

LUBRICATION PROPERTIES OF DIFFERENT PENTAERYTHRITOL-OLEIC ACID REACTION PRODUCTS

¹Abolfazl Semnani, ²Hamid Shakoori Langeroodi, ³Mahboube Shirani

¹University of Shahrekord, Iran

²Barzin Sepand Sepahan Company, Iran

³University of Jiroft, Iran

Abstract. The esterification reactions between pentaerythritol and oleic acid have been followed in the presence of para toluene sulfonic acid catalyst at 4:1, 2:1, 1.5:1, and 1:1 acid –alcohol mole ratios. Considering the lubrication properties of the resulting products in each reaction indicates systematic increase of vis@40 °C, vis@100 °C, pour point, and flash point upon decreasing of the moles of oleic acid. In the case of viscosity index the reverse trend is observed. The lubrication properties were also compared with the corresponding data regarding some of mineral and synthetic base oils. The advantages and disadvantages of esteric products relative to recent oils were discussed. Finally, several industrial oils were equalized successfully by using the esteric base oils.

Keywords: pentaerythritol, oleic acid, esteric base oils, mineral oils, synthetic oils

Introduction

Esters have been used successfully in lubrication for more than 50 years. They are also the preferred stocks in many severe applications. The polarity of ester molecules leads to high attraction among them and polar species. This has a direct impact on their properties such as low vapor pressure, low volatilities, high flash points, high solvency, hydroscopic character, lubricity, and thermal and hydrolytic stability. The low toxicity and excellent biodegradability are the two dominant features of ester molecules (Laukotka, 1985; Van der Waal & Kenbeek, 1993).

Monoesters, diesters, phthalates, C36 dimerates, trimellitates, polyol pyromellitate esters, and numerous other types of esters are widely used in lubricant industry (Malek & Immenthun, 1972; Hirzy, 1977; Randles, 1992; Phillips, 2006; Ash & Ash, 2006; Carr et al., 1999; Kato et al., 1998; Rudnick, 2013).

Polyol esters are made by the reaction of multifunction alcohol with the monofunctional acid. Polyol esters do have the advantage of higher hydrolytic and thermal stability. They are used in a wide variety of applications such refrigeration compressors, aviation

greases, air compressors, metal working and etc. (Carr et al., 1999; Kato et al., 1998).

Phthalate esters are specific subgroup of diesters. They are prepared by reacting phthalic anhydride with a mono-functional alcohol. Phthalate esters are one of the most cost-effective esters therefore they are often used in industrial scales for instance in air compressors to replace mineral oils. They have low pour points or good viscosity index (Rudnick, 2013).

Despite the existence of various esters based products, it seems that development of synthetic lubricants based on new esters, as well as introduction of new methods for the synthesis of existing esters, will have progressive effect in lubricant ester industry. We have been recently involved in the investigation on lubricants (Langerood & Semnani, 2009; Shugarman, 2006; Kolwzan & Gryglemicz, 2003; Trayer & Fitch, 2001). In this paper, we report the results of synthesis and industrial application of several polyolesters.

Experimental

Synthesis of base oil 4:1

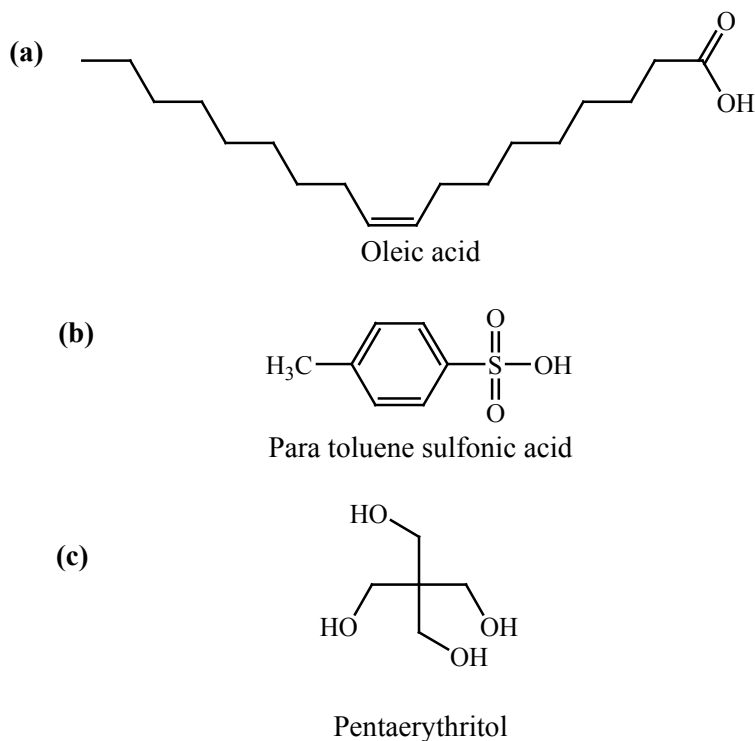
380 kg of oleic acid was transferred to a 500 liter Batch vessel. The vessel was put on the heater-stirrer. While stirring, the solution was heated to 200 °C. During heating and stirring, 45.6 kg pentaerythritol and 400 g paratoluene sulfonic acid were added to batch gradually. The heating and stirring was continued for 8 hours. The resulting solution was cooled. Then, neutralized by addition of 400 g of $\text{Ca}(\text{OH})_2$. The neutralized solution was filtered and the filtrate was used for the next steps. The chemical structures of Oleic acid, Para toluene sulfonic acid, and are shown in Scheme 1.

Synthesis of base oil 2:1

340 kg of oleic acid was transferred to a 500 liter Batch vessel. The solution was stirred and heated to 100 °C. At this temperature and during stirring, 40 kg of pentaerythritol and 400 g of para toluene sulfonic acid were added gradually. Then, the temperature was elevated to 160 °C. The process took for two hours. In the next step, 41.8 kg of pentaerythritol and 400 g of para toluene sulfonic acid were added again. Following addition, the temperature was increased to 200 °C and remained for 8 hours. Finally, 800 g of $\text{Ca}(\text{OH})_2$ was added for neutralization and the solution was filtrated. The filtrate was employed for the next steps.

Synthesis of base oil 1.5:1

318 kg of oleic acid was transferred to a 500 liter Batch vessel. The solution was stirred and heated to 100 °C. At recent temperature and during stirring, 50 kg of pentaerythritol and 400 gr of para toluene sulfonic acid were added gradually. Then, the

**Scheme 1**

temperature was increased to 160 °C and kept for two hours. In next step, 52.1 kg of pentaerythritol and 400 g of para toluene sulfonic acid were added again. Subsequently, the temperature was increased to 200 °C and kept for 8 hours. Finally, with the purpose of neutralization, 800 g of $\text{Ca}(\text{OH})_2$ was added and the solution was filtrated. The filtrate was applied for the next steps.

Synthesis of base oil 1:1

282 kg of oleic acid was transferred to a 500 liter batch vessel. The solution was stirred and heated to 100 °C. At recent temperature and during stirring, 50 kg of pentaerythritol and 400 g of para toluene sulfonic acid were added gradually. Then, the temperature was elevated to 160 °C. The recent conditions were remained for two hours. In the next step, 65.8 kg of pentaerythritol and 400 g of para toluene sulfonic acid were added again. Then, the temperature was increased to 200 °C and kept for 8 hours. Finally, with the

purpose of neutralization, 800 g of $\text{Ca}(\text{OH})_2$ was added and the solution was filtrated. The filtrate was employed for the next steps.

Instrumentation

The viscosities of all the compounds were determined by viscometer Anton Baar model SVM 3000. Flash points were evaluated by flash point tester Herzog model HC 852. Pour points were determined by pour point tester Herzog, model HC 852. The colors were determined by Dr. Long instrument. The FZG values were determined by Strama MPS instrument.

Test methods

The test methods were followed as: ASTM D-445 for vis@ 40 °C and 100 °C, ASTM D-2270 for viscosity index, ASTM D-92 for flash point, ASTM D-97 for pour point, ASTM D-1298 for specific gravity, ASTM D-892-11 for foam, ASTM 1500 for color, and DIN 51354 for FZG.

Equalization of compressor oil Ultracoolant by 4:1

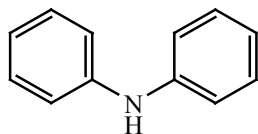
70.6 kg of 4:1 and 29.4 kg of di-2-ethylhexylphthalate (DOP) from Abtin Company were transferred to a Batch vessele. Without heating, the solution was stirred for one hour. Following this step, 100 mg silicon antifoam B14 from Infinium Company, 0.5 kg of pour point depressant (PPD) M-Kay from Krishna Company, 1kg diphenylamine antioxidant from Merck Company, and additive package RC9224 from Rein Chemi Company were added to initial solution. While stirring, the temperature was elevated to 60 °C. Heating and stirring was continued for one hour. The final adduct was used for next steps.

Equalization of gear oil Shell Hyperia by 2:1

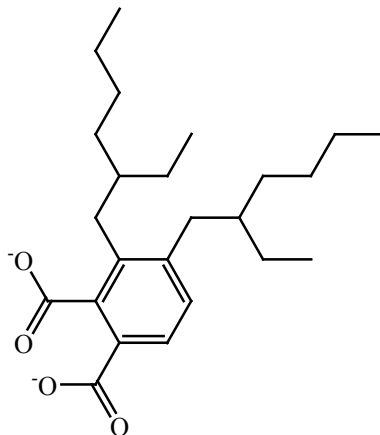
100 kg of 2:1 was transferred to a Batch vessel. 1.5 kg of additive package Hitech 343 from Afton Company and 0.5 kg of pour depressant (PPD), V-351 from Rohmax Company was added in next step. The resulting mixture was stirred for one hour and the final adduct was used for next steps.

Equalization of compressor oil Shell Madrela 220 by blending of 4:1 and 2:1

4.4 kg of 4:1 and 15.6 kg of 2:1 were transferred to a Batch vessel. Subsequently, 1 kg of diphenylamine antioxidant from Merck Company, 50 mg of silicon antifoam B14 from Infinum Company, and 1kg pour point depressant V-351 from Rohmat Company were added to initial solution. The resulting mixture was then stirred for half an hour and the final adduct was used for next steps.



Diphenylamine



Di-2-ethylhexylphthalate (DOP)

Scheme 2*Equalization of gear oil Shell Omela HD 460 by 1.5:1*

100 kg of 1.5:1 was transferred to a Batch vessel. Then 0.5 kg of additive package Hitech 343 from Afton Company and 1 kg pour point depressant V-351 from Rohmat Company was added to vessel. The resulting mixture was stirred for half an hour and the final solution was used for next steps.

Equalization of gear oil Mobilgear by 1:1

100 kg of 1:1 was transferred to a Batch vessel. Then, 1.5 kg of additive package Hitech 343 from Afton Company and 0.5 kg of pour point depressant V-351 from Rohmat Company was added to vessel. The resulting solution was stirred for half an hour and the final product was used for next steps.

Results and discussion

Physical properties of the reaction adduct of different combinations of oleic acid-pentaerythritol are given in Table 1. The plots of vis @ 40 °C and vis @ 100 °C are also shown in Fig. 1. As it is indicated, upon increasing the number of oleic acid, vis @ 40 °C and vis @ 100 °C will decrease. This can be attributed to the higher molecular interactions in lighter oleate esters which results in enhancement of hydrogen bonding between ester molecules as well as extension of dipole-dipole interactions between esteric units. Also the viscosity index vs. no. of oleic acid molecules is shown in Fig. 2.

Table 1. Physical properties of different esteric adducts

Property	Test method	4:1	2:1	1.5:1	1:1
Vis@ 40 °C	ASTM D-445	68	247	463	630
Vis@ 100 °C	ASTM D-445	12.5	25	34	45
VI	ASTM D-2270	187	129	109	85
Flash point	ASTM D-92	245	280	295	305
Pour point	ASTM D-97	-21	-18	-15	-12
Color	ASTM D-1500	6	Black	Black	Black
Specific gravity	ASTM D-1298	0.9227	0.9503	0.9729	0.9910

The effect of molecular interactions effects are further reflected in flash point and pour point. As it is anticipated, in parallel to growing the oleate number in final ester, both of the properties have been grown (Table 1 and Fig. 3).

Physical properties such as vis @ 40 °C and vis @ 100 °C as well as viscosity index, flash point pour point and etc. are some of the most important factors which in base oil selection, should be considered. In fact the recent lubrication properties are the basis of the evaluation of the performance of certain base oil (Nepogod'ev et al., 1983; Wu, 1989). So, herein the physical properties of different adducts are compared with some of the mineral and synthetic base stocks.

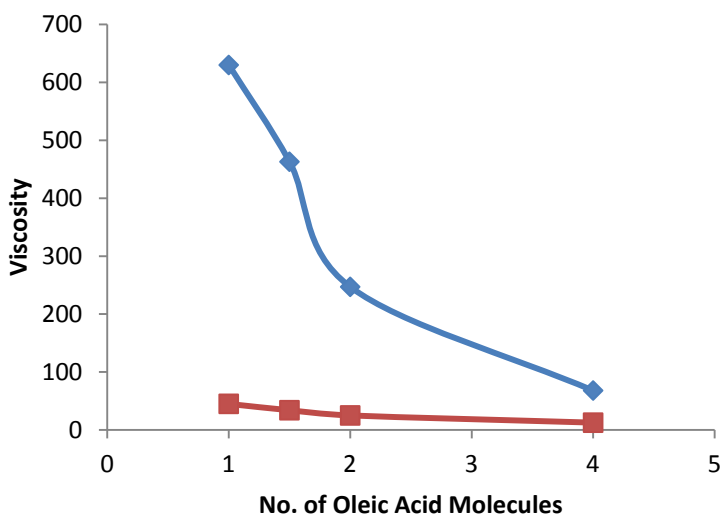


Fig. 1. Plots of vis@40 °C (top) and vis@100 °C (bottom) vs. no. of oleic acid molecules

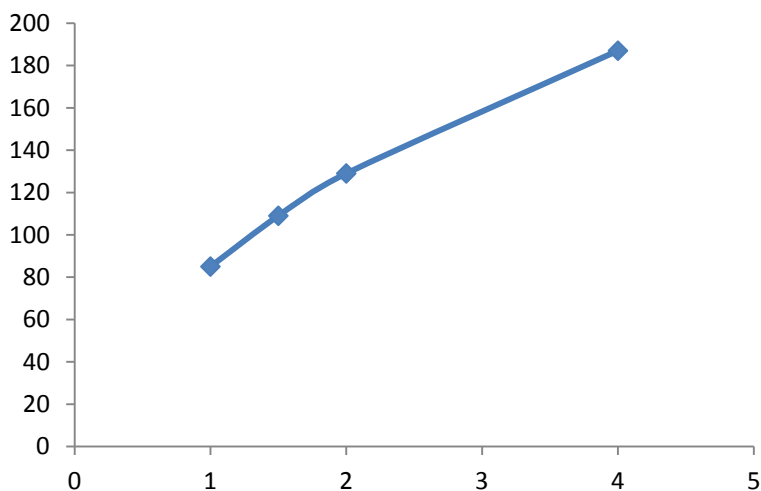


Fig. 2. Plots of viscosity index vs. no. of oleic acid molecules

Firstly, properties of 4:1 were compared with mineral oil SN-500 from Sepahan Company. The final obtained results are collected in Table 2. As the data show, the vis @ 40 °C of the 4:1 and SN-500, are 68 and 105, respectively. This means that vis @ 40 °C of 4:1 is exactly the same as the ISO class (Rudnick, 2013). Meanwhile, the vis @ 40 °C of SN-500 is out of the range. Consequently, the oil formulation by 4:1 can be followed without any other base oil or VI improvers. Oil preparation of SN-500 involves the usage of another base oil or application of VI improver. Therefore for vis @ 40 °C, the preferred base oil is 4:1.4.

Table 2. Comparison of physical properties of 4:1 and SN-500 Sepahan

Property	Test method	4:1	SN-500 Sepahan
Vis@ 40 °C	ASTM D-445	68	105
Vis@ 100 °C	ASTM D-445	12.5	11.1
VI	ASTM D-2270	187	88
Flash point	ASTM D-92	245	245
Pour point	ASTM D-97	-21	-3
Color	ASTM D-1500	6	2
Specific gravity	ASTM D-1298	0.9217	0.8909

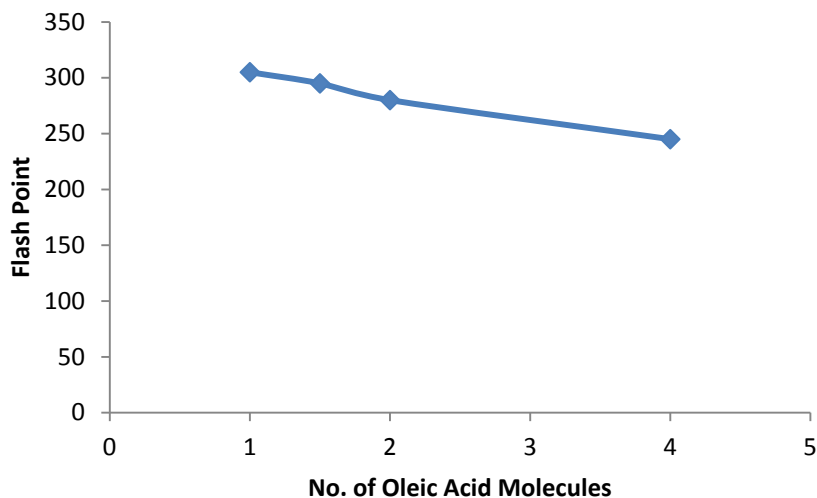


Fig. 3. Plots of flash point vs. number of oleic acid molecules

The viscosity index of 4:1 is considerably higher than that of SN-500 (Table 2) which can be considered as an important advantage of the former relative to the later. Lower pour point is its other benefit. On the other hand, the color of 4:1 is somewhat darker than that of SN-500 and with regarding to this factor, the application of this base oil in motor oils is limited.

Physical properties of 2:1 were compared with the corresponding values due to Nynas BNS 600. The data (Table 3) are indicative of advantages of higher flash point and lower pour point, and disadvantage of dark color of 2:1 relative to Nynas BNS 600. Similar to 1:1, the recent defect causes that the application of 2:1 in motor oils to be limited.

Table 3. Comparison of physical properties of 2:1 and Nynas BNS 600

Property	Test method	2:1	Nynas BNS 600
Vis@ 40 °C	ASTM D-445	247	600
Vis@ 100 °C	ASTM D-445	25	22
VI	ASTM D-2270	129	114
Flash point	ASTM D-92	280	237
Pour point	ASTM D-97	-18	-12
Color	ASTM D-1500	Black	4
Specific gravity	ASTM D-1298	0.9503	0.9100

In the next step physical properties of 1.5:1 relative to Bright stock 150 were investigated. Based on the data (Table 4), 1.5:1 show the benefits of higher flash point and higher VI. Owing the dark color is its major defect.

Table 4. Comparison of physical properties of 1.5:1 and Bright Stock 150

Property	Test method	1.5:1	Bright Stock 150
Vis@ 40 °C	ASTM D-445	463	460
Vis@ 100 °C	ASTM D-445	34	30
VI	ASTM D-2270	109	85
Flash point	ASTM D-92	295	270
Pour point	ASTM D-97	-15	-6
Color	ASTM D-1500	Black	4
Specific gravity	ASTM D-1298	0.9729	0.9129

Table 5. Comparison of physical properties of 1:1 and PAO-40

Property	Test method	1:1	PAO-40
Vis@ 40 °C	ASTM D-445	630	396
Vis@ 100 °C	ASTM D-445	4509	39
VI	ASTM D-2270	85	147
Flash point	ASTM D-92	305	281
Pour point	ASTM D-97	-12	-36
Color	ASTM D-1500	Black	0.5
Specific gravity	ASTM D-1298	0.9910	0.8525

Finally physical properties of 1:1 were compared with PAO-40 (Table 5). Relative to PAO-40, 1:1 does have much lower VI. Higher pour point and dark color are its disadvantages. Greater flash point is the benefit of the oil. The plot of pour point vs. no. of oleic acid molecules is shown in Fig. 4.

It should be noticed that the viscosities @ 40 °C of all of the esteric base oils, is in a level, that without VI improvers, they can be used for oil formulation. This will reduce the problems which originate from the employment of VI improvers and can be considered as general advantage of all of the esteric oils.

The advantages and disadvantages of esteric base oils relative to mentioned reference oils are summarized in Table 6. An overview in the Table shows that esteric oils can fairly compete with other equivalent base oils.

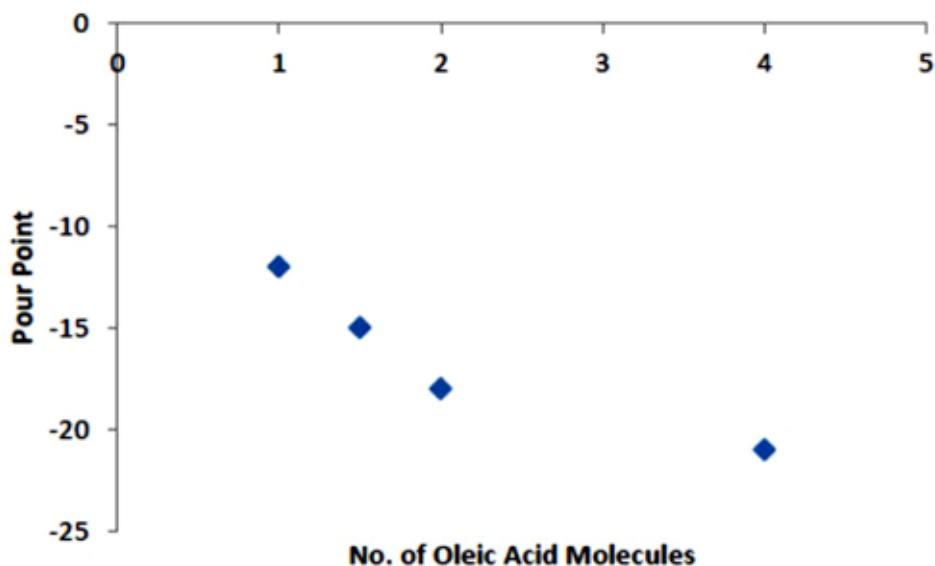


Fig. 4. Plots of pour point vs. no. of oleic acid molecules

The 4:1 esteric oil was employed in the equalization of compressor oil Ultracoolant which is a product from Ingersolland Company. The details of adduct formulation of are given in Table 7. Data due to comparison of physical properties of simulated and original oil are also given in Table 7. Despite the simulated oil show the minor defects such as lower VI (12 units), lower flash point (6 °C), and higher pour point (5 °C), its application in air compressor of national oil Company of Iran caused lower voice as well as faster and easier start up. In addition the final price of ester based oil is considerably lower than Ultracoolant which can be regarded as an important priority of the former relative to the latter.

Gear oil Shell Hyperia S220 from Shell Company was simulated by 2:1 esteric oil. The simulated oil does have the lower VI and higher flash point relative to reference one (Table 8). Its application in cement industry was highly economic (the final price was 20% of the Shell Hyperia S220).

The mixture of 4:1 and 2:1 were used for the equalization of compressor oil Shell Madrela from Shell Company. The details of simulation as well as, the physical properties of esteric and reference oils are given in Table 9. As it is observed the viscosity index of esteric oil is considerably lower than original one. Meanwhile, its flash point is higher. It was applied in some of the instruments of National Iranian oil Company, without any problem. The application of the oil was more economic.

Table 6. Advantages and disadvantages of different esteric oils in comparison with some other base oils

Esteric oil	Reference oil	Advantages	Disadvantages
4:1	SN-500 Sepahan	Unnecessary of using VI improvers, higher flash point, lower pour point.	Dark color
2:1	Nynas BNS 600	Unnecessary of using VI improvers, higher flash point, lower pour point.	Dark color
1.5:1	Bright Stock 150	Unnecessary of using VI improvers, higher flash point, lower pour point.	Dark color
1:1	PAO-40	Unnecessary of using VI improvers, higher flash point VI	Dark color, higher pour point, lower

Table 7. Information due to formulation of compressor oil based on 4:1 and comparison of its physical properties with those of Ultracoolant

Formulation		Property	Test Method	Formulated oil	Ultracoolant
Component	Wt	Vis@40 °C	ASTM D-445	49	48
		Vis@100 °C+9	ASTM D-445	9	9
Base oil 4:1	70.6 kg	Viscosity index	ASTM D-2270	160	172
DOP	29.4 kg	Flash point	ASTM D-92	265	271
Pour point depressant M-Kay	0.5 kg	Pour point	ASTM D-97	-45	-50
		Specific gravity	ASTM D-1298	0.9929	0.9812
Diphenylamine antioxidant	1 kg				
Additive Package RC9224	0.8 kg	Foam	ASTM D-892	5/0/10/0	Nil
		Color	ASTM D-1500	6	1.5
Antifoam B14	100mg				

Table 8. Information due to formulation of gear oil based on 2:1 and comparison of its physical properties with those of Shell Hyperia S220

Formulation		Property	Test method	Formulated oil	Shell Hyperia S220
Component	Wt	Vis@40 °C	ASTM D-445	250	222
		Vis@100 °C	ASTM D-445	25	26
Base oil 2:1	100 kg	Viscosity index	ASTM D-2270	120	162
		Flash point	ASTM D-92	280	263
Pour point depressant V-351	0.5 kg	Pour point	ASTM D-97	-48	-48
		Specific gravity	ASTM D-1298	0.9220	0.8501
Additive package Hitech 343	1.5 kg	FZG	DIN 51354	>12	>12
		Color	ASTM D-1500	6	2

Table 9. Information due to formulation of compressor oil based on blend of 4:1 and 2:1 and comparison of its physical properties with those of Shell Madrela 220

Formulation		Property	Test Method	Formulated oil	Shell Madrela 220
Component	Wt	Vis@40 °C	ASTM D-445	200	198
		Vis@100 °C	ASTM D-445	22	34.8
Base oil 4:1	15.6 kg	Viscosity index	ASTM D-2270	160	223
Base oil 2:1	84.4 kg				
Pour point depressant V-351	1 kg	Flash point	ASTM D-92	300	260
		Pour point	ASTM D-97	-39	-39
Diphenylamine antioxidant	1 kg	Specific gravity	ASTM D-1298	0.9439	1.0021
Additive package RC-9321	0.8 kg	Foam	ASTM D-892-11	5/0 / 1/0 / 5/0	0/0 / 0/0 /0/0
		Color	ASTM D-1500	5	0.2
Antifoam B14	50 mg				

The equalization of gear oil Shellomelahd 460 from Shell Company was performed by 1.5:1 esteric base oil. The details of simulation as well as, the physical properties of esteric and reference oils are given in Table 10. Lower VI and higher flash point are its advantage and disadvantage, respectively. The application of this oil in some of the instruments of National Iranian oil Company was successful and economic.

Gear oil Mobilgear 680 from Exxonmobil Company was simulated by 1:1. The simulated oil does have (Table 11) the profits of lower pour point and higher flash point. On the other hand the viscosity index of this oil is somewhat (5 units) less than reference one. Application of this oil in cement industry was successful.

Table 10. Information due to formulation of gear oil based on 1.5:1 and comparison of its physical properties with those of Shell Omela HD 460

Formulation		Property	Test method	Formulated oil	Shell Omela HD 460
Component	Wt	Vis@40 °C	ASTM D-445	400	458.3
		Vis@100 °C	ASTM D-445	34	45.5
Base oil 1.5:1	100 kg	Viscosity index	ASTM D-2270	100	155
		Flash point	ASTM D-92	300	240
Pour point depressant V-351	0.5 kg	Pour point	ASTM D-97	-42	-42
		Specific gravity	ASTM D-1298	0.9419	0.8900
Additive package Hitech 343	0.5 kg	FZG	DIN 51354	>12	>12
		Color	ASTM D-1500	Black	1

Table 11. Information due to formulation of gear oil based on 1:1 and comparison of some of its physical properties with those of Mobilgear 680

Formulation		Property	Test method	Formulated oil	Mobilgear 680
Component	Wt	Vis@40 °C	ASTM D-445	680	680
		Vis@100 °C	ASTM D-445	45	39.2
Base oil 1:1	100 kg	Viscosity index	ASTM D-2270	85	90
		Flash point	ASTM D-92	300	285
Pour point depressant V-351	0.5 kg	Pour point	ASTM D-97	-18	-9
		Specific gravity	ASTM D-1298	0.9815	0.9192
Additive package Hitech 343	1.5 kg	FZG	DIN 51354	>12	>12
		Color	ASTM D-1500	Black	4

Conclusions

Based on the obtained results it can be concluded that: (1) The performance characteristics of different esoteric base oils are acceptable; (2) The application of base oils is limited to industrial scales due to their color which makes the solution colorful; (3) The base oils can be used without VI improvers. Not only this is important from economic aspects, but also, will decrease the problems which produce through addition of VI improvers; (4) The vis@40 °C of all of the base oils show excellent agreement with ISO classification. Consequently, the formulation of oils with desired ISO classes will be possible without utilization of any other base oil; (5) Formulated oils based on esteric adducts are compatible with reference oils. In addition they have lower price; (6) Upon increase of the number of hydroxyl groups in ester molecules, the vis @ 40 °C and vis @ 100 °C as well as flash point will increase systematically. Meanwhile the pour point will increase.

Acknowledgement. The financial support of this work by research council of Shahrekord University is highly appreciated. The authors were also partially supported by the Center of Excellence for Mathematics, University of Shahrekord.

REFERENCES

- Ash, M. & Ash, I. (2004). *Handbook of preservatives*. Goa: Synapse Info Resources.
- Carr, D.D., McHenry M.A. & Schaefer, T.G. (1999). Poly (neopentyl polyol) ester based coolants and improved additive package. *US Patent* 08/918,177.
- Hirzy, J.W. (1977). Modified polyester polyblends and preparation thereof. *US Patent* 05/633,207.
- Kato, K., Sato, Y. & Shiokawa, Y. (1998). Polyol ester based-lubricant. *Patent EP0801129A2*.
- Kolwzan, B. & Gryglewicz, S. (2003). Synthesis and biodegradability of some adipic and sebacic esters. *J. Synthetic Lubrication*, 20, 99-107.
- Langeroodi, H.S. & Semnani, A. (2009). Behavior of esters in blend and its possible application. *African J. Pure & Applied Chem.*, 3 241-246.
- Laukotka, E.M. (1985). Lubrication of gears with synthetic lubricants. *J. Synthetic Lubrication*, 2, 39-62.
- Malec, R.E. & Immethun, P.A. (1972). Complex esters. *US Patent* 3,637,501.
- Nepogod'ev, A.V., Mitin, I.V. & Vipper, A.V. (1983). Volatility of synthetic oils in engines. *Chem. Technol. Fuels Oils*, 19 243-247.
- Phillips, W.D. (2006). The high-temperature degradation of hydraulic oils and fluids@. *J. Synthetic Lubrication*, 23, 39-70.
- Randles, S.J. (1992). Environmentally considerate ester lubricants for the automotive and engineering industries. *J. Synthetic Lubrication*, 9, 145-161.
- Rudnick, L.R. (2013). *Synthetics, mineral oils, and bio-based lubricants: chemistry and technology*. New York: CRC Press.
- Shugarman, A.L. (2006). *Lubricant base oils: analysis and characterization of petroleum and liquid fossil fuels analysis: encyclopedia of analytical chemistry*. New York: Wiley.
- Troyer, D. & Fitch, J.C. (2001). *Oil analysis basics*. Tulsa: Noria corporation.
- Van der Waal, G. & Kenbeek, D. (1993). Testing, application, and future development of environmentally friendly ester base fluids. *J. Synthetic Lubrication*, 10, 67-83.
- Wu, M.M. (1989). High viscosity index synthetic lubricant compositions. *Patent* 4827074 A.

✉ **Dr. Abolfazl Semnani** (corresponding author)

Department of Chemistry
University of Shahrekord
P.O. Box 115, Shahrekord, Iran
E-mail: a.semnani1341@gmail.com