

*Full Length Research Paper*

# Behavior of esters in blend and its possible application

Hamid Shakoori Langeroodi<sup>1</sup> and Abolfazl Semnani<sup>2\*</sup>

<sup>1</sup>Sepahan Petro Kimia Company, Jey Industrial City, Isfahan, Iran.

<sup>2</sup>Faculty of Sciences, University of Shahrekord, P. O. Box 115, Shahrekord, Iran.

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**By estrification of corresponding acids and alcohols, polyol ester of pentaeritritol–tetra–oleate (PETO) and diester of dioctyladipate (DOA), were synthesized. Each synthesis was confirmed through the comparison of some important physical and chemical properties of obtained adducts, with those of reported values. Following this step, three blends of PETO and DOA were prepared and their important physical properties were evaluated. Due to desirable physical properties, of a PETO: DOA mixture, with 32:68 weight ratio, it was assigned as the suitable one and named as Synester F4. This new group (V) esteric base oil was employed for production of two motor oils with standard 15W40CH4. The application of produced oils in two diesel engines was successful.**

**Key words:** Synthetic base oils, polyol ester, diester, PETO, DOA, viscosity index, fash point, pour point, 15W40CH4.

## INTRODUCTION

Prior to the early nineteenth century, one of the main classes of lubricants in use were natural esters contained in animal fats such as sperm oil, lard oil, or in vegetable oil such as rapeseed or castor oil. The earliest recorded use of animal fats is 1400 BC, when they were used to lubricate chariot axles. Around 1937, Dr. Zorn of I. G. Faben in Germany began investigate work on synthetic lubricants. During World War II a range of synthetic oils were developed for commercial production. The great difficulty encountered in Russia in starting trucks and tanks in winter 1941 to 1942 due to the cold, provided an impetus to the development of synthetic ester lubricant. Among these, esters of long chain alcohols and acids proved to be excellent as low temperature lubricants. Following World War II, the further development of esters was closely linked to that of aviation gas turbine (Rudnick, 2006).

Esters are now used in many application including automotive and marine engine oils, compressor oils, hydraulic fluids, gear oils and grease formulations. The low toxicity and excellent biodegradability of ester molecules now afford benefits to those performances (Coffin

et al., 1979; Wyman et al., 1987; Van Ormer, 1987; Witts, 1989; Waddington, 1983; Ridderikhoff, 2003). Mono-esters, diesters, phthalates, C36 dimerates, trimellitates, polyol esters and numerous other types of esters are used in lubricant industry (Rudnick, 2006).

Polyol esters are made by reacting multifunctional alcohol with a monofunctional acid. Polyol esters have the advantage of higher hydrothermally and thermal stability. They are used in a wide variety of applications such as refrigeration compressors, aviation greases, air compressors, metal working and etc (Farron et al, 1984).

Reacting a linear diacidic with a linear, but more usually a branched monofunctional alcohol makes a diester. Diesters have very good viscosity indices and pour points. One disadvantage of diesters is their low molecular weight. This results in limited ISO range coverage (Rudnick, 2006; Whiting, 1988).

Despite, the extensive application of single esters and their excellent advantages (Rao, 1996; Duchowski, 1996). The disadvantages such as high volatility (high NOACK) and low viscosity of some of esters (NIIR Board, 2003), causes some limitation in their single usage. This defect can considerably be improved by balancing the properties via blending (Schick and Kaminski, 1979; Patrick et al., 2005). In this paper we report, the use of mixture of polyol ester and diester as base oil, followed

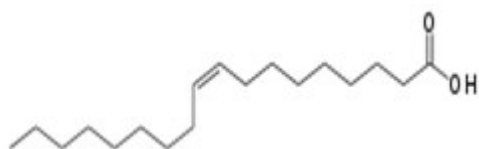
\*Corresponding author. E -mail: [a\\_semnani@yahoo.com](mailto:a_semnani@yahoo.com).

by its successful application in motor oil.

## EXPERIMENTAL

### Synthesis and characterization of PETO

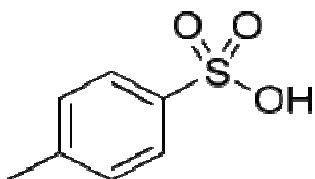
350.25 kg oleic acid (1240 mol), 42.2 kg pentaerythritol (310 mol) and 400 g (nearly 0.1% by weight of the sum of the weights of acid and alcohol) of para toluene sulfonic acid were transferred to a 500 liter stainless still tank. The tank was equipped with stirrer, thermometer and heating means. While stirring, the mixture was heated to 200 °C. After 8 h, a dark oily clear liquid was obtained. The solution was cooled and neutralized by addition of 100 g Ca(OH)<sub>2</sub>. The resulting mixture was shaken vigorously and filtrated. The filtrate was tested by standard methods.



Oleic acid



Pentaerythritol



Para toluene sulfonic acid

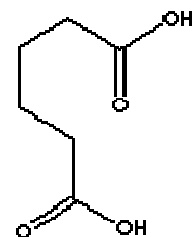


R= Oleate  
Pentaerythritol – tetra – oleate (PETO)

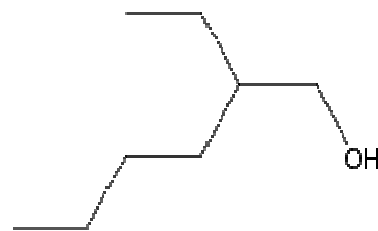
### Synthesis and characterization of DOA

146.14 kg adipic acid (1000 mol), 260 kg 2-ethylethanol (2000 mol) and 400 g (nearly 0.1% by weight of the sum of the weights of ester and alcohol) para toluene sulfonic acid were transferred to a 500 liter stainless still tank. While stirring, the mixture was heated at 110 °C for 8 h. A transparent oily product was obtained. The solution was cooled and neutralized by addition of 100 g Ca(OH)<sub>2</sub>. The re-

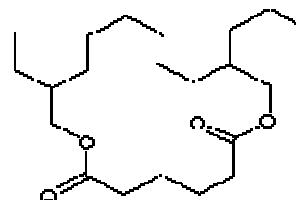
sulting solution was shaken vigorously and filtrated. The filtrate was tested by standard methods.



Adipic acid



2- Ethyl hexanol



Dioctyladipate (DOA)

## Instrumentation

All of the viscosities were determined by viscometer tester Anton Bar model SVM 300. Flash points (FP) were evaluated by flash point tester Herzog model HFP 386. Pour points (pp) were determined by pour point tester Herzog model HCP 852. Cold cranking simulator (CCS) values were obtained by CCS tester Canon 2100. The color scale was determined by Dr. Long instrument. The total acid number (TAN) values were determined by metrohm 624, pH/ion meter, the NOACK values were identified by Petrolab and the IR spectra were recorded on a Perkin Elmer 781 spectrometer by Nujol oil.

## Test methods

**The test methods were followed as:** ASTM D-445 for vis. at 40 and 100 °C, ASTM D-2270 for viscosity index (VI), ASTM D-92 for flash point, ASTM D-97 for pour point, ASTM D-1298 for specific gravity, ASTM D-5293 for cold cranking simulator, ASTM D-1500 for color scale, ASTM D-1959 for iodine value, ASTM D-94 for saponification value, ASTM D-664 for total acid number, ASTM D-5800 for NOACK and ASTM D-1957 for hydroxyl value.

## Optimization of ester mixtures

Several 400 g mixtures containing different weight percentages of PETO and DOA were prepared and examined by standard method.

**Table 1.** Comparison of determined and reported physical properties of DOA.

| Property             | Test method | Obtained value                                     | Reported value <sup>a</sup>                        |
|----------------------|-------------|--|--|
| Vis. at 40 °C        | ASTM D-445  | 8  | 7.9  |
| Vis. at 100 °C       | ASTM D-445  | 2.4  | 2.4  |
| Viscosity index      | ASTM D-2270 | 120  | 124  |
| Flash point          | ASTM D-92   | 190  | 190  |
| Pour point           | ASTM D-97   | -60  | -68  |
| Specific gravity     | ASTM D-1298 | 0.92   | 0.92   |
| Iodine value         | ASTM D-1959 | 0.1  | 0.1  |
| Soapfinication value | ASTM D-94   | 299  | 300.22   |
| Total acid number    | ASTM D-664  | 0.09   | 0.07   |
| NOACK 256 %/1 h      | ASTM D-5800 | 42.8   | 44.3   |
| Hydroxyl value       | ASTM D-1957 | 0  | 0  |
| IR bands             | -           | 3051, 1758, 1412,<br>1246 and 753 cm <sup>-1</sup> | 3055, 1760, 1416,<br>1250 and 750 cm <sup>-1</sup> |

<sup>a</sup>Data taken from Booster ER (1984); and Aldrich Chemical Co. (1998).

**Table 2.** Comparison of determined and reported physical properties of PETO.

| Property             | Test method | Obtained value                                    | Reported value <sup>a</sup>                       |
|----------------------|-------------|---|---|
| Vis. at 40 °C        | ASTM D-445  | 65  | 68  |
| Vis. at 100 °C       | ASTM D-445  | 12  | 12.2  |
| Viscosity index      | ASTM D-2270 | 187   | 187   |
| Flash point          | ASTM D-92   | 260   | 260   |
| Pour point           | ASTM D-97   | -18   | -18   |
| Specific gravity     | ASTM D-1298 | 0.92  | 0.92  |
| Iodine Value         | ASTM D-1959 | 89  | 88  |
| Soapfinication value | ASTM D-94   | 186   | 188   |
| Total acid number    | ASTM D-664  | 0.7   | 0.5   |
| NOACK 256 %/1 h      | ASTM D-5800 | 1.0   | 1.0   |
| Hydroxyl value       | ASTM D-195  | 9   | 10  |
| IR bands             | -           | 1712, 1460, 1282,<br>931 and 712 cm <sup>-1</sup> | 1710, 1462, 1285,<br>937 and 715 cm <sup>-1</sup> |

<sup>a</sup>Data taken from Booster ER (1984); Rao AM (1996); Rudnick LR (2006).

The test methods were followed by the same instruments in previous sections. The mixture with desirable properties was employed for motor oil production.

### Preparation of two motor oils

The optimized mixture of PETO and DOA was employed for preparing two motor oils with standard 15W40CH4. The oils were prepared by blending of SN-500 SN-150 beside optimized mixture, as base oil, as well as Viscoplex 4677 and Lubrizol 4980 A, as additive. The physical properties were evaluated with the same instruments in section of test methods.

### Application of Oils in two diesel engines

The prepared motor oils, was employed in two diesel engines of Scania and Volvo B7. After 10000 km; important physical properties

of used oils such as viscosity at 40 and 100 °C, viscosity index, flash point, pour point, total acid number, total base number, color and specific gravity were tested by standard methods. The results were compared with those of fresh ones.

## RESULTS AND DISCUSSION

Most important performance properties of DOA, as well as, the corresponding test methods are collected in Table 1. The good agreement between determined and reported values (Rudnick, 2006) indicate that the obtained adduct is DOA. Similar data due to PETO are collected in Table 2. In this case, also, determined and reported values (Rudnick, 2006; Schick and Kaminski, 1979; Hosseini and Eric, 2006) show a good consistency. So, the proper synthesis of PETO is also confirmed.

**Table 3.** Comparison of some of properties of different PETO: DOA blends.

| Property            | Test method   | PETO : DOA weight ratio | Obtained value     |
|---------------------|---------------|-------------------------|--------------------|
| Vis. at 40 °C       | ASTM D-445    | 76:24 , 59:41 , 32:68   | 46.2 , 26.2 , 14.5 |
| Vis. at 100 °C      | ASTM D-445    | 76:24 , 59:41 , 32:68   | 8 , 6 , 4          |
| Vis. index          | ASTM D-2270   | 76:24 , 59:41 , 32:68   | 142 , 187 , 170    |
| Fash point          | ASTM D- 92    | 76:24 , 59:41 , 32:68   | 247 , 234 , 215    |
| Pour point          | ASTM D- 97    | 76:24 , 59:41 , 32:68   | -40 , -36 , -40    |
| Specify gravity     | ASTM D- 1298  | 76:24 , 59:41 , 32:68   | 0.92 , 0.92 , 0.92 |
| CCS at – 15 °C      | ASTM – D-5293 | 76:24 , 59:41 , 32:68   | 1846 , 748 , 724   |
| CCS at – 20 °C (CP) | ASTM – D-5293 | 76:24 , 59:41 , 32:68   | 3068 , 850 , 786   |
| CCS at -25 °C       | ASTM– D-5293  | 76:24 , 59:41 , 32:68   | 5453 , 1279 , 882  |
| CCS at –30 °C       | ASTM– D-5293  | 76:24 , 59:41 , 32:68   | 10350 , 1995 , 948 |
| Color scale         | ASTM– D-1500  | 76:24 , 59:41 , 32:68   | 8 , 7 , 4          |

Physical properties such as vis. at 40 and 100 °C, viscosity index, pour point, flash point and cold cranking simulator, are some of the most important factors, which, before employment of a base oil should be considered (Rudnick, 2006). For a common base oil, the acceptable viscosities at 40 and 100 °C are in the ranges of 14 to 34 and 5 to 39, respectively (Rudnick, 2006; Troye, 2002; Booster, 1984; Denis and Briant, 2000). On the other hand, higher flash point, higher viscosity index lower pour point and especially lower cold cranking simulator, are some of the most important performance advantages for a base oil (Rudnick, 2006; Troye, 2002; Booster, 1984).

In order to obtain a desirable PETO: DOA blend, three PETO: DOA mixtures, with different weight ratios were prepared and their physical properties were determined. The weight ratios of different PETO: DOA blends are 76:24, 59:41 and 32:68. They are named as Synester F8, Synester F6 and Synester F4, respectively. The final results are shown in Table 3.

As it can be seen from Table 3, the viscosities of F4 at 40 and 100 °C are 14.5 and 4 which are the acceptable values for a common base oil (Rudnick, 2006; Troye, 2002; Booster, 1984; Denis and Briant, 2000). On the other hand, the similar viscosities due to F6 and F8 are also desirable values. So, from the point of view of viscosity at 40 and 100 °C, there is no preference between none of blends.

Despite the highest flash point and lowest pour point of, F8, relative to other blends, it has the defects of (i) lowest viscosity index and (ii) highest CCS values. The great CCS value causes the fuel consumption to be increased which is a serious disadvantage for a base oil. So, among different blends, F8 should be discarded.

Concerning the VI and FP factors, it seems that, F6, having the maximum VI value and higher FP than F4, is preferable. However, it shows the important disadvantage of higher CCS at different temperatures. In addition the PP of, F6, is more than F4.

It is well known, that commercially, the color scale, is an important factor (Troyer and Fitch, 2001). In fact gain-

ing a base oil, in which, the color scale is as low as possible, would be ideal. Based on this bias, F4 with lowest weight percentage of PETO (that is, the lower color component), which results in lowest color would be the best choice.

The advantages and disadvantages of each blend are summarized in Table 4. Based on the information of Table 4, it can be concluded that the overall conditions of F4 is better than F8 and F6. Consequently, among the three blends, F4, is selected.

Properties of synester F4 has been compared with some equivalent oils (Table 5). The selected base oils are SN400I, SN100 NLP and VHVI III, which are mineral (Rudnick, 2006) and PAO4 which is synthetic (Miller and Synth, 1984; Carpenter, 1994).

As, it can be seen from the data, the VI of F4 is more than the other oils, which can be assigned as an important advantage of this oil, relative to others. Beside this feature, it has the benefit of highest flash point. Also, the viscosities at 40 and 100 °C of F4 are normal values.

Among the different base oils of Table 5, the lowest PP and CCS belongs to PAO4. This can be considered as an important advantage for this base oil and it seems that the recent base oil is compatible with F4. However, considerable difference between VI values of F4 and PAO4, as well as, higher solubility and its adaptability with additives, causes that F4 to be preferred to PAO4. It should be noticed that by having high solubility and adaptability with additives, the preparation of blends of motor oil will be easy. In fact, such properties cause that without heating the preparation of blends and the addition of VI improvers to be possible. So, the blending can be followed merely by mixing, which causes that the whole process to be economic.

According to the above advantages of F4, relative to other equivalent base oils, it can be claimed that F4 is a novel product that can compete strongly with other equivalent base oils.

In addition of previous mentioned advantages of F4, relative to SN100I, SN100NL, VHVI and PAO4, F4 is an

**Table 4.** Advantages and disadvantages of different blends.

| Blend       | Advantages  | Disadvantages  |
|-------------|---|--|
| Synester F8 | Acceptable viscosities at 40°C and 100°C highest flash point, lowest pour point                                   | Lowest viscosity index, highest CCS, undesirable color |
| Synester F6 | Acceptable vis. at 40°C and 100°C highest viscosity index, high flash point                                       | Highest pour point, high CCS, moderate color           |
| Synester F4 | Acceptable viscosity at 40°C and 100°C high viscosity index, high flash point, lowest pour point, desirable color | Lowest flash point                                     |

**Table 5.** Comparison of physical properties of Synester F4 with some equivalent base oils.

| Property        | Base oil            |                      |                       |                   |             |
|-----------------|---------------------|----------------------|-----------------------|-------------------|-------------|
|                 | SN100I <sup>a</sup> | SN100NL <sup>a</sup> | VHVI III <sup>a</sup> | PAO4 <sup>a</sup> | Synester F4 |
| Vis. at 100°C   | 381                 | 4.02                 | 3.7                   | 3.8               | 4           |
| Vis. at 40°C    | 18.6                | 20.1                 | 16.2                  | 16.7              | 14.5        |
| Viscosity index | 89                  | 94                   | 121                   | 124               | 170         |
| Flash point     | 200                 | 197                  | 206                   | 213               | 215         |
| Pour point      | -15                 | -15                  | -18                   | -72               | <-40        |
| CCS at -20°C    | Solid               | Solid                | Solid                 | 830               | 850         |

<sup>a</sup>Data taken from Booster ER (1984).

**Table 6.** Specifications of two motor oils (a and b) in class 15W40CH4 which have been made by Synester F4.

| Base Oils and additives | Composition        |                    | Property         | Oil(a) | Oil(b) |
|-------------------------|--------------------|--------------------|------------------|--------|--------|
|                         | (wt%) <sub>a</sub> | (wt%) <sub>b</sub> |                  |        |        |
| SN-500                  | 24.4               | 24.5               | Vis. at 100°C    | 15.02  | 15.42  |
| SN-150                  | 50.2               | 47.1               | Vis. at 40°C     | 98     | 100.4  |
| Synester F4             | 10                 | 13                 | Viscosity index  | 146    | 143    |
| Viscoplex 4677          | 2.3                | 2.3                | CCS              | 6540   | 6130   |
| Lubrizol 4980 A         | 13.1               | 13.1               | Flash point      | -215   | 215    |
| -                       | -                  | -                  | Pour point       | -36    | -36    |
| -                       | -                  | -                  | Specific gravity | 0.89   | 0.89   |

esteric base oil and because of the following reasons (Rudnick, 2006) lubricant producers are promoted to use esters:

- i) Because of their polarity, esters are highly adaptable with metals. However, because of non-polarity the adaptability of PAO and mineral oils is not as much as esters.
- ii) The lubricity of esters is significantly higher than PAO and mineral oils.
- iii) The performance of esters at high pressure is better than PAOs and mineral oils.
- iv) The VI of esters is high. Despite this can also be seen in DOA, but the VI of mineral oils is low.
- v) Biodegradation of esters is considerable. In the case of PAOs, this property depends on VI and mineral oils are not decomposable.
- vi) The esters are highly soluble. The solubility of PAOs is

very low and mineral oils can be dissolved moderately.

The specifications of two motor oils in class 15W40CH4, which have been made by F4, are collected in Table 6. The motor oil (a) is made from blending of SN-500, SN-150, plus F4 as base oils and in the amounts of 24.4, 50.5 and 10% by weight respectively. The Viscoplex 4-677 and Lubrizol 4980 in the amounts of 2 and 13.1% are used as, additives. The corresponding values for motor oil (b) are 24.5, 47.4, 13.2 and 13.10.

As it can be seen, in both cases, the vis. at 40 and 100°C, as well as, VI, CCS, FP and PP are acceptable and the 15W40CH4 standard is fairly passed. On the other hand, by increasing the weight percentage of F4 from 10% in oil (a) to 13% in oil b, the CCS has been dropped 410 units, which can be assigned as a valuable specification. In fact, a minor increase in F4, results in a

**Table 7.** Comparison of some of important performance properties of oil (a) after 10000 km usage in diesel engines of Scania and Volvo B7 with the same oil at in fresh state.

| Property         | Fresh oil | Used oil in Scania | Used oil in Volvo |
|------------------|-----------|--------------------|-------------------|
| Vis. at 40°C     | 98        | 90                 | 89                |
| Vis. at 100°     | 15        | 12.9               | 12.8              |
| VI               | 146       | 143                | 140               |
| FP               | 215       | 190                | 188               |
| TAN              | 1.8       | 2.2                | 2.4               |
| TBN              | 10        | 9                  | 8.1               |
| Color            | 2         | 3.5                | 3.9               |
| Specific gravity | 0.89      | 0.93               | 0.94              |

profound decrease in CCS. This also causes the reduction in fuel consumption.

In order to ascertain the performance characteristics of novel products, the oils were examined in diesel motors of Scania and Volvo. The results of typical tests, after 10000 km usage of oil (a) are collected in Table 7. The data due to fresh oil (a) are also included. As it can be seen, the variations of different properties are in acceptable range (Denis et al., 2000). Similar results were also obtained from oil (b). So, it can be surly claimed that the new products are good candidates for application in diesel engines.

The reduction of motor voice, lowering the fuel consumption and better initial start are of other advantages of these novel motor oils.

## Conclusion

Based on the obtained results it can be concluded that:

1. Synester F4 can be introduced as a new product.
2. The properties of F4 is such a way that it can fairly compete with common base oils.
3. Synester F4 do have the important advantage of high VI.
4. By using Synester F4, the preparation of blends at room temperature would be possible.
5. The CCS factor, which is very important in motor oil performance. Can be lowered significantly upon minor increment of F4 (3%) in motor oil.
6. Application of mixed esters instead of single ones, causes the availability of base oils with extensive desirable properties.

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