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Full Length Research Paper

Relative thermal stability of metal soaps of *Ximenia americana* and *Balanites aegyptiaca* seed oils

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Metal soaps of *Ximenia americana* seed oil (XSO) and *Balanites aegyptiaca* seed oil (BSO) were prepared by metathesis in aqueous alcohol solution. The thermal stability of the metal carboxylates (soaps) was studied thermogravimetrically in the temperature range 50 – 500°C under nitrogen. The thermal stability of the carboxylates was assessed in terms of temperatures at which various extents of decomposition were attained and weight loss at the initial stage of decomposition. The weight loss for all the metal soaps was less than 10% at temperature up to 250°C. The activation energies at the initial stage of decomposition of the metal carboxylates modelled using Broido's equation are in the range 6.93 – 14.14 kJmol^{-1} for XSO while those of BSO ranged between 15.52 – 28.41 kJmol^{-1}. Based on these results, metal soaps of BSO are thermally stable than those of the corresponding XSO soaps. The results suggest potential application of carboxylates of *X. americana* and *B. aegyptiaca* seed oils in some industrial applications.

Key words: Metal soaps, thermal stability, carboxylates, thermogravimetric, decomposition.

INTRODUCTION

Seed oils are important sources of nutritional oils, industrial and pharmaceutical raw materials (Oderinde et al., 2009), and current emphasis on sustainable development has made it imperative to search for industrial raw materials from renewable sources. Seed oils are at the centre of this search as many useful products and industrial materials have been produced from them. One of such materials is metal carboxylates otherwise called metal soaps. Metallic soaps have been described as alkaline-earth or heavy-metal long-chain carboxylates (Barth, 1982), which are insoluble in water, but soluble in non-aqueous solvents. They have the general formula $(RCO_2)_2M$, where M is a metal such as Zn, Cd, Pb, Ba, Ca, Co, Cu, Al, Fe, etc and R is a linear or branched alkyl group. Metal soaps are manufactured by using one of the following processes: double decomposition, direct reaction of carboxylic acid with metal oxides, hydroxides and carbonates and direct reaction of metals with molten fatty acid (Gonen et al., 2005). These reactions are usually carried out in an aqueous medium for alkaline and alkaline-earth soaps or in an organic medium, such as alcohol or benzene, for metallic soaps (Upadhyaya and Sharma, 1997; Akanni et al., 1992). Metal carboxylates have played an important role in the development of poly vinyl chloride (PVC) as an important commercial polymer (Owen and Msayib, 1989). Soaps, alkaline and alkaline-earth as well as metallic soaps are employed in various fields (Poulenat et al., 2004).

The soaps of the heavy metals have important applications in the manufacture of greases, paints or inks, plastics, cosmetics, textiles, pharmaceuticals, etc, in which they are employed as lubricants, driers, catalysts, wetting agents, thickening agents, stabilizers, waterproofing agents, fungicides and pesticides (Egbuchunam et al., 2005; Egbuchunam et al., 2007). Silver salts of fatty acids are being used as source of silver in thermographic and photothermographic materials (Binnemans et al., 2004). Calcium and magnesium soaps are used as corrosion inhibitors in non-polar media; lead, manganese, cobalt and zinc soaps are used in paints to accelerate drying while copper soap exhibits fungicidal properties (Salager, 2002). Most of these studies have been carried out using soaps prepared from pure fatty acids with little attention paid to the use of triglycerides as starting

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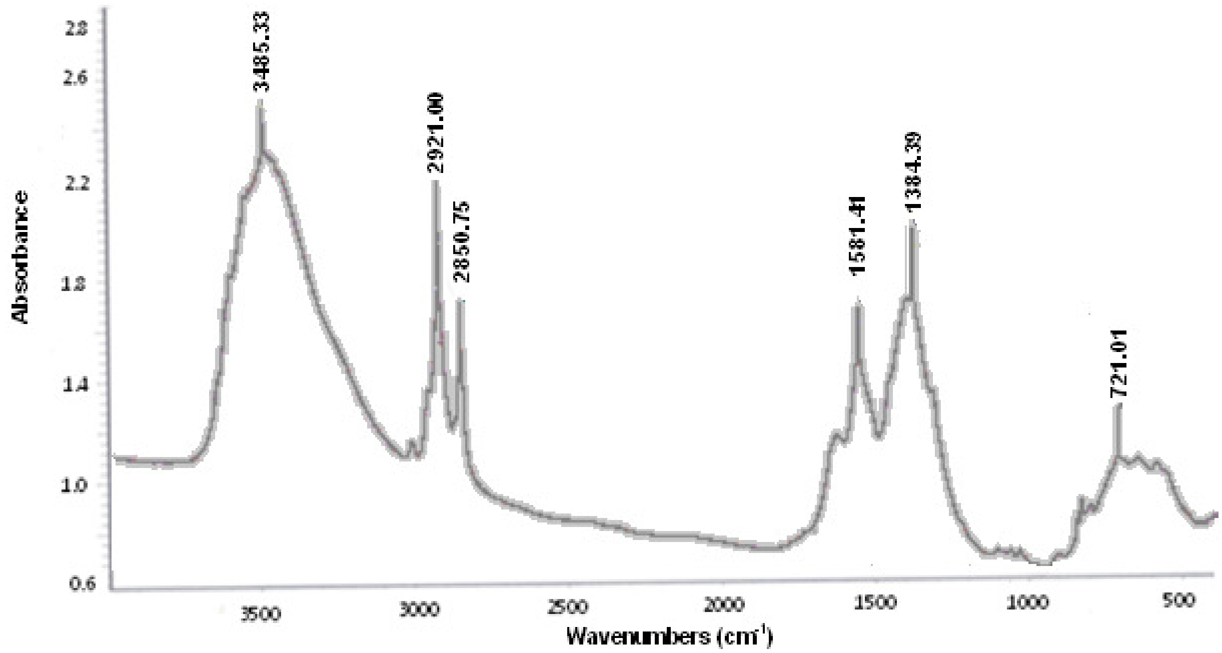

Figure 1. Typical FTIR of the metal soap.

materials for the preparation of the soaps (Egbuchunam et al., 2007). Report by some workers (Egbuchunam et al., 2005; Okieimen et al., 2006) have shown that metal soaps of some vegetable oils are fairly heat stable and may be suitable as stabilizer of PVC. *X. americana* seed oil (XSO) is obtained from the seeds of the plant *X. americana* while *B. aegyptiaca* seed oil (BSO) is obtained from the seeds of the plant *B. aegyptiaca*.

XSO is polyunsaturated and drying oil with the following characteristics: specific gravity 0.972, refractive index 1.472, and iodine value 158.30; it contains oleic acid (66.72%), linoleic acid (16.53%), stearolic acid (0.92%) (fatty acid with a triple bond) and saturated acids (4.38%). BSO is polyunsaturated and semi-drying oil that has the following characteristics: specific gravity 0.961, refractive index 1.468, and iodine value 102.60; it contains oleic acid (34.52%), linoleic acid (51.49%), and saturated acids (13.79%) (Folarin, 2008). At present, the two oils have no commercial value in Nigeria. This work examines the preparation and characterisation of some metal soaps of *X. americana* and *B. aegyptiaca* seed oils in terms of their thermal stability.

MATERIALS AND METHODS

Preparation of metal soaps of the oils

Metal soaps of *X. americana* seed oil (XSO) and *B. aegyptiaca* seed oil (BSO) were prepared by metathesis in aqueous alcohol solution following the method described by Burrows et al. (1981). The soaps were dried in oven at 60°C to constant weight. The BDH analar (99%) salts used are $Pb(NO_3)_2$; $BaCl_2.2H_2O$; $Cd(NO_3)_2.4H_2O$; $ZnSO_4.7H_2O$ and $CaCl_2$.$2H_2O$.

Characterisation of the metal soaps

Fourier transforms infrared (FTIR) spectra of the metal soaps were recorded with Nicolet Avatar 330 FTIR at a resolution of 4 cm^{-1} between wave numbers 4000 to 400 cm^{-1}. The presence of characteristic bands of carboxylate ions confirmed the formation of the metal soaps. Measurement of the thermal properties of metal soaps of XSO and BSO were carried out using a Perkin-Elmer Pyris 6 TGA thermal gravimetric analyser. The activation energies for the decomposition of the metal soaps at the initial stage were determined using Broido's equation (Broido, 1969).

RESULTS

Typical FTIR spectrum of a metal soap of the seed oils is shown in Figure 1. As no modifications occur on the alkyl chain of triglyceride during soap preparation, the spectra show absorption bands which are characteristics of the oils. Typical antisymmetric stretching vibration for carboxylate occurs between 1513 and 1561 cm^{-1}. CH_2 antisymmetric and symmetric stretching vibrations occur with varying intensities in the region 2916 to 2923 cm^{-1} and 2849 to 2851 cm^{-1} respectively. The thermograms for the metal soaps of *X. americana* seed oil (XSO) are presented in Figure 2 while those of metal soaps of *B. aegyptiaca* are presented in Figure 3. For the metal soaps of XSO, it can be seen that Zn and Pb soaps show a one-stage decomposition process up to 500°C while Cd, Ba and Ca soaps show a two-stage decomposition process. Cd soap shows an initial more or less stable region occurring up to 220°C, followed by a region of slow decomposition (220 to 300°C) and this is followed by a relatively stable region up to 450°C. The decomposition patterns of Ba and Ca soaps appeared

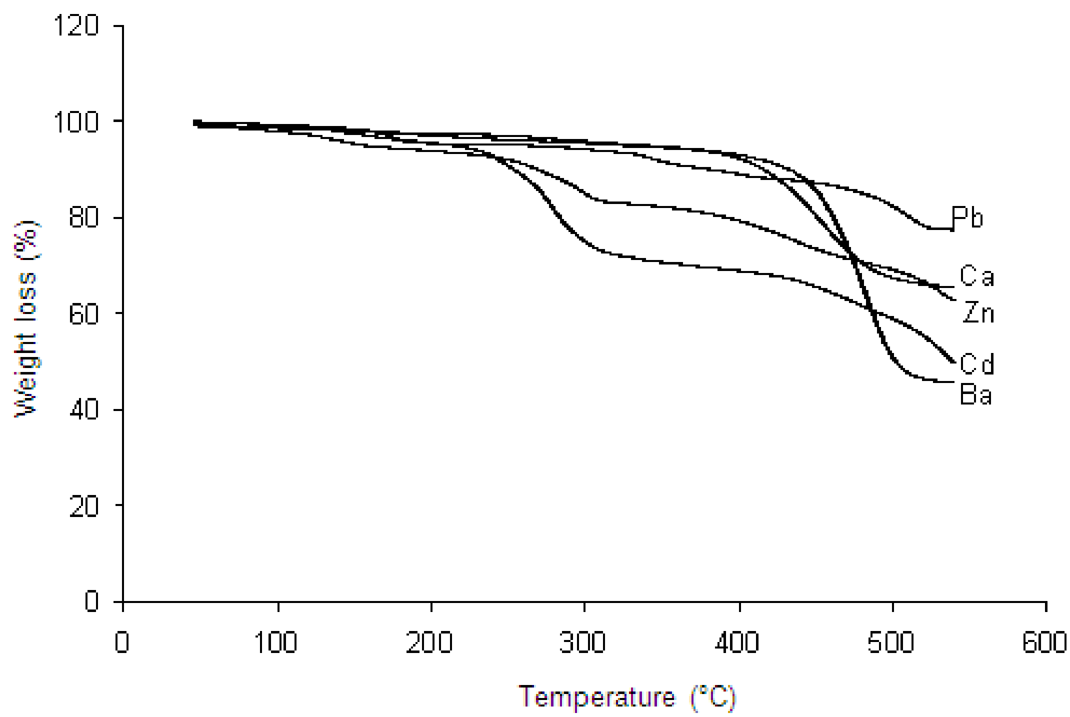

Figure 2. Thermogram of metal soaps of *X. americana* seed oil (XSO).

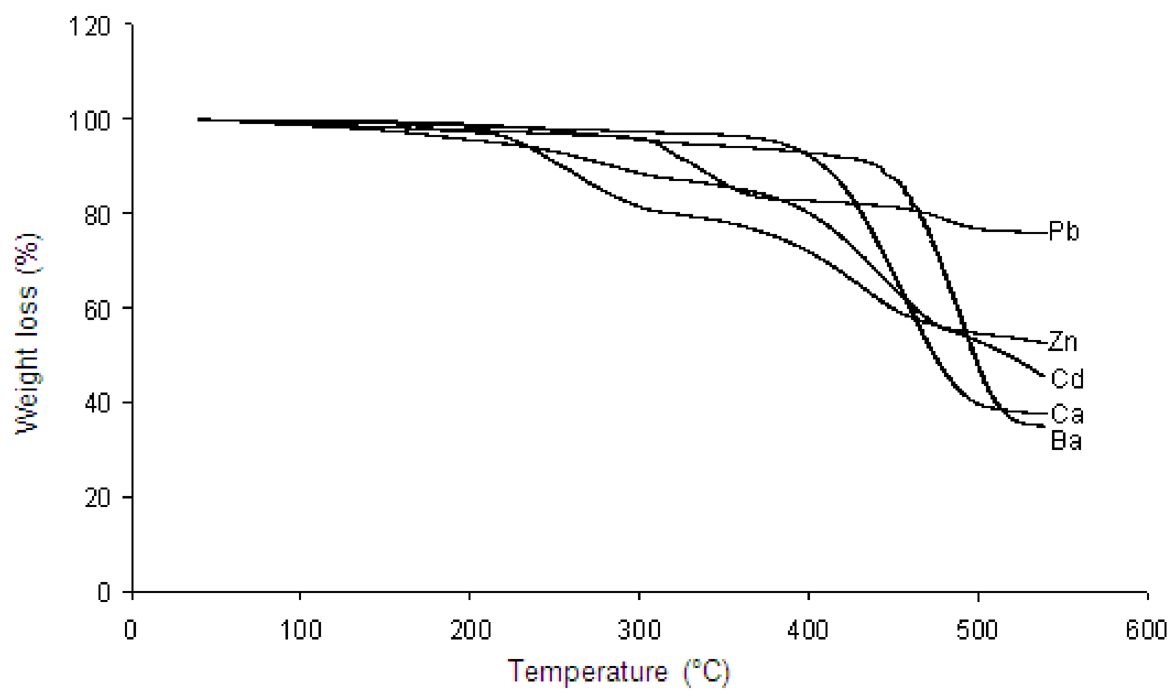

Figure 3. Thermogram of metal soaps of *B. aegyptiaca* seed oil (BSO).

similar albeit more marked with the former soap. The Ba soap shows a stable region up to about 450°C followed by a region of rapid decomposition (450 to 500°C). Ca soap shows a stable region up to about 420°C followed by a region of rapid decomposition (420 to 490°C). All soaps of BSO show a two – stage decomposition process. They all have initial stable regions with varying temperatures. Zn soap of BSO is stable up to 400°C with

Table 1. Evaluation of relative thermal stability of the metal soaps: Temperatures at which various extents of decomposition were attained and percentage residual weight at the end of decomposition.

Metal soap	Temperature at which decomposition was attained (°C)						RW (%) at 500°C
	1%	2%	5%	10%	30%	50%	
Zn-XSO	57.6	96.5	156.0	268.7	489.1	-	69.09
Cd-XSO	114.8	137.8	220.3	253.6	368.5	542.5	59.24
Pb-XSO	51.0	160.3	261.5	434.3	-	-	82.33
Ba-XSO	118.9	154.5	340.2	434.3	477.6	504.3	52.05
Ca-XSO	71.8	147.5	324.1	415.8	492.3	-	67.42
Zn-BSO	84.5	131.1	214.7	284.4	434.0	-	54.61
Cd-BSO	92.2	164.1	224.3	254.2	409.3	520.8	53.32
Pb-BSO	162.6	177.3	308.9	333.7	-	-	76.76
Ba-BSO	190.7	235.8	377.6	441.5	477.5	497.5	47.74
Ca-BSO	153.8	188.8	361.4	408.3	445.8	473.7	39.69

RW = Residual weight.

Table 2. Percentage residual weight of the metal soaps at the initial stage of decomposition (170 to 220°C).

Metal soap	Temperature(°C)					
	170	180	190	200	210	220
Zn-XSO	94.55	94.31	94.08	93.85	93.60	93.31
Cd-XSO	96.54	96.17	95.83	95.52	95.17	95.00
Pb-XSO	97.27	96.09	95.59	95.37	95.28	95.22
Ba-XSO	97.74	97.62	97.51	97.44	97.38	97.31
Ca-XSO	97.66	97.46	97.25	97.05	96.85	96.67
Zn-BSO	96.82	96.37	96.00	95.58	95.20	94.77
Cd-BSO	97.84	97.63	97.43	97.23	96.93	96.25
Pb-BSO	98.41	97.92	97.78	97.68	97.55	97.40
Ba-BSO	99.22	99.13	99.00	98.86	98.68	98.45
Ca-BSO	98.85	98.74	98.61	98.49	98.37	98.25

percentage weight loss not higher than 20%. This is followed by a region of rapid decomposition (400 to 480°C). Cd soap shows initial stable region up to 220°C followed by a region of slow decomposition (220 to 300°C). Pb soap was stable up to 280°C followed by a region of slow decomposition (280 to 340°C). Ba soap shows an initial stable region up to 440°C followed by a region of rapid decomposition (440 to 500°C). The decomposition pattern of Ca soap is similar to that of Ba. It shows an initial stable region up to 400°C followed by a region of rapid decomposition (400 to 480°C).

DISCUSSION

As shown in Figure 1, typical antisymmetric stretching vibration for carboxylate occurs between 1513 and 1561 cm^{-1}. These results are consistent with values reported for antisymmetric stretching vibrations of some metal soaps (Gonen et al., 2005; Okieimen et al., 2005) and confirmed the formation of metal soaps during metathesis. The absorption band occurring in the region 3200 to 3500 cm^{-1}, centred at about 3400 cm^{-1} indicates the presence of OH group and is attributed to hydroxides of metals formed during metathesis (Egbuchunam et al., 2007).

The thermal decomposition patterns of the metal soaps are shown in Figures 2 and 3. These patterns are similar to a previous report for metal soaps of rubber seed oil (Okieimen et al., 2006). The relative stability of the metal soaps of XSO and BSO was evaluated from the temperatures at which various extents of decomposition occurred and the residual weight of the soaps at 500°C (Table 1), the percentage weight of the metal soaps at the initial stage of decomposition (Table 2), percentage weight loss at temperature up 250°C (Table 3) as well as activation energy at the initial stage of decomposition (Table 4). Weight loss of up to 2% is frequently

Table 3. Weight loss (%) of metal soaps at temperature up to 250°C.

Metal soap	Weight loss (%)
Zn-XSO	8.0
Cd-XSO	9.3
Pb-XSO	4.9
Ba-XSO	3.0
Ca-XSO	3.8
Zn-BSO	6.9
Cd-BSO	9.1
Pb-BSO	3.2
Ba-BSO	2.5
Ca-BSO	2.1

Table 4. Activation energy for the decomposition of the metal soaps of XSO and BSO at the initial stage of decomposition.

Metal Soap	Activation energy ($kJmol^{-1}$)
Zn-XSO	8.31
Cd-XSO	13.10
Pb-XSO	14.41
Ba-XSO	6.93
Ca-XSO	9.35
Zn-BSO	17.50
Cd-BSO	16.63
Pb-BSO	24.30
Ba-BSO	28.41
Ca-BSO	15.52

associated with loss of moisture associated with the soaps. At 5% conversion, the result in Table 1 shows that, for XSO metal soaps, the relative stability of the soaps is in the order Ba-XSO>Ca-XSO>Pb-XSO>Cd-XSO>Zn-XSO and for the metal soaps of BSO, the relative stability of the soaps is Ba-BSO>Ca-BSO>Pb-BSO>Cd-BSO>Zn-BSO. The weight loss occurring at temperatures up to 250°C is less than 10% for all the soaps (Table 2). Thus, the results show that the thermal stability of metal soaps of XSO and BSO are comparable with the stability of soaps of stearic acids within the temperature range (170 to 220°C) frequently used in processing of PVC (Okieimen et al., 2006). The residual weights of the metal soaps at 500°C which could be oxides or carbonates of the respective metals (Akanni et al., 1992) was highest for Pb-XSO (82%) and least for Ba-XSO (52%). For BSO soaps, the value was highest for Pb-BSO (76%) and lowest for Ca-BSO (39%) as could be observed in Table 1. It would appear from these results that soaps of XSO are relatively more stable than the soaps of BSO at higher temperature. However, a cursory look at Tables 2 and 3 does not corroborate this observation.

In Table 3, it is apparent that the soaps of BSO are more stable at 250°C than the corresponding ones for XSO based on the percentage weight loss. For corresponding metal soaps, the percentage weight loss at 250°C is higher by 80% for Ca-XSO than Ca-BSO. For cadmium soaps however, the difference is less marked (2%). In Table 2, the percentage residual weights of the metal soaps at the initial stage of decomposition in the temperature range 170 to 220°C, show higher stability of the metal soaps of BSO compared with the corresponding ones of XSO. Specifically, at 190°C the percentage residual weight loss for the metal soaps is higher, albeit nominally, by 2% for Zn-BSO compared with Zn-XSO. Thus, metal soaps of BSO are more stable than the corresponding ones of XSO at the degradation temperature range 170 to 220°C. Thermal decomposition of metal soaps follows first order kinetics (Egbuchunam et al., 2005; Okieimen et al., 2006).

The kinetics for decomposition of the first stage of the metal soaps was modelled using Broido's equation. The activation energies for the initial stage of the decomposition of the metal soaps (170 to 220°C) determined using Broido's equation (Table 4) indicate that XSO soaps have lower activation energies than the corresponding BSO soaps. The decomposition was carried out under nitrogen atmosphere and it is assumed that decomposition is the only reaction taking place. Under atmospheric conditions, degradation and oxidation reactions of the soaps occur together simultaneously and/or consecutively (Okieimen et al., 2006) and this will alter the value of the activation energy. For XSO soaps, the activation energies are in the range 6.93 to 14.41 $kJmol^{-1}$, the highest and the least values being for Pb-XSO and Ba-XSO soaps respectively. Similarly, for BSO, the range of activation energies for the metal soaps is 15.52 to 28.41 $kJmol^{-1}$, the highest and the least values are for Ba-BSO and Ca-BSO soaps respectively. Thus, it can be seen that metal soaps of BSO are thermally stable than those of XSO at the initial stage of decomposition. The activation energies for the metal soaps are comparable with values reported for some metal soaps of rubber seed oil, RSO namely Ba-RSO (19.55 $kJmol^{-1}$), Cd-RSO (10.95 $kJmol^{-1}$) and Ca-RSO (13.46 $kJmol^{-1}$) (Okieimen et al., 2006). Some metal soap of carboxylic acids have been shown to be susceptible to thermal decomposition producing ketones, the metal oxide and carbon dioxide. It might be expected that unsaturation would confer instability on metal soaps of unsaturated acids (Okieimen and Ebhoaye, 1992). Thus, the observed differences in the stability of the metal soaps of XSO and BSO may be due to differences in the levels of unsaturation in the fatty acid moiety of the oils. Based on iodine value of 158.3 $gI_2 100g^{-1}$, XSO is a drying oil while BSO a semi-drying oil with iodine value of 102.6 $gI_2 100g^{-1}$ (Folarin, 2008).

Conclusions

In this study, zinc, cadmium, lead, barium and calcium soaps of *X. americana* seed oil and *B. aegyptiaca* seed oil were prepared by metathesis in aqueous alcohol. The thermal stability was determined by thermogravimetric analysis. The results confirmed earlier report that high level of unsaturation in the fatty acid moiety of the oil is antithetical to thermal stability of metal soaps. The data obtained represent significant new findings and provide additional impetus for the development of value-added, industrially useful products from the two seed oils.

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REFERENCES

Akanni SM, Okoh EK, Burrows HD, Ellis, HA (1992). The valent thermal behaviour of divalent and higher valent metal soaps: a review. Thermochim Acta. 208: 1- 41.

Barth TFW (1982). Soaps In: McGraw-Hill Encyclopedia of Science and Technology. McGraw-Hill Inc. USA.

Binnemans K, Van Deun R, Thijs B, Vanwelkenhuysen I, Geuens I (2004). Structure and mesomorphism of silver alkanoates. Chem. Mater., 16: 2021-2027.

Broido A (1969). A simple, sensitive graphical method of treating thermogravimetric analysis data. J. Polym. Sci., A2. 7: 1761-1773.

Burrows HD, Ellis HA, Akanni MS (1981). Proceeding of the second European symposium on thermal analysis (Dallimore, D, Ed.). Heydes London.

Egbuchunam TO, Okieimen FE, Aigbodion AI (2005). Studies in the thermal stability of metal soaps of parkia seed oil. Chem. Tech. J., 1: 18-23.

Egbuchunam TO, Balkose D, Okieimen FE (2007). Structure and thermal behaviour of polyvalent metal soaps of rubber seed oil. Nig. J. Chem., Soc. 32: 107-116.

Folarin OM (2008). Thermal stabilization of poly (vinyl chloride) by *Ximenia americana* (Wild Olive) and *Balanites aegyptiaca* (Betu) seed oils and their derivatives. PhD Thesis, Chemistry Department, University of Agriculture, Abeokuta, Nigeria.

Gonen M, Balkose D, Inal F, Ulku S (2005). Zinc stearate production by precipitation and fusion processes. Ind. Eng. Chem. Res., 44(6): 1627-1633.

Oderinde RA, Ajayi I A, Adewuyi A (2009). Characterisation of seed and seed oil of *Hura crepitans* and kinetics of degradation of the oil during heating. EJEAFChe. pp. 201-208.

Okieimen FE, Ebhoaye JE (1992). Thermal dehydrochlorination of PVC in the presence of metal soaps derivatives from rubber seed oil. Eur. Polym., J. 28: 1423-1425.

Okieimen FE, Pavithran C, Bakare IO (2005). Epoxidation and hydroxylation of rubber seed oil: one-pot multi-step reactions. Eur. J. Lipid Sci. Technol., 107: 330-336.

Okieimen FE, Egbuchunam TO, Bakare OI, Sogbaike CE (2006). Investigation on the thermal stability of Ba, Cd, Ca and Zn soaps of rubber seed oil. Nig. J. Chem. Soc., 31: 136-140.

Owen ED, Msayib KJ (1989). Catalyzed degradation of poly(vinyl chloride) III. Zinc (11) chloride catalysis. J. Polym. Sci. Polym. Chem., A27: 399-408.

Poulenat G, Sentenac S, Mouloungui Z (2004). Double decomposition reactions for the production of alkaline and alkaline-earth oleic soaps under salting-out conditions. Ind. Eng. Chem. Res., 43(7): 1574-1579.

Upadhyaya SK, Sharma PS (1997). Thermal, Infrared and X-ray diffraction studies on manganese and zinc soaps. Asian J. Chem., 9: 388-394.