domestic and industrial painting operations.

Keywords: Jatropha curcas, paint drier, precipitation, soluble soap

Introduction

The importance of paints and coatings cannot be overemphasized as they are applied both domestically in painting our homes, and industrially in painting of process equipment. These paints and coatings usually take relatively long time to dry which increases the chances of the painted surfaces being marred and may also lead to delay in industrial operations in cases where industrial equipments are painted. The drying time of these paints and coatings can be reduced by the addition of substances known as driers. Driers are various compounds added to paints and coatings to increase the drying rate of the paints or coatings. Driers improve the drying characteristics of corrosive paints even at lower temperatures and in relatively humid environments [13].

Driers are metallic soaps and can be represented by the general formula $(RCOO)_xM$. Where R is an aliphatic radical (mainly from organic acids found in vegetable oil) and M is the drier metal with a valence of X, and they differ from normal soaps via their solubility differences in organic solvents and water insolubility[5]. Driers must be soluble in the drying oil, therefore agro-based oils is a major raw material in the production of paints driers[3]. Driers from agro based oils are usually manufactured as pastes, liquids or solids and their physical properties depends on the type and amount of metal present, nature of acid used, and mode of preparation. Several agro based oils can be used in the production of driers, but majority of these agro based oils are edible and thus, if used to produce driers might lead to food insecurity and increased cost of producing the driers, therefore non-edible oils such as jatropha seed oil should be used in producing paint driers [16].

The term “Jatropha” is generally used to refer to the species *J. curcas*, although about 170other species of the plant are known [10]. *Jatropha curcas* belongs to the family Euphorbeaceae, a large drought-resistant shrub with several attributes and potentials that has attracted interest all over the world as a potential bio-fuel plant [13]. It is tall(about 6m high), possess a straight trunk with large branches and green leaves whose length and width is about 6 and 15cm respectively. This tree have a lifespan of more than 50 years, and can survive on marginal soils with low nutrient content 10]. Oil from jatropha seeds is referred to as jatropha seed oil; a non-edible vegetable oil which can serve as a feedstock for biodiesel production, making soap, glue, dye and driers[13].

According to [3], there are basically two classes of paint driers; primary driers and secondary driers. Primary (or active) driers at moderate temperature and humidity promote oxidation, and the formation and decomposition of peroxide and when used alone would simply dry the surface of the film, while the paint subsurface would remain moist. Examples of primary drier metals includes Cobalt, Manganese, Iron, and Lead [12]. On the other hand, secondary (or auxiliary or through) drier metals includes Barium, Zirconium, Calcium, Zinc, and Lithium. At moderate temperatures and humidity these driers do not display any catalytic activity themselves, but rather improves the action of primary driers, especially with regards to through drying of the coatings and are therefore referred to as "through driers" [8].

Three driers preparation methods are known; precipitation (double decomposition), fusion, and direct metal reaction methods[6]. The precipitation method involves the reaction of potassium or sodium salt of the organic acid with the appropriate metal salt in an aqueous medium, the fusion process involves

the reaction of metal hydroxides, oxides, carbonates or other salts directly with the selected organic acids at 150–200 °C, and the direct metal reaction process involves the oxidation of finely divided metal powder over a catalyst with air and in the presence of the organic acids [4].

The precipitation method is the most preferred method of producing paint driers, this is because the precipitation method does not require any catalyst, and takes place at room temperature. This method is represented by the chemical reactions:

$$RCOOH + KOH\ (aq) \rightarrow RCOOK + H_2O \quad (1)$$

$$ZnCl_2(aq) + 2RCOOK\ (aq) \rightarrow (RCOO)_2Zn + 2KCl \quad (2)$$

The organic acid in the oil is first reacted with KOH or NaOH, this reaction is known as saponification reaction to form soluble soap. This soluble soap is further reacted with the drier metal salt in an aqueous medium. The metallic soap (drier) is the precipitate formed from the second reaction, which is filtered, washed, dried and ground [9].

A number of non-edible agro-based oils have been characterized but a vast majority have not yet been explored for the production of paint driers. [14] produced and characterized Zinc, Nickel and Copper paint driers from sand box oil, which was found to be effective in various combinations in a gloss paint. [9] prepared Zinc and Cobalt driers from melon and sesame seed oils which was tested in a binder solution and yet proved effective in accelerating the drying rate of the solution. Despite the several works on vegetable oils in paint drier making, little information have been provided on the optimal combination of primary and secondary driers for lowest drying time of paints and coatings. This research is focused on the use of the precipitation method for the production of Cobalt and Zinc driers from *Jatropha curcas* seed oil. The optimal driers combination for best results was also examined.

2.0 Materials and Method

2.1 Materials

The materials used for this research work are: *Jatropha curcas* seed, n-hexane, potassium hydroxide (KOH), zinc(ii)chloride ($ZnCl_2$), cobalt(iii)chloride ($CoCl_3$), distilled water, and emulsion paint.

2.2Sample Preparation and Extraction of the *Jatropha curcas Seed* Oil

Jatropha curcas seeds were obtained from Ibadan in Oyo state. The seeds were removed from their pods and sun dried for two weeks after which they were deshelled and comminuted using a mortar and a pestle. Soxhlet apparatus was used to extract the oil from the ground jatropha seeds using n-hexane, and the oil-solvent mixture was placed in a water bath set at 75 ^{0}C for the n-hexane to evaporate.

2.3 Determination of Peroxide Value

5 g of the oil sample was weighed into a 250 mL conical flask, 30 cm^3 of a solution mixture containing 60% glacial acetic acid and 40% chloroform was added to the oil sample. The flask was stirred to dissolve the solvent mixture. Afterwards, 5 cm^3 of the saturated potassium iodide solution was added. The solution was placed in the dark for 5 minutes and 3$cm^3$of distilled water was added, followed by

0.5cm^3 of 1% starch solution. The mixture was titrated with 0.1 M $Na2S_2O_3$with constant shaking. The titration continued until the blue colour disappeared [9].A blank titration was also carried out without the sample. The peroxide value was calculated using:

$$POV\left(\frac{meq}{kg}\right) = \frac{(S-B)M\ x\ 1000}{wt\ of\ sample} \quad (3)$$

2.4 Determination of Specific Gravity

10 mL of the oil sample was weighed on a weighing balance and the resulting weight (in grams) of the measured oil was divided by the volume of the oil to obtain the oil density. The specific gravity of the oil was calculated from the following expression:

$$Specific\ Gravity = \frac{density\ of\ oil\ (\mathrm{g/cm3})}{density\ of\ water\ (\mathrm{g/cm3})} \quad (4)$$

2.5 Determination of Acid Value

1.10 g of the oil was poured into a conical flask. 25mL of ethanol was added to dissolve the oil followed by 2 drops of phenolphthalein. The solution mixture was heated by soaking in a water bath for 10 minutes after which it was allowed to cool. Afterwards, the mixture was titrated against 0.1 N potassium hydroxide solution until the pink color appeared [11]. Acid value was calculated using this formula:

$$Acid\ value\ \left(\frac{mg}{g}\right) = \frac{56\ x\ N\ x\ V}{Wt\ of\ sample} \quad (5)$$

2.6 Determination of Moisture Content

2 g of the oil was placed in a pre-weighed petri dish and kept in an oven set at 60 ^{0}C. After every 5 minutes, the sample was removed, cooled in a desiccator for 10 minutes and then weighed. The cycle continued until the weight of the sample was constant.

The moisture content was calculated as follows:

$$Moisture\ content(\%) = \frac{(\mathrm{w1-w2})}{\mathrm{w1}}\ x\ 100\% \quad (6)$$

2.7 Determination of Saponification Value

2 g of the oil was weighed into a 250mL conical flask containing 25mL of 0.5N alcoholic potassium hydroxide solution. The solution mixture was heated in a boiling water bath for 1 hour with occasional shaking. While the solution was still hot, 3 drops of phenolphthalein indicator was added and the excess potassium hydroxide was titrated with 0.5 N hydrochloric acid. The initial and final titre values were recorded accordingly. The above procedure was repeated without the sample [11].The saponification value was calculated using the formula:

$$SV\left(\frac{mg}{g}\right) = \frac{56.1(Vb-Va)x\ N\ of\ Hcl}{wt\ of\ sample} \quad (7)$$

2.8 Determination of Iodine Value

A 0.1 g of the *Jatropha curcas* seed oil was dissolved in 15 mL of carbon tetrachloride. 20 mL of Wijs solution was added from a burette. With the components thoroughly mixed and the flask stopped, the mixture was allowed to stay in the dark for 2 hours at room temperature. Afterwards, 150 mL of water and 20 mL potassium iodide were added to the solution mixture. The solution was titrated with sodium

thiosulphate using starch indicator. Similar titration was also carried out with a blank sample [2]. The iodine value was thereafter calculated using:

$$Iodine\ value\left(\frac{mg}{g}\right) = \frac{12.7\ (B-S)N}{W} \quad (8)$$

2.9 Preparation of Soluble Soap

The cold process of soap production was used to prepare a soap. 15 g of KOH was dissolved in 10 mL of distilled water and was allowed to stay for 5 minutes for proper dissolution. The prepared solution of KOH was then poured gently into a beaker containing 10 g of the oil, and the resulting solution was stirred properly. Thereafter the solution was heated gently on a heating mantle for 5minutes with constant stirring and then left to stay for1 hour. 30 mL of saturated NaCl solution was added to the paste formed to remove the soap from water, glycerol and any excess KOH present and also make it to cake. The soap floated on the liquid and was filtered off, washed with distilled water and dried under the sun for 48 hours [15]. The preparation of the soap is illustrated below;

$$RCOOH+KOH \rightarrow RCOOK+H_2O \quad (9)$$

2.10 Preparation of Cobalt and Zinc Driers

The precipitation method was used to prepare the cobalt and zinc driers. An aqueous solution containing 10% (w/v) of $CoCl_3$ was poured into another aqueous solution containing 5% (w/v) of the soluble soap with continuous stirring. The precipitate formed from the reaction is the cobalt drier which was filtered off, washed with distilled water and dried under the sun for 24 hours. The same process was repeated for zinc drier [9].

2.11Characterization of the Driers

The color of the drier was determined by the sense of sight. The texture was determined by placing small quantities of the driers on a finger and rubbing it against another finger. 1g of the driers were separately poured into two beakers containing 100mL of water and 100 mL of kerosene at room temperatures and their dissolutions were carefully observed to determined their solubility in water and kerosene (at room temperature). Thereafter, the beakers containing the driers and water were agitated to determine the foaming characteristics of the driers.

2.12 Evaluation of the Efficiency of the Prepared Paint Driers

A purchased emulsion paint was well-thinned with water and used to effectively study the driers combination that will yield the lowest drying time and the effect of increase in mass of driers in a fixed volume of the paint. 5 samples of 1 g of the driers were prepared containing both the Cobalt and Zinc driers as shown in Table 1

Table 1: Driers Percentage in various samples

Sample	Sample 1	sample 2	sample 3	sample 4	sample 5
Co/Zn drier (%/%)	100/0	75/25	50/50	25/75	0/100

Each of these samples was mixed with 100mL of the thinned emulsion paint, and then applied on a wall with the aid of a brush and the paint drying was carefully observed to determine which combinations of the driers is best suitable for use. The paint was also applied without the drier.
The percentage combination of driers with the least drying time was selected and with the total mass of driers varied, it effect on the drying time on a fixed volume of paint was examined. The following concentrations were used; 2/100, 3/100, and 5/100 weight of driers (g) / volume of paint (mL). The drying time of the paint mixtures was studies under three categories:

i. Dust-Free Time (DFT)
This is when dusts will no longer stick to the surface of newly applied paints or coatings. At this stage, the paint film was dried enough so that fine particles of dust dropped onto the surface was removed by gentle blow of air over the surface. This time was observed and noted.

ii. Dry-for-Recoat Time (DFRT)
Dry-for-recoat time is the time required for the applied paints to reach a drying stage where by a second coating can be successfully applied on it without causing any surface irregularities. To determine this, a second coating was gently applied on parts of the dust-free paint, the time in which the second coating adhered nicely without marring the surface of the initially applied paint was noted as the dry-for-recoat time.

iii. Dry-Hard Time (DHT)

Crudely, painters have evaluated the dry hard time of paints and coatings by twisting an impressed thumb on the painted surface and checking for damages. A thumb was frequently pressed on the paint surface until the pressure of the thumb could no longer mar the surface. The period of time was noted.

3.0 Results and Discussion

Table 2: Physiochemical Properties of *Jatropha curcas* Oil

Parameter	Value
Iodine value (mg/g)	108
Peroxide value (meq/g)	2.87
Acid value (mgKOH/g)	3.80

Saponification (mgKOH/g)	187.99
Moisture (%)	0.40
Specific gravity	0.89

The results of the physiochemical properties of the extracted *Jatropha curcas* oil are presented in Table 2. Acid value is a measure of the free fatty acids in an oil sample, and a very low acid value (≤ 1 mgKOH/g) implies an edible vegetable oil [18]. The acid value of the extracted oil was determined to be 3.80 mgKOH/g which means that the oil is non-edible and therefore if used to produce paint driers, will not affect the food chain.

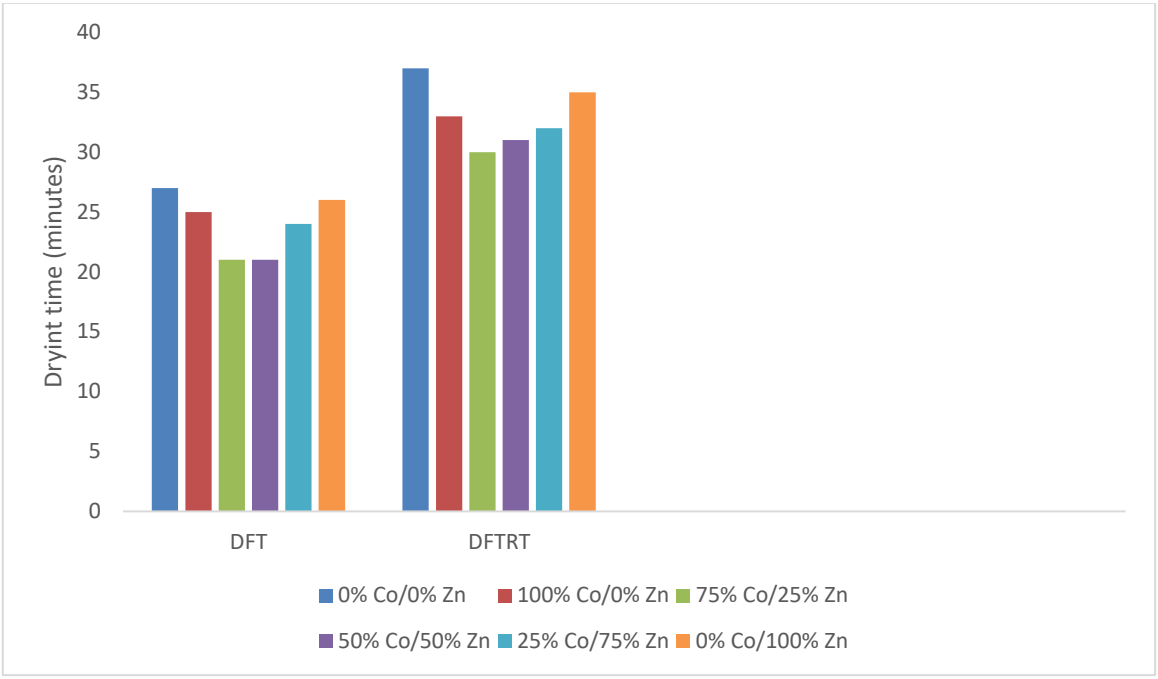
Iodine value shows the degree of unsaturation of the oil. The iodine value for the extracted *jatropha* oil (108 mg/g) indicates relatively high degree of unsaturation and can be classified as a semi-drying oil; absorbs atmospheric oxygen slowly and produces only soft film after prolong exposure to air. This is a good property of oils suitable for use in the production of paint driers [14]. Peroxide value is an indication of the oil stability to oxidation. It is an assay used in measuring the level of oxidative rancidity of the oil. The *Jatropha curcas* seed oil has a peroxide value of 2.87 meq/g. This low value attest to the oxidative stability of the oil which implies that the oil is not rancid and will take a very long period of time to go stale [7].

Saponification value is an indicator of the amount of potassium hydroxide required to saponify 1g of the oil. The larger the saponification value, the more the tendency of the oil to form a soap. The saponification value of the extracted oil (187.99 mgKOH/g) implies that the oil has good a tendency to form soap and can therefore be used to make paint driers[1].

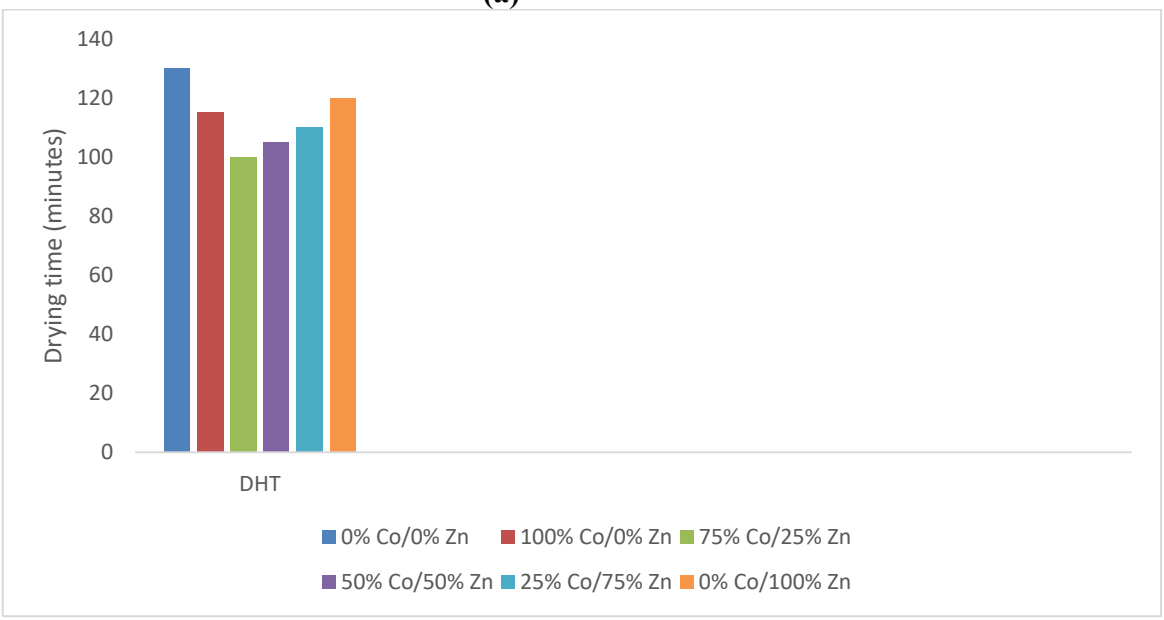
Table 3: Physiochemical Properties of the Prepared Driers

Test	Cobalt drier	Zinc drier
Color	dark blue	white
Texture	powder	powder
Solubility	insoluble in water and soluble in kerosene	insoluble in water and soluble in kerosene
Foaming characteristics	does not foam in water	does not foam in water

From Table 3 which shows the properties of the prepared driers, it can be seen that while the cobalt drier is dark blue, the zinc drier is white. Also, both driers are powdery, insoluble in water but soluble in kerosene, and does not foam in water. The properties of these driers are comparable with the data reported for paint driers from sand box oil by [14]. Paint driers does not discolor paint due to their addition in small quantities.



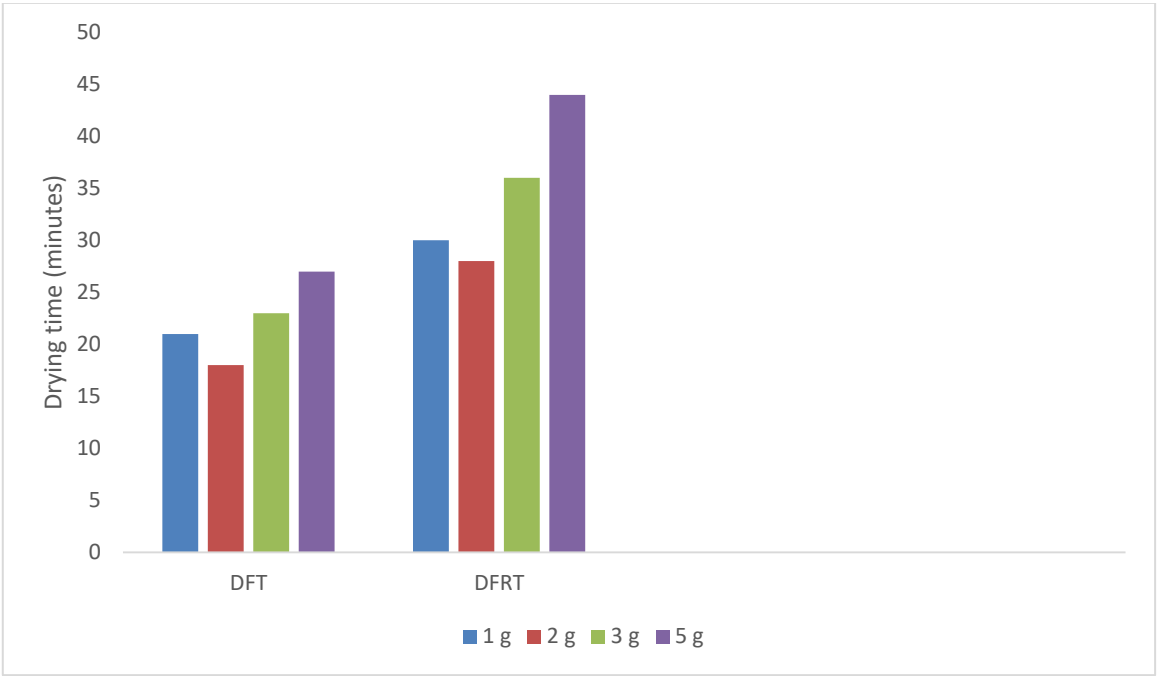
(a)



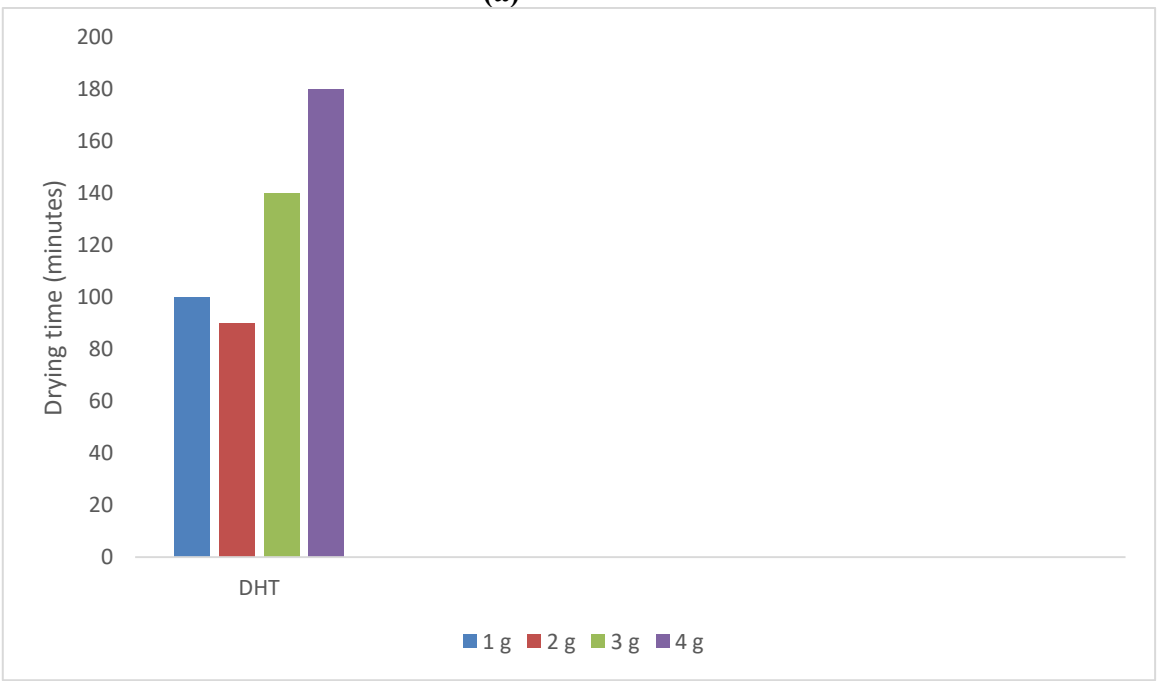
(b)

Fig 1: Optimization of the Driers Combination Using a Fixed Mass of Driers (1g) Mixed with 100mL of Paint (a) DFT (Dust-Free Time) and DFRT (Dry- for-Recoat Time) (b) DHT (Dry-Hard Time)

The results from the optimization experiment to ascertain which combination of the driers will result in the fastest drying time of an emulsion paint is shown in Figure 1. Cobalt drier is the primary or surface drier, while zinc drier is the auxiliary or through drier. When the driers were combined, the respective drying times were lower than when used individually, this is because the effective accelerated drying of paints and coatings involves simultaneous fast drying from the surface and subsurface of the paints and coatings. 75% cobalt and 25% zinc drier combination gave the best drying time of 21 minutes, 30 minutes, and 100 minutes for the Dust-Free Time (DFT), Dry for Recoat Time (DFRT), and Dry-Hard Time (DHT) respectively when 1g of the driers mixture is poured in 100mL of paint



(a)



(b)

Figure 2: Effect of Increase in Mass of Driers (75% Co and 25% Zn) on a Fixed Volume (100ml) of Paint (a) DFT (Dust-Free Time) and DFRT (Dry- for-Recoat Time) (b) DHT (Dry-Hard Time)

The effect of increase in mass of the driers (75% Co and 25% Zn), in a fixed volume (100mL) of paint was studied, and the results is shown in figure 2. From the results, it can be seen that the lowest drying time was obtained from 2g of the driers. Also as the mass of driers increased from 2g, the drying time of the paint also increased. This is because a paint is a thick slurry and can only dissolve limited amount of soluble solids (in this case, the driers), and the undissolved excess driers will lead to chalking of the applied paint on the wall surface, making the overall painting operation to be ineffective.

4.0 Conclusion

The drying time of paints and coatings depends on several factors including the composition of the paints, temperature and relative humidity. This research work shows that *Jatropha* curcas oil can be used to synthesize paint driers with appreciable characteristics which can significantly reduce the drying time of paints when compared to applying these paints without the driers under relatively stable atmospheric conditions. From the experiments carried out and results obtained, it can be deduced that individually the driers will reduce the drying time of paints minimally, but when combined, the effects of the driers is maximized and the optimum driers combination is 75% cobalt and 25% zinc driers which changed the Dust-Free Time (DFT), Dry for Recoat Time (DFRT), and Dry-Hard Time (DHT) of the paint from 27, 37, and 130 minutes to 21, 30, and 100 minutes respectively when 1g of the driers was mixed with 100mL of a thinned paint. It can also be concluded that 2g of the driers in 100mL of paint is the maximum concentration for an effective painting operation.

5.0 Acknowledgement

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