SYNTHESIS OF ZINC-DIFATTYALKYLDITHIOCARBAMATES AND THEIR ANTIOXIDANT ACTIVITIES

Komar Sutriah[1,*], Zainal Alim Mas'ud[2], and Tun Tedja Irawadi[2]

[1]*Department of Agriculture Engineering, Bogor Agricultural University, Kampus Dramaga, Bogor 16680, Indonesia*

[2]*Department of Chemistry, Bogor Agricultural University, Kampus Dramaga, Bogor 16680, Indonesia*

Received September 15, 2011; Accepted April 19, 2012

ABSTRACT

Zinc-difattyalkyldithiocarbamates are organosulfur compounds with many functions, including as an antioxidant in a lubrication system. They were synthesized by reacting secondary fatty amine with $ZnCl_2$ and CS_2 giving result zinc-difattyalkyldithiocarbamates of around 77-87%. The synthesized products were characterized using infrared (IR) spectroscopic techniques. The IR spectra of zinc-difattyalkyldithiocarbamates showed sharp bands at 1450-1550 cm^{-1} for thioureida υ (C-N), 950-1050 cm^{-1} for υ (C-S), and in the far-red area 300-400 cm^{-1} for sulfur-metal bond. Products recovery was evaluated by AAS and the purity was analyzed by HPLC. Seven variants of zinc-difattyalkyldithiocarbamates were obtained. Antioxidant activity was evaluated by rancimat test regarding their induction time. At 125 ppm levels all variants showed higher value in each of their induction time as compared to those of butylated hydroxyanisole and butylated hydroxytoluene, commercial antioxidants No.1, and commercial antioxidants no.2. Three variants, i.e. Zn-bis(dilauryl)dithiocarbamate, Zn-bis(laurylpalmityl)dithiocarbamate, and Zn-bis(laurylstearyl)dithiocarbamate had higher values in their induction time than the other variants. The values are 16.67, 26.54, and 16.11 h, respectively.

***Keywords**: antioxidants; dithiocarbamate complex; Zn-difattyalkyldithiocarbamate*

ABSTRAK

Zn-difattyalkyldithiocarbamates merupakan senyawa organosulfur yang memiliki banyak fungsi, termasuk sebagai antioksidan dalam sistem pelumasan. Zn-difattyalkyldithiocarbamates disintesis dengan mereaksikan antara fattyamin sekunder dengan $ZnCl_2$ dan CS_2 yang memberikan hasil sekitar 77-87%. Hasil sintesis ini dikarakterisasi dengan teknik spektroskopi infra merah. Spektrum infra merah dari Zn-difattyalkyldithicarbamates menunjukkan serapan tajam pada 1450-1550 cm^{-1} untuk thioureida υ (CN), 950-1050 cm^{-1} υ (CS), dan di daerah infra merah jauh pada 300-400 cm^{-1} untuk ikatan sulfur logam. Perolehan kembali produk dievaluasi dengan AAS dan kemurniannya dengan HPLC. Tujuh variasi Zn-difattyalkyldithicarbamates diperoleh. Aktivitas antioksidan dievaluasi dengan uji ransimat yang mengukur waktu induksi dari produk. Pada tingkat konsentrasi 125 ppm semua varian menunjukkan hasil yang lebih tinggi dari butylated hydroxyanisole (BHA) dan Butylated hydroxytoluene (BHT), antioksidan komersial 1 dan antioksidan komersial 2. Tiga varian, yaitu Zn-bis(dilauryl)dithiocarbamate, Zn-bis(laurylpalmityl)dithiocarbamate, dan Zn-bis(laurylstearyl)dithiocarbamate memiliki nilai waktu induksi yang lebih tinggi dibanding varian lainnya. Nilai dari variasi tersebut, yaitu 16,67; 26,54; dan 16,11 jam.

***Kata Kunci**: antioksidan; kompleks ditiokarbamat; Zn-difattyalkyldithiocarbamate*

INTRODUCTION

Currently, all lubricants contain at least one antioxidant agent for stabilization and other performance-enhancing purposes. Since oxidation has been identified as a major cause of loss of lubricant quality, it is important to improve the stability. The oxidation processes result in a variety of harmful species of chemicals which eventually reduces the lubrication function and shortens life service of the lubricant.

Oxidation process initiated by hydrocarbon exposure to both oxygen and heat. The processes can be greatly accelerated by transitional metals such as copper, iron, and nickel [1]. Dithiocarbamates are organosulfur compounds which easily form complexes with metal ions, and if they are in the form of coordination with a metal, they will have wide variety functions and applications. The applications of these compounds are in the field of automotive as additives in lubricants, as insecticides and fungicides in agriculture, as an acceleration of vulcanization in the

* Corresponding author. Tel/Fax : +62-251-8319894/8323571
Email address : komar.sutriah@yahoo.com

Table 1. The important absorption area of IR spectrum for alkyldithiocarbamate complexes

Wavenumber (cm^{-1})	Bond	Description
1680– 1640	C=N	
1530–1430	C---N	$S_2C–NR_2$ & wavelength type of medium-strong absorption
1001	C-S	Acquitted
around 1000	C-S	One strong band absorption indicates bidentate, 2 strong absorptions indicate monodentate
around 2400- 2650	S-H	Strong band absorption
Finger print area	M-C, M-S	Absorption type from weak to strong

*Sources: [3,14-17]

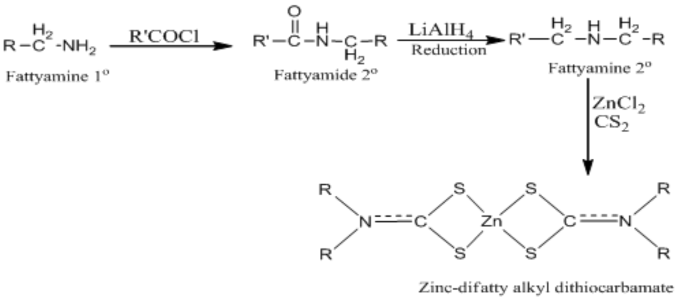

Fig 1. Synthesis of Zn-difattyalkyldithiocarbamate complexes

geology, as antioxidant in pharmaceuticals [2-3], and as an antibacterial and antifungal [4-5]. Metal-dithiocarbamate heterocyclic such as potassium (1,1-dioxothiolan-3-yl)-dithiocarbamate was reported having potency as selective fungicides [6]. Addition of antioxidant is to prevent oxidation and sludge formation to keep the engine clean. Many kinds of compounds used as lubricant additives include dithiocarbamate metals, amine and phenolic compounds, and dithiophospate metals [2].

Asthana restated that the methylene-bis-(di-*n*-butyl dithiocarbamate) is an excellent antiwear additive and has good antioxidant characteristics [7]. These compounds are used in gear oils and grease lubricant. Griffo & Keshavan using additional substances that serves as antiwear and antifriction in "high performance rock bit grease" in the form of Pb-diamyl dithiocarbamate, Mo-di-*n*-butyldithiocarbamate, Zn-dithiocarbamate, and Sb-dithiocarbamate [8]. However, most of alkyl dithiocarbamate compounds used as lubricants was reported having a short chain alkyl derived from mineral oils.

The aim of this work is to study the synthesis of difattyalkyldithiocarbamates compounds using secondary fatty amines derived from vegetable oil. Various long chain of fatty acid (C12-C18) will increase their liphophilicity that will have implications on increasing their solubility in the lubricant base, and provides additional cushioning aspects that supposedly improve its performance as an antioxidant and anti-friction compounds.

Anti-oxidation mechanism in lubricants is divided into two pathways, namely through primary antioxidant (radical scavenger) and secondary antioxidant (peroxide decomposition). The antioxidant action starts with the reduction of an alkyl hydroperoxides to a less reactive alcohol with the sulfide being oxidized to a sulfoxide intermediate [1]. A preferred mechanism for the subsequent reaction of sulfoxide intermediate is the intramolecular beta-hydrogen elimination, leading to the formation of a sulfonic acids (RSOH), which can further react with hydroperoxides to form sulfur-oxy acids. At elevated temperatures, sulfinic acid (RSO_2H) may decompose to form sulfur dioxide (SO_2), which is a particularly powerful Lewis acid for hydroperoxide decomposition through the formation of active sulfur trioxide and sulfuric acid. Previous work has shown that one equivalent of SO_2 was able to catalytically decompose up to 20,000 equivalents of cumene hydroperoxide. Further enhancement of the antioxidancy of sulfur compounds is that, under certain conditions, the intermediate sulfur-oxyacids (RSO_2H) can scavenge alkyl peroxy radicals, thus giving the sulfur compound (included dithiocarbamate) has primary antioxidant characteristics.

Synthesis pathways of complex compounds Zn-dialkyl dithiocarbamate is presented in Fig. 1 while the infrared (IR) spectrum of dithiocarbamate compound is presented in Table 1.

EXPERIMENTAL SECTION

Materials

Materials used in this work were secondary fatty amines, $ZnCl_2$, diethyl ether, CS_2, NaOH, BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene), an additive 1 (oil booster advanced additive for motorcycle), and additive 2 (antiwear additive), RBDPO (refined bleached deodorized palm oil).

Table 2. The synthesis yield of Zn-difattyalkyldithiocarbamate complexes

Secondary Fattyamine	Complexes	Yield (%)
Dilauroylamine	Zn-bis(dilauroyl)dithiocarbamate	77.68 (*n*=8)
Lauroylpalmitilamine	Zn-bis(lauroylpalmityl)dithiocarbamate	86.75 (*n*=3)
Lauroyloleilamine	Zn-bis(lauroyloleyl)dithiocarbamate	78.80 (*n*=3)
Lauroylstearilamine	Zn-bis(lauroylstearyl)dithiocarbamate	85.48 (*n*=3
Palmitiloleilamine	Zn-bis(palmitiloleyl)dithiocarbamate	77.04 (*n*=5)
Palmitilstearilamine	Zn-bis(palmitilstearyl)dithiocarbamate	80.64(*n*=4)
Stearyloleilamine	Zn-bis(stearyloleyl)dithiocarbamate	79.63 (*n*=7)

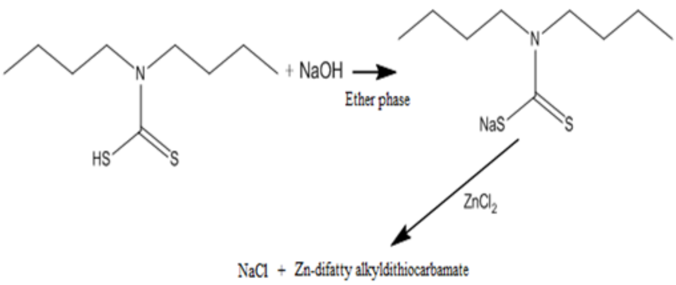

Fig 2. Synthesis Reaction of Zn-difattyalkyldithiocarbamate complexes

Instrumentation

Equipments used in this work were an open synthesis reactor, closed synthesis reactor (*Buchy Syncore Reactor*), Shimadzu AA6300 Atomic Absorption Spectrophotometer (AAS), Infrared Spectrophotometer Shimadzu IR Prestige 21 Fourier transform (FTIR), High Performance Liquid Chromatography Shimadzu-SP.10A (HPLC), and Metrohm Rancimat Model 743.

Procedure

Scheme of Synthesis Zn-difattyalkyldithiocarbamate

Secondary fatty amines were synthesized from secondary fatty amides with a closed reflux reactor according the method of [9]. Secondary fatty amines as intermediate products were converted to Na-difattyalkyldithiocarbamates, hereinafter complexed with Zn-metal to form Zn-difattyalkyldithiocarbamates. The progress of synthesis was monitored through the changes in the absorption band of FTIR spectrum, retrieval test of Zn with AAS, and conformity purity test with HPLC. The performance test of the product as an antioxidant substance was made by the rancimat method using RBDPO as a base lubricant.

Synthesis of Zn-difattyalkyldithiocarbamate Complex

Synthesis of Zn-difattyalkyldithiocarbamates were conducted according to the modified method of [3,10-11], using closed reflux system. One mmol of secondary fatty amine dissolved in 30 mL diethyl ether then added with 0.2 mL CS_2 and 1 mmol NaOH. After 17 h reaction 0.5 mmol Zn as $ZnCl_2$ was added and the reaction was continued for 7 h. Organic phase was separated and washed with distilled water 3 times, then ether (the solvent) was evaporated by a rotary evaporator at a temperature of 30 °C.

Monitoring of the reaction

The equipment used for monitoring the reaction was a set of FTIR, AAS, and HPLC. FTIR was used to monitor the changes of functional group in the implemented conversion reaction. Any changes on functional groups would affect the absorption spectral band of the product and then compared with the spectral band of reactants and supported by theoretical studies. This qualitative monitoring aims to keep the synthesis process remain within the planned corridor design of the synthesis of Zn-difattyalkyldithio carbamate complex. AAS was used, for supporting the qualitative data in the monitoring of Zn during the progress of synthesis and the final products.

Anti-oxidation test (Rancimat method)

Various amount of Zn-difattyalkyldithiocarbamate in grams was added into the RBDPO oil, and then homogeneously stirred. A total of 3.0 g of each mixture was then inserted into sample cell and tested at 120 °C for 24 h. The data were expressed in induction hour.

RESULT AND DISCUSSION

The Synthesized Zn-difattyalkyldithiocarbamates

Zn-dithiocarbamate complexes were obtained from the reaction between Zn^{2+} and dithiocarbamate. Difattyalkylamines and carbon disulfide were reacted to form difattyalkyldithiocarbamates and further reacted with $ZnCl_2$ to form Zn-difattyalkyldithiocarbamate complexes. The proposed reaction for the synthesis of Zn-difattyalkyldithiocarbamate complex from their corresponding reactants initiated with secondary fatty amine is shown in Fig. 2.

Synthesis Zn-difattyalkyldithiocarbamate was preceded by reaction between difattyalkyldithiocarbamates with NaOH to increase its sulfur reactivity in binding zinc atoms of $ZnCl_2$. In addition, alkaline conditions (NaOH) would increase the reactivity of nitrogen atoms of difattyalkylamine. In

Table 3. Purity of Zn-bis(dodecyllauryl)dithiocarbamate

Compound	tR (min)	Peak Area	Composition (%)
Secondary fattyamine	2.93	148068	2.3
Zn-bis(dodecyllauryl)dithiocarbamate	3.51	21249257	93.6

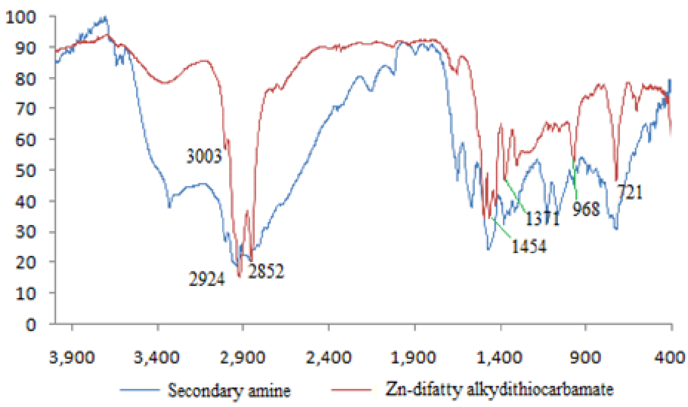

Fig 3. Infrared spectra of secondary fatty amine and Zn-difattyalkyldithiocarbamate complex

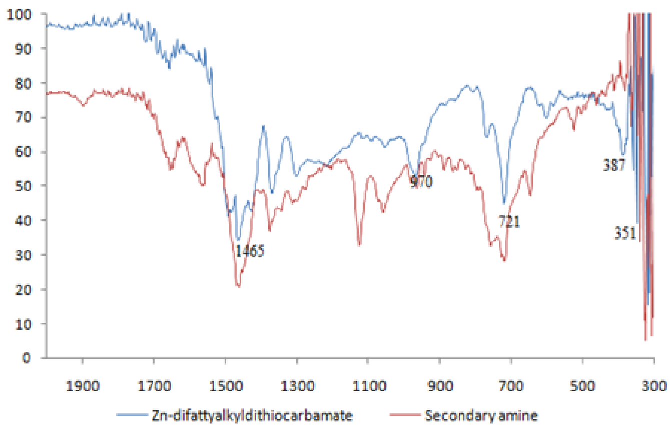

Fig 4. Far infrared spectra of secondary fattyamine and Zn-difattyalkyldithiocarbamate complex

alkaline conditions, lone pairs electrons on nitrogen atoms are ready to react, but in the contrary, in acidic conditions, the nitrogen atom will form an amine salt that is not reactive. Furthermore, the formation of Zn^{2+} complex compounds through exchange reaction is in the line with Lewis acid-base concept.

The progress of synthesis reaction of Zn-difattyalkyldithiocarbamate complex was monitored using FTIR. The important infrared absorption bands of dithiocarbamate complex according to [12], are υ (C-N) and υ (C-S). Uptake thioureida υ (C-N) are usually located on the wavenumber of 1450-1550 cm^{-1} while the υ (C-S) are on the wavenumber of 950-1050 cm^{-1}. Sharp absorption band at wavenumber of 1471-1478 cm^{-1} is due to C-N bond strain. The existence of this absorption band indicates that the difattyalkyldithiocarbamate has acted as a bidentate ligand. Absorption band υ (C-S) on the wavenumber of 952-957 cm^{-1} also shows a charactistic of dithiocarbamate as a bidentate ligand. Absorption band located in the far infrared region (400-300 cm^{-1}) due to strain mode is known as a metal-sulfur bond, υ (M-S).

The results indicate absorption band located in the infrared region of 2800-2950 cm^{-1} is corresponding to CH_3 asymmetric stretch, 1454-1462 cm^{-1} shows C-N stretch, and 968 cm^{-1} shows C-S group, which characterized dithiocarbamate as a bidentate ligand. The presence of absorption band in the far infrared region, i.e. 351 cm^{-1} indicates the presence of Zn-S bond. Fig. 3 and 4 show the IR absorption spectra of Zn-difattyalkyldithiocarbamate complexes and secondary fatty amines.

In addition to IR spectra, the synthesis and the purity of product were also monitored through elemental analysis of the products, i.e. Zn-bis(dodecyllauryl)dithiocarbamate and in its extracting solution, and conformity purity test of this product. The amount of Zn added as $ZnCl_2$ to the synthesis mixture was 65.2 mg, and around 48.78 mg of Zn was detected in the product and in the extracting solution was 0.029 mg Zn. Therefore, the recovery of Zn was 74.8%. This fact indicates that the Zn-bis(dodecyllauryl)dithiocarbamate complex is completely converted. The result of conformity purity test using HPLC indicated high purity of Zn-bis(dodecyllauryl)dithiocarbamate (Table 3).

Antioxidant Activity of Zn-difattyalkyldithio carbamate

Stability to oxidation is an important criterion for a good performance of lubricant. Air and humid environment in high temperature from friction of engine rotation can cause oxidation. The products of the oxidation process of lubricant include carboxylic acids, ketones, alcohols, and other polymeric materials which come together to form sludge. The unsaturated components of the sludge and high level of acidity causes viscosity increases and ultimately reduce engine performance. It has been observed that when oxidation starts, carbonyl formation is accelerated. Acid number increases due to the increase in type as well as amount of carboxylic acids or carbonyl compounds formed by long oxidation process. To prevent or to lengthen live service of a lubricant, additives that have

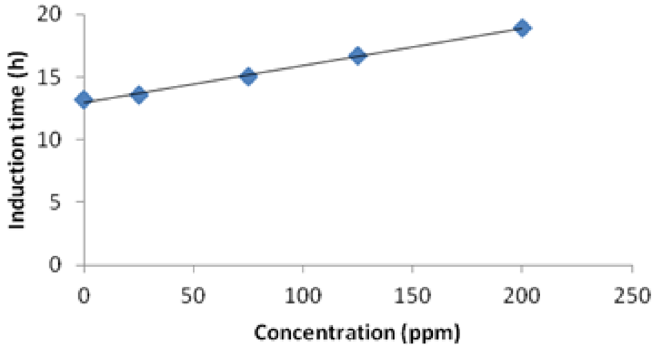

Fig 5. Range of measuring antioxidant activity using rancimat method

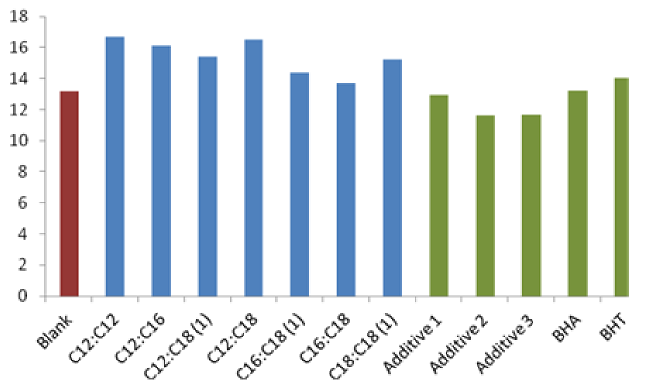

Fig 6. Antioxidant activities of Zn-difattyalkyl dithiocarbamates using Rancimat method

antioxidant activities are added so that they inhibit the formation of sludge, keep engine clean that in the end will have positive impact on engine performances. Many kinds of compounds used as lubricant additives include dithiocarbamate metals, amine and phenolic compounds, and dithiophospate metals [2].

One way to measure antioxidant activity is employing Rancimat method. The principle of the test is accelerated oxidation process by airflow and heat (temperature 120 °C). The antioxidant activity is expressed as induction time (in hours) which is the time required to oxidized sample material from zero to maximum level of oxidation. The faster induction time, the easier the material oxidized, and *vice versa* [13]. Before testing the antioxidant stability of a sample, verifying the ability range of the measuring instrument is required to obtain concentration interval that gives the best measurement sensitivity. The verifying results the instrument used is 0.00-200 ppm as shown in Fig. 5. From the data obtained, the concentration of 125 ppm was selected as the dose that provides the best measurement sensitivity, which then was used as the dose for testing our samples. The measurements results of antioxidant activity of seven Zn-difattyalkyldithio carbamates sample variants are shown in Fig. 6.

The curve in Fig. 5 follows a pattern according to the linear regression equation $Y = 0.029X + 12.95$ with a correlation coefficient $r^2 = 0.996$. Besides explaining the range of measurement capabilities, the curve also explains the sample concentration increment that will increase induction time.

The measurement results showed that the highest induction time was obtained by group of Zn-difattyalkyldithiocarbamate complex synthesized from dodecyllauryl amine (C12: C12), octadecyllauryl amine (C18: C12), and hexadecyllauryl amine (C16: C12). By looking at the induction time of these synthesized compounds, Zn-bis(dilauryl)dithiocarbamate reaches the highest value. It was synthesized from fatty amine (dodecyllaurylamine). The longer the induction time period, the longer the product inhibits the rate of oxidation, then the higher the antioxidant activity.

From the seven variants of Zn-difattyalkyldithio carbamate products tested, alkyl (lauryl) turned out to have the best antioxidant activity, as compared to other alkyl chains. It seems that the longer fatty acid chain in dithiocarbamate complex, the lower the value of antioxidant activity. The number of double bond have more dominant effect on increasing the antioxidants stability as compared to that of the increment in the number of carbon chains in fatty alkyl group in the tested complex compounds. Molecular symmetry factor has a positive contribution to the antioxidant power. Zn-bis(dilauryl)dithiocarbamate has symmetry form that show best antioxidant power compared to the other two, i.e. Zn-bis(laurylpalmityl)dithiocarbamates and Zn-bis(laurylstearyl)dithiocarbamate, which are both are non-symmetry geometric

For comparison study, four commercial additives were used, i.e. BHA (food additive), BHT (food additive), additive 1 (oil booster advanced additive for motorcycle), and additive 2 (antiwear additive). Among those four the one that give best value in oxidative activities was BHT. At 125 ppm dose tested, except Zn-bis(stearyl palmityl)dithiocarbamate, all variants of Zn-difattyalkyldithiocarbamates exhibited antioxidant activity higher than that of BHT, and all variants of Zn-difattyalkyldithiocarbamates also showed antioxidant activity higher than those of lubricant additives 1 and lubricant additives 2.

These results suggest a very promising Zn-difattyalkyldithiocarbamates as antioxidant additives in the lubrication system, because it has better performance antioxidant activity than that of additive 1, nonetheless that additive 1 is a commercially available in market. In addition, the low dose (125 ppm) application of Zn-difattyalkyldithiocarbamates suggest also it has high prospective uses as additives for food systems, pharmaceutical, and cosmetics from the aspect of their lower probable toxicity.

Other supporting factor that produces high effectiveness of the antioxidant activity of Zn-difattyalkyldithiocarbamate is molecular structure that has surfactant characters. Zn-dithio group which is hydrophilic part will be oriented to the surface of liquid oil or surface of metals engine, while fatty acid groups are lipophilic part that will oriented to oil bulk of lubricant. The orientation of the two groups of compounds in the liquid lubricant will act as the protectors of the effective surface of liquid oil oxidation processes that have a positive impact on its performance. It is better than that of radical capture mechanisms exhibited by BHA and BHT. With the orientation of such a molecule, Zn-difattyalkyldithiocarbamates are likely serve as a bearing on the lubrication system which is expected to have other activities as anti-friction agent.

CONCLUSION

Complex Zn-difattyalkyldithiocarbamate is synthetized with yield of 77%-87%. Zn-difattyalkyldithiocarbamate complex has a higher antioxidant activity than those of BHT, BHA, additive-2, and additive-1. From 7 (seven) types of Zn-complex products of difattyalkyldithiocarbamate tested at dose concentrations of 125 ppm, the best antioxidant power is generated by the Zn-bis(dilauryl)dithiocarbamate, Zn-bis(laurylpalmityl)dithiocarbamate, and Zn-bis(laurystearyl)dithiocarbamate with induction time 16.67 h, 16.54 h, and 16.11 h, respectively. Induction time for this product is better when compared with BHT, BHA, additive-2, and additive-1 with induction time 14.02, 13.26, 12.97, and 11.60 h, respectively. Zn-difattyalkyldithiocarbamates have very promising activity for application as antioxidant additives in lubrication system, because it shows better performance than that of antioxidant additive-1 which is a commercial antioxidant additive. In addition, the use of low dose (125 ppm), Zn-difattyalkyldithiocarbamate is also has good prospective as antioxidant additives in food systems, pharmaceutical and cosmetics because of its toxicity problem seems very little.

ACKNOWLEDGEMENT

This work was funded by the Directorate General of Higher Education through Grant for Post Graduate Program and facilitated by the Integrated Laboratory, Bogor Agricultural University.

REFERENCES

1. Rudnick, L.R., 2009, *Lubricant Additive: Chemistry and Applications*, 2nd ed., CRC Press: New York, 4–28.
2. Gogoi, P.K., and Sonowal, J., 2005, *Indian. J. Chem. Technol.*, 12, 50–54.
3. Kaludjerovic, G.N., Djinovic, V.M., Trifunovic, S.R., Hodzic, I.M., and Sabo, T.J., 2002, *J. Serb. Chem. Soc. 67*, 2, 123–126.
4. Husain, A., Nami, S.A.A., Singh, S.P., Oves, M., and Siddiqi, K.S., 2011, *Polyhedron* 30, 1, 33–40.
5. Nabipour, H., 2011, *Int. J. Nano. Dim.,* 1, 3, 225–232.
6. Vasiliev, A.N., and Polackov, A.D., 2000, *Molecules* 5, 8, 1014–1017.
7. Asthana, P., 2006, Micro- And Nano- Scale Experimental Approach To Surface Engineer Metals, *Thesis*, Texas A&M University.
8. Griffo, A., and Keshavan, M.K., 2007, High Performance Rock Bit Grease, *US Patent*, No. 7749947.
9. Sutriah, K., Mas'ud, Z.A., Irawadi, T.T., and Jamaran, I., 2011, *J. Kim. Ter. Ind,* LIPI (*in press*)
10. Nakanishi, H., Iwasaki, H., and Koganei, K., 2000, Zinc-molybdenum-based dithiocarbamate derivative, method of producing the same, and lubricant composition containing the same, *US Patent,* No. 6096693.
11. Zhang, W., Zhong, Y., Tan, M., Tang, N., and Yu, K., 2003, *Molecules*, 8, 5, 411–417.
12. Thirumaran, S., Venkatachalam, V., Manohar, A., Ramalingam, K., Bocelli, G., and Cantoni, A., 1998, *J. Coor. Chem.,* 44, 3-4, 281–288.
13. Tensiska, Wijaya, H., and Andarwulan, N., 2003, *J. Teknol. Ind. Pangan*. 14, 1, 29–39.
14. Awang, N., Baba, I., and Yamin, B.M., 2006, *Malay. J. Anal.*, 10, 2, 251–260.
15. Raya, I., Baba, I., and Yamin, B.M., 2006, *Malay. J. Anal.,* 10, 1, 93–98.
16. Shahzadi, S., Ahmad, S.U., Ali, S., Yaqub, S., and Ahmed, F., 2006, *J. Iran. Chem. Soc.,* 3, 1, 38–45.
17. Trifunović, S.R., Marković, Z., Sladić, D., Andjelković, K., Saboo, T., and Minić, D., 2002, *J. Serb. Shem. Soc., 67*, 2, 115–122.