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Preparation of Zinc-Cobalt Driers from Melon and Sesame Seed Oils

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ABSTRACT

Oils from melon and sesame seeds were extracted and their physicochemical properties were evaluated as; iodine value, 126 mg I_2 g^{-1} and 113 mg I_2 g^{-1}, saponification value, 197 mg KOH g^{-1} and 189 mg KOH g^{-1}, acid value, 4.71 mg KOH g^{-1} and 5.64 mg KOH g^{-1}, free fatty acid, 2.37 mg KOH g^{-1} and 2.92 mg KOH g^{-1}, peroxide value, 1.76 mg kg^{-1}, and 1.98 mg kg^{-1}, specific gravity, 0.91 and 0.92 respectively. Melon and sesame seed oils were utilized in the preparation of metal soaps of zinc and cobalt. The physicochemical properties of the metallic soap were determined using standard procedures. A binder – drier solution was prepared using an alkyd resin and xylene and the metallic soaps were incorporated into the solution as driers. The reduction in the drying drying time with increase in the concentration of the metallic soaps indicated that the metallic soaps acted as catalysts in the coating.

Keywords: Paint driers, melon, sesame, physicochemical properties, seed oils.

INTRODUCTION

The use of metallic soaps as binder- drier solution in coatings and paint industries has taken a centre stage in global discourse. The drying effect of various metal soaps in surface coatings has been studied by many researchers. It is observed that a combination of two or more metals is better than either of them separately because each one has a specific action in the drying process e.g. lead is usually considered to be a “thorough drier” and cobalt a “surface drier”, manganese is more surface than thorough. Zinc retards surface drying but promotes drying by keeping the surface open for continued oxygen penetration and absorption [1, 2].

Driers are a group of water insoluble metallic soaps which contain either alkaline earth metals, for example Aluminium, calcium or heavy metals such as Zinc, copper etc., combined with monobasic carboxylic acids of seven to twenty-two carbon atoms and they work by catalyzing the uptake of dioxygen and decomposition of hydro peroxides to free radicals, resulting in hardened cross-linked polymer networks that bind the pigment to the painted surface of the treated object.

The most commonly used driers are metal soaps of carboxylic acids. The first modern ones were developed in the early 1920’s with the preparation of metal naphthenates [3-5]. The driers that are used today are based upon synthetic acids, like 2-ethyl hexanoic acid and versatic acid. Versatic acids have a tertiary carbon atom adjacent to the carboxylic acid group resulting in a highly branched structure. The reason for using branched carboxylic acids is to achieve a high solubility in a polar environment; that is the oil-paint binder system and to prevent precipitation of the complex. The introduction of water-borne and high-solid alkyd paints has led to the development of new drier systems [6].

The metals that have been used in drier compounds can be grouped in three categories: primary driers (also called active or oxidation driers), secondary driers (also called thorough-driers) and auxiliary driers [7-9]. In this work, oils were extracted from melon and sesame seeds and then utilized in the preparation of zinc-cobalt driers.

MATERIALS AND METHODS

Materials: Chemicals used were of analytical grade and were products of BDH Chemicals Ltd, Poole England unless otherwise stated. Melon and sesame seeds were collected from Ipav, Gboko in Benue State, Nigeria. The sample was authenticated by a Botanist, Mr. Joshua Waya of the Department of Biological Sciences Benue State University, Makurdi-Nigeria. The seeds were dehulled, screened, oven dried and ground. The oils were extracted in a Soxhlet apparatus using petroleum ether (40-60) ^oC and solvent removed in vacuo.

Determination of peroxide value: 5 g of each oil sample was weighed into 250 mL conical flask, and heated at 25 ^oC for 1 hour. 30 cm^3 of the solution mixture consisting of 60 % glacial acetic acid and 40 % of chloroform was added to the oil sample. The flask was stirred to dissolve the solvent mixture. 5 cm^3 of saturated potassium iodide solution was then added. The solution was placed in a dark cupboard for 5 minutes and 3 cm^3 of distilled water was added. 0.5 cm^3 of 1 % starch solution was added and it was titrated with 0.1 M $Na_2S_2O_3$ with vigorous shaking until the blue colour just disappeared [9, 10].
Thereafter, the peroxide value of the oils was calculated using equation 1

$$POV\ [meq/kg] = \frac{(V_1 - V_o) \times 1000 \times T}{W} \qquad 1$$

Where, POV is peroxide value, V_o and V_1 are 0.1 mol/L of sodium thiosulphate solution in the blank and main test respectively, T is titre of the thiosulphate solution, W is the weighed portion of substance in grams.

Iodine value: A 0.1 g of melon and sesame seed oil was dissolved separately in 15 mL of carbon tetrachloride. 25 mL of Wijs' solution was added from a burette. The components were thoroughly mixed with the flask stopped and the mixture was allowed to stand in the dark for 2 h at room temperature. Thereafter 150 mL of water and 20 mL potassium iodide were added to the reaction mixture. The solution was titrated with sodium thiosulphate using starch indicator [11-13]. A similar titration was also carried out with a blank sample and the iodine value was thereafter calculated using equation 2 below;

$$\text{Iodine value (mg/g)} = (T_2 - T_1)M \times 12.7 \qquad 2$$

Determination of acid value: 25 mL of diethyl ether was mixed with 25 mL of ethanol and 1 mL of phenolphthalein indicator solution was added. This was then neutralized with 0.1 M KOH solution. 1 g of melon and sesame seed oil was dissolved in the neutralized solvent mixture. This was then titrated with 0.1 M NaOH with continuous shaking until a pink color which persisted for 115 sec was obtained [14].

$$Acid\ value\ (mg\ KOH/g) = \frac{40 \times C \times V}{weight\ of\ sample} \qquad 3$$

The acid value was calculated using equation 3. Where; C is concentration of KOH used, v is volume of mass of KOH.

Determination of refractive index value: The refractive index of the oil was determined by using Abbe refractometer at 306 K after which temperature correction was made to obtain the correct refractive index of the oil. The expression used to correct for temperature effect is shown in equation 4 below.

$$RI_{correct} = (T - 20)K \times 0.0000078 = RI \qquad 4$$

Where $RI_{correct}$ is the refractive index after temperature correction, RI is refractive index obtained before temperature correction was made, T is temperature.

Determination of specific gravity: The specific gravity of the melon and sesame seed oil was calculated as follows using equation 5 [15].

$$\text{Specific gravity} = 0.8475 + 0.003 \times \text{SV} + 0.00014 \times \text{IV} \qquad 5$$

Where SV is Saponification value and IV is Iodine value.

Moisture content: 2 g of each oil sample was weighed into a Petri dish which was dried in an oven, cooled in desiccator and weighed. The Petri dish with oil was then placed in an ovum at a temperature of 373 K for 45 min at the end of the drying period, the sample was removed and cooled in the desiccator for 15 min and weighed. The moisture content was calculated as follows using equation 6 [16].

$$\text{Moisture content (\%)} = \frac{(\text{a}-\text{b})}{\text{w}} \times 100\ \% \qquad 6$$

Where a is the weight of Petri dish and sample before oven drying, b is weight of Petri dish and sample after oven drying, w is weight of sample.

Determination of saponification value: 1 g of each of oil was measured and poured into a flask and 12.5 mL of alcoholic potassium hydroxide solution was added into the flask and was placed on a boiling water bath for 40 min accompanied by shaking. After the time interval of 40 min, the flask was then removed and 0.4 mL of the 1 % phenolphthalein indicator was added. Thereafter, while still warm, it was titrated with 0.5 M HCl, until the faint pink color permanently disappeared and a titer value was obtained. Similar titration was also carried out with a blank sample. The saponification values for the oils were calculated using equation 7 [15, 16].

$$\text{Saponification value (mg/g)} = \frac{(\text{V}_\text{b}-\text{V}_\text{a})}{\text{W}} \times \text{N} \times 56.1 \qquad 7$$

Where, V_b is the value of HCl used in the blank, V_a is the value of HCl used in titration with the oil, W is the weight of the oil used, N is the normality of HCl solution, 56.10 is the equivalent weight of potassium hydroxide.

Preparation of soluble soap: The cold process of soap production was used to prepare the soap. 15 g of KOH was dissolved in 10 mL of distilled water and was allowed to stand 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 stirred properly. The resulting solution mixture was then heated gently on a heating plate for 5 min with continuous stirring. The solution was then removed from the heating plate and allowed to stand for 1 hour. 30 mL of saturated solution of Na Cl was then added to the paste formed. This process which is termed “salting out” was used to remove the soap from water, glycerol, and any excess KOH present and also made it to cake [17]. The soap floated on the liquid and was then filtered off, washed with distilled water and dried under the sun for 48 hours [17]. The preparation of the soap is illustrated in equation 8 below;

$$RCOOH + KOH \rightarrow RCOOK + H_2O \qquad 8$$

Preparation of cobalt and zinc drier: The precipitation method was used to prepare cobalt drier, consider reaction 8 for cobalt. 10 % (w/v) of $CoCl_3$ was prepared by dissolving 10 g of $CoCl_3$ in 100 mL of distilled water and 5 % (w/v) of soap solution was made by dissolving 5 g of the soap prepared in 100 mL of distilled water accompanied by stirring. Thereafter, the two solutions were mixed with continued stirring until slurry was formed. The slurry formed was then filtered off, washed with distilled water and dried under the sun for 24 h. The same process was repeated for zinc drier [18].

Preparation of Binder-Drier solution: The required 5 g of alkyd resin was measured and thinned to 50 % using 2.5 g of xylene. With the aid of a stirring rod, the solution was mixed properly; the preparation of the binder was carried out in ten beakers in which the metallic soaps were incorporated in the coating at different concentration and combination.

In the first five beakers, cobalt (primary drier) was incorporated in the binder and a combination of cobalt (primary drier) and zinc (auxiliary drier) were also incorporated in another five beakers ensuring that the concentration was kept constant.

Also 1.5 g of alkyd resin was measured and thinned to 50 % using 0.5 g of xylene. The mixture was mixed properly and with the aid of a stirring rod the binder was casted on a glass slide, without incorporating any of the metallic soap and the time taken for the film to dry was noted [19].

Casting of the prepared binder on a glass slide: The formulated binder-drier solution was casted on a glass slide with the aid of a stirring glass rod. The solution was casted evenly on the surface of a glass slide to a uniform film in triplicates at each concentration of the coat formulation and the glass slides were exposed to atmospheric oxygen and allowed to dry.

Physicochemical properties: The physicochemical properties of the metallic soaps (melting point, moisture content, apparent bulk density, and total ash content) were determined using the method described by Dalen and Mamza [16].

Extraction of the oils: Melon and sesame seeds purchased from open market were sieved to remove solid particles. The samples were dried in a Gallenkamp hot air oven model OV 160 overnight to reduce moisture content. The dried seeds were milled using local grain mill REF 121 (100 µm mesh size). The oils were thereafter extracted using Soxhlet apparatus with petroleum ether as the solvent.

RESULTS AND DISCUSSION

The physicochemical properties of melon and sesame seed oils were evaluated as; iodine value, 126 mg I_2 g^{-1} and 113 mg I_2 g^{-1}, saponification value, 197, and 189, acid value, 4.71, mg KOH g^{-1} and 5.64 mg KOH g^{-1}, free fatty acid, 2.37 mg KOH g^{-1}, and 2.92 mg KOH g^{-1}, peroxide value, 1.76 mg kg^{-1}, and 1.98 mg kg^{-1}, specific gravity, 0.91 and 0.92 respectively. The Iodine number is defined as the number of grams of iodine which will add to 100 g of fat or oil. Iodine value shows the degree of unsaturation of the constituent fatty acids in an oil or fat and is thus a relative measure of the unsaturated bonds present in the oil or fat. Iodine value is expressed in grams of iodine absorbed by 100 g of oil or fat. Unsaturated compounds absorb iodine (in suitable form) and form saturated compounds. The amount of iodine absorbed in percentage is the measure of unsaturation in the oil. No oil has zero iodine value and oils are classified as drying, semi drying and non-drying on the basis of iodine value. The iodine value of melon and sesame seed oils approximates to the range of semi drying oils (120 - 150 mg g^{-1}). Within this range, oils possess the property of absorbing oxygen on exposure to the atmosphere, remain thickened and sticky but do not form a hard dry film and hence are used in soap production. The high saponification values indicate that the oils could be good for soap making. The low peroxide values of the oils; 1.76 mg kg^{-1}, and 1.98 mg kg^{-1}, mean that they are less liable to oxidative rancidity at room temperature. A specific gravity of 0.91 and 0.92 for melon and sesame seed oils show that they are less dense than water and is a measure of the degree of unsaturation.

Table 1. Physicochemical properties of melon and sesame seed oils

Parameters	Melon oil	Sesame oil
Iodine value (mg/g)	126	113
Peroxide value (mg/kg)	1.76	1.98

Acid value (mgKOH/g)	4.71	5.64
Saponification value (mgKOH/g)	197	189
Free fatty acid value (mgKOH/g)	4.71	5.64
Specific gravity (g/cm^3)	0.91	0.92

Table 2. The physicochemical properties of the prepared cobalt drier from melon and sesame seed oils

Tests	Melon seed oil	Sesame seed oil
Colour	Purple	Purple
Texture	Powder	Powder
Moisture content	0.18	0.16
Apparent bulk density	0.29	0.36
Foaming characteristics	Poor	Poor
Solubility	Insoluble in water but soluble in kerosene, acetone ant methanol	Insoluble in water but soluble in kerosene, acetone ant methanol

Table 3. The physicochemical properties of the prepared zinc drier from melon and sesame seed oils

Tests	Melon seed oil	Sesame seed oil
Colour	White	White
Texture	Powder	Powder
Moisture content	0.11	0.12
Apparent bulk density	0.22	0.31
Foaming characteristics	Poor	Poor
Solubility	Insoluble in water but soluble in kerosene, acetone ant methanol	Insoluble in water but soluble in kerosene, acetone ant methanol

Table 4. The Drying time of cobalt drier (primary) in minutes

Mass ratio of drier	Set to touch time	Surface dry time	Dry hard time	Dust free time
Blank	9	98	125	137
0.1	8	83	103	128
0.2	7	75	94	119
0.3	6	70	88	108
0.4	5	59	76	102
0.5	5	51	70	96

Table 5. Drying time of cobalt/ zinc drier (primary and auxiliary) in minutes

Mass ratio of drier	Set to touch time	Surface dry time	Dry hard time	Dust free time
Blank	9	98	125	137
0.05/0.05	6	82	93	121
0.1/0.1	6	79	86	111
0.15/0.15	5	70	80	100
0.2/0.2	4	66	72	93
0.25/0.25	4	61	68	84

The results from tables 2 and 3 above show the physicochemical properties of cobalt and zinc driers respectively which are in agreement with other researchers [19, 20, 21]. The metallic soaps which were produced by precipitation method are quite effective since good yields of zinc and cobalt soaps were obtained. Cobalt drier has a purple colour while zinc was white; hence the use of zinc drier will be most suitable at all concentrations in paints while cobalt drier has to be used in low concentrations or decolorized before use. This observation places cobalt drier at a greater advantage over cobalt driers especially for white paint formulations.

APPLICATIONS

This research work has shown that melon and sesame seed oils can be used to synthesize paint driers with appreciable characteristics such as reducing the drying time of a gloss coating. It was found to perform well at cobalt/zinc combination. The use of cobalt and zinc in the preparation of the metallic soap required in the paints could greatly reduce the amount of foreign inputs necessary for the production of paints.

CONCLUSIONS

The performance of these driers from the observed evaluation of drying time of the film coating on glass slide, revealed that the drier reduced the drying time of the gloss coating with increase in concentration of the drier in the gloss coat formulation, and it was also established from the research work that the coating casted on the glass slide in absence of a metallic drier took a longer period of time to dry as compared with those in which the metallic drier was incorporated. This observation validates the fact that metallic driers enhanced the drying time of the coat produced and on a general note, enhance the drying of paints.

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