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THE EFFECT OF DIOCTYLPHTHALATE ON INITIAL PROPERTIES AND FIELD PERFORMANCE OF SOME SEMISYNTHETIC ENGINE OILS

¹Azadeh Ghasemizadeh, ²Abolfazl Semnani, ³Hamid Shakoori Langeroodi, ¹Alireza Nezamzade Ejhieh

¹Islamic Azad University, Iran ²University of Shahrekord, Iran ³Petrokimia Sepahan Company, Iran

Abstract. Several semisynthetic engine oils containing solvent neutral-150 (SN-150) and solvent neutral-500 (SN-500) as mineral constituent and di-2-ethyl-hexylphthalate (DOP) as synthetic constituent has been formulated. Physical properties of the prepared oils have been measured by standard methods. The concentration of twenty three elements in the oils has also been determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The physical measurements and chemical analysis were repeated after 5000 kilometer of running. By comparison of the obtained data, the influence of ester on initial properties of fresh formulated oils, as well as its impact on the field performance of used ones have been investigated. The result indicate that upon ester introduction properties such as biodegradability, coefficient of friction, wear, suppression of additive depletion, CCS, color, and pour point will be modified. However, specifications such as oxidation stability and hydrolytic stabilities will be downgraded. The overall obtained data indicate that, upon 20% increase of DOP content most of the useful properties of ester will be gained.

Keywords: lubricants, SN-150, SN-500, ester, DOP, engine oils, ICP-OES, engine oil, biodegradability, wear

Introduction

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. 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 (Rudnick, 2006; Venkaramani et al., 1989; Debian & Hänssle, 1985; Boyde, 2000; Szydywar, 1984; Ridderikhoff & Ooserman, 2005; Nagendramma, 2011; Gandule & Dwivedi, 2001; Wits, 1989; Kenbeek & Van der Waal, 1991). The low toxicity and excellent biodegrability of ester molecules now afford benefits to those performances (Rudnick, 2006; Hahn et al., 2003; Hömer, 2002).

Reacting a linear diacidic with a linear, but more usually a branched monofunctional alcohol makes a diester. One disadvantage of diesters is their low molecular weight. This results in limited ISO range coverage (Rudnick, 2006; Mang & Dresel, 2005; Al-Magly et al., 1990). Phthalates are a specific subgroup of diesters. These compounds are made by reacting phthalic anhydride with a monofunctional alcohol (Rudnick, 2006). Iso-heptyl, iso-octyl, 2-ethyl hexyl, iso-nonyl, and isotridecyl are examples of commercially available phthalates, which do have versatile viscosity and viscosity index (Rudnick, 2006). Phthalate esters are one of the most cost-effective esters and as such they often used in industrial applications.

Solvent extraction creates base oils which are known as solvent raffinates or solvent neutrals (SN) consist of solvent refined paraffinic oils that are processed to meet specific targets for saturates and sulphur content (Wessol & Pirro, 2001). This ensures good solubility characteristics for additive in product formulations and good antioxidant properties for high temperature applications (Rudnick, 2006). These base oils have high VI and low pour points for good low temperature performance (Mang & Dresel, 2005). Solvent neutral base oils are identified with a number which represents the SUS viscosity measured in Saybolt Universal Seconds at 40°C (Fenna, 2004). For example SN-150 and SN-500 do have the SUS viscosity equal to 150 and 500, respectively.

Blending of two or more different base oils makes it possible to achieve various property combinations of the resulting material (Bantchev & Biresaw, 2008; Hu & Jiang, 1998; Asadusca & Erhan, 2003; Haycock et al., 2005; Tanveer & Prasad, 2006). The possibility of the accumulation of the useful properties of the mixture components in the obtained blend is an attractive aspect of mixing.

Oil analysis involves sampling and analyzing oil for various properties and materials to monitor wear and contamination in an engine, transmission, or hydraulic system (Troyer & Fitch, 2001). In an oil analysis, the concentration of a number of elements as well as the quantity of some of the physical properties such as viscosity, viscosity index, density, flash point, pour point, total acid and base numbers, and water content (Evans, 2008; Roylance & Hunt, 1999) is determined. The resulting data are then employed for the diagnosis of the conditions of oil and motor (Evans, 2008; Roylance & Hunt, 1999). Oil analysis can detect, fuel dilution of lubrication oil, dirt contamination in the oil, antifreeze in the oil, excessive bearing wear, and misapplication of lubricants. Early detection can reduce repair bills, diminish catastrophic failures, increase machinery life, and lessen nonscheduled downtime (Fitch, 2001; Toms & Toms, 2008).

We have recently been involved in the investigation of lubrication oils (Langeroodi & Semnani, 2009; 2013; Semnani & Langeroodi, 2013; Ashrafi et al., 2013; Rahimi et al., 2012a; 2012b). In this paper, we report the results of the study on the effect of DOP ester on initial properties, as well as field performance of some of semisynthetic gasoline engine oils SAE 20w50, API Sl.

Experimental

Materials

Base oils SN-500 and SN-150 from Behran oil Company were used directly. Methanol, hydrochloric acid, perchloric acid, different buffers, propane-2-ol, chloroform, potassium hydroxide, acetic acid, acetic anhydride, chlorobenzene, sodium perchlorate, xylene, acetone, and solid carbon dioxide were purchased from Merck Company and used without any further processing. Spex multielement primary standards set were used for ICP-OES elemental analysis.

Formulations

This was performed by blending of appropriate amounts of base oils followed by addition of fixed amounts of additives to the mixtures, and stirring for 10 minutes at 50°C. The details of formulations as well as, physical properties of formulated oil are given in the section of results and discussion.

Sampling

At the final running kilometer the sampling was performed immediately after turning off the car. Adequate amount of oil sample was taken by 100mL syringe.

Test methods

The test methods were followed as: ASTM D-445 for viscosity at 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-1500 for color, ASTM D-664 for total acid number, ASTM D-664 for total base number, ASTM D-6304 for water content, ASTM D-5800 for Noack, ASTM D-5293 for CCS, CEC L-33-A-93 for biodegradability, ASTM D-5183 for coefficient of friction (COF), ASTM D-4742 for oxidation stability.

Instrumental

All of the viscosities, viscosity indices and specific gravities were determined by viscometer Anton Paar 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. TBNs were determined by robotic titrosampler Metrohm model Dosiono 800. TANs were determined by titrator

Metrohm model Titrino MPT 789. The elemental analysis of the formulated oils, was performed by ICP-OES Perkin Elmer model Optima 5300 V. The detection limits (DLs) were obtained under simultaneous multielement conditions with the axial of a dual-view plasma using a cylonic spray chamber and a concentric nebulizer. All detection limits are given in microgram per liter and were determined using organometallic standards.

Results and discussion

The information due to versatile formulation of engine oils with different DOP content are given in Table 1. As it can be seen, the percentage of ester in different base oils varies from 0 to 40. The interval between the amount of ester in successive lubricants is 10%. In all of the formulated oils, the mixture of SN-150 (in variable amounts) and SN-500 (in constant amounts) has been employed as part of the base oil. Also, all of the engine oils contain similar additives with the same quantity. Thus, during the usage, upon monitoring the physical and chemical properties of various formulated oils, the effect of ester on their performance can be detected.

Table 1. Information due to formulation of engine oils containing different weight percentage of ester

Content	Percentage of Ester						
	0	10	20	30	40		
	Weight of Components (gr)						
SN-150	2800	2400	2000	1600	1200		
SN-500	800	800	800	800	800		
DOP	0	400	800	1200	1600		
Additive Package	280	280	280	280	280		
9325							
VI improver	120	120	120	120	120		

Table 2. Physical properties of SN-150, SN-500, and DOP

Property	Test Method	Value		
		SN 150	SN-500	DOP
Viscosity@40°C (cSt)	ASTM-D 445	33.3	105.1	26
Viscosity@100°C(cSt)	ASTM-D 445	5.61	12.20	4.2
Viscosity Index	ASTM-D 2270	105.9	93.0	14
Flash Point (°C)	ASTM-D 92	200	240	230
Pour Point (°C)	ASTM-D 97	-15	-3	-45

T.A.N (mg KOH/g)	ASTM-D 664	0.01	0.01	0.1
T.B.N mg (KOH/g)	ASTM-D 664	0.5	0.6	-
Sp.gr @ 15C (gr/mL)	ASTM-D1298	0.8732	0.8900	0.9821
Color	ASTM-D 1500	1.0	2.5	0.0
Noack %	ASTM-D 5800	10.6	4.3	20.1
Water Content (ppm)	ASTM- D 6304	35	30	100
CCS@ -15°C (cP)	ASTM-D 5293	31514	40000	1100

Physical properties of SN-150, SN-500, and DOP are given in Table 2. Comparison of different data indicates that kinematic viscosity of DOP and, as well as, its viscosity index are less than analogous values due to each of the mineral oils. So, it is anticipated that upon addition of DOP to each of the SN oils, or their blends, the mentioned properties to be diminished. On the other hand, the flash point of the ester is close to SN-500 (10 units difference), and considerably larger than SN-150 (30 units difference). Thus, it is expected that the flash point of the ternary mixtures of SN-150:SN-500:DOP, to be in close proximity to SN-500 or DOP values. Because of much lower pour point, it is imagined, that the ester does have substantial diminishing effect on this property. Higher TAN of DOP can be assigned to slight hydrolysis of ester. The Noack of DOP is not as good as the mineral oils; which means that upon addition of ester to the cited liquids, Noack enhancement will not occur. Water content of DOP is more than SN oils; which means that upon increase of ester fraction, the probability of happening of water simulated reactions will be increased. Significantly lower CCS of DOP, indicate that addition of ester will be along with CCS improvement. Finally, the zero color of DOP point out that after ester addition, positive impact on color will be observed.

Physical properties of virgin formulated oils, containing different ester percentage are given in Table 3. According to rheological properties of the formulated oils, all of them can be regarded as SAE 20W50. Due to amounts of employed additives, they are considered as API SL. It is observed that upon increase of ester content, the viscosity at 40 and 100°C, as well as viscosity index decrease systematically. Flash point does not show any systematic trend. Pour point has been decreased. Specific gravity has been raised up. Color has been improved. TAN have been raised up slightly, and TBN remained constant. Noack has been adjusted. Water content has been increased. CCS has been advanced.

The TBN and TAN mainly origin from additives. On the other hand in all of the formulations identical additives in equal amounts has been used. Thus, relatively constant values of cited properties are not unusual. The observed physical changes, upon addition of DOP (Table 3), are in accordance with prediction based on comparison of physical properties of mineral oils and DOP (Table 2).

It is interesting to note that upon addition of DOP to SN oils, the COF values have

Table 3. Typical properties of engine oils containing various percentages of ester; values in percentages are due to the oils after 5000 km usage

Property	Test method	Ester percentage						
		0	10	20	30	40		
				Value				
Viscosity@40°C	ASTM D-445	130.7	122.5	103.2	97.6	88.2		
(cSt)		(108.2)	(117.2)	(101.7)	(93.2)	(84.8)		
Viscosity@100°C	ASTM D-445	17.3	15.6	14.2	12.0	11.4		
(cSt)		(17.0)	(14.9)	(13.9)	(11.6)	(10.9)		
Viscosity Index	ASTM D-2270	142.1	140.6	139.6	137.2	135.7		
-		(157.4)	(154.3)	(152.0)	(147.6)	(145.5)		
Flash Point (°C)	ASTM D-92	225	222	220	230	235		
		(218)	(217)	(218)	(214)	(206)		
Pour Point (°C)	ASTM D-97	-18	-21	-24	-27	-27		
		(-21)	(-24)	(-21)	(-24)	(-18)		
Specific Gravity	ASTM D-1298	0.8779	0.8865	0.8983	0.9135	0.9291		
(gr/ mL)		(0.8864)	(0.8968)	(0.9040)	(0.9206)	(0.9384)		
Color	ASTM D-1500	5.5	5.0	4.5	4.0	3.0		
		(Dark)	(Dark)	(Dark)	(Dark)	(Dark)		
TAN (mg KOH/g)	ASTM D-664	0.01	0.02	0.03	0.04	0.05		
		(2.3)	(2.9)	(3.9)	(4.0)	(4.5)		
TBN (mg KOH/g	ASTM D-664	7.6	7.3	7.3	7.5	7.4		
		(2.9)	(3.1)	(3.9)	(4.1)	(4.4)		
Noack%	ASTM D-5800	4.8	5.1	5.7	5.8	5.9		
		(-)	(-)	(-)	(-)	(-)		
Water content	ASTM- D-6304	30	35 (29)	43	47	52		
		(26)		(38)	(4)	(4)		
CCS @ -15°C	ASTM D-5293	6650	6100	5726	5132	4350		
		(-)	(-)	(-)	(-)	(-)		
Coefficient of fric-	ASTM 5183	0.17	0.15	0.11	0.09	0.06		
tion		(-)	(-)	(-)	(-)	(-)		
Primary Biodegrad-	CEC L-33-A-93	17%	26%	33%	36%	38%		
ability		(-)	(-)	(-)	(-)	(-)		
Oxidation Stability	ASTM D-4742	213	199	183	170	164		
(min)		(-)	(-)	(-)	(-)	(-)		

been decreased (Table 3). This can be attributed to the polar functional groups in DOP molecule. Boundary lubrication in a dynamic system is primarily governed by the formation of stable tribological film. Carbonyl functional group in DOP molecule in conjunction with oil-additive-metal interaction during the metal rubbing process can significantly improve the wear resistance and extreme pressure lubrication. Increasing the polar functionality has a positive impact on wear protection resulting from stronger

adsorption on metal surface as well as stronger lateral interaction between the ester molecules (Adhvaryu et al., 2004).

Biodegradability defined as the ability to be rapidly decomposed by living organisms. The data in Table 3 indicate that primary biodegradability of formulated oil which merely has been formulated by mineral oil is low. However, upon ester addition, has been increased systematically. It is well known that one liter of oil can pollute thousands of liters of water. Hence using biodegradable lubricants is very important. As a consequence, increasing the cited property, can be regarded as an important advantage of ester containing formulations.

In contrast to enhanced biodegradability, ester addition caused reduction in oxidation stability (Table 3) in thin film oxygen uptake (TFOUT) test. This means that upon ester addition simultaneous enhancement of biodegradability and oxidation stability is not obtained. So, any formulation should be balanced according to the desired properties.

The results of measurements of physical properties of the oils with different ester content and after 5000 km usage are also given in Table 3 (the values in parenthesis). In order to have a better understanding about the amount and the direction of changes, upon usage the percentage of relative alterations due to each of the properties are also demonstrated in Table 4. Comparison of the data due to used oil with those of fresh ones (Table 3), indicate that in all cases, viscosities at 40 and 100°c have been reduced.

The viscosity of used engine oil can drop for reasons of fuel dilution or because of high water content and or shearing of VI improvers. Viscosity can increase because of heavy contamination of the oil by the soot, polymerization, vaporization losses, and emulsions due to water contamination and /or oxidation of the oil. Obviously the final status of the oil viscosity depends on the combination effects of decreasing and increasing factors. If the falling factors are overcome to the rising ones, the drop in viscosity will happen. An increase in the property will be observed in reverse conditions. The observation of the drop in viscosity indicates that dropping factors have conquered to increasing ones. The new produced gap in the viscosity at 40 and 100°, in the used oil, caused that viscosity index to be increased. Interestingly, the percentage of relative variations of viscosity index (Table 4), show decreasing trend upon ester increase, i.e. addition of more ester, prevent from extensive change of viscosity index.

Because of low flash points of most fuels a drop in flash temperature can usually related to fuel dilution. Occasionally, very high localized temperatures can lead to thermal cracking within the oil which results in diminishing the flash point. The formulations contain 0, 10, and 20% have shown minor decrease (-0.9% to -2.2%) in flash point (Tables 3 and 4). So, the possibility of fuel dilution or thermal cracking, in recent formulations, is discarded. However, tremendous decrease in flash point is observed for the formulations containing 30% (-6.9%) and 40% (-12.3%) of ester (Tables 3 and 4).

According to lower oxidation stability (Table 3), as well as, exists low hydrolytic

stability of ester (+0.02kg/gr). It seems that recent observation can be assigned to some oxidation and some hydrolytic cleavage of ester molecules; which causes the production of low molecular weight compounds, and subsequent drop of the flash point. The significant decrease of water content in used oils (Table 4) further support this idea.

TAN is a measure of the acidic constituents in petroleum products. The acidity of used oil is of interest to measure the degree of oxidation. TBN characterizes the alkaline reserve in petroleum products. In contrast relatively fixed values which is observed for TAN and TBN of the fresh oils (Table 3), the equivalent values due to used oils have been changed to various degrees (Tables 3 and 4). As it is seen, upon augmentation of ester fraction, the relative changes of TAN, enlarges more and more (Tables 3 and 4). Meanwhile, the absolute and relative alterations due to TBN values have been dropped off continuously (Table 4). The former observation can be attributed to production of acidic adducts under hydrolytic effect of water on ester which will be increased upon ester percentage. The later can be assigned to improved ability of the formulated oil (upon ester increment) in preventing depletion of additive reserves.

Table 4. The percentage of variations of typical properties of different DOP containing engine oils, after 5000 km usage

Property	Test Method		Ester Percentage					
		0	10	20	30	40		
				Value				
Viscosity@40°C (cSt)	ASTM D-445	-17.2	-4.3	-1.5	-4.5	-3.9		
Viscosity@100°C (cSt)	ASTM D-445	-1.7	-4.4	-2.1	-3.3	-4.3		
Viscosity Index	ASTM D-2270	10.7	9.7	8.9	7.6	7.2		
Flash Point (°C)	ASTM D-92	-2.2	-2.2	-0.9	-6.9	-12.3		
Pour Point (°C)	ASTM D-97	16.6	14.2	-12.5	11.1	33.3		
Specific Gravity (gr/ mL)	ASTM D-1298	1.0	1.2	0.6	0.8	1.0		
Color	ASTM D-1500	>100	>100	>100	>100	>100		
TAN (mg KOH/g)	ASTM D-664	>100	>100	>100	>100	>100		

TBN (mg KOH/g	ASTM	-61.8	-57.5	-46.6	-45.3	-41.3
	D-664					
Noack%	ASTM	-	-	-	-	-
	D-5800					
Water Content (ppm)	ASTM	-13.3	-17.1	-13.1	-91.5	-92.3
	D-6403					
CCS @ -15°C	ASTM	-	-	-	-	-
	D-5293					
Coefficient of Friction	ASTM	-	-	-	-	-
	D-5183					
Primary	CEC L-33-A-93	-	-	-	-	-
Biodegradability						
Oxidation Stability	ASTM	_	-	<u>-</u>	-	<u>-</u>
(min)	D-4742					

Table 5. Initial concentrations of various elements in different DOP containing engine oils

No	Element	Weight Percentage of DOP (DL= Detection limit)					
		0	10	20	30	40	
1	Zn	1060.6	1052.3	1061.6	1063.7	1065.7	
		(700.5)	(778.6)	(816.2)	(836.2)	(857.6)	
2	P	712.4	711.5	706.4	710.5	704.8	
		(539.6)	(585.2)	(593.4)	(605.9)	(611.6)	
3	Mg	1030.0	1026.0	1028.0	1025.0	1027.0	
		(831.5)	(937.1)	(953.0)	(956.0)	(963.0)	
4	Si	8.6	8.1	7.6	7.7	8.0	
		(11.8)	(11.1)	(8.9)	(8.3)	(6.4)	
5	Ca	183.3	176.3	181.4	172.5	179.5	
		(80.3)	(95.8)	(99.9)	(105.9)	(117.1)	
6	Ba	0.4	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>	
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7	В	5.7	7.3	6.2	6.0	10.0	
		(6.4)	(7.2)	(6.4)	(6.5)	(11.3)	
8	Mo	4.5	3.6	4.2	5.3	5.1	
		(6.1)	(4.3)	(5.1)	(5.9)	(6.1)	
9	Al	6.7	6.5	6.6	7.0	6.9	
		(8.2)	(5.2)	(4.5)	(4.0)	(3.2)	
10	Ag	0.4	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>	
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11	Cr	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""><th><dl< th=""></dl<></th></dl<></th></dl<>	<dl< th=""><th><dl< th=""></dl<></th></dl<>	<dl< th=""></dl<>
11	Cr					
		(6.5)	(5.8)	(5.2)	(4.6)	(4.0)
12	Ni	4.3	4.0	3.6	4.2	4.7
		(7.1)	(6.8)	(5.8)	(6.3)	(5.9)
13	Na	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
		(<dl)< td=""><td>(9.8)</td><td>(10.1)</td><td>(10.5)</td><td>(11.4)</td></dl)<>	(9.8)	(10.1)	(10.5)	(11.4)
14	Mn	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
		(4.7)	(3.8)	(3.0)	(2.8)	(2.3)
15	Fe	3.1	3.9	4.0	4.3	4.9
		(53.5)	(32.3)	(8.0)	(8.0)	(9.1)
16	Cu	0.3	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
		(0.6)	(0.3)	(0.2)	(<dl)< td=""><td>(<dl)< td=""></dl)<></td></dl)<>	(<dl)< td=""></dl)<>
17	Sn	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
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18	Ti	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
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19	V	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
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20	Pb	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
		(4.1)	(3.0)	(2.2)	(1.3)	(<dl)< td=""></dl)<>
21	Cd	0.7	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
		(0.9)	(<dl)< td=""><td>(<dl)< td=""><td>(<dl)< td=""><td>(<dl)< td=""></dl)<></td></dl)<></td></dl)<></td></dl)<>	(<dl)< td=""><td>(<dl)< td=""><td>(<dl)< td=""></dl)<></td></dl)<></td></dl)<>	(<dl)< td=""><td>(<dl)< td=""></dl)<></td></dl)<>	(<dl)< td=""></dl)<>
22	Sb	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""></dl<></td></dl<>	<dl< td=""></dl<>
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23	K	3.1	3.7	5.5	5.7	5.1
		(0.5)	(1.9)	(2.0)	(2.0)	(1.9)

The concentrations of twenty three elements which are included in various unused engine oils are given in Table 5. The data can be divided to three groups: (i) elements that their concentrations are more than 10 ppm; (ii) elements having concentrations less than 10 ppm; and (iii) elements that their concentrations are less than detection limit (DL). In fresh formulated oil, the existence elements, originate from two sources of base oil and additives. Usually the concentrations of the elements in the base oil are less than 10 ppm, sulfur is exclusion. Thus, the existence of the elements which their concentration in fresh oil is more than 10 ppm can mainly be attributed to employed additives. In all of the formulated oils, identical additives, in equal concentrations have been employed. So, it is expected that, in all of the formulated oils, the amounts of additive originated elements to be nearly equal. Really, the anticipated prediction has been observed. The concentrations of additive originated elements have not varied significantly in different oils.

Upon the oil application, depletion in additives is occurred. In fact, at high engine temperature, the additives are degraded and some of the resulting degradation products are absorbed by the filter or contacting surfaces (Wessol & Pirro, 2001). Which result in lowering of the concentrations of the corresponding elements in the oil.

Wear metals will appear in the oil because of wearing of different parts of engine, Fe is the most common of the wear metals. Present in some form in virtually all equipment. Its widespread presence means that there are many sources of the wear particles. It can be found in cylinder liners, piston rings, valve train, crankshaft, rocker arms, spring gears, lock washers, nuts, pins, connecting rods, engine blocks, oil pump. Copper, tin, aluminum, lead, and chromium, are some of the other wear elements.

The concentrations of different elements in various formulated oils after 5000 km usage are also given in Table 5. With the aim of more clarity, the relative alterations are also given in Table 6. Upon the comparison of the former numbers, with the data due to virgin oils, the reduction in quantities of additive originated elements is confirmed. Upon ester increase, a systematic lessening in absolute percent of reduction is observed (Table 6). This means that increase of ester fraction has a positive impact on depletion of additives. The data are in accordance with the mode of TBN changes (Tables 3 and 4). As it was noted, in formulations with higher ester content, lower decrease in TBN have been occurred. Enhancement effect on suppression of additive depletion is an important advantage. Such property indicates that upon long term operation of the oil, enough additive reserve will be present, and ensures the proper performance of the oil.

Table 6. The percentage of variations of concentrations of various elements, in different DOP containing engine oils, after 5000 km usage

No	Element	Weight Percentage of DOP					
		0	10	20	30	40	
1	Zn	-34.0	-26.0	-23.1	-21.4	-19.5	
2	P	-24.2	-17.8	-16.0	-14.7	-13.2	
3	Mg	-9.6	-8.7	-7.3	-6.7	-6.2	
4	Si	37.2	37.0	17.1	-4.5	5.0	
5	Ca	-56.2	-45.7	-44.9	-38.6	-34.8	
6	Ba	0	-	-	-	-	
7	В	12.2	10.0	3.2	8.3	13.0	
8	Mo	35.5	19.4	21.4	11.3	19.6	
9	Al	22.4	-20	-31.8	-42.9	-53.6	

10	Ag	-	-	-	-	-
11	Cr	-	-	-	-	-
12	Ni					
13	Na	-	-	-	-	-
14	Mn	-	-	-	-	-
15	Fe	» 100	> 100	100.0	86.0	85.7
16	Cu	100	-	-	-	-
17	Sn	-	-	-	-	-
18	Ti	-	-	-	-	-
19	V	-	-	-	-	-
20	Pb	-	-	-	-	-
21	Cd	28.5	-	-	-	
22	Sb	-	-	-	-	-
23	K	-83.0	-48.6	-63.6	-64.9	-62.7

The demonstrated data in Tables 5 and 6, indicate that upon addition of ester, significant reduction in the wear of Fe containing parts, have been occurred; which is in agreement with the observation of reduction in coefficient of friction in ester containing blends.

An overall view to the obtained data, specifies that by employing 20% ester, a balance of integrated properties will be obtained. In fact most of the ester benefits are achieved in formulation containing 20% DOP. Upon further augment, significant advantage will not attained. Thus, it can be claimed that the recent percent is an optimum value for ester formulation. Because of higher price of esters, such a result does have economic importance.

Conclusion

Based on the obtained data it can be concluded that: (A) Upon blending of DOP with SN base oils, gasoline engine oils, with appropriate lubrication properties can be obtained; (B) The increase of ester percentage result in enhancement of properties such as biodegradability, coefficient of friction, wear, suppression of additive depletion, CCS, color, and pour point; (C) Lower oxidation stability and higher hydrolytic stability are the disadvantages of ester containing formulations; (D) Most of the advantages of ester will be gained until 20%. So, upon further ester addition, considerable enrichment in the formulated oils will not be obtained.

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☑ Dr. Abolfazl Semnani (corresponding author)

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