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Novel Acyloxy Derivatives of Branched Mono- and Polyol Esters of Sal Fat: Multiviscosity Grade Lubricant Base Stocks

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ABSTRACT: Sal fat, a nontraditional seed oil, was chemically modified to obtain base stocks with a wide range of specifications that can replace mineral oil base stocks. Sal fatty acids were enriched to 72.6% unsaturation using urea adduct method and reacted with branched mono alcohol, 2-ethylhexanol (2-EtH), and polyols namely neopentyl glycol (NPG) and trimethylolpropane (TMP) to obtain corresponding esters. The esters were hydroxylated and then acylated using propionic, butyric, and hexanoic anhydrides to obtain corresponding acylated derivatives. The acylated TMP esters exhibited very high viscosities (427.35−471.93 cSt at 40 °C) similar to those of BS 150 mineral oil base stock range, ISO VG 460, while the acylated NPG esters (268.81−318.84 cSt at 40 °C) and 2-EtH esters viscosities (20.94−24.44 cSt at 40 °C) exhibited viscosities in the range of ISO VG 320 and 22 respectively with good viscosity indices. Acylated NPG esters were found suitable for high temperature and acylated 2-ethylhexyl esters for low viscosity grade industrial applications. It was observed that the thermo-oxidative stabilities of all acylated products were found better compared to other vegetable oil based base stocks. Overall, all the sal fat based lubricant base stocks are promising candidates with a wide range of properties, which can replace most of the mineral oil base stocks with appropriate formulations.

KEYWORDS: sal fat, branched mono alcohol, polyols, acylation, multi viscosity grade, thermo-oxidative stability

INTRODUCTION

Most of the lubricants available in the market are mineral oil based. As the fossil fuels are diminishing rapidly, the demand for renewable, biodegradable, nontoxic lubricants is increasing day-by-day. Today over 60% of the lubricants are lost to the environment;[1] hence, there is an increasing concern for environmental pollution from excessive petroleum based lubricants especially in lost lubrication, military application and outdoor actions such as forestry, mining, railroad, fishing, and agriculture hydraulic fluids. In this context, vegetable oils rich in oleic acid are considered to be potential substitutes for mineral oil based lubricating oils and synthetic esters.[2] They possess superior viscosity index, lubricity characteristics, and high solubilizing power for additive molecules. Despite their enormous potential to be cost and performance competitive to mineral-based fluids, they have inherent short comings such as poor oxidative, thermal, and hydrolytic stabilities, which is due to the presence of unsaturation, allylic autoxidation, their propensity for E/Z isomerizations (cis/trans isomerizations)[3] and also due to the presence of β- hydrogen in triglyceride.[4,5]

Chemical modification of vegetable oils is an attractive way to solve these problems and can pave way to renewable raw materials.[6] Introduction of branched and bulky molecules into the structure of fatty acids can enhance the properties required for biolubricant and cosmetic applications. However, introduction of bulky groups such as polyols may hinder the cold-flow properties of the vegetable oils-based esters.[7] These short comings can be overcome by modification at unsaturation by hydrogenation, epoxidation, hydroxylation, etherification, acylation etc.,[8−14] also the removal of β- hydrogen atom in the triglyceride by the reaction with polyols and branched alcohols.[15−19]

Most of the reported literature involved either modification of unsaturation or removal of β- hydrogen to develop vegetable oil based lubricant base stocks with various specifications. On the other hand, some of the most widely used lubricants at high temperatures and pressures, such as the forging or industrial gear oils lubrication, demand high viscosities with good oxidation stabilities and low pour points. However, there exists no report on vegetable oil modification suitable for the above applications. With this background an attempt was made to modify sal fat to obtain base stocks with a suitable range of viscosities for forging and metal working fluid applications.

Sal tree (*Shorea robusta*), one of the nontraditional oil yielding tree, widely grown in India and under exploited. Sal forests form a major source of timber and can also yield nontimber forest products including fodder,[20] seed for oil, bark for tannin and gum,[21] and leaves for plate making. The tree can adapt well in all types of climates and is a good source for rural development. In the present study sal fat was chemically modified to develop base stocks with high viscosities, good oxidation stabilities and low pour points. The fat being rich in saturation, 56.5% can be exploited to develop base stocks with good oxidation stabilities. Our earlier work on sal fat based polyol esters[17] generated base stocks with viscosities ranging from 10 to 56. With an intention to develop high viscosity grade base stocks and improve the pour point and oxidation stabilities, sal fatty acids were enriched with oleic acid, followed by esterification with alcohols such as branched mono- and polyols such as 2-ethylhexanol, NPG, and TMP, respectively.

Further, to develop high viscous base stocks, the unsaturation in branched mono- and polyol esters was modified to the acylated derivatives. The base stocks with the above modifications are novel and are reported for the first time.

■ MATERIALS AND METHODS

Materials. Sal fat was procured from M/s. Paras Vanaspathi, Raipur, India. Hydrogen peroxide, formic acid, sulfuric acid, acetic acid, 4 N hydrobromic acid, iodine monochloride (ICl), potassium hydroxide, hydrochloric acid, *n*-butanol, pyridine, chloroform, acetic anhydride, 2-ethylhexanol (2-EtH), NPG, TMP, *p*-tolunesulfonic acid (p-TSA), 4-(dimethylamino)pyridine (DMAP), xylene, aluminum oxide active basic, sodium hydroxide (NaOH), methanol, urea, and sodium sulfate were procured from M/s SD. Fine chemicals Pvt. Ltd., (Mumbai, India). Propionic, butyric, and hexanoic anhydrides were procured from Sigma-Aldrich (St. Louis, MO, U.S.A.). Hexane, methanol, and ethyl acetate were purchased from Industrial Solvents and Chemicals Pvt. Ltd. (Mumbai, India). All the solvents and reagents were of analytical grade and used directly without purification.

Methods. *Spectral Analysis.* Infrared (IR) spectra were obtained on a 1600 FT-IR PerkinElmer Spectrometer (Norwalk, CT) with a liquid film between NaCl cells. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded in CDCl$_3$ on Avance 300 MHz spectrometer. Chemical shifts relative to TMS as internal standard are given as δ values in ppm. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded in CDCl$_3$ on a Varian (75 MHz) spectrometer.

Thermogravimetric Analysis (TGA). TGA studies were carried out in nonisothermal mode in a Mettler Toledo TGA instrument to get the decomposition pattern of the base stocks. About 5 mg of the sample was taken in an aluminum crucible and heated slowly up to 600 °C at a rate of 10 °C/min under nitrogen atmosphere. The TGA degradation onset temperature was obtained by extrapolating the horizontal baseline and intercept of this line with tangent to the downward portion of the weight curve was taken as onset temperature.

Physico-Chemical Analyses. The lubricant properties namely, acid value, hydroxyl value, density, specific gravity, kinematic viscosity, viscosity index, pour point, flash point, copper corrosion, TGA degradation onset temperature, oxidative stability, weld load, and wear of the lubricant base stocks were also determined using standard AOCS and ASTM methods. All the analyses were carried out in duplicates and the results are the average of the two values.

Procedure for Enrichment of Unsaturation in Sal Fatty Acids. Sal fatty acid methyl esters (SFAME) 100 g were taken in methanol (1000 mL, 1:10 w/v ratio of SFAME) and urea (200 g, 1:2 w/w ratio of SFAME) was added. The contents were stirred mechanically under reflux until urea was completely dissolved. The contents were cooled to room temperature and stored at 0−5 °C for 12 h. The material was then filtered to remove urea complex and concentrated. The filtrate was extracted with hexane, washed with diluted HCl to remove traces of urea followed by water until it was acid free.[22] The hexane extract was concentrated on rotary evaporator to obtain oleic acid rich SFAME (51 g, 51% yield). The fatty acid composition of enriched SFAME (72.6%, by GC) is shown in Table 1.

The enriched sal fame was hydrolyzed to get oleic acid rich sal fatty acids (ORSFA). ORSFA was further reacted with branched mono-alcohol (2-ethylhexanol) and polyols (NPG, TMP) in the presence of a p-TSA and xylene medium at 135−140 °C to obtain corresponding oleic acid rich branched mono and polyol esters (ORS2-EtHE, ORSNPGE, ORSTMPE).[17]

Table 1. Fatty Acid Composition (wt %) of Oleic Acid Rich Sal Fat

	fatty acid composition (wt %)				
sample name	16:0	18:0	18:1	18:2	20:0
oleic acid rich sal FAME	9.5	15.8	67.7	4.9	2.1

Hydroxylation of Oleic Acid Rich Sal 2-Ethylhexyl Esters. In a typical experiment, ORS2-EtHE (300 g, 0.764 mol), formic acid (85%) (43.35 mL, 1.14 mol), and concentrated sulfuric acid (3.37 mL, 2% weight of formic acid and hydrogen peroxide) were stirred under mechanical stirring at 5−10 °C. Hydrogen peroxide solution, 30% concentration (234.23 mL, 2.29 mol), which was pre-equilibrated at the same temperature was added slowly to the contents through addition funnel for a period of 2 h. This precaution was taken to prevent over heating of the system due to the exothermic nature of epoxidation. After addition of the H$_2$O$_2$ the temperature was slowly raised to 60 °C. After 3 h, the temperature of the reaction was raised to 90 °C and stirred for 24 h. The course of the reaction was monitored by withdrawing aliquots of the reaction mixture at various time intervals and analyzed for oxirane value. After complete conversion, the reaction mixture was cooled, extracted with ethyl acetate, and washed with water until it was acid free. The final product was analyzed for acid value, oxirane value, iodine value, and hydroxyl value. The structure of hydroxylated ORS2-EtHE was characterized by IR, ^{1}H NMR, and ^{13}C NMR.

A similar procedure was followed for the preparation of hydroxy ORSNPGE (HydORSNPGE) and hydroxy ORSTMPE (HydORSTMPE) taking ORSNPGE (0.477 mol), formic acid (46.1 mL, 1.19 mol), sulfuric acid (3.5 mL), and hydrogen peroxide solution, 30% concentration (2.38 mol); ORSTMPE (0.325 mol), formic acid (37.78 mL, 0.97 mol), sulfuric acid (3.26 mL), and hydrogen peroxide solution, 30% concentration (2.28 mol) respectively. The hydroxylated polyol esters were analyzed for acid, oxirane, iodine, and hydroxyl values. The structures of the compounds were characterized by IR, ^{1}H NMR, and ^{13}C NMR.

HydORS2-EtHE. IR (neat, cm^{-1}): 3448 (—OH), 2925 (C—H), 1736 (—C=O), 1168 (C—(C=O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.89 (t, C$\underline{H}_3$—CH$_2$—), 1.19−1.41 (m, (—C$\underline{H}_2$—)$_n$), 1.46−1.51 (m, —CH(OH)—C$\underline{H}_2$—), 1.54−1.72 (m, —CH$_2$—C$\underline{H}_2$—CH$_2$—C=O), 2.31 (t, —CO—C$\underline{H}_2$—CH$_2$—), 3.36−3.45 (m, —C$\underline{H}$—OH), 3.98 (d, —CH—C$\underline{H}_2$—O—CO—CH$_2$—); ^{13}C NMR (CDCl$_3$, δ ppm): 10.96, 14.02, 14.08, 22.64, 22.95, 23.76, 24.94, 25.03, 25.56, 25.64, 28.89−29.67, 30.38, 31.89, 34.36, 34.43, 38.70, 66.63, 74.49, 174.09.

HydORSNPGE. IR (neat, cm^{-1}): 3460 (—OH), 2928 (C—H), 1740 (—C=O), 1162 (C—(C=O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.88 (t, C$\underline{H}_3$-CH$_2$—), 0.96 (s, C$\underline{H}_3$—C—C$\underline{H}_3$), 1.14−1.39 (m, (—C$\underline{H}_2$—)$_n$), 1.40−1.53 (m, —CH(OH)—C$\underline{H}_2$—), 1.54−1.7 (m, —CH$_2$—C$\underline{H}_2$—CH$_2$—C=O), 2.31 (t, —CO-—C$\underline{H}_2$—CH$_2$—), 3.36−3.45 (m, —C$\underline{H}$—OH), 3.87 (s, —C—C$\underline{H}_2$—O—CO—CH$_2$—); ^{13}C NMR (CDCl$_3$, δ ppm): 14.08, 21.7, 22.63, 23.83, 24.93, 25.51, 25.63, 28.98−29.88, 31.83, 33.54, 34.21, 34.56, 68.95, 74.39, 74.45, 173.77.

HydORSTMPE. IR (neat, cm^{-1}): 3461 (—OH), 2924 (C—H), 1742 (—C=O), 1160 (C—(C=O)—O). ^{1}H NMR (CDCl$_3$, δ ppm): 0.88 (t, C$\underline{H}_3$—CH$_2$—), 1.21−1.38 (m, (—C$\underline{H}_2$—)$_n$), 1.44−1.53 (m, —CH(OH)—C$\underline{H}_2$—, —C—C$\underline{H}_2$—CH$_3$), 1.54−1.67 (m, —CH$_2$—C$\underline{H}_2$—CH$_2$—C=O), 2.30 (t, —CO—C$\underline{H}_2$—CH$_2$—), 3.36−3.43 (m, —C$\underline{H}$—OH), 4.01 (s, —C—C$\underline{H}_2$—O—CO—CH$_2$—); ^{13}C NMR (CDCl$_3$, δ ppm): 7.30, 14.08, 22.6, 22.9, 23.8, 24.87, 25.65, 28.9−29.6, 31.83, 33.54, 34.12, 40.5, 42.7, 63.62, 74.4, 173.5.

Propionylation of HydORS2-EtHE. HydORS2-EtHE (300 g, 0.716 mol), propionic anhydride (2.148 mol), DMAP (0.3 g, 0.1% DMAP based on weight of HydORS2-EtHE), and xylene (150 mL) were taken in a three-necked round-bottom flask and stirred at 135−140 °C for 8 h. The progress of the reaction was monitored by TLC using hexane/ethyl acetate (80:20 v/v) and IR. The crude product was distilled at 140 °C and 5 mm Hg to remove excess propionic anhydride and xylene. The residue was extracted into ethyl acetate, washed with water, passed over anhydrous sodium sulfate, and concentrated using a rotary evaporator and dried under reduced pressure to obtain acylated product. The product was further purified to remove traces of propionic acid by passage through a basic alumina column to obtain propionylated ORS2-EtHE (PrORS2-EtHE) with an acid value of <0.2. The product was analyzed for hydroxyl value. The

structure of the product was confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectral studies.

Similar procedure was followed for the butanoylation and hexanoylation of HydORS2-EtHE (HydORS2-EtHE) and alkanoylation of HydORSNPGE and HydORSTMPE, by taking HydORSNPGE (300 g, 0.439 mol) and alkanoic anhydride (2.198 mol); HydORSTMPE (300 g, 0.439 mol) and alkanoic anhydride (2.097 mol), respectively. The products were analyzed for acid and hydroxyl values. The structures of all the alkanoylated esters were confirmed by IR, ^{1}H NMR, and ^{13}C NMR spectral studies.

Propionylated Esters of Oleic Acid Rich Sal 2-Ethylhexyl Esters (PrORS2-EtHE). IR (neat, cm^{-1}): 2928 (C—H), 1739 (—C═O), 1182 (C—(C═O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.85–0.92 (m, C$\underline{H}_3$—CH$_2$—), 1.15 (t, C$\underline{H}_3$—CH$_2$—C═O), 1.20–1.39 (m, (—C$\underline{H}_2$—)$_n$), 1.47–1.53 (m, —C$\underline{H}_2$—CH—CO), 1.53–1.65 (—C$\underline{H}_2$—CH$_2$—C═O), 2.26–2.40 (m, —CH$_2$—C$\underline{H}_2$—C═O), 3.94–4.02 (m, —CH—C$\underline{H}_2$—O—CO—), 4.98–5.03 (m, O═C—O—C$\underline{H}$—); ^{13}C NMR (CDCl$_3$, δ ppm): 9.25, 10.94, 13.99, 22.63, 22.93, 23.71, 24.90, 25.05, 27.61, 28.86–29.65, 30.34, 30.66, 31.77, 31.86, 34.33, 34.39, 38.66, 66.56, 73.57, 173.97, 174.09.

Butanoylated Esters of Oleic Acid Rich Sal 2-Ethylhexyl Esters (BuORS2-EtHE). IR (neat, cm^{-1}): 2929 (C—H), 1736 (—C═O), 1178 (C—(C═O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.86–0.91 (m, C$\underline{H}_3$—CH$_2$—), 0.95 (t, C$\underline{H}_3$—(CH$_2$)$_2$—C═O), 1.19–1.39 (m, (—C$\underline{H}_2$—)$_n$), 1.47–1.53 (m, —C$\underline{H}_2$—CH—CO), 1.53–1.71 (—C$\underline{H}_2$—CH$_2$—C═O), 2.26–2.33 (m, —CH$_2$—C$\underline{H}_2$—C═O), 3.94–4.02 (m, —CH—C$\underline{H}_2$—O—CO), 4.98–5.03 (m, O═C—O—C$\underline{H}$—); ^{13}C NMR (CDCl$_3$, δ ppm): 10.96, 13.66, 14.00, 18.52, 22.61, 22.94, 23.76, 24.94, 25.03, 25.08, 28.89–29.66, 30.38, 30.73, 31.79, 31.89, 34.35, 34.42, 36.25, 38.71, 66.60, 73.48, 173.15, 174.00.

Hexanoylated Esters of Oleic Acid Rich Sal 2-Ethylhexyl Esters (HeORS2-EtHE). IR (neat, cm^{-1}): 2927 (C—H), 1735 (—C═O), 1171 (C—(C═O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.85–0.92 (m, C$\underline{H}_3$—CH$_2$—), 1.20–1.39 (m, (—C$\underline{H}_2$—)$_n$), 1.46–1.52 (m, —C$\underline{H}_2$—CH—CO), 1.53–1.67 (—C$\underline{H}_2$—CH$_2$—C═O), 2.26–2.34 (m, —CH$_2$—C$\underline{H}_2$—C═O), 3.94–4.01 (m, —CH—C$\underline{H}_2$—O—CO—), 4.98–5.03 (m, O═C—O—C$\underline{H}$—); ^{13}C NMR (CDCl$_3$, δ ppm): 10.94, 13.85, 13.99, 22.28, 22.63, 22.92, 23.71, 24.70, 24.90, 24.99, 25.07, 28.86–29.65, 30.34, 30.72, 31.27, 31.77, 31.86, 34.30, 38.66, 66.56, 73.43, 173.33, 173.97.

Propionylated Esters of Oleic Acid Rich Sal NPG Esters (PrORSNPGE). IR (neat, cm^{-1}): 2927 (C—H), 1740 (—C═O), 1177 (C—(C═O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.88 (t, C$\underline{H}_3$—CH$_2$—), 0.96 (s, C$\underline{H}_3$—C—C$\underline{H}_3$), 1.15 (t, C$\underline{H}_3$—CH$_2$—C═O), 1.2–1.35 (m, (—C$\underline{H}_2$—)$_n$), 1.44–1.53 (m, —C$\underline{H}_2$—CH—CO), 1.54–1.67 (m, —C$\underline{H}_2$—CH$_2$—C═O), 2.27–2.40 (m, —CH$_2$—C$\underline{H}_2$—C═O), 3.88 (s, —C—C$\underline{H}_2$—O—CO—CH$_2$—), 4.98–5.03 (m, O═C—O—C$\underline{H}$—); ^{13}C NMR (CDCl$_3$, δ ppm): 9.28, 14.08, 21.7, 22.63, 23.74, 24.85, 24.93, 25.05, 27.61, 29.03–29.88, 30.66, 31.77, 31.83, 32.9, 34.18, 34.56, 68.95, 73.61, 173.65, 173.97.

Butanoylated Esters of Oleic Acid Rich Sal NPG Esters (BuORSNPGE). IR (neat, cm^{-1}): 2926 (C—H), 1736 (—C═O), 1175 (C—(C═O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.88 (t, C$\underline{H}_3$—CH$_2$—), 0.91–1.01 (m, C$\underline{H}_3$—C—C$\underline{H}_3$, C$\underline{H}_3$—(CH$_2$)$_2$—C═O), 1.19–1.36 (m, (—C$\underline{H}_2$—)$_n$), 1.45–1.54 (m, —C$\underline{H}_2$—CH—CO), 1.55–1.73 (m, —C$\underline{H}_2$—CH$_2$—C═O), 2.3 (t, —CH$_2$—C$\underline{H}_2$—C═O), 3.87 (s, —C—C$\underline{H}_2$—O—CO—CH$_2$—), 4.97–5.05 (m, O═C—O—C$\underline{H}$—); ^{13}C NMR (CDCl$_3$, δ ppm): 7.3, 13.87, 14.07, 22.3, 22.6, 22.86, 24.73, 24.87, 25.1, 28.99–29.64, 30.72, 31.27, 31.77, 34.09, 34.30, 40.5, 63.56, 73.42, 173.32.

Hexanoylated Esters of Oleic Acid Rich Sal NPG Esters (HeORSNPGE). IR (neat, cm^{-1}): 2927 (C—H), 1740 (—C═O), 1170 (C—(C═O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.86–0.91 (m, C$\underline{H}_3$—CH$_2$—, —CO—(CH$_2$)$_4$—C$\underline{H}_3$), 0.96 (s, C$\underline{H}_3$—C—C$\underline{H}_3$), 1.20–1.36 (m, (—C$\underline{H}_2$—)$_n$), 1.46–1.53 (m, —C$\underline{H}_2$—CH—CO), 1.54–1.66 (m, —C$\underline{H}_2$—CH$_2$—C═O), 2.26–2.35 (m, —CH$_2$—C$\underline{H}_2$—C═O), 3.87 (s, —C—C$\underline{H}_2$—O—CO—CH$_2$—), 4.97–5.03 (m, O═C—O—C$\underline{H}$—); ^{13}C NMR (CDCl$_3$, δ ppm): 13.88, 14.08, 21.72, 22.3, 22.65, 23.75, 24.73, 24.96, 25.1, 26.04, 26.14, 29.06–29.9,

30.74, 31.3, 31.78, 31.89, 32.93, 34.2, 34.27, 34.33, 34.46, 34.61, 38.53, 42.8, 68.96, 73.46, 73.72, 173.32, 173.61, 173.71.

Propionylated Esters of Oleic Acid Rich Sal TMP Esters (PrORSTMPE). IR (neat, cm^{-1}): 2926 (C—H), 1741 (—C═O), 1180 (C—(C═O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.88 (t, C$\underline{H}_3$—CH$_2$—), 1.15 (t, C$\underline{H}_3$—CH$_2$—C═O), 1.2–1.36 (m, (—C$\underline{H}_2$—)$_n$), 1.42–1.54 (m, —C$\underline{H}_2$—CH—CO), 1.55–1.66 (—C$\underline{H}_2$—CH$_2$—C═O), 2.24–2.42 (m, —CH$_2$—C$\underline{H}_2$—C═O), 4.0 (s, —C—C$\underline{H}_2$—O—CO—CH$_2$—), 4.96–5.05 (m, O═C—O—C$\underline{H}$—); ^{13}C NMR (CDCl$_3$, δ ppm): 7.3, 9.25, 14.05, 22.63, 22.86, 23.74, 24.84. 25.05, 27.6, 28.88–29.64, 30.66, 31.83, 34.12, 40.49, 63.56, 73.61, 173.38, 173.97.

Butanoylated Esters of Oleic Acid Rich Sal TMP Esters (BuORSTMPE). IR (neat, cm^{-1}): 2926 (C—H), 1740 (—C═O), 1177 (C—(C═O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.88 (t, C$\underline{H}_3$—CH$_2$—), 0.95 (t, —CO—(CH$_2$)$_2$—C$\underline{H}_3$), 1.2–1.34 (m, (—C$\underline{H}_2$—)$_n$), 1.44–1.53 (m, —C$\underline{H}_2$—H—CO), 1.53–1.71 (—C$\underline{H}_2$—CH$_2$—C═O), 2.25–2.34 (m, —CH$_2$—C$\underline{H}_2$—C═O), 2.38 (t, —CH$_2$—C$\underline{H}_2$—C═O), 4.01 (s, —C—C$\underline{H}_2$—O—CO—CH$_2$—), 4.97–5.03 (m, O═C—O—C$\underline{H}$—); ^{13}C NMR (CDCl$_3$, δ ppm): 7.3, 13.64, 14.05, 18.5, 22.63, 22.89, 23.739, 24.87, 25.07, 29.20, 29.64, 30.72, 31.83, 34.12, 36.22, 40.50, 63.57, 73.46, 173.13, 173.42.

Hexanoylated Esters of Oleic Acid Rich Sal TMP Esters (HeORSTMPE). IR (neat, cm^{-1}): 2927 (C—H), 1740 (—C═O), 1168 (C—(C═O)—O); ^{1}H NMR (CDCl$_3$, δ ppm): 0.83–0.95 (m, C$\underline{H}_3$—CH$_2$—, —CO—(CH$_2$)$_4$—C$\underline{H}_3$), 1.21–1.37 (m, (—C$\underline{H}_2$—)$_n$), 1.43–1.53 (m, —C$\underline{H}_2$—CH—CO), 1.55–1.69 (m, —C$\underline{H}_2$—CH$_2$—C═O), 2.24–2.41 (m, —CH$_2$—C$\underline{H}_2$—C═O), 4.01 (s, —C—C$\underline{H}_2$—O—CO—CH$_2$—), 4.95–5.06 (m, O═C—O—C$\underline{H}$—); ^{13}C NMR (CDCl$_3$, δ ppm): 7.3, 13.87, 14.08, 22.28, 22.6, 22.86, 24.78, 25.1, 29.03–29.67, 30.72, 31.27, 31.82, 34.24, 40.49, 63.56, 73.43, 173.33.
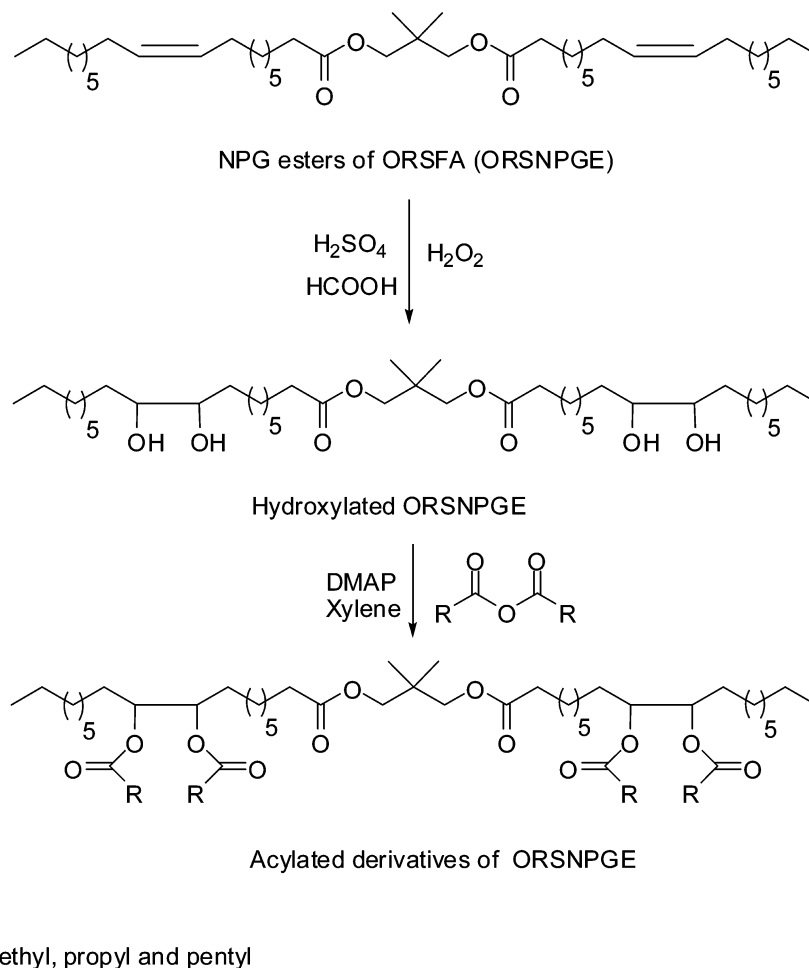
■ RESULTS AND DISCUSSION

Sal fat (containing 56.5% saturated fatty acids) based polyol esters synthesized in our earlier study[17] showed viscosities ranging between ISO viscosity grades 10 to 68 suitable for high temperature applications. However, the base stocks were found to exhibit high pour points.[17] With this background, an attempt was made to further chemically modify sal fat to generate high viscosity base stocks which are in more demand for high temperature industrial applications such as gear oil applications (involving BS 150 lubricant base stocks), forging lubricants and metal working fluids. As these base-stocks require very high viscosities and low pour points, sal fatty acids were chemically modified employing a four step process. Initially, oleic acid rich sal fatty acid esters were prepared employing urea complexation method and then hydrolyzed to get oleic acid rich sal fatty acids. These fatty acids were esterified with branched mono- and polyols such as 2-EtH, NPG, and TMP to prepare esters in 95.5 to 93% yields.

The branched mono- and polyol esters were hydroxylated using one pot synthesis of epoxidation followed by hydroxylation using Prilezhaev dihydroxylation method.[23] The hydroxylated products were analyzed for oxirane value, hydroxyl value, and iodine value and characterized using spectral techniques. The products with low oxirane < 0.1, iodine ≤ 1.5, and high hydroxyl values of 168−119, indicated complete hydroxylation of branched mono- and polyol esters. The presence of prominent —OH stretching band (~3450) as observed in IR spectra along with disappearance of ═C—H and epoxy stretching bands supported the complete hydroxylation. The presence of a multiplet at ~1.40−1.53 ppm related to —CH(OH)—C$\underline{H}_2$— and multiplet at ~3.36−3.45 ppm related to —C$\underline{H}$—OH in ^{1}H NMR and also characteristic

Scheme 1. Synthesis of Acylated Neopentyl Glycol Esters of Oleic Acid Rich Sal Fatty Acids

NPG esters of ORSFA (ORSNPGE)

H_2SO_4

HCOOH $\quad H_2O_2$

Hydroxylated ORSNPGE

DMAP

Xylene

Acylated derivatives of ORSNPGE

R= ethyl, propyl and pentyl

peaks at ∼74.5 ppm related to C_9 and C_{10} hydroxyl carbons in ^{13}C NMR further confirmed complete hydroxylation.

Further, the hydroxylated branched mono- and polyol esters were acylated by using propionic anhydride, butyric anhydride, and hexanoic anhydrides in the presence of DMAP and xylene medium at 135−140 °C, as branching helps in reducing the pour points and improving oxidation stability.[24] The progress of the reaction was monitored by TLC using hexane/ethyl acetate (80:20 v/v) and IR spectra. The lower hydroxyl value (≤3.1) indicated the completion of acylation. A total of nine products were prepared and thoroughly characterized using spectral data (IR, ^{1}H NMR, and ^{13}C NMR). The scheme involved in the preparation of the above esters is shown by taking NPG esters of ORSFA acylation as a representative in Scheme 1.

In IR spectra, the noticeable disappearance of −O−H stretching band in the region of (∼3450) cm^{-1} and appearance of prominent intensity of carbonyl functionality at ∼1740 cm^{-1} were also observed; this is due to increasing the ester functionality in the products confirming complete acylation.

In ^{1}H NMR spectra, the presence of triplet at 1.15 ppm related to methyl protons of the propanoyl side chain, multiplet at 4.98−5.03 ppm related to acylated C_9 and C_{10} protons and also increase in area of peak at 2.2−2.4 ppm, related to methylene protons α to the corbonyl group of the acyl side chain, indicated the complete propanoylation of branched mono- and polyol esters. In butanoylation the presence of new

peak, triplet at 0.95 ppm related to methyl protons of the butanoyl side chain and multiplet at 4.98−5.03 ppm related to acylated C_9 and C_{10} protons and also increase in area of peak at around 2.2−2.3 ppm, related to methylene protons α to the corbonyl group of the acyl side chain, confirmed the butanoylation of branched mono- and polyol esters. The presence of multiplets at around 0.83−0.95 ppm, 4.98−5.03 ppm related to acylated C_9 and C_{10} protons and also increasing the area of peak at 2.26−2.4 ppm due to methylene protons α to the carbonyl group of the acyl side chain confirmed the complete hexanoylation of branched mono- and polyol esters. The dissappearance of multiplet at 3.36−3.45 ppm related to −C<u>H</u>−OH further supported the acylation.

In ^{13}C NMR spectra, the peaks at around 9.25 ppm related to propanoyl side chain methyl carbon, 73.6 ppm of C_9 and C_{10} carbons of propanoylated esters and 173.97 ppm confirmed the propanoylation. The peaks at around 13.7 ppm related to butanoyl side chain methyl carbon, C_9 and C_{10} carbons of butanoylated esters 73.4 and 173.4 ppm indicates the butanoylation. The presence of peaks at 13.88 ppm related to hexanoyl side chain methyl carbon, 73.4 ppm of C_9 and C_{10} carbons of hexanoylated esters and 173.4 ppm confirmed the hexanoylation of branched mono- and polyol esters.

All the nine base-stocks were characterized for lubricant properties such as density, specific gravity, kinematic viscosity, viscosity index, pour point, flash point, thermogravimetric analysis (TGA), rotating pressurized vessel oxidation test

Table 2. Physico-Chemical and Lubricant Properties of Propionylated Oleic Acid Rich Sal 2-Ethylhexyl Esters (PrORS2-EtHE), Butanoylated Oleic Rich Sal 2-Ethylhexyl Esters (BuORS2-EtHE), and Hexanoylated HeORS2-EtHE Oleic Rich Sal 2-Ethylhexyl Esters

test		method	PrORS2-EtHE	BuORS2-EtHE	HeORS2-EtHE
total acid number		AOCS Te 2a-64	0.28	0.33	0.35
hydroxyl value		AOCS Cd 13-60	1.2	2.3	1.8
density at 15 °C (g/cm^3)		ASTM D 4052	0.91412	0.91369	0.90012
specific gravity at 15 °C		ASTM D 4052	0.91494	0.91451	0.90093
kinematic viscosity (cSt)	40 °C	ASTM D 445	23.44	22.65	20.94
	100 °C		4.91	4.89	4.71
viscosity index (VI)		ASTM D 2270	137	144	150
pour point (°C)		ASTM D 97	−3	−3	−6
flash point (°C)		ASTM D 93	238	244	252
TGA onset temp. (°C)			254	266	272
copper corrosion		ASTM D 130	1a	1a	1a
oxidative stability (min) (RPVOT)		ASTM D 2272	18	20	16
weld load (kg)		IP 239	130	130	140
wear (mm)		ASTM D 4172	0.63	0.65	0.73

Table 3. Physico-Chemical and Lubricant Properties of Propionylated Oleic Acid Rich Sal Neopentyl Glycol Esters (PrORSNPGE), Butanoylated Oleic Acid Rich Sal Neopentyl Glycol Esters (BuORSNPGE), and Hexanoylated Oleic Acid Rich Sal Neopentyl Glycol Esters (HeORSNPGE)

test		method	PrORSNPGE	BuORSNPGE	HeORSNPGE
total acid number		AOCS Te 2a-64	0.21	0.35	0.33
hydroxyl value		AOCS Cd 13-60	1.1	2.3	2.9
density at 15 °C (g/cm^3)		ASTM D 4052	0.95401	0.95101	0.94584
specific gravity at 15 °C		ASTM D 4052	0.95487	0.95687	0.94669
kinematic viscosity (cSt)	40 °C	ASTM D 445	318.84	301.73	268.81
	100 °C		32.45	31.94	30.09
viscosity index (VI)		ASTM D 2270	142	146	150
pour point (°C)		ASTM D 97	3	0	−3
flash point (°C)		ASTM D 93	300	314	329
TGA onset temp. (°C)			347	349	357
copper corrosion		ASTM D 130	1a	1a	1a
oxidative stability (min) (RPVOT)		ASTM D 2272	20	20	18
weld load (kg)		IP 239	165	170	180
wear (mm)		ASTM D 4172	0.78	0.73	0.69

Table 4. Physico-Chemical and Lubricant Properties of Propionylated Oleic Acid Rich Sal Trimethylolpropane esters (PrORSTMPE), Butanoylated Oleic Acid Rich Sal Trimethylolpropane (BuORSTMPE), and Hexanoylated Oleic Acid Rich Sal Trimethylolpropane HeORSTMPE

test		method	PrORSTMPE	BuORSTMPE	HeORSTMPE
total acid number		AOCS Te 2a-64	0.15	0.31	0.29
hydroxyl value		AOCS Cd 13−60	1.5	2.5	3.1
density at 15 °C (g/cm^3)		ASTM D 4052	0.97181	0.96826	0.96065
specific gravity at 15 °C		ASTM D 4052	0.97268	0.96913	0.96151
kinematic viscosity (cSt)	40 °C	ASTM D 445	471.93	463.33	427.35
	100 °C		41.73	42.49	43.82
viscosity index (VI)		ASTM D 2270	138	143	157
pour point (°C)		ASTM D 97	9	6	3
flash point (°C)		ASTM D 93	333	351	375
TGA onset temp. (°C)			376	382	385
copper corrosion		ASTM D 130	1a	1a	1a
oxidative stability (min) (RPVOT)		ASTM D 2272	20	16	15
weld load (kg)		IP 239	180	185	190
wear (mm)		ASTM D 4172	0.78	0.72	0.69

(RPVOT), weld load, and wear (Tables 2, 3 and 4) using standard test methods.

Kinematic Viscosity. Viscosity of lubricant is the resistance to flow and is directly related to the film formation. It was

observed that in case of acylated TMP esters of oleic acid rich sal fatty acids the viscosities ranged between 427 to 468 cSt at 40 °C which could be due to larger number of acyl groups.[18] A lubricant oil with high viscosity flows very slowly and is good to

form stable film between two moving surfaces.[25] The base-stocks in this viscosity range lie within the viscosity of BS 150 mineral oil and those required for high temperature applications such as forging lubricants and metal working fluids. With the shift in polyol from TMP to NPG, the viscosities of the corresponding acylated NPG esters (268.81 to 318.84 cSt) showed a decrease by about 150−200 units. This could be due to the smaller number of acyl groups and difference in molecular size compared to TMP esters. Similar observations were found in case of rubber based polyol esters.[16] These viscosities are related to ISO VG 320 and well suited for the industrial applications such as SAE gear oil No. 80W-140, bearing lubricants and positive displacement blowers, forging lubricants and metal working fluids. On further acylation of 2-ethylhexyl esters, the viscosities drastically fell by several folds ranging from 20.94 to 23.44 cSt, related to ISO VG 22 viscosity grade base stocks. These low viscosity grade base stocks are in more demand today in several industrial applications.[9]

Among the nine acylated TMP, NPG, and 2-EtH esters, the viscosities and densities were found to decrease as the alkyl chain increased from propyl to butyl, butyl to hexanoylated polyol esters. The degree of attenuation in viscosity of acylated lubricant basestocks was observed with increased substituent group chain length. This could be the effect of branching in the chain, which tends to introduce sphericity in the molecule, causing attenuation in the viscosity.[8] Similar observations were found in viscosities of acylated derivatives of milkweed oil,[8] branched polysaccharides,[26] branched synthetic polymers[27,28] and oligomerized estolides of oleic acid.[29]

Viscosity Index (VI). VI describes the change of viscosity with change in temperature. A high VI indicates there is little change over a wide temperature range. The acylated polyol esters exhibited high viscosity indices ranging from 138 to 157 in acylated TMP esters, 142−150 in acylated NPG esters and 137−150 in the acylated 2-ethylhexyl esters indicating their multirange applications.[15,30] Even though the VI increased with the molecular weight of the acyl group, it slightly decreased with branching. A similar trend was reported by Yao et al.[31] for ricinoleic acid−based acylated products. The VI values of the reported acylated derivatives are comparable to those of synthetic oils and superior to those of mineral oils.[8,9,32,33] Based on viscosity index, sal oleic acid rich acylated polyol esters belong to group II and group III, category of base fluids as per API classification. The viscosity indices are also well within the specifications required for BS 150 mineral oil base stocks, forging, and metal working fluid applications.

Pour Point. Pour point indicates the low temperature fluidity of lubricants. Vegetable oils have a tendency to form macrocrystalline structures at low temperature through uniform stacking of the "bend" triacylglycerol backbone. Such macro-crystals restrict the easy flow of the system due to loss of kinetic energy of individual molecules during self-stacking. The property can be improved by increasing the unsaturation and modification at the unsaturation and also at −COOH. Presence of a polyol and branched mono alcohol attached to the fatty acid does not allow the molecules to come closer due to steric interactions, preventing easy stacking of the individual molecules resulting in better fluidity of the total mixture. Among the nine base stocks, acylated TMP esters of oleic acid rich sal fatty acids exhibited high pour points (3 to 9 °C) compared to the corresponding acylated NPG (−3 to 3 °C) and acylated 2-EtH esters of oleic acid rich sal fatty acids (−3 to −6 °C). It was observed that the pour points of the base stocks

under study are much lower compared to corresponding sal fatty acid based branched mono and polyol esters.[17] This could be due to effective disruption of molecular packing in the former with high degree of branching due to acylated groups compared to the later. The pour points of TMP esters are higher compared to that of BS 150 mineral oil base stocks, which can be further reduced by using appropriate pour point depressants and diluents.[14] The pour point decreased with branching as seen in the corresponding acylated 2-ethylhexyl esters of oleic acid rich sal fatty acids (−6 to −3 °C). Similar observation was reported for acylated jatropha alkyl esters[9] and acylated soy bean oil derivatives.[13] The base stocks with low pour points are useful for machine tool and hydraulic systems applications.[34]

Flash Point. Flash point is useful in determining a biolubricant volatility, fire resistance, and transportation and storage temperature requirements. The flash point should be high to allow the safe operation and minimum volatilization at the maximum operating temperature. The flash point values of all the 9 acylated branched mono- and polyol esters as observed in the range 238−375 °C are useful for multirange applications. Among all the acylated derivatives acylated TMP esters exhibited high flash points (333−375 °C) followed by acylated NPG esters (300−329 °C) and acylated 2-EtH esters (238−252 °C). The high flash point of the acylated TMP esters is due to the high molecular weight and side chain branching. The flash point specification for hydraulic oils as per IS: 3098 is 150 °C. All the acylated derivatives with flash point of ≥165 °C lie well within the range of hydraulic oils.[35] The lubricant base stocks with high flash point ≥300 °C are suitable for the applications that are in more demand, such as gear oil lubricants and aviation jet engine lubricants.[36]

TGA. The thermal stability of a fluid is its ability to resist decomposition on exposure to high temperatures. It establishes the ultimate high-temperature limit for a tribological system fluid that will ensure continual unimpaired service. The most significant change in fluid properties caused by thermal decomposition of organic molecules is an increase in vapor pressure caused by the shearing of molecules into smaller, more volatile fragments. Ester functionality is more prone to thermolysis and removal of β-hydrogen in the triglyceride by reacting with a polyol and branched alcohols improves the thermal stability.[37]

Among the nine base stocks prepared, the acylated TMP esters exhibited very high thermal stabilities as observed by their TGA onset temperatures, 376−385 followed by NPG esters, 347−357. The stability of the branched mono esters was found to decrease drastically due to disturbance in crystalline packing.[37] However, the values were found higher compared to the undecenoic acid−based polyol esters and other vegetable oil based polyol esters.[15,39] The high thermal stabilities of the acylated TMP and NPG esters are suitable as substitutes to BS 150 mineral oil base stocks and for high temperature applications such as forging and metal working fluid applications.

Rotating Pressurized Vessel Oxidation Test (RPVOT). Oxidation stability is another important property which determines the degree of resistance of the lubricant to oxidation. In general, the ester group is oxidatively stable and increases the stability of the adjacent carbon atoms.[38,39] Removal of the β-hydrogen in the triglyceride by reacting with a polyol and branched alcohols improves the oxidation stability. In general, TMP esters are more stable compared to

NPG and branched esters.[37] However, in the present study, it was observed an increase in unsaturation by urea adduct complexation, followed by reaction with polyols and branched alcohols, which on further acylation increased the oxidation stabilities of all the base stocks. The oxidation stabilities of all the base stocks were higher or comparable to other vegetable oil-based synthetic esters.[9,15,16,33] All the nine base stocks with good oxidation stabilities can be well exploited as mineral oil base stock substitutes in a variety of lubricant formulations.

Extreme Pressure Test (Weld Load). Weld load is another important property of lubricant base stocks, which determines the load-carrying capacity of the lubricants. The weld load capacity of the acylated ORSTMP esters is found to be more (180−190 kg), followed by acylated ORSNPG esters (155−170 kg) and acylated ORS2-EtHE (130−140 kg). All the 9 acylated base stocks were is found to possess high load carrying capacity compared to other reported polyols.[16,17]

Wear. This property indicates the antiwear properties of the lubricant between two sliding surfaces preventing the surfaces from the dimensional loss of one solid, with or without any actual decoupling and loss of material. In case of polyol esters, the effect of nature of the polyol involved has hardly any effect on the property.[40] Similar observation was seen in the TMP and NPG acylated products understudy. However, all the acylated polyol and branched mono-esters exhibited good antiwear properties suitable for high pressure and high temperature applications such as the forging and metal working fluid applications.

In conclusion, Sal fat was chemically modified to develop acylated branched mono and polyol esters of oleic acid rich sal fatty acids with a wide range of properties matching with BS 150 mineral oil base stocks in case of TMP acylated products, forging and metal working fluid applications in case of NPG acylated products. The modification resulted in low viscous 2-EtH acylated products suitable for metal working and hydraulic fluid applications. The thermal and oxidative stabilities of the base stocks have been improved with the above modification and found comparable to synthetic esters. Overall, all the base stocks with stringent properties are promising candidates to replace most of the mineral oil base stocks in a variety of industrial applications either as such or after formulations.

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Notes
The authors declare no competing financial interest.

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