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# Synthesis, Characterization and Evaluation of Overbased Magnesium Fatty Acids Detergent for Medium Lubricating Oil

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## Abstract

A series of overbased magnesium fatty acids such as caprylate, caprate, laurate, myristate, palmitate, stearate and oleate) were synthesized by the reaction of the fatty acids with active – 60 magnesium oxide and carbon dioxide ($CO_2$) gas at 60 $^oC$ in the presence of ammonia solution as catalyst, toluene / ethanol solvent mixture (9:1vol/vol) was added.

The prepared detergent additives were characterized by FTIR, $^1$HNMR and evaluated by blending each additive in various concentrations with medium lubricant oil fraction (60 stock) supplied by Iraqi Midland Refineries Company. The total base number (TBN, mg of KOH/g) was determined, and the results of TBN were treated by using two-way analysis of variance (ANOVA) test. It was found that the number of carbons in the fatty acid ($C_8$-$C_{18}$) used for overbased detergent preparation had slight effect on the TBN of the oil, while detergent concentrations (1-5% wt/wt) had a significant effect on the TBN of the blended oil.

The oxidation stability of the oil blends with 2% of overbased magnesium palmitate and overbased magnesium stearate detergents was evaluated, and the results showed that these blends gave higher oxidation stability compared with the blends with standard antioxidant supplied by Midland Refineries Company.

**Keywords:** Overbased detergent, Fatty acid, Lubricant oil, TBN.

## Introduction

Lubricants are an important family among products of the refining industry. A lubricant performs a number of critical functions, these include lubrication, cooling, cleaning and suspending, and protecting metal surfaces against corrosive damage [1].

Lubricant comprises a base fluid and an additive package. Additives can be defined as substances which improve the performance of lubricants, either by imparting new properties to a base oil (cleaning and suspending ability, antiwear performance, and corrosion control), or by enhancing properties already present (viscosity, viscosity index, pour point, and oxidation resistance). The use of additives began in the 1930's and enormous growth has been seen since in both their production rates and the scope of their applications [2].

Modern equipment must be lubricated in order to prolong its lifetime. One of the most critical properties of the automotive lubricants, especially engine oils, is their ability to suspend undesirable products from thermal and oxidative degradation of the lubricant. It has been found necessary to incorporate detergent additives in oils for such service in order to avoid the engine failure [3].

Modern diesel engine lubricants derive most of their alkalinity from overbased detergents such as sulfonates/phenates/salicylates of calcium, or magnesium [4].

Over-based detergents are salts of alkaline earth metals such as calcium and magnesium that contain more alkaline metal than that required for their manufacture. Thus, they have both a good detergent property and an excellent ability to neutralize strong acids. Detergent additives prevent or disperse an accumulation of sludge in the crankcase at high or low temperatures [5].

The term “overbased” refers to the fact that the quantity of base incorporated in the particle cores is greater than that needed to neutralize the acid surfactant. The neutralizing strength of an overbased detergent is measured by its total base number (TBN). TBN is defined as the quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide that is required to neutralize all basic constituents present in 1 g of overbased detergent [6].

Recently, the use of environmentally friendly lubricant base oils [7-9] increased, as did the necessity of studying their environmentally friendly additives. New environmentally friendly overbased detergents were synthesized [10-14].

This work deals with preparation of lubrication oil overbased detergents from different fatty acid and testing their efficiency.

## Experimental Work Materials

### 1. Chemicals

Table (1) shows the properties and manufacturers of the used chemicals.

Table 1, Chemicals and their properties and manufactures

| No. | Chemicals | Molecular weight | Mp., °C | Purity,% | Supplier |
|---|---|---|---|---|---|
| 1. | Caprylic acid | 144.22 | 15-17 | 98 | BDH chemicals Ltd. |
| 2. | Capric acid | 172.27 | 29-31 | 99 | BDH chemicals Ltd. |
| 3. | Lauric acid | 200.32 | 43-44 | 98 | H and W Ltd. |
| 4. | Myristic acid | 228.38 | 53-54 | 97 | H and W Ltd. |
| 5. | Palmitic acid | 256.43 | 61-63 | 99 | BDH chemicals Ltd. |
| 6. | Stearic acid | 284.48 | 67-69 | 95 | MERCK |
| 7. | Oleic acid | 282.47 | 13-14 | 97 | H and W Ltd. |
| 8. | Magnesium oxide | 40.31 | _ | 99 | BDH chemicals Ltd. |
| 9. | Toluene | 92.14 | (Bp., °C) 110-111 | 99 | Fluka AG |
| 10. | Ethanol | 46.07 | (Bp., °C) 79-81 | 95 | BDH chemicals Ltd. |
| 11. | Ammonium hydroxide | 17.03+aq | _ | 20-25 in water | Fluka AG |
| 12. | $CO_2$ gas | 44 | _ | High purity | National gas manufacturing company |

### 2. Base Oil

Base lubrication oil 40 stock and 60 stock supplied by Midland Refineries Company, 40 stock was used as a diluents in preparation of overbased magnesium fatty acid detergents, while 60 stock was used for preparation of oil blends with the prepared detergents.

The properties of these oils were listed in table (2).

Table 2, Properties of base lubricating oil 40 stock and 60 stock

| No. | Specification | 40 stock | 60 stock | Standard test method |
|---|---|---|---|---|
| 1. | Kinematic viscosity at 40 °C, cSt (mm²/s) | 13.16 | 62.71 | ASTM-D 445 |
| 2. | Kinematic viscosity at 100 °C, cSt (mm²/s) | 3.12 | 8.13 | ASTM-D 445 |
| 3. | Viscosity index | 94 | 95 | ASTM D- 2270 |
| 4. | Specific gravity at 60/60 oF | 0.856 | 0.88 | ASTM D-4052 |
| 5. | Pour point ,°C | -12 | -9 | ASTM D-97 |
| 6. | Flash Point (C.O.C),°C | 198 | 240 | ASTM D-92 |
| 7. | Color | 1.0 (Pale yellow) | 2.5 (yellowish) | ASTM D-1500 |

**Instrumentation**

Fourier transform infrared (FTIR) spectra were recorded on Shimadzu FTIR-8400S Spectrophotometer, Department of Chemistry, College of Science , Baghdad university as KBr disc to detect the functional groups in the region 4000-400 $cm^{-1}$ .

$^{1}H$-NMR spectra were recorded on a Burker model ultra-shield DPx-400MHz, Cardiff University, U.K., using $CDCl_3$ as solvent and tetramethylsilane $Si(CH_3)_4$ as internal reference . All data are given as chemical shifts δ (ppm) downfield from tetramethylsilane.

**Synthesis of Overbased Magnesium Fatty Acid Detergents**

The synthetic procedure of overbased magnesium fatty acids detergent is similar to that described by Yonglei Wang, and Wumanjiang Eli [13], but the xylene and methanol solvent change to toluene and ethanol, respectively.

Different magnesium fatty acid detergents were prepared, using a three neck 500 mL round bottom flask fitted with a gas dispersion tube, condenser, and mechanical stirrer as a reactor shown in Fig. (1).

0.05 mol of the desired fatty acid and 20 g of diluents oil were added to the flask and dissolved in 100 mL of mixture of toluene and ethanol (9:1), then 20.15 g of active-60 magnesium oxide (0.5 mol) was added to the diluted mixture. The resulted mixture was stirred for 1 h and then heated up to 65 $^{o}C$. 10mL of ammonia solution was added to the mixture and 60 mL/min of gaseous CO2 for 3.5 h was then introduced into the reactor through gas dispersion tube via the gas flow meter. The desired overbased magnesium fatty acid detergent was obtained by filtration through fluted filter paper for residue removal, and filtrate evaporation to remove the solvents.

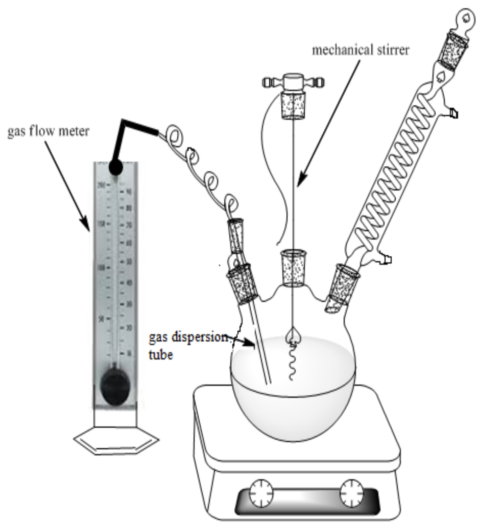


Fig. 1, Schematic diagram of the reactor

**Formulation of Oil Blends**

Blends of different prepared overbased magnesium fatty acid detergents ($C_8$ - $C_{18:0}$ and $C_{18:1}$) were prepared by dissolving each detergent in a mixture of toluene and xylene

(1:1) at 60 °C for 1 hour. The prepared 60 stock oil blends contain different dosages (1%, 2%, 3.5% and 5%) of each of synthesized detergent.

### Test Methods

Total base number (TBN, mg of KOH/g) was determined according to American Society of Testing and Materials ASTM D-4739, This standard method is based on the potentiometric titration of the basic constituents in an oil with standardized hydrochloric acid to a fixed endpoint.

Oxidation stability was determined according to IP 280, which measures the tendency for a lubricant to generate sludge and/or solid oxidation byproducts.

Total oxidation products (TOP) include products formed from decomposition of hydro peroxides regardless of their chemical form. Thus, TOP is a good indicator of total conversion and overall extent of oxidation.

### Results and Discussion

The chemical structure and total base number for the prepared magnesium overbased detergents are listed in table (3).

Table 3, Nomenclature, structure, color and TBN of synthesized overbased detergents

| No. | Abbreviation | Common name | Systematic name | Chemical structure | Color | TBNmg KOH/g |
|---|---|---|---|---|---|---|
| 1. | C8:0 | Magnesium caprylate | Magnesium octoate | (CH3(CH2)6COO)2Mg. nMgCO3 | Pale yellow | 76 |
| 2. | C10:0 | Magnesium caprate | Magnesium decanoate | (CH3(CH2)8COO)2Mg. nMgCO3 | white | 103 |
| 3. | C12:0 | Magnesium laurate | Magnesium dodecanoate | (CH3(CH2)10COO)2Mg. nMgCO3 | white | 123 |
| 4. | C14:0 | Magnesium myristate | Magnesium tetradecanoate | (CH3(CH2)12COO)2Mg. nMgCO3 | Pale yellow | 258 |
| 5. | C16:0 | Magnesium palmitate | Magnesium hexadecanoate | (CH3(CH2)14COO)2Mg. nMgCO3 | Pale yellow | 346 |
| 6. | C18:0 | Magnesium stearate | Magnesium octadecanoate | (CH3(CH2)16COO)2Mg. nMgCO3 | white | 420 |
| 7. | C18:1 | Magnesium oleate | 9-Octadecenoic acid magnesium salt | (CH3(CH2)7CH=CH-(CH2)7COO)2Mg. nMgCO3 | Pale yellow | 398 |

The structureof the synthesized compounds were confirmed by FTIR, and $^1$H NMR spectroscopy as shown in table (4).

FTIR spectra of the prepared compounds showed asymmetric 2918-2927 cm$^{-1}$ for ($CH_2$) group, while symmetric stretching band for ($CH_2$) group appeared between 2850- 2854 cm$^{-1}$.

A band in the region 719-723 cm$^{-1}$ refers to the methylene rocking vibration for straight chain [15].

The carboxylate ion gave a strong asymmetrical stretching band between 1578-1560 cm$^{-1}$ [16].

$^1$H NMR spectra of two of the prepared compounds ($C_{16:0}$ and $C_{18:0}$) showed the signals at δ 0.8 for $CH_3$ and δ 1.2-1.3 for $(CH_2)_n$ because the long chain R group have resonances that occur over a very narrow range. The two protons near to carboxylate ($CH_2COO$) appeared at δ 1.9-2.0 [17].

Table 4, FTIR and $^1$H- NMR spectral data of synthesized overbased detergents

| No. | Abbreviation | Major FTIR absorptions cm-1 | | | | 1H-NMR (δ ppm) | | |
|---|---|---|---|---|---|---|---|---|
| | | νCH3 | νCH2 | ν(C=O) | δCH2 rocking | CH3 | (CH2)n | CH2–CO |
| 1. | C8:0 | νas.2956 | νas.2927 νs.2854 | 1577 | 723 | | | |
| 2. | C10:0 | νas.2958 | νas.2923 νs.2854 | 1560 | 721 | | | |
| 3. | C12:0 | νas.2955 | νas.2924 νs.2854 | 1578 | 721 | | | |
| 4. | C14:0 | νas.2954 | νas.2920 νs. 2850 | 1560 | 721 | | | |
| 5. | C16:0 | νas.2954 | νas.2918 νs.2850 | 1568 | 719 | 0.8 | 1.3 | 2.0 |
| 6. | C18:0 | νas.2956 | νas.2922 νs.2850 | 1571.8 | 721 | 0.8 | 1.2 | 1.9 |
| 7. | C18:1 | νas.2955 | νas.2924 νs.2854<br>ν(=CH)<br>3006.8 | 1570 | 723 | | | |

The surfactants that are used to prepare the overbased detergent contain a polar hydrophilic head and a long, non-polar organic chain. The polar head-group typically links to calcium, magnesium or barium cations. The colloidal particle consists of a core of basic metal carbonate or a mixture of metal carbonate and metal hydroxide depending on the cation species. The core of the colloidal particle is stabilized by a monolayer of surfactant and the core radius is in a size range of 1.5 — 10 nm. [18]

The schematic diagram of prepared overbased magnesium fatty acid detergent particle may be present in Fig. (2).

Total base number were determined for the 60 stock oil blends with different overbased magnesium fatty acid detergent in different dosages according to ASTM D-4739, and the results are shown in table (5).

The results of TBN were treated by using two-way analysis of variance (ANOVA) tests to measure the effects of two factors ,number of carbons in the synthesized overbased detergents ($C_8$-$C_{18}$) and their concentrations (1-5% wt/wt) in the blended oil simultaneously.

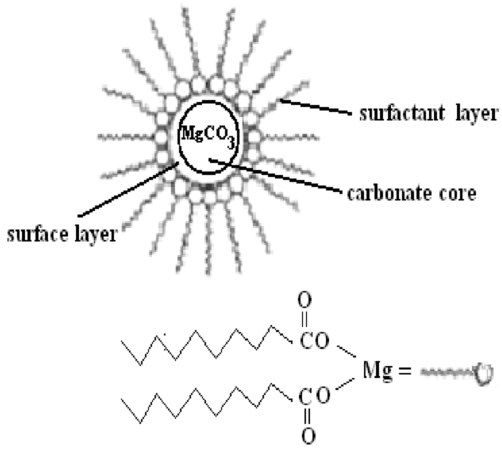


Fig. 2, Schematic diagram of prepared overbased detergent particle

Table (6) shows the effect between subjects and summarized ANOVA. This table show the sum of squares, degree of freedom, mean squares, F-value and the significant test results .The significant level of using different carbon numbers in the detergent have a value of 0.620 which means that there is no significant difference because the significant level is greater than 0.05 (95% confidence), while the significant level obtained for blends with different weight percentage of different additives have the value 0.00, and this means that there is a significant difference in the effect of adding different percentage of detergent.

Table 5, Total base number (TBN, mg of KOH/g) of blend oils

| No. | wt% of detergent in the oil | Blank | Oil with overbased Mg-caprylate ($C_8$) | Oil with overbased Mg-caprate ($C_{10}$) | Oil with overbased Mg-laurate ($C_{12}$) | Oil with overbased Mg-myristate ($C_{14}$) | Oil with overbased Mg-palmitate ($C_{16}$) | Oil with overbased Mg-oleate ($C_{18:1}$) | Oil with overbased Mg-stearate ($C_{18:0}$) |
|---|---|---|---|---|---|---|---|---|---|
| 1. | 1 | 0.87 | 1.63 | 1.41 | 1.63 | 1.66 | 1.69 | 1.71 | 2.84 |
| 2. | 2 | 0.87 | 1.28 | 2.34 | 2.7 | 2.74 | 2.9 | 4.93 | 4.85 |
| 3. | 3.5 | 0.87 | 4.9 | 5.6 | 5.8 | 5.9 | 8.8 | 10.4 | 10.9 |
| 4. | 5 | 0.87 | 6.8 | 7.55 | 10.38 | 12.8 | 15.9 | 24.5 | 20.6 |

Table 6, The effect between subjects and summarized ANOVA.

| Source | Sum of Squares | Degree of freedom | Mean Square | F-value | Significant |
|---|---|---|---|---|---|
| Corrected model | 167.467 | 6 | 27.911 | 0.745 | 0.620 |
| Carbon compound | 167.467 | 6 | 27.911 | 0.745 | 0.620 |
| Correlated model | 641.647 | 3 | 213.882 | 16.396 | 0.000 |
| Weight added | 641.647 | 3 | 213.882 | 16.396 | 0.000 |

Fig.s (3) and (4) show the TBN and efficiency of oil blends with prepared overbased magnesium fatty acid ($C_8$–$C_{18}$) detergents respectivly.

These figures show that the overbased magnesium palmitate ($C_{16}$) , stearate ($C_{18:0}$) and oleate ($C_{18:1}$) detergents give the higher TBN and efficiency. Since the cost of oleic acid is higher than palmitic and stearic acids, they can be recommended for lubricant oil detergent preparation.

Usually the excepted percentage of detergent used for engine crankcase lubricants is not less than 2% [19].

For further, evaluation of the selected overbased magnesium palmitate and overbased magnesium stearate, the base oil (60 stock) as well as its blends with 2% by weight of detergents were subjected to severe oxidation condition in the presence of a soluble iron and copper catalyst at 120 $^{o}$C for 164 hours while being subjected to a constant one-liter/hour flow of oxygen.

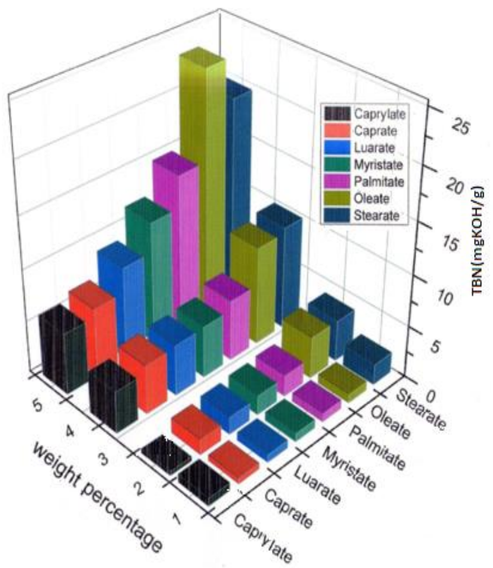


Fig. 3 The TBN of oil blends with prepared overbased magnesium fatty acid ($C_8$–$C_{18}$) detergents at different weight percentages

Results given in table (7) show that the blends with 2% by weight overbased Mg-palmitate ($C_{16}$) or overbased Mg-stearate ($C_{18:0}$) have higher oxidation stability compared with the blend of the same oil with standard antioxidant used by Midland Refineries Company.

Overbased detergents, especially organo-alkaline earth salt compounds, are type of metal deactivators antioxidants, which act as film-forming agents in two ways. First, they coat the metal surface, thus preventing metal ions from entering the oil. Second, they minimize corrosive attack of the metal surface by physically restricting access of the corrosive species to the metal surface [3]. Thus, the overbased magnesium palmitate and overbased magnesium stearate, can show an antioxidant effect, because the carbonate in their structure performs acid neutralization, and the linear structure of the soap forms the protective surface film.

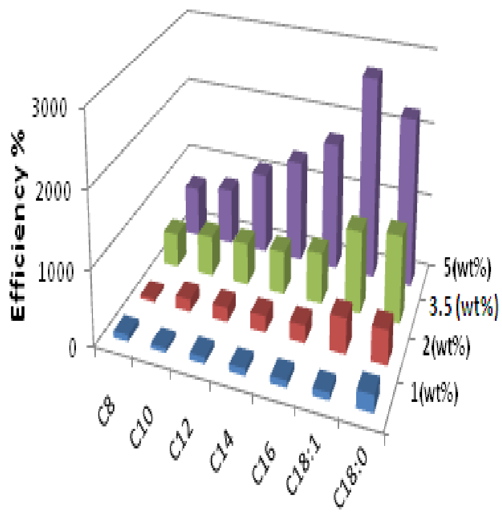

Fig. 4 The efficiency of oil blends with prepared overbased magnesium fatty acid ($C_8$–$C_{18}$) detergents

Table 7, Oxidation stability results

| Characterization | Blank | Oil with overbased Mg-palmitate ($C_{16}$) | Oil with overbased Mg-stearate ($C_{18:0}$) | Standard |
|---|---|---|---|---|
| Volatile acidity, mg of KOH/g | 0.0025 | 0.0037 | 0.0037 | 0.0060 |
| Soluble acidity, mg of KOH/g | 0.2571 | 0.04939 | 0.01234 | 0.1230 |
| Total acidity, mg of KOH/g | 0.259 | 0.05309 | 0.01604 | 0.1290 |
| Total sludge, wt% | 0.280 | 0.01114 | 0.00 | 0.0880 |
| Total Oxidation Products (TOP %) | 0.363 | 0.0281 | 0.05146 | 0.1298 |

## Conclusions

1. A series of overbased magnesium fatty acids ($C_8$-$C_{18:0}$ and $C_{18:1}$) were synthesized and evaluated by blending each additive in various concentrations with 60 stock base oil, and the TBN was determined.
2. It was found that the number of carbons in the fatty acid ($C_8$-$C_{18}$) had slight effect on the TBN of the blended oil, while additive concentrations had a significant effect on the TBN of the blended oil.
3. Blends of 2% of overbased magnesium palmitate and overbased magnesium stearate detergents showed better oxidation stability than the standard antioxidant supplied by Midland Refineries Company.

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