Short Communication Report

SOME PHYSICO-CHEMICAL PROPERTIES OF PREPARED METALLIC SOAP-DRIERS OF ALUMINIUM, COPPER AND ZINC.

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Considerable work has been done on the drying effects of various soaps in surface coatings. Payne (1954) reported the drying behaviour of twenty metals and their various soaps and observed a wide range of activity of the metals with Cobalt, Vanadium and Manganese. Kirk-Othmer (1985) observed that the combination of two or more metals is preferred because each one has a specific action in the drying process e.g. lead is usually considered to be "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.

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 e.t.c., combined with monobasic carboxylic acids of seven to twenty-two carbon atoms (Ulmanns, 2001). These drier soaps are soluble in organic solvents and are the most important group of metallic soaps used as additives in coatings (paints, vanishes, ink, lacquers) to speed up the physical change from the liquid to the solid state thereby reducing the drying time (Omeike, 1996). Primary (active) driers initiate drying process on their own, with Cobalt being the most active drier since it effects rapid surface drying and is generally used in conjunction with auxiliary driers to improve or modify the final properties of the coatings (Kirk-Othmer, 1985). Driers can be prepared by fusion or precipitation method. The precipitation process consists of two chemical steps:

$$RCOOH + NaOH \longleftrightarrow RCOONa + H_2O \quad \ldots (1)$$
$$2RCOONa + MSO_4 \longleftrightarrow M(RCOO)_2 + Na_2SO_4 \quad \ldots (2)$$

The present study investigates the optimum pH ranges for precipitation of Al, Cu and Zn soaps and their metal contents suitability as driers for surface coatings.

Sample Collection: Palm kernel oil was obtained at Katako market in Jos Plateau State. The oil was vacuum filtered at 25 ^{0}C. Parameters such as Acid, Iodine and Saponification numbers were determined by conventional methods. All reagents and solvents were analyte grades (AR)

Preparation of Soluble Soaps: From the saponification value of the oil, calculated amount of 50 % w/v NaOH was obtained. To 500 g of the oil was added the calculated amount of 50 % w/v NaOH solution in a stepwise manner. Excess of few drops were added to ensure complete saponification. Furthermore, the soap solution formed was warmed over a steam bath while stirring for about 30 mins and thereafter overnight to solidify. The dried soap was ground into powdery form.

Determination of pH of Soap: 10 g of the powdered soap was weighed and dissolved in distilled water in a 100 ml volumetric flask. This was made up to prepare 10 % soap solution. The pH of the 19 % soap solution was determined using a pH meter.

Preparation of Metallic Soaps: 0.5 M solution metals salts of Aluminium ($AlCl_3$), Copper ($CuSO_4 . 7H_2O$) and Zinc ($ZnSO_4$) were prepared and kept in amber bottles. To 20cm^3 of 10 % soap solution was added 10 cm^3 of 0.5 M HCl and in each case, titrated against each of the metal salt solution until complete precipitation was observed. The initial pH and final readings of the pH of the soaps were taken and recorded.

Moisture content: 5 g of the metallic soaps (Copper, Zinc, Aluminum) were weighed into a pre-weighed petridish and placed in a hot oven at 105 ^{o}C. The crucible and its contents were weighed at fixed intervals to constant weight after cooling in desiccators. The moisture content was found by weight difference.

Ash and Sulphated Ash Content Determination: The moisture free metallic soap was weighed into a pre-weighed crucible and placed in a furnace regulated at 500 ^{o}C and heated for 6 hrs. The furnace was then allowed to cool after which the crucible was placed in desiccators for further cooling before weighing. This procedure was similarly repeated for the sulphated samples when few drops of concentrated H_2SO_4 were added. Ash or sulphated ash contents were calculated as:

$$\% \text{ Ash} = \frac{b}{a} \times 100$$

Weight of empty crucible	= x
Weight of metallic soap before ashing	= a
Weight of crucible + ash	= y
Weight of ash	= y – x = b

Apparent Bulk Density: A particular weight was taken and put into a measuring cylinder, then the cylinder was tapped on a rubber surface 50 times. This was repeated 6 times and for each interval the volume was taken. After this, the average volume was taken. This was repeated for the three metallic soaps and the Apparent Bulk Density was calculated from the expression:

$$ABD\ (g / cm^3) = \frac{\text{Weight of soap} \times 0.62}{\text{Tapped volume of soap sample } (cm^3)}$$

Metal Content: This was determined by Atomic Absorption Spectrophotometer (AAS) machine. The colours and appearances of the metallic soaps were observed and noted.

Solubility Test: Solubility of the metallic salts in various solvents was carried out by introducing a small amount of the metallic soaps into the solvents one at a time. This was stirred and observations were made.

Melting Range: This was carried out on gallenkamp melting point apparatus.

The results of the physical properties of palm kernel oil are shown in Table 1 while Table 2 shows some physical properties of the prepared metallic soaps.

Aluminium showed electronegativity of (1.5) while oxygen had (3.5) with the difference of 2.0 translating to 63 % ionic character (Dillard & Goldberg, 1978). For Copper, the EN is (1.9) and the difference between Copper and Oxygen was (1.6) giving an ionic character of 47 %, while Zinc had EN value of (1.6) with difference of (1.9) with Oxygen and an ionic character of 59%.

TABLE 1. SOME PHYSICAL AND CHEMICAL PROPERTIES OF PALM KERNEL OIL

Parameter	Value
Specific cravity (24 ^{O}C)	0.900
Relative viscosity 30 ^{O} C	1.2604
Refractive index (28 ^{O}C)	1.4410
Moisture content (%)	0.511
Acid value (mg KOH/g)	14.92
Saponification value (mg KOH/g)	252.42
Iodine value g iodine / 100g oil	10.152

TABLE 2. PHYSICOCHEMICAL PROPERTIES OF THE PREPARED METALLIC SOAPS

SOAP	pH range	Metal content (%)	Colour & appearance	Moisture content (%)	Melting point (°C)	Apparent Bulk Density	Total Ash content (%)	Sulphated Ash content (%)	Solubility (room temp)
Aluminium	5.50 - 4.10	7.09	White powder	0.86	115	0.67	7.80	11.16	benzene acetone partly soluble in kerosene
Copper	7.00 - 4.40	3.60	Green powder	0.40	100	0.77	14.46	12.61	benzene acetone toluene Partly soluble in kerosene
Zinc	6.70 - 5.30	2.20	White powder	0.45	110	0.77	17.30	26.22	Partly soluble in benzene

TABLE 3. ELECTRONEGATIVITY (EN) VALUES OF THE METALS

Parameters	Soap		
	Aluminum	Copper	Zinc
Valency of metal	+3	+2	+2
EN values of metal	1.5	1.9	1.6
EN value of oxygen (O)	3.5	3.5	3.5
EN difference	2.0	1.8	1.9
Ionic character (%)	63	47	59

Results from this work is similar to the findings of Vogels (1989) and Dalen (2004) with respect to values for the physico-chemical properties of palm kernel oil (Table 1). Phillip (1992) reported that the precipitation of metallic soaps occurred at different pH ranges depending on their precipitation equilibria and atomic weight of the metal involved (equations 1 and 2). Accordingly, copper soap precipitates first at pH range 7.00- 4.40, followed by Zinc soap at pH 6.70 – 5.30 and Aluminum at pH 5.30 – 4.10.

The melting points of the metallic soaps are in the order of Al > Zn > Cu which could be explained by the following:

(1) The nature and the type of bonds between the metal ion and the carboxylate anion, because the stronger the bond, the higher the melting point (Phillip, 1992)
(2) The number of electrons that a metal has available for bonding called valence electrons which are responsible for bond strength. Al, has a valency of +3, while Cu and Zn both have +2 as their valencies (Dillard & Golberg, 1978)
(3) The differences in the electronegativity (EN) values of the metals and the oxygen to which they are directly bonded (Table 3).

Generally, the melting points of the soaps are between 100-115 ^{o}C which makes them suitable for application at these temperatures since high melting points pose solubility and handling problems. Foster & Frank (1990) reported similar results for percentage metal contents in the order Al > Cu > Zn. When percentage metal contents are compared with the ash contents it was observed that the higher the percentage metal content, the lesser the corresponding total ash and sulphated ash contents of the metallic soaps. This means non-combustible organic and inorganic matter (Metal content) are present in inverse proportion.

In commercial application of driers in coating formulations, it has become a standard practice to specify the amount of drier metal content to use with oils and resins rather than the amount of drier (Foster & Frank, 1990). Earlier reports (Heaton, 1949; Payne, 1954) indicated the amount of drier or auxiliary to be calculated from their own metal content in drier specification for oils and the requirements are usually stated at a given percentage of the metal content to oil (resin) ratio, with typical specifications as 0.6 % Lead, 0.04 % Cobalt, 0.04 % Manganese as metal content to oil. This study demonstrates that metal contents of 7.09 % for Al, 3.8 % for Cu and 2.2 % for Zn are very essential for the specification of the amount of drier to give a certain metal content required for a particular formulation and subsequent application.

The metallic soaps produced by precipitation titrimetry method are quite effective since good yields of Al, Cu and Zn soaps were obtained.

The results of the physicochemical properties of the metallic soaps tally appreciably with their constants reported observed by other investigators.

Even though Al soap mostly employed as a lubricant to modify film properties, Zn and Cu soaps are used as auxiliary driers. Their physical properties suggest that they can be used with other primary driers. However, further work must be carried to determine their suitability or otherwise for surface coating applications. From this study, the use of palm kernel oil, though a non-drying oil to prepare driers is not only suitable but also a cheap source of raw material since it is available locally and could serve as additional oil for use by paint industries in Nigeria.

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