

Introduction A lubricant provides a protective film which allows for two touching surfaces to be separated, thus lessening the friction between them. Lubricating oil is a liquid lubricant that reduces friction, protects against corrosion, reduce electric currents and cool machinery temperature. It is most often used in the automobile industry and is applied to bearings, dies, chains, cables, spindles, pumps, rails and gears to make them run smoother and more reliably. Lubricating oil is a substance introduced between two moving surfaces to reduce the friction and wear between them. Lubricating oils consist of a liquid paraffinic or vegetable oil and surface active agents, antioxidants and anticorrosive additives. Metal soaps in pure form or dispersed in paraffinic oils are used as lubricants. Felder et al [1] used sodium and calcium soap coatings on steel wires for drawing the wires. Calcium stearate had good lubricating efficiency at low wire drawing rates [1]. The possibility for the production of a motor oil with improved operating characteristics and a higher stability by applying of composite additives has been studied by Palichev et al [2]. For this purpose two multifunctional additives, synthesized by them have been used. They used additives containing calcium stearate and calcium salts of nitrated polypropylene and oxidized paraffin, urea, ethylene diammine, stearic acid. The additives improved the anticorrosion, viscosity-temperature, antiwear and antisludge properties of the lubricant [2]. The optimum concentration of the additive, which enables the production of a high-quality motor lubricant, has been found to be 5% [2]. Cutting oils were obtained by adding CaSt₂ to dry paraffin oil up to 5 % together with other additives [3]. Thus the gelation was prevented and an easily flowing cutting oil was obtained. Savrik et al [4] prepared lubricants using base oil, surface active agent Span 60 and zinc borate particles. They used 1% Span 60 and 1 % zinc borate. Surface active agent Span 60 was found to be very effective in reducing the friction coefficient and wear scar diameter in four ball tests. As surface active agents metal soaps are also used. Metal soaps are transition metal salts of the fatty acids and the alkaline earth elements. Although, the alkali salts of the fatty acids such as sodium and potassium are water soluble, metal soap is water insoluble but more soluble in non-polar organic solvents. Calcium stearate Ca (C₁₇H₃₅COO)₂, in short form CaSt₂ is the one of the important ionic surfactants of metal soaps. Calcium Stearate, is a non-toxic, white powdery substance. It is a calcium salt derived from stearic acid and is widely used in cosmetics, plastics, pharmaceuticals and lubricants [5]. Metal soaps can be obtained by neutralization of long chain organic acids with bases or by precipitation process. Moreria et al [6] investigated formation of CaSt₂ from stearic acid and calcium hydroxide in different solvents and a complete conversion to CaSt₂ was obtained in ethanol medium [6]. The precipitation process generally produces metal soap in powder form by the reaction of aqueous solutions of a water soluble metal salt and a fatty acid alkali metal salt at a temperature below the boiling point of water at atmospheric pressure. Filtering, washing, drying are the important steps in this method. Calcium stearate is produced in pure form by using this process [5]. Production of a lubricant by using a neutral base

oil and calcium stearate is the aim of this study. The lubricating effects were tested by a four ball tester for this purpose.

MATERIALS AND THE METHOD

Materials

Calcium chloride, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (98%, Aldrich), and sodium stearate, (NaSt) $\text{C}_{17}\text{H}_{35}\text{COONa}$ (commercial product, Dalan Kimya A.Ş., Turkey), were used in the synthesis of CaSt_2 . The acid value of stearic acid, used in the NaSt synthesis, was 208.2 mg of KOH/g of stearic acid and it consists of a C_{16} - C_{18} alkyl chain and with 47.7% and 52.3% by weight, respectively[5]. Spindle Oil from TUPRAS Izmir was used as base oil in the preparation of the lubricants.

Preparation of calcium stearate powder

Calcium stearate powder was prepared from sodium stearate and calcium chloride by precipitation from aqueous solutions according to reaction 1.

$$2\text{C}_{17}\text{H}_{35}\text{COO}^- + \text{Na}^+(\text{aq}) + \text{Ca}^{2+}(\text{aq}) \rightarrow (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca}(\text{s}) + 2\text{Na}^+(\text{aq}) \quad (1)$$

5.000 g (0.016 mol) of sodium stearate, (NaSt) was dissolved in 200 cm³ of deionized water in a stainless steel reactor at 75°C. 1.7984 g (0.012 mol) of calcium chloride (50% excess) was dissolved in 100 cm³ of deionized water at 30°C and added to sodium soap solution at 75°C. The mixture was stirred at a rate of 500 rpm at 75°C by a mechanical stirrer for 30 min. Since the by-product, NaCl , is soluble in water the reaction media was filtered by using Büchner funnel and flask under 600-mmHg vacuum level. To remove the NaCl completely, wet CaSt_2 was washed by 200 cm³ deionized water once and then, wet CaSt_2 cake was dried in a vacuum oven under 2×10^{-4} Pa pressure. The KBr disc spectrum of the powder was taken with Shimadzu FTIR spectrophotometer. The SEM micrograph of the dried powder was taken with Scanning electron microscopy (Philips XL30 SFE). Lubricant preparation 1g of CaSt_2 and 100 cm³ spindle oil were mixed together at 160 °C at 880 revolution min⁻¹ rate for 30 minutes and then cooled to 25°C by continuously stirring. At the mixing experiments, a heater and magnetic stirrer (Ika Rh Digital KT/C) and a thermocouple (IKA Werke) were used. The experiment was repeated with 2 g of CaSt_2 in 100 cm³ oil.

Lubricant characterization

The dispersion of CaSt_2 in base oil was observed by optical microscopy. The phase change behavior of CaSt_2 and lubricants with increasing temperature was observed with an optical microscope equipped with a hot plate. The stabilities of the lubricants having different calcium stearate contents were determined by measuring the rate of settling of calcium stearate particles in base oils. The chemical structures of calcium stearate and the prepared lubricants were investigated by FTIR spectroscopy. The tribologic behavior of the lubricants was tested with a four ball tester. Four ball tests were done using the four ball tester from DUCOM Corporation (Fig. 1) to determine the friction coefficient and wear scar diameter of the lubricants. The test was performed according to ASTM D 4172-94 at 392 N and 1200 rpm and the test duration was 1 h. The wear scar diameter was reported as the average of the wear scar diameter of the three fixed balls.

Fig. 1 - Four ball tester

The visible spectrum of base oil separated by centrifugation from base oil was taken by using Perkin Elmer UV-Vis spectrophotometer by using base oil without any additive as the reference.

Optical microscope

Melting behavior of CaSt_2 in powder form and in dispersed form in the

base oil on a microscope slide was observed by using the transmission optical microscope (Olympus, CH40) with a heated hot stage controlled by a temperature controller (Instec, STC 200C). The samples were heated at 50C/min rate from room temperature up to 190oC. The photographs were taken with Camedia Master Olympus Digital camera. Results and discussion

CaSt2 powders FTIR spectrum of calcium stearate powder obtained by precipitation process is shown in Fig. 2. The characteristic peaks of calcium stearate at 1542 cm⁻¹ and 1575 cm⁻¹ were observed. These bands are due to antisymmetric stretching bands for unidendate and bidendate association of carboxylate groups with calcium ions [5, 7]. Antisymmetric and symmetric methylene stretching, and methylene scissoring bands (naCH₂, nsCH₂, and dsCH₂) were observed at about 2914 cm⁻¹, 2850 cm⁻¹ and 1472 cm⁻¹ respectively. These bands are due to the alkyl chain in the calcium stearate structure [5, 7].

Fig. 2 - FTIR spectrum of bulk CaSt2

Fig. 3 - SEM micrograph of CaSt2 powder

The SEM micrograph of the CaSt2 powder shown in Fig. 3 indicated that the particles were flat in shape and had a broad size distribution ranging from 200 nm to 1µm. The average diameter of particles was 600 nm.

FTIR spectra of lubricants

The prepared lubricants were also examined by FTIR spectroscopy. Their FTIR spectra are shown in Figure 4. The peaks at 2918 and 2848 cm⁻¹, 1454cm⁻¹ are due to stretching and bending vibrations of the methylene groups in base oil structure. The stretching and bending vibrations of the methyl group are observed at 2951 and 1385 cm⁻¹. At 3414 cm⁻¹ a broad peak related to hydrogen bonded OH groups are present. The antisymmetric stretching bands for unidendate and bidendate association of carboxylate groups with calcium ions at 1542 cm⁻¹ and 1575 cm⁻¹ are observed as small peaks in the spectra.

Fig. 4 - FTIR spectra of lubricants with a - 1% CaSt2 b - 2% CaSt2

Stability of lubricants and the particle size of the CaSt2 dispersed in base oil

The stability of the lubricant suspensions was determined by recording the height of the line separating the oil phase and the suspension phase. Due to gravity settling of the particles the level of this line decreases continuously with time as seen in Fig. 5. The settling velocity is directly proportional to the radius of the particle as shown in Equation 2 [8].

$$\frac{dx}{dt} = \frac{2r^2(\rho - \rho_o)g}{9\eta} \quad (2)$$

Where; $\frac{dx}{dt}$ is rate of settling (cm/s); ρ_o is the density of medium (g/cm³), ρ is the density of particle (g/cm³), η is viscosity of medium (g/(cm.s)), r is radius of particle (cm), g is 981 cm/s². The radius of particles was calculated from the slopes of the lines in Figure 6. The results were evaluated for the settling of particles within 15 days. The oil density and viscosity used for the calculations are 0.86 g/cm³ and 0.35 ((g/cm.s)). The density of CaSt2 is 1.12 g/cm³. The initial rate of settling was calculated as 0.188x10⁻⁷ cm/s and 0.635x10⁻¹²cm/s for oils with 1 % and 2 % CaSt2 respectively from Fig. 6. Apparent radius of the CaSt2 particles dispersed in base oil was 1.88 µm and 0.11 µm respectively for 1 % and 2 % CaSt2 added samples respectively. The CaSt2 particles were molten and recrystallized in base oil during preparation of the lubricant. Thus they have a different particle size than the original powder. At higher CaSt2 content the formed CaSt2 crystals were in smaller size due to

fast nucleation and slow growth of crystals. The gelation of CaSt2 and base oil system is also another possibility affecting apparent size of particles. Fig. 5 - Settling of CaSt2 particles in base oil on the a. 1st day, b. 15th day after mixing Fig. 6 - The height of the boundary between clear base oil and CaSt2 particles settling in base oil Melting behavior of pure CaSt2 and CaSt2 in mineral oil CaSt2 powder melts at 120°C as determined by DSC and at 148°C by optical microscopy in a previous study [3]. In Fig. 7 micrographs of the CaSt2 powders before and after melting are seen. Before melting CaSt2 appears as a white powder and on melting it is transformed into a transparent liquid. It was found that CaSt2 had a melting temperature of 142.8°C by optical microscopy in the present study. CaSt2 particles in base oil also showed a similar phase transition behavior as bulk CaSt2. They were dispersed as particles in base oil at room temperature. The particles kept their shape up to 113°C and they melted and mixed with mineral oil homogeneously at 128°C as seen in Fig. 8. Fig. 7 - Optical micrographs of CaSt2 powder at (a) 142.8 °C and (b) 156.6 °C Fig. 8 - Optical micrographs of CaSt2(1 %) dispersed in mineral oil at (a) 113°C (b) 128°C Friction and wear behavior of the lubricants The lubricants with CaSt2 efficiently decreased the friction and wear between metal surfaces. The four ball test results are shown in Table 1, wear scar's optical micrographs are seen in Fig. 9 and the change of friction coefficient during 1 hour test duration is seen in Fig. 10. Fig. 9 - Optical micrographs of the wear scar diameters of the one of the fixed balls of four ball tests for (a) 1% CaSt2 (b) 2% CaSt2 containing lubricant The friction coefficient and wear scar diameter of base oil 0.099 and 1402 nm were reduced to 0.0730 and 627.61 nm respectively for the lubricant having 1 % CaSt2. For 2 % CaSt2 containing lubricant the friction coefficient and the wear scar diameter were 0.815 and 0.540 respectively. As the CaSt2 content increased better lubricating efficiency were observed. The four ball tests are done at 75°C. At this temperature CaSt2 is in solid form in base oil. However by the kinetic energy of the rotating ball over fixed balls the temperature of the oil should have been increased to melt the CaSt2 crystals in base oil and to cover the surface of the balls by a smooth lubricating layer. The solid CaSt2 particles similar to other nano particles can also fill the crevices and holes on the steel surface reducing the friction and wear. Fig. 10 - Change of the friction coefficient with time for a. 1% CaSt2 b. 2% CaSt2 containing lubricants Table 1 - Friction coefficient and wear scar diameter of base oil and lubricants with 1% and 2 % CaSt2

Property	Base oil [2]	Base oil with 1 % CaSt2	Base oil with 2 % CaSt2
Friction coefficient	0.099	0.0730	0.8150
Wear Scar Diameter, nm	1402	627.61	540.88

The effect of four ball tests on the color of the base oil The lubricants change their color due to oxidation, hydrolysis and thermal degradation during its use. Contaminants from the eroding surfaces also change the color of the oil. The solid colorants in the lubricating oil can be filtered and the filter surface color can be measured [9]. In the present study the color change of the lubricating oils during four ball tests were investigated by visible spectroscopy. The visible spectra of the lubricants shown in Figure 11 were taken using the base oil Fig.

11 - Visible spectra of the base oil 1. before four ball tests, 2. after four ball tests for 1% CaSt₂ and 3. before four ball tests and 4. after four ball tests for 2% CaSt₂ as the reference. The base oil with 1% CaSt₂ were lighter in color than the reference base oil as indicated by the negative absorbance values in Figure 11. CaSt₂ adsorbed the coloring material initially existing in the base oil. After four ball test the base oil become dark yellow due to oxidation and crosslinking reactions in base oil. The base oil having 2% CaSt₂ had higher absorbance values at all wavelengths and the absorbance was maximum at 420 nm. It also had a darker color after the test. Thus CaSt₂ improves the lubricating efficiency of the base oil, but it does not increase the oxidative and thermal stability. Adding antioxidants to the system would help the thermal and oxidative stability which could be the subject of further investigations.

Conclusion Calcium stearate powder prepared from sodium stearate and calcium chloride by precipitation from aqueous solutions and Light Neutral Base oil were mixed together to obtain lubricating oils. It was found that CaSt₂ powder had a melting temperature of 142.8°C and in the base oil it melted above 128°C. From rate of settling of the particles in base oil the size of dispersed particles were found to be 1.88 µm and 0.11 µm respectively for lubricants having 1% and 2 % CaSt₂. The friction coefficient (0.099) and wear scar diameter of base oil (1402 nm) were reduced to 0.0730 and 627.61 nm respectively for the lubricant having 1 % CaSt₂. Lower wear scar diameter (540 nm) was obtained for lubricant with 2% CaSt₂. Calcium stearate when added to base oil reduces the friction and wear of metal surfaces sliding on each other. It covers the cracks and grooves of the metal surface with a smooth film. Thus it is an efficient lubricant additive. However CaSt₂ did not increased oxidative and thermal stability of the base oil. Thus further studies for the antioxidant selection should be made.