

# Study of Novel Ecofriendly Multifunctional Lube Additives Based on Pentaerythritol Phenolic Ester

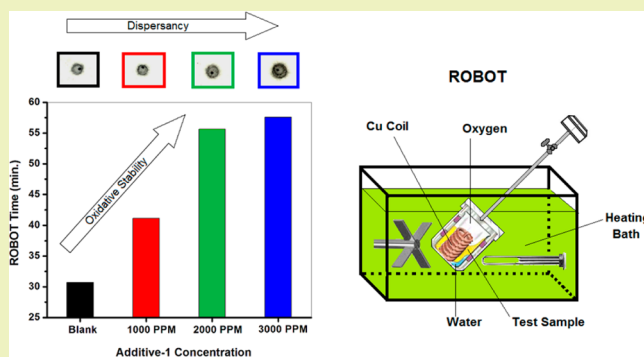
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## Supporting Information

**ABSTRACT:** The concept of an “ecofriendly lubricant” has drawn much attention due to environmental issues related to conventional lubricants. Mere innovations in lube base oils are not enough. The introduction of new ecofriendly additives is also necessary to address such issues. Therefore, there is a need for the development of new multifunctional additives (MFA) that are environmentally benign. In view of this, the mixed esters of pentaerythritol monooleate with gallic acid (additive 1) and 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (additive 2) have been synthesized. Both additives 1 and 2 were characterized by FT-IR, NMR, TG, and CHNS analyses. They were evaluated for antioxidant and detergent dispersant along with lubricity properties using the rotary bomb oxidation test, blotter spot test, and four ball test. The thermo-oxidative stability of the base oil was found to increase significantly in the presence of additives 1 and 2 at 3000 ppm concentration. The antioxidant, detergent dispersant, and lubricity properties of additive 1 have been found to be better than those of additive 2.

**KEYWORDS:** Lubricant, Pentaerythritol, Multifunctional additive, Antioxidant, Lubricity improver, Detergent dispersant property



## INTRODUCTION

The mineral oil-based lubricants cause severe environmental problems due to their disposal to land and water after use. The air is also affected indirectly by degraded products and volatile organic compounds (VOC) of lube oil. Their toxic and nonbiodegradable nature has drawn the attention of modern researchers to develop new environmentally benign lubricant technologies.<sup>1</sup> In the last few decades, synthetic oils along with vegetable oil-based esters have come out as an alternate choice. Synthetic lube oils offer some major advantages with respect to their performance characteristics that are not obtainable with mineral oils. Their molecular structure can be modulated to achieve the desired level of predictable properties. However, they are too costly and may be toxic also.<sup>2</sup>

Vegetable oil-derived base oils are emerging as the potential choice for formulating environmentally friendly lubricants because of their inherent technical properties and biodegradable nature. They are also preferred over synthetic fluids because their source is renewable and cheaper.<sup>3–6</sup> The major drawbacks associated with vegetable oil-based base stocks include low thermo-oxidative stability, nontolerance to acidic or alkaline media, etc.<sup>1,4–7</sup> These drawbacks may be overcome using new and effective additives in lubricant formulations.

In principal, most lubricants are comprised of a base lube oil (>85%) and an additive package. A dozen additives are added to meet all the specifications of the lube formulations. In order to reduce the number of such additives, the demand of multifunctional additives (MFA) is quite high. Conventional

MFAs including zinc dialkyldithiophosphate (ZnDDP), sulfonate, manich base, etc are not biodegradable, and hence,<sup>8</sup> maintaining the biodegradable nature of biolubes in the presence of an additive is one of the main challenges.<sup>9–11</sup> This aspect can be exemplified using the case of ZnDDP, which works well in biolubricant base but suffers from the limitations related with environmental concerns arising from S, P, and metal atoms. An additional problem with using ZnDDP is the poisoning of catalytic convertors in automobiles.<sup>12</sup> Sulfonate and manich bases have similar problems. In view of these problems, attention has been paid toward the development of ecofriendly MFAs.

A series of novel long-chain dimercaptiothiadiazole derivatives has been prepared and tested as antiwear (AW) and extreme pressure (EP) ecofriendly additives in vegetable oil using a four ball tester.<sup>13</sup> Condensation products of various amines with di(alkylphenyl) phosphorodithioic acid, derived from cashew nutshell liquid, have been evaluated as ashless antioxidant, antiwear, friction-modifying, and extreme pressure additives in lubricant compositions.<sup>14</sup> Soybean lecithin, which is a mixture of various phospholipids, is used for synthesizing an environmentally friendly, boron-containing, friction-reducing, antiwear, extreme pressure additive in synthetic base fluids by the reaction of boric acid.<sup>15</sup> N-oleoyl alanine, prepared by reactions of alanine with oleoyl chlorides under alkali solution,

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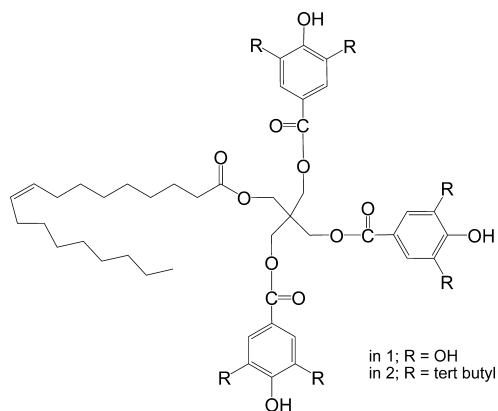
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has been tested as new environmentally friendly multifunctional lubricating additive in mineral base oil on a four ball friction tester.<sup>16</sup> Another report includes the synthesis of a multifunctional fuel additive for diesel fuel and biodiesel using rapeseed oil methyl ester. This vegetable oil-based multifunctional additive is reported to show the same or even better detergent dispersant properties compared to the traditional PIB succinimides and also provided other functional effects along with a corrosion inhibiting property and lubricity improving character.<sup>17</sup>

Long chain esters of cystine ( $Cys_2$ ), which is essential amino acid obtained from natural sources, have been tested as multifunctional additives. Tribological evaluation reveals that these diesters of cystine exhibit antiwear properties comparable with conventional ZnDDP in rapeseed oil.<sup>18</sup>

Some of the heterocyclic (bentriazole, benthiazole, benzimidazole, benzoxazole, thiazole, cyclotriphosphazene and triazine) derivatives have been reported to be excellent ashless multifunctional lubricating oil additives as they cause less pollution than others and also possess excellent extreme pressure, antiwear, anticorrosion, and antioxidant properties and high thermal stabilities.<sup>19–26</sup> A dioctyl [2-(benzothiazol-2-yl) disulfide ethyl] borate ester (BTSB) is also reported as a multifunctional additive when tested in rapeseed oil. Its EP (extreme pressure) property is found to be better than that of ZnDDP. It exhibits a better friction-reducing property and an almost equivalent antioxidant property compared with ZnDDP, but its antiwear property is slightly worse. It is also effective in protecting copper from corrosion.<sup>27</sup>

Further, in view of the requirement for the development of new ecofriendly, biolubricant, multifunctional additives, in the present manuscript, we report the synthesis, characterization, and evaluation of two additives, i.e., **1**, which is a mixed ester of pentaerythritol with oleic and gallic acid, and **2**, a mixed ester of pentaerythritol with oleic and 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (Figure 1). The synthesized additives were



**Figure 1.** Molecular structure of synthesized compounds **1** and **2**.

characterized by FT-IR, NMR, TG, CHNS analysis, etc. and evaluated for their antioxidant, detergent dispersant, and lubricity properties in *N*-butyl palmitate/stearate, a biolubricant reference fluid.<sup>28,29</sup> The rotary bomb oxidation test (ASTM D2272) was used for evaluating the antioxidant property. Detergent dispersant properties were evaluated using the blotter spot test method (modified ASTM D7899), while the lubricity property was evaluated by using the four ball test (ASTM D4172A).

## EXPERIMENTAL SECTION

**Materials.** Pentaerythritol monooleate was purchased from Wilson Laboratories, Mumbai, and used as received. Gallic acid, 3,5-di-*tert*-butyl-4-hydroxybenzoic acid, 4-(dimethylamino)pyridine (DMAP), and *N,N'*-dicyclohexylcarbodiimide (DCC) were purchased from Sigma-Aldrich. *N*-Butyl palmitate/stearate was purchased from Merck Millipore. *N,N*-dimethylformamide (DMF, HPLC grade) was purchased from Himedia. DMF was refluxed to be free from any moisture content. All other chemicals were of the highest available grade and were used without further purification.

**Synthesis of Additives 1 (Pentaerythritol Monooleate Gallate).** Pentaerythritol monooleate (4.0 g), gallic acid (5.1 g), *N,N'*-dicyclohexylcarbodiimide (6 g), and 4-(dimethylamino)pyridine (1.2 g) in 70 mL of *N,N*-dimethylformamide were taken into a 250 mL three-necked round-bottomed flask equipped with a stirrer, thermometer, water trap, and condenser. The mixture was heated to 150 °C for about 5 h. In order to avoid the decomposition of the reactants, all the processes were carried out in nitrogen atmosphere. Finally the reaction content was poured into water, and then precipitate was filtered, washed with 2 N HCl water and then with  $NaHCO_3$  to remove the DCC and DMAP, and then dried in a vacuum oven at 85 °C overnight. The dark brown compound was obtained as liquid additive **1**. Yield: 2.9 g.

**Synthesis of Additives 2 (Pentaerythritol Monooleate 3,5-di-*tert*-butyl-4-hydroxybenzoate).** Pentaerythritol monooleate (4.0 g), 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (7.5 g), *N,N'*-dicyclohexylcarbodiimide (6 g), and 4-(dimethylamino)pyridine (1.2 g) in 70 mL of *N,N*-dimethylformamide were taken into a 250 mL three-necked round-bottomed flask equipped with a stirrer, thermometer, water trap, and condenser. The mixture was heated to 150 °C for about 5 h. In order to avoid the decomposition of the reactants, all the processes were carried out in a nitrogen atmosphere. Finally, the reaction content was poured into water, and then precipitation was filtered, washed with 2 N HCl water and then with  $NaHCO_3$  to remove the DCC and DMAP, and then dried in a vacuum oven at 85 °C overnight. The dark brown compound was obtained as liquid additive **2**. Yield: 3.3 g.

## MEASUREMENTS

**Characterization.** Fourier transform infrared (FT-IR) spectra of both additive **1** and **2** (KBr pellets) were recorded using a Thermo-Nicolet 8700 research spectrophotometer with a 4  $cm^{-1}$  resolution. The synthesized additives were also characterized using NMR.  $^1H$  and  $^{13}C$  NMR measurements were carried out on a Bruker Avance 500 spectrometer in the proton noise-decoupling mode with a standard 5 mm probe. Thermogravimetry curves were recorded with a PerkinElmer EXSTAR TG/DTA 6300 using aluminum pans. The experiments were carried out under continuous nitrogen flow of 200  $mL\ min^{-1}$ , and the temperature ramp was set at 10 °C  $min^{-1}$ . The mass loss was recorded from 30 to 550 °C. CHNS analysis was performed on the PerkinElmer Series II CHNS/O 2400 analyzer.

**Biodegradability Testing.** The biodegradability test was done as per the ASTM D5864 procedure.<sup>30</sup> Three test sample oils were prepared and tested: sample 1 having only base ester, i.e., *N*-butyl palmitate/stearate; sample 2 having 0.5% additive **1** in base ester; and sample 3 having 0.5% additive **2** in base ester. The biodegradation of the oil is induced by an inoculum of a mixed population of microorganisms taken from activated sludge obtained from local sewage. Common oil biodegradability (aerobic aquatic biodegradation) tests are performed in the presence of oxygen and water. In a typical test, a sample of the oil is incubated at 77 °F (25 °C) for 28 days. Ultimate biodegradation is determined according to the evolution of carbon dioxide ( $CO_2$ ) from the tested sample over that produced in a blank, which contains inoculum only. As per ASTM, it should be fully biodegradable if producing 65% of  $CO_2$  of the total calculated value.

**Thermal Stability and Antioxidant Performance Analysis.** Thermal stability and antioxidant performance analysis were conducted on a RBOT (rotating bomb oxidation test) apparatus manufactured by Stan-hope Seta, U.K. using ASTM method D2272-

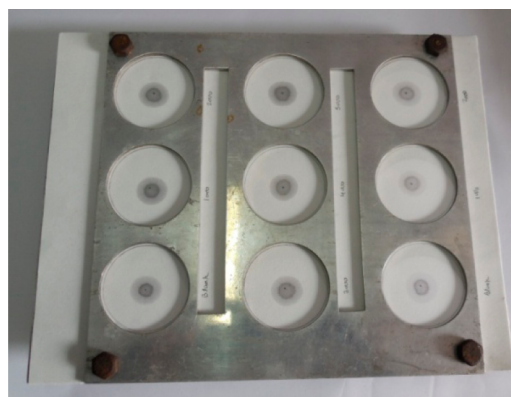
11.<sup>31</sup> Additives in base oils were run at 150 °C. Keeping the temperature below 150 °C will lead to longer duration tests. At this temperature, the difference between blank and doped oil is significant. Samples were measured near 50.0 ± 0.5 g and 5.0 mL of reagent water added to the sample. The copper catalyst was measured and cleaned with 220 grit silicon carbide sand paper and was used immediately. The wire was converted into a spring-coil shape having an outside diameter of 44–48 mm, weight of 55.6 ± 0.3 g, and height of 40–42 mm. The bomb was assembled and slowly purged twice with oxygen. The bomb was charged with 90.0 ± 0.5 psi (620 kPa) of oxygen then tested for leakage by immersing in water. The test was considered completed after the pressure dropped more than 175 kPa from the original pressure. All samples were run in duplicate, and the average time is reported in Table 1.

**Table 1. RBOT Test Results at 150 °C**

sample no.	compounds	concentration (ppm)	RBOT time
1	blank ( <i>N</i> -butyl palmitate/stearate)	0	30 min 42 s
2	propyl gallate	1000	58 min 23 s
3	propyl gallate	2000	1 h 25 min
4	lauryl gallate	1000	1 h 36 min
5	lauryl gallate	2000	2 h 39 min
6	octyl gallate	1000	1 h 39 min
7	octyl gallate	2000	2 h 13 min
8	octadecyl 3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate	1000	1 h 23 min
9	octadecyl 3-(3,5-di- <i>tert</i> -butyl-4-hydroxyphenyl)propionate	2000	1 h 41 min
10	3,5-di- <i>tert</i> -4-butylhydroxytoluene	1000	1 h 8 min
11	3,5-di- <i>tert</i> -4-butylhydroxytoluene	2000	1 h 32 min
12	additive 1	1000	41 min 9 s
13	additive 1	2000	55 min 38 s
14	additive 1	3000	57 min 35 s
15	additive 2	1000	31 min 11 s
16	additive 2	2000	35 min 42 s
17	additive 2	3000	43 min 30 s

**Detergency and Dispersing Efficiency.** The screening test for evaluation of detergency and dispersing efficiency of the compounds was done by the blotter spot test according to modified ASTM D7899.<sup>32</sup> A 1000 mL sample of base oil (polyol ester) was put in a beaker, and 5.0 g of lamp black (cosmetic grade prepared from lamp shoot) was dispersed in it. It was used as the stock oil or blank. Then an additive was added in 5 g of this stock oil to make the 1000–5000 ppm concentration solutions. It was stirred for 2–3 h at about 40–50 °C with the help of magnetic stirrer. The solution was made homogeneous. This sample was used for the spot test. A sheet of filter paper (Whatman number 1) was clamped in an aluminum frame having nine circle holes of equal area (Figure 2). Circles boundaries were marked with pencil. Oil samples were drawn with a dropper, and one drop of sample was placed on the center mark of each filter paper circle. The spreading of oil on the filter paper was developed by keeping it for 10–12 h. The filter paper or blotter spot for soot and oil was inspected. The carbon spot area and oil spot area were recorded (Figure 3).

**Tribological Test.** Lubrication properties of the synthesized additives were evaluated on a four ball test machine (Ducom, India) in terms of friction coefficient and wear scar diameter (WSD). All tests were carried out as per the ASTM D4172A standard test method.<sup>33</sup> In a typical experiment, a 12.7 mm steel ball under the load is rotated against three stationary steel balls clamped in the holder. During these experiments, the four balls were covered with lube samples (additive 1 or 2 in *N*-butyl palmitate/stearate base oil in different concentrations). Tests were performed at a rotating speed of 1200 rpm; load, 198 N; temperature, 75 °C; and time, 60 min.



**Figure 2.** Experimental arrangement for blotter test.

## RESULTS AND DISCUSSION

Developing new ecofriendly biolubricant MFAs is a topic of current interest due to environmental issues related with lubricant disposal after use. Phenolic esters have been used as ecofriendly antioxidant additives recently and have been found to be relevant in this context. A new ester phenolic antioxidant based on dipentaerythritol was synthesized via first esterification reaction with 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionic acid and second via esterification reaction with isostearic acid. The rotary bomb oxidation test (RBOT) demonstrated that this phenolic antioxidant has excellent antioxidant efficiency.<sup>34</sup> Here, two new similar molecules were designed to be used as multifunctional additives (Figure 1).

**Synthesis.** These new designed molecules were synthesized following Schemes 1 and 2. The esterification of the hydroxyl group using anhydrides or acyl halides as the esterifying agent is one of the most routinely used transformations in organic synthesis. Synthesis through this route will add one more step to synthesize additive 1 and 2 with our reaction scheme. In order to avoid one step, we have tried carbodiimide-mediated coupling used in combination with a catalytic amount of DMAP. DCC (*N,N'*-dicyclohexylcarbodiimide) works as an activating reagent for gallic acid and 3,5-di-*tert*-butyl-4-hydroxybenzoic acid for the esterification of pentaerythritol monooleate. The use of DCC avoids the need for prior activation of the carboxylic acid and allows the esterification to be achieved with acids in the presence of sensitive functionalities. The 4-(*N,N*-dimethylamino)pyridine (DMAP) Steglich catalyst was used.<sup>35–37</sup> We found only DCC/DMAP offered high yields, while others such as DCC alone and DCC/HOBT (1-hydroxybenzotriazole) resulted in low yields. To optimize the solvent condition, we have tested several solvents including DMF, CH<sub>2</sub>Cl<sub>2</sub>, and toluene, but we found DMF more suitable in terms of high yield and reaction time.

**Biodegradability.** Biodegradability of the synthesized compounds was evaluated using ASTM D5864.<sup>30</sup> The experimental value of cumulative CO<sub>2</sub> evolved for sample 1 (*N*-butyl palmitate/stearate) has been found to be 73.46%. This value for sample 2 (0.5% additive 1 in base ester) is 71.53 and for sample 3 (0.5% additive 2 in base ester) is 70.43. All these values are greater than 65, indicating a complete biodegradable nature. It clearly indicates that additives 1 and 2 do not affect the biodegradability of the base ester to a significant extent and can be considered as environmentally friendly.

**FT-IR Characterization.** The designed additives were synthesized via esterification reaction where alcoholic and

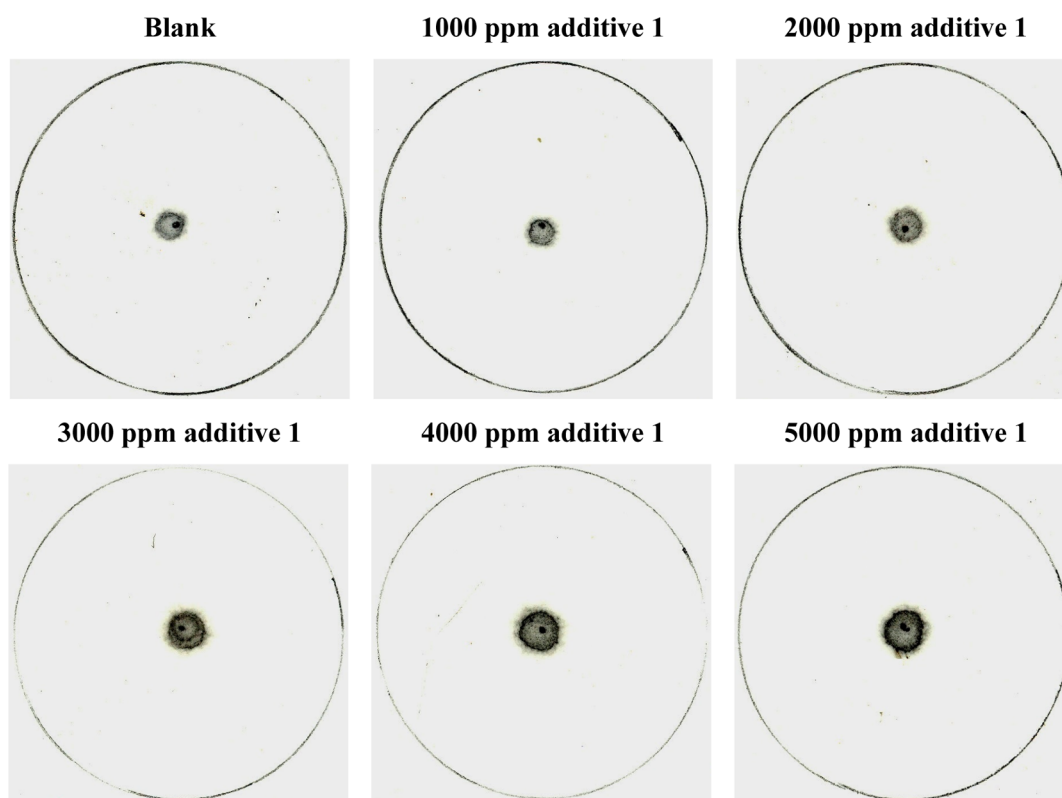
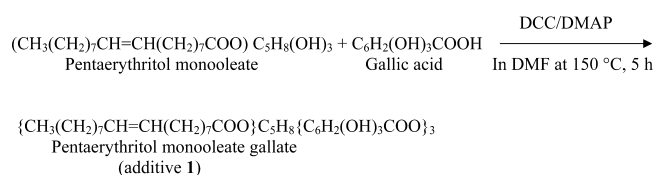
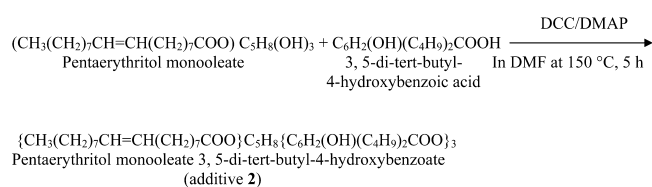


Figure 3. Blotter spot test results of additive 1.

#### Scheme 1



#### Scheme 2

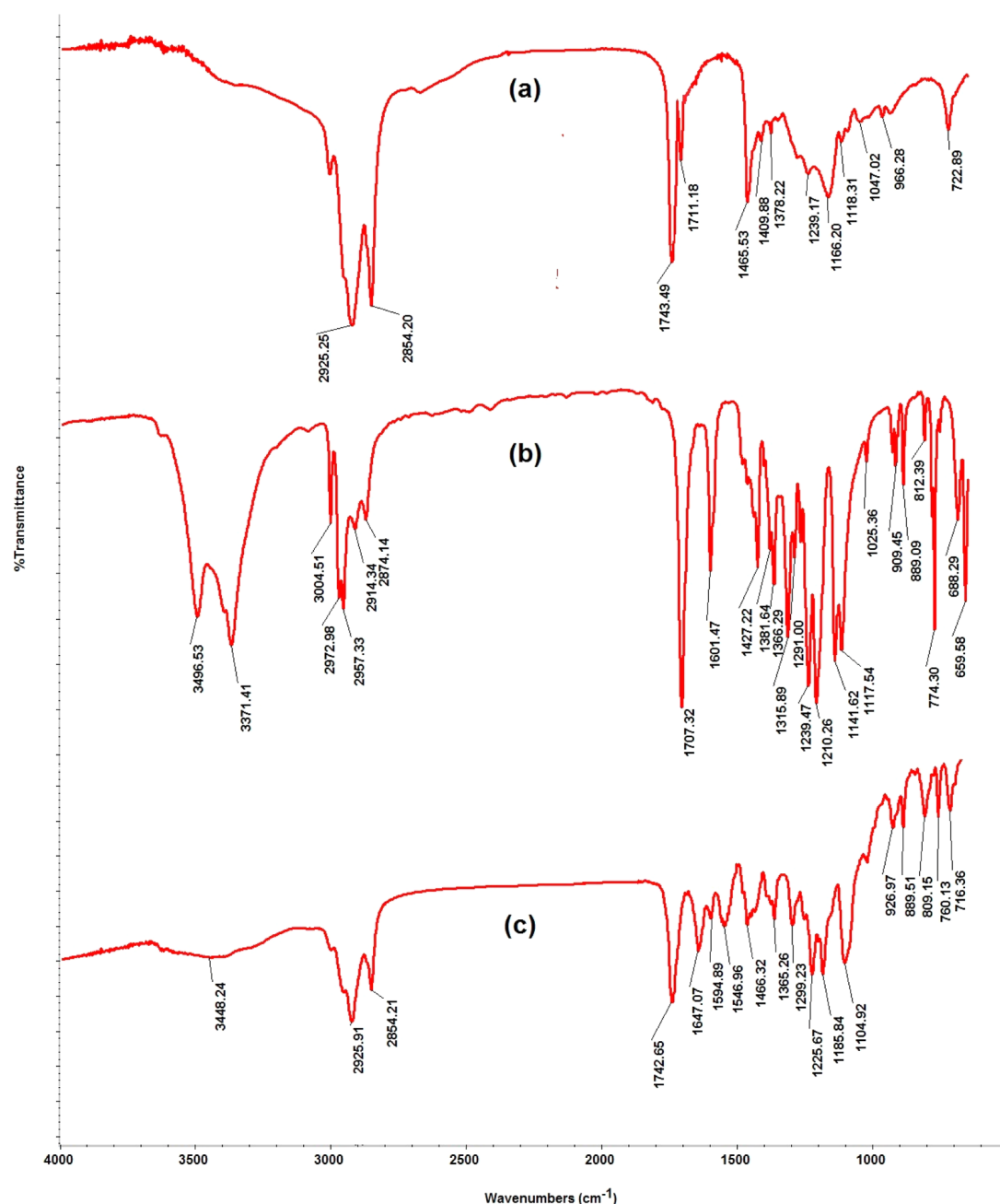


carboxylic functional groups are changed to ester. Therefore, FT-IR may be an effective method to detect the successful synthesis. The pentaerythritol monooleate, 3,5-di-*tert*-butyl-4-hydroxybenzoic acid and additive 2 are represented by the spectral data in Figure 4. In the FT-IR of pentaerythritol monooleate, the bands at 2925 and 2854  $\text{cm}^{-1}$  represent asymmetric and symmetric C–H stretching vibrations, respectively, for  $\text{CH}_3$  and  $\text{CH}_2$  groups. The band appearing at 1378  $\text{cm}^{-1}$  characterizes the symmetric C–H bending vibrations in the  $\text{CH}_3$  group and the band at 1465  $\text{cm}^{-1}$  for the  $\text{CH}_2$  group. The bands at 1166 and 722  $\text{cm}^{-1}$  represent the C–H wagging and rocking bending vibrations, respectively, for the  $\text{CH}_2$  group. A sharp and very strong absorption band at 1743  $\text{cm}^{-1}$  in the spectra of the pentaerythritol monooleate represents the C=O stretching vibration of the ester group. A weak band at 1711  $\text{cm}^{-1}$  is also observed corresponding to

the carbonyl group of the fatty acids, which may exist as an impurity due to partial hydrolysis. Also the characteristic multiple bands in the C–O stretching region are observed in the region of 1260–1239  $\text{cm}^{-1}$ .<sup>38,39</sup> The diminished OH stretching band near 3305  $\text{cm}^{-1}$  is also observed, which corresponds to the unesterified polyol hydroxyl groups.

As far as the FT-IR spectra of 3,5-di-*tert*-butyl-4-hydroxybenzoic acid is concerned, the band at 3496 and 3371  $\text{cm}^{-1}$  corresponds to the hindered phenolic OH stretching and acidic OH stretching, respectively. The aromatic C–H band appears at 3004  $\text{cm}^{-1}$ , while the asymmetric and symmetric C–H stretching vibrations along with the coupled vibrations of  $\text{CH}_3$  were observed between 2972 and 2874  $\text{cm}^{-1}$ . The sharp band at 1707  $\text{cm}^{-1}$  is also observed corresponding to the C=O stretching of the carboxylic group. Aromatic C=C stretching appears at 1601  $\text{cm}^{-1}$ . The bands at 1427 and 1366  $\text{cm}^{-1}$  appear due to asymmetric and symmetric  $\text{CH}_3$  bending. Phenolic C–O stretching appears at 1239  $\text{cm}^{-1}$ . Carboxylic C–O stretching appears at 1315  $\text{cm}^{-1}$ . Aromatic C–H in-plane bends appears between 1141 and 1117  $\text{cm}^{-1}$ . Aromatic C–H out-of-plane bends appear at 774 and 688  $\text{cm}^{-1}$ .

Now the successful synthesis of additive 1 could be established by the FT-IR spectra. The disappearance of the polyol OH stretching band near 3305  $\text{cm}^{-1}$  is evidence for the complete esterification of the hydroxyl groups in pentaerythritol monooleate. The presence of a phenolic OH stretching band at 3448  $\text{cm}^{-1}$  along with the aromatic C=C stretching bands at 1647, 1594, and 1546  $\text{cm}^{-1}$  is evidence of the hindered phenolic group incorporation in the pentaerythritol monooleate. Further, the existence of the C=O stretching vibration at 1742  $\text{cm}^{-1}$  is strong evidence of successful synthesis. The coexistence of the fatty alkyl chain along with the tertiary butyl group in hindered phenol is evident by the appearance of the



**Figure 4.** FT-IR spectra: (a) pentaerythritol monooleate, (b) 3,5-di-*tert*-butyl-4-hydroxybenzoic acid, and (c) additive 2.

characteristic strong bands at 2925 and 2854 cm<sup>-1</sup> attributing to the asymmetric and symmetric C–H stretching vibrations (CH<sub>3</sub> and CH<sub>2</sub> groups), respectively. The bands at 1378 and 1465 cm<sup>-1</sup> correspond to the symmetric C–H bending vibrations of CH<sub>3</sub> and CH<sub>2</sub>, respectively. Also phenolic C–O stretching appears at 1225 cm<sup>-1</sup>. Ester C–O stretching appears at 1299 cm<sup>-1</sup>. Aromatic C–H in-plane bends appear at 1104 cm<sup>-1</sup>. All these results indicate that the free OH of pentaerythritol monooleate has been reacted with the 3,5-di-*tert*-butyl-4-hydroxybenzoic acid leading to additive 2 formation. Similar structure elucidation by FT-IR was done for additive 1 (Figure S1, Supporting Information).

**NMR.** Along with the FT-IR analysis, NMR also presents some strong evidence in favor of the structures of additives 1 and 2. Figure 5 shows the <sup>13</sup>C NMR of additive 1. The signals, observed in the range of 0–40 ppm, correspond to carbons of

the oleoyl fatty chain and pentaerythritol. Signals for aromatic carbons are observed between 120 and 150 ppm. The presence of the >C=O (C19) signal at 173.5 ppm is strong evidence of the Steglich coupling of gallic acid. Similarly, in the <sup>13</sup>C NMR of additive 2 (Figure S2, Supporting Information), the signals observed in the range of 0–40 ppm are attributed to the carbons of the oleoyl fatty chain and pentaerythritol and CH<sub>3</sub> of the tertiary butyl groups of the phenolic reactant. Also, aromatic carbons are observed between 120 and 150 ppm and the >C=O (C19) signal at 166.5 ppm. The C12 signal of the precursor, i.e., pentaerythritol monooleate, appearing at 48 ppm gets shielded upon esterification and appears at 37 and 39.5 ppm in additives 1 and 2, respectively.

The <sup>1</sup>H NMR spectra of additives were also recorded, and characteristic signals were found for all protons corresponding

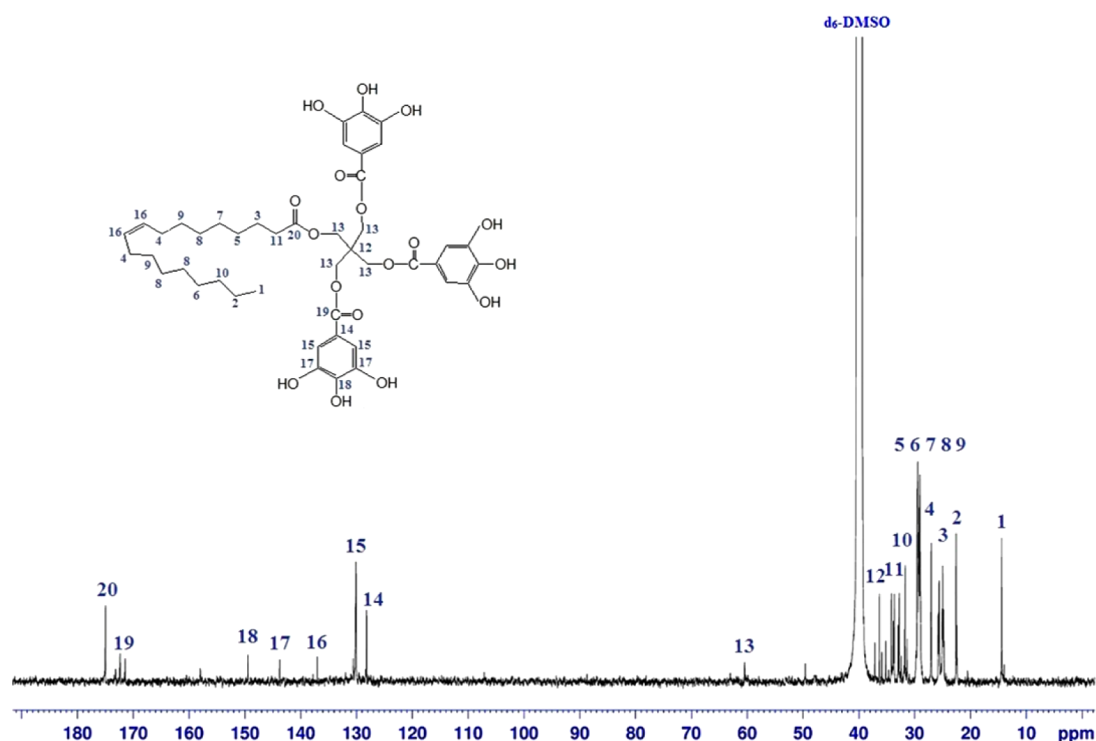


Figure 5.  $^{13}\text{C}$  NMR of additive 1 in  $\text{DMSO-}d_6$  at  $25\text{ }^\circ\text{C}$ .

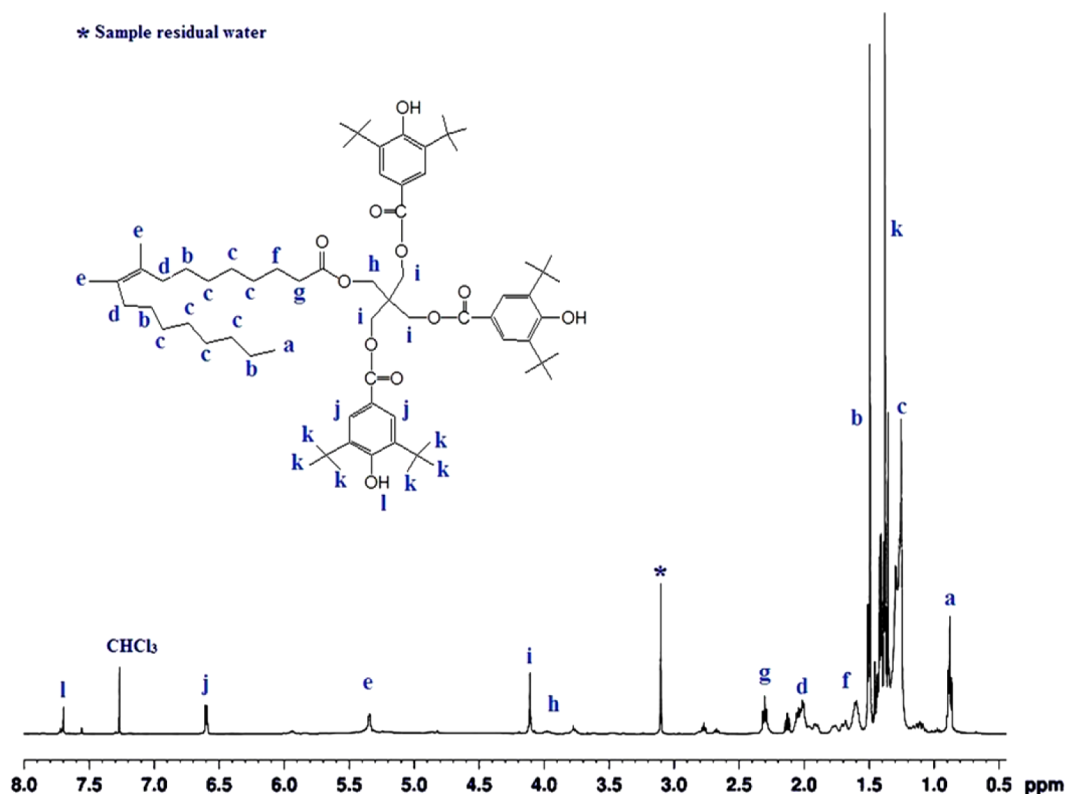


Figure 6.  $^1\text{H}$  NMR of additive 2 in  $\text{CDCl}_3$  at  $25\text{ }^\circ\text{C}$ .

to the fatty chain, substituted aromatic ring, and phenolic OH as shown in the  $^1\text{H}$  NMR spectrum of additive 2 (Figure 6).

**CHNS Analysis.** The CHNS analysis shows that additive 1 ( $\text{C}_{44}\text{H}_{56}\text{O}_{17}$ ) has C, 60.45; H, 7.12; and O, 32.43%, which is very similar to that of that of the theoretical values (C, 61.67; H, 6.59; O, 31.74%). A similar conclusion was revealed by the

CHNS analysis of additive 2. The CHNS results for additive 2 ( $\text{C}_{68}\text{H}_{104}\text{O}_{11}$ ) are C, 73.84; H, 8.38; and O, 17.83%. Esterification of all three hydroxyl groups of pentaerythritol monooleate with gallic acid (additive 1) and 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (additive 2) is supported by the results of CHNS analyses.

**Thermal Stability.** The TG/DT analytical results (Figures 7 and 8) indicate that both additives (i.e., 1 and 2) possess

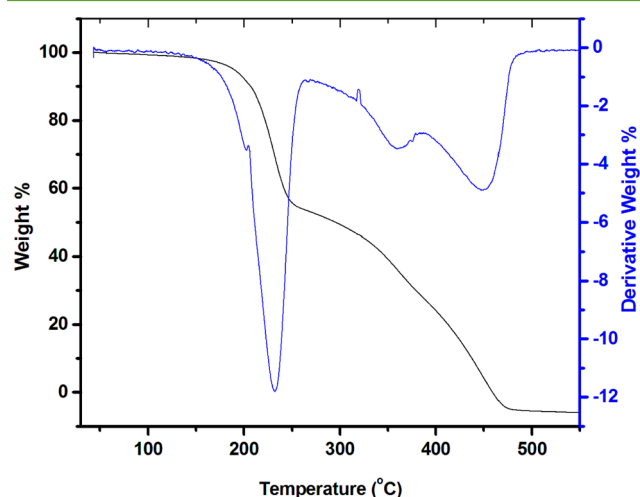


Figure 7. TG/DT of additive 1.

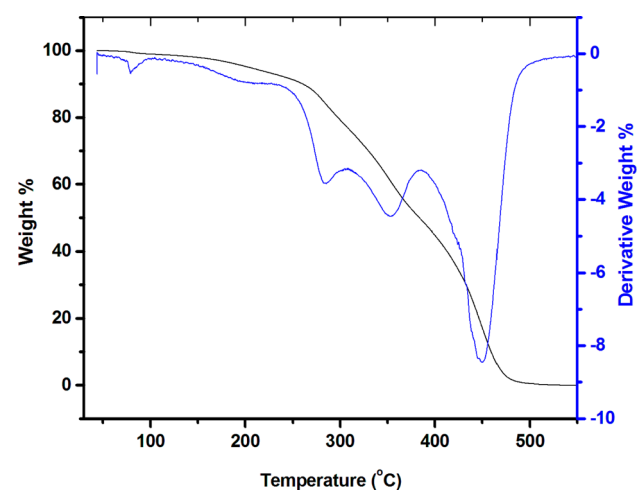


Figure 8. TG/DT of additive 2.

good thermal stability, and their decomposition temperatures are 232.27 and 285.25 °C, respectively. The temperature value at the maximum decomposition rate of the first degradation stage is taken as the decomposition temperature.

On the basis of the results of the elementary analysis and IR and NMR spectral analyses, it can be concluded that the prepared compounds are identical to the proposed molecular structures.

**Antioxidant Property.** Hindered phenolic compounds are well-known antioxidant additives. The mechanism is well established.<sup>40</sup> Incorporation of hindered phenolic groups in pentaerythritol monooleate through the esterification reaction with the gallic acid (additive 1) and 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (additive 2) is supposed to provide antioxidant behavior.

The ASTM D2272 method was employed using RBOT to understand antioxidant behavior of both additives. *N*-Butyl palmitate/stearate is taken as the reference lube base oil in this study. Some standard antioxidant additives compounds were also tested to compare the antioxidant potential. Optimization of temperature for the test was carried out by performing the rotatory bomb oxidation test (RBOT) at different temperatures

for the reference lube base oil, and 150 °C was found to be suitable. At higher temperatures, oxidation time was very short to give a significant difference of induction times for various additives. However, at lower temperatures, induction time was too long. A different dose of antioxidants was used between 1000 and 3000 ppm.

It can be inferred from the results of RBOT (Table 1) that additive 1 at 3000 ppm concentration enhances the RBOT time of the reference oil from 30 min 42 s to 57 min 35 s. This is a 1.5 times increase. The concentration effect of additive 1 is remarkable, and RBOT time periods increase with an increase in its concentration. The response of additive 2 is not equally encouraging at low concentration as it enhances the RBOT time only to the value of 43 min 30 s at 3000 ppm concentration. As far as the comparison of antioxidant potential with the standard compounds is concerned, the additives are less effective. These results indicate that additive 1 is having a greater antioxidant character than additive 2. The reason may be attributed to the higher number of hindered phenolic groups in additive 1.

**Detergent Dispersant Property.** Additives 1 and 2 were evaluated for their detergency and dispersant capabilities as per the modified ASTM D7899 method, which is also known as blotter spot test. The detergency and dispersing power can be evaluated in terms of several parameters such as the size of the center spot, color of the center spot, size of the diffusion zone, color of the diffusion zone (black, gray), and density (translucent or opaque). However, our study has been confined only to the measurement of the size of the spot (Figure 3 and Figure S3, Supporting Information) where dispersancy measurement is done according to the method developed by Diraison et al.<sup>41</sup> The dispersions of the samples were measured using eq 1

$$\text{Dispersancy (\%)} = \frac{\text{Diameter of black spot}}{\text{Total diameter of the oil spot}} \times 100 \quad (1)$$

On its basis, a comparative chart has been prepared by observing the spot on the filter paper for 24 h. The efficiency of dispersants has been categorized as up to 30% very bad dispersancy, 30–50% bad dispersancy, 50–60% normal dispersancy, 60–70% good dispersancy, and above 70% very good dispersancy; we have categorized the performance of additives samples in five classes Very Good (VG), Good (G), Normal (N), Bad (B), and Very Bad (VB). It can be inferred from the results of the blotter spot test (Table 2) that additive 1 is dispersing soot in base oil far better than additive 2. The dispersion is found to increase with an increase in concentration from 1000–5000 ppm. In additive 2, this effect is not prominent. The reason is related to the polarity, which is higher in the case of additive 1 because of the existence of the nine phenolic hydroxyl groups in additive 1. This polarity provides an ideal molecular structure to form the micelles. The tertiary butyl groups in additive 2 decreases the polarity in comparison to additive 1.

**Tribological Properties.** The synthesized additives were tested (Table 3) for the lubricity properties using ASTM D4172A on the Ducom four ball test machine using 198 N load, 1200 rpm rotating speed, and different concentrations (1000, 1500, 2000, 2500, and 3000 ppm) of the additive compounds in *N*-butyl palmitate/stearate reference base oil at 75 °C for 60 min. Both samples showed an increased lubricity and friction reducing capacity in terms of WSD and average

**Table 2. Blotter Spot Test Evaluation of Additives 1 and 2**

sample no.	name of the additive <sup>a</sup>	concentration (ppm)	performance evaluation <sup>b</sup>
1	blank ( <i>N</i> -butyl palmitate/stearate)	–	VB
2	standard (PIB succinimide of tetraethylene pentamine)	1000	VG
3	additive 1	1000	VB
4	additive 1	2000	B
5	additive 1	3000	N
6	additive 1	4000	G
7	additive 1	5000	VG
8	additive 2	1000	VB
9	additive 2	2000	N
10	additive 2	3000	N
11	additive 2	4000	N
12	additive 2	5000	G

<sup>a</sup>PIB, polyisobutylene. <sup>b</sup>VB, Very Bad; B, Bad; N, Normal; G, Good; and VG, Very Good.

**Table 3. Four Ball Test Results**

sample no.	compounds	concentration (ppm)	WSD ( $\mu\text{m}$ )	average friction coefficient
1	blank	–	507.50	0.10375
2	additive 1	1000	609.17	0.10421
3	additive 1	1500	486.67	0.08394
4	additive 1	2000	470.49	0.07431
5	additive 1	2500	450.25	0.06234
6	additive 1	3000	525.14	0.09321
7	additive 2	1000	615.00	0.12199
8	additive 2	1500	502.43	0.10234
9	additive 2	2000	494.58	0.09321
10	additive 2	2500	487.64	0.09114
11	additive 2	3000	495.74	0.09874

friction coefficient of the *N*-butyl palmitate/stearate. The WSD value, i.e., 507.50  $\mu\text{m}$  for the base oil, increases to 609.17 and 615.00 upon adding 1000 ppm of additives 1 and 2, respectively, while the base oil average friction coefficient 0.10375 increases to a value of 0.10421 (additive 1) and 0.12199 (additive 2) at this concentration. The 1000 ppm concentration of both additives is not enough for film formation over the metallic surface. Both the WSD and average friction coefficient decreases with an increase in concentration up to 2500 ppm of additives 1 and 2. At 2500 ppm, both samples were shown to increase the lubricity of *N*-butyl palmitate/stearate. When 2500 ppm of additives 1 and 2 was used, the WSD was found to decrease to a value of 450.25 and 487.64  $\mu\text{m}$ , respectively. This reveals that both additives show some film forming tendency over the metallic surface at this concentration as the average friction coefficient is also found to decrease from its value of 0.10375 for base oil to 0.06234 and 0.09114, respectively, for additives 1 and 2 (Table 3). The concentrations higher than 2500 ppm affect negatively the lubricity characteristics. Comparatively, additive 1 is more effective than additive 2 in providing lubricity and friction reduction between the metallic contacts. It is a well-known fact that the lubricity by any material is a consequence of its ability to form film on metallic surfaces. The metallic surface has an affinity toward the polar functionalities of additives due to the existence of the residual forces on the surfaces. In case of additive 1, a more phenolic group (OH) exists than in additive

2, along with similar ester functional groups ( $-\text{COOC}-$ ). This polar end ( $-\text{O}-$ ) acts as the head to stick to the surface, while the long carbon chain of the oleoyl fatty chain works as an arm, which remains toward the bulk of the second interacting surface. This provides a film between the two moving surfaces and avoids direct contact between them, imparting lubricity. However, bulkiness of the tertiary butyl groups in the additive 2 molecules reduces the film formation capacity. This is a clear indication that additive 1 is a good candidate as a lubricity improver due to better film formation and more friction reducing effect.

## CONCLUSIONS

New multifunctional additives 1 (pentaerythritol monooleate gallate) and 2 (pentaerythritol monooleate 3,5-di-*tert*-butyl-4-hydroxybenzoate) were synthesized via an esterification reaction. These molecules were designed by keeping the view that the introduction of the hindered phenolic group via esterification of the free hydroxyl groups in the pentaerythritol monooleate will not only provide an antioxidant property but also that the polar end formation will enable these molecules to work as a detergent dispersant. Of course, the inherent existing lubricity in the pentaerythritol monooleate will also increase due to the addition of more polar ester functionalities. The long oleoyl fatty chain will continue to help in providing the additives solubility in biolubricant base oil.

According to this designed molecular structure, we have synthesized additives 1 and 2, and then the characterization by FT-IR and NMR analyses reveals the successful synthesis of both compounds. The comparative study of the antioxidant, detergent dispersant, and lubricity properties of the compounds in *N*-butyl palmitate/stearate base oil was done using the rotary bomb oxidation test (ASTM D2272), modified blotter spot test (ASTM D7899), and four ball test (ASTM D4172A). Both compounds are found to have these activities, but additive 1 is comparatively more active. Although our additives are not superior to the commercially used MFA, additive 1 is an excellent antioxidant and good detergent dispersant and has minimal lubricity improver characteristics in the used reference biolubricant base oil. Conclusively, additive 1 could be a good candidate for a MFA biolubricant having antioxidant, detergent dispersant, and lubricity properties.

## ASSOCIATED CONTENT

### Supporting Information

FT-IR characterization spectrum of additive 1 and <sup>13</sup>C NMR of additive 2 along with blotter spot test results of additive 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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