

Lube Oil Blending and Use of Polymers as Additive

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ABSTRACT. Heavy petroleum fractions can be mixed with neutrals to give blends having somewhat higher viscosity index than the arithmetical mean of the initial stocks. But the use of polymeric materials so-called viscosity index improvers yields far higher viscosity index values. In this study, it was observed that polymethacrylate is more effective as an oil viscosity index improver than ethylene-propylene copolymer. Alkylated polystyrene is also suitable for use as a viscosity index improver for lubricating oils. As the degree of alkylation increases, the polymer becomes more soluble in oil, consequently the viscosity index improving performance of the polymer increases.

Viscosity index VI, is an empirical number indicating the effect of change of temperature on the viscosity of an oil. Its value can be calculated from the viscosity measurements of fluids at 100°F and 210°F as mentioned in literature (Bonet 1956). For this purpose, in the first part of this study two kinds of polymers were considered and their blends in four different base stock oils were studied.

Then, some additives as VI improvers were produced by alkylating polystyrenes of different molecular weights with different alkylating agents. The effectiveness of these additives were examined after blending with various base stock oils.

Molecular weight, the degree of alkylation and the size of alkyl group were the main factors studied for their influence upon the VI improving effect of the polymer.

Material and Methods

The various blends were prepared by using basically two types of base stock lubricating oils; namely paraffinic and naphthenic. The properties of base stock oils are given in Table 1. In order to determine the effectiveness of the polymer in question, binary mixtures of different polymer concentrations were prepared for each oil class.

After blending, viscosities and viscosity indices of these oils were calculated according to ASTM methods.

Polystyrenes were alkylated with different tertiary alkyl-chlorides in the presence of anhydrous aluminium chloride catalyst while having the polystyrene(s) dissolved in an inert solvent such as cyclohexane as it was done in earlier works of Semerci and Yorulmaz (1980).

Polystyrene having a molecular weight of 210,000 was alkylated with tertiary butyl chloride and tertiary pentyl chloride. Alkylation of polystyrene of 210,000 molecular weight was also carried out, varying the amount of alkylating agent, thus obtaining products of two different degree of alkylation.

Another polystyrene which had a molecular weight of 140,000 was alkylated with tertiary butyl chloride.

Discussion

The study of two kinds of polymeric additives and their VI improving performances are given in Tables 2 and 3. It is seen that polymethacrylate is more effective than the olefinic copolymer which is ethylene-propylene copolymer (EPC). The effectiveness of olefinic copolymer as a VI improver decreases with increasing viscosity of the base oil more than that of polymethacrylate.

The outstanding ability of polymethacrylates to produce blends possessing excellent viscosity-temperature properties may be attributed to the fact that they are polymeric esters (Horne 1949). Esters, as a class of compounds are notable for possessing good viscosity-temperature characteristics (Evans and Young 1947). A desirable property of the polymethacrylate viscosity index improver is that the increase in viscosity index is accompanied by relatively little increase in viscosity at the lower temperature (100°F).

It is also proposed that alkylated polystyrene is suitable for use as viscosity index improver for lubricating oils (Bonet 1956).

The effectiveness of the alkylated polystyrene products were examined by making some changes in the structure of the products such as; changing the degree of alkylation, the molecular weight of the starting polystyrene reactant and the alkylating agent.

Tertiary alkyl groups were attached to the polystyrene rings in para form without disturbing the structure of the main polymer chain. Polystyrene is insoluble in oil, the attached alkyl groups make it soluble, thus provide the primary requisite for the polymer to be used as a VI improver.

The results obtained with p-tertiary butyl polystyrene additives, PBS(2), PBS(L), PBS(1) produced are given in Table 4 and Table 5.

Another product, PBS(1), was obtained by using an amount of alkylating agent which was half of that was used in the formulation of the product, PBS(2). It was observed that the VI improving performance of this product is about 6% less than the previous one.

The possible explanation for this reduced performance is as follows: As the degree of alkylation is decreased the polymer molecules form a loosely knit network due to unalkylated styrene monomer blocks in the polymer which are not very soluble in oil. Because of this effect, a low polymer concentration results in a steep rise of the solution viscosity. In other words, it contributes more to low temperature viscosity resulting in a decreased thickening performance compared to the one which has higher degree of alkylation.

Another product, PBS(L), can be obtained by alkylating a lower molecular weight polystyrene. It is observed that the product of higher molecular weight shows higher performance than that of lower molecular weight. So, for a given type of viscosity index improver it can be said that within limits, the higher the molecular weight the more effective or efficient it becomes.

But as the length of the molecule increases, its susceptibility to mechanical shear also increases thus limiting the degree of polymerization of polymers that can be utilized. Of course, a high molecular weight polymer will have a relatively larger effect on the viscosity since it influences the behaviour of more solvent molecules than could a lower molecular weight polymer.

As the last product the higher molecular weight polystyrene was alkylated with tertiary pentyl chloride, PPS. The thickening performance of this product was not as good as the one produced from tertiary butyl chloride. It was observed that this product contributes more to the base oil viscosity while having less viscosity index increasing effect compared to the p-tertiary butyl polystyrene. The increase in viscosity may be attributed to the increased branching in the configuration of the polymer molecule.

The addition of a viscosity index improver inevitably raises the viscosity of the oil. The initial viscosity and viscosity index of an oil largely determine the results produced by a fixed amount of VI improver.

For oils of about the same viscosity, the thickening effect is slightly less for paraffinic oils than naphthenic stocks. But even with latter type a 70 pale oil can be

brought to 100 VI with a surprisingly little thickening.

When using a VI improver to obtain a considerable increase in VI, it is of course necessary to use a base stock of lower viscosity than desired for the final blend in order to allow for the viscosity increase accompanying the addition of polymer. For this reason, it is important for the polymer to produce the desired VI gain with as little thickening as possible. So the selection of the viscosity and viscosity index of a base stock is of particular importance in using improver to obtain blends qualifying for two or more viscosity grades. Usually it is desired to use the minimum amount of polymer for this purpose.

At low concentration of polymer in solvent oil, the polymer is completely dispersed and exerts its optimum thickening effect. However, as the concentration of polymer in solvent oil is increased the relative thickening power decreases, until at higher concentrations further addition of polymer has less effect on viscosity.

As result, the choice of which particular VI improver for use when formulating a multi-grade oil depends on some important and related factors as given below:

- Viscosity of finished oil
- Viscosity of oil after its use
- Availability of base stocks
- Product availability and cost

Conclusion

It was concluded that the polymethacrylate viscosity index improver is more effective than the olefinic copolymer.

Polystyrene can be used as a viscosity index improver when it is alkylated with suitable tertiary alkyl halides as alkylating agents.

Degree of alkylation is an important parameter in formulation of p-tertiary alkyl polystyrene VI improver. As the degree of alkylation increases the polymer solubility in oil increases, consequently the VI improving performance of the additive increases.

The molecular weight has an overriding effect on the VI improving performance of a VI improver. As the molecular weight increases the effectiveness of the polymer as a VI improver increases.

As the size of the alkyl group attached to the styrene ring increases, the VI improving effect of the polymer decreases while its contribution to base oil viscosity increases.

Base oil viscosity is an important factor in multigrade oil formulation. As the base oil viscosity increases the thickening effect of the polymer decreases, so the

selection of polymer-base oil couple is of particular important in formulation of a desired grade of oil.

The thickening effect of a polymer increases with concentration of oil up to a certain limit. Addition of additive beyond this concentration has less effect on VI of the oil, that is the VI of the oil remains almost constant but the viscosity of the oil increases.

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Table 1(a). Properties of Base Stock Oils

Properties	Standards	Units	Pale Oil-70	Spindle Oil	SAE 10	SAE 30
Appearance	—	—	clear	clear	clear	clear
Viscosity 100 F°	ASTM D-445	cst.	13.97	15.37	36.41	119.24
Viscosity 210 F°	ASTM D-445	cst.	2.79	3.51	6.07	12.51
Viscosity Index	ASTM D-2270	—	16.0	107.5	110.0	102.0
Pour Point	ASTM D-97	C	-40(max)	-6(max)	-15	-9
Color	ASTM D-1500	—	1.5(max)	1.5(max)	2(max)	3(max)
Flash Point COC	ASTM D-92	C	154.4	166	216	240

Table 1(b). Properties of Polystyrene - PETREN K-500

Properties	Standard	Units	
Melt Flow Index	ASTM 1238-G	gr/10 min	9-14
Solution Viscosity	ASTM D-445	cst.	10-15
Volatile Content	COSDEN PS-39L	% wt.	0.8-0.9(x)
Monomer Content	CSN-640321	% wt. Kg/cm^2	0.25 max
Tensile Strength	ASTM D-638-58T	%	320/260(x)
Tensile Elongation	ASTM D-638-58T	Kg/cm^2	N.A.
Flexural Strength	ASTM D-790-58T	$Kg/cm/cm$	570/500(x)
Izod Impact	ASTM D-256-56	°C	1.3/0.19(x)
Vicat Temperature	ASTM 1525-65T	—	78/75(x)
Av.Mol.wt.	—	—	210000

(x) When purity of polystyrene is 99.4 - 99.5%.

Table 1(c). Properties of Polystyrene - 625

Properties	Standards	Units	
Melt Flow Index	ASTM 1238-G	gr/10 min	14-17
Solution Viscosity	ASTM D-445	cst.	9.5-12.5
Volatile Content	COSDEN PS-39L	% wt.	0.5/0.7
Monomer Content	CSN-640321	% wt.	0.3
Izod Impact	ASTM D-256-56	$Kg/cm/cm$	—
Av.Mol.wt.	—	—	140,000

Table 2(a). Viscosity-Temperature Characteristics of Pale Oil-70/Polymethacrylate Blends

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil	
				Crankcase	Gear
0.0	13.97	2.79	16.0	—	—
2.0	17.47	3.69	103.0	—	—
4.0	20.37	4.72	127.5	—	—
6.0	27.58	6.48	141.5	—	—
8.0	30.32	7.92	156.5	10W/10	—
10.0	37.32	9.99	161.5	10	—
12.0	40.77	10.78	161.0	20	—
14.0	55.57	13.80	158.0	20	—

Table 2(b). Viscosity-Temperature Characteristics of Spindle Oil/Polymethacrylate Blends

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil	
				Crankcase	Gear
0.0	15.37	3.51	107.5	—	—
2.0	19.00	4.47	126.0	—	—
4.0	20.81	5.44	147.0	—	—
6.0	25.66	7.00	158.0	—	—
8.0	29.41	8.34	165.0	—	—
10.0	35.80	10.27	167.5	10	—
12.0	38.94	11.12	167.5	10	—
14.0	49.39	13.94	167.5	10	—

Table 2(c). Viscosity-Temperature Characteristics of SAE 10/Polymethacrylate Blends

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil	
				Crankcase	Gear
0.0	36.41	6.07	110.0	10	—
2.0	40.66	6.88	116.0	10	—
4.0	46.85	8.08	122.5	20W/20	—
6.0	54.51	9.58	128.0	20W/20	—
8.0	64.05	11.77	135.0	20W/20	—
10.0	66.78	13.35	142.5	10W/30	—
12.0	79.04	15.73	144.0	10W/50	80
14.0	88.81	17.56	145.5	20W/50	80

Table 2(d). Viscosity-Temperature Characteristics of SAE 30/Polymethacrylate Blends

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil	
				Crankcase	Gear
0.0	119.24	12.51	102.0	30	—
2.0	123.33	13.90	108.5	40	—
4.0	136.28	15.91	113.0	50	—
6.0	147.63	18.40	119.5	50	—
8.0	157.63	20.96	125.5	50	80/90
10.0	166.26	23.70	131.0	20W/60	80/90
12.0	187.84	27.28	134.0	20W/70	80/140
14.0	208.96	29.92	135.0	—	80/140

Table 3(a). Viscosity-Temperature Characteristics of Pale Oil-70/Ethylene-propylene Copolymer Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil	
				Crankcase	Gear
0.0	13.97	2.79	16.0	—	—
2.0	17.06	3.52	90.0	—	—
4.0	19.63	4.05	106.5	—	—
6.0	24.03	4.80	114.0	—	—
8.0	27.78	5.71	125.0	10W/10	—
10.0	32.15	6.50	128.0	10W/10	—
12.0	39.35	7.69	130.5	10W/20	—
14.0	48.88	8.98	130.0	20W/20	—

Table 3(b). Viscosity-Temperature Characteristics of Spindle Oil/Ethylene-propylene Copolymer Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil	
				Crankcase	Gear
0.0	15.37	3.51	107.5	—	—
2.0	17.57	3.93	113.0	—	—
4.0	22.72	4.75	117.5	—	—
6.0	25.51	5.26	122.0	10W/10	—
8.0	29.48	5.95	125.5	10W/10	—
10.0	34.85	6.90	128.5	10W/10	—
12.0	41.27	7.94	130.5	10W/20	—
14.0	50.70	9.25	130.0	10W/20	—

Table 3(c). Viscosity-Temperature Characteristics of SAE 10/Ethylene-propylene Copolymer Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil Crankcase	Gear
0.0	36.41	6.07	110.0	10	—
2.0	42.29	6.78	111.0	10	—
4.0	48.47	7.57	113.0	20W/20	—
6.0	62.46	9.18	114.5	20W/20	—
8.0	64.49	9.62	117.0	20W/20	—
10.0	76.87	11.16	118.5	20W/20	—
12.0	86.76	12.47	120.0	20W/30	—
14.0	100.62	14.62	120.5	20W/40	—

Table 3(d). Viscosity-Temperature Characteristics of SAE 30/Ethylene-propylene Copolymer Blends.

Addi- tive % by vol.	Vis- cosity 100° F	Vis- cosity 210° F	Vis- cosity Index	Blended Cr- ankcase	Oil Gear
0.0	119.24	12.51	102.0	30	—
2.0	130.15	13.64	104.0	40	—
4.0	145.36	15.00	105.5	40	80
6.0	160.13	16.42	107.0	50	80
8.0	185.79	18.51	108.5	50	80/90
10.0	202.60	19.93	109.5	50	90
12.0	223.27	21.58	110.0	50	90
14.0	267.33	24.51	110.5	60	90

Table 4(a). Viscosity-Temperature Characteristics of Pale Oil-70/PBS(2) Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil Crankcase	Gear
0.0	13.97	2.79	16.0	—	—
1.0	22.06	4.80	122.5	—	—
2.0	33.06	6.96	134.5	10W/10	—
3.0	48.07	9.97	141.0	10W/20	—
4.0	67.00	13.83	145.0	10W/30	—
5.0	97.67	19.02	145.5	10W/50	—
6.0	133.33	24.73	146.0	10W/60	—
7.0	173.98	30.73	146.0	—	80/140

Table 4(b). Viscosity-Temperature Characteristics of Spindle Oil/PBS(2) Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil Crankcase	Gear
0.0	15.37	3.51	107.5	—	—
1.0	22.79	5.12	129.0	—	—
2.0	31.33	7.17	142.5	10W/20	—
3.0	41.58	9.48	147.5	10W/20	—
4.0	60.64	13.31	149.0	10W/30	—
5.0	77.00	16.90	151.5	10W/50	80
6.0	110.39	22.82	151.0	10W/60	80
7.0	136.51	26.97	150.5	70	80/140

Table 4(c). Viscosity-Temperature Characteristics of SAE 10/PBS(2) Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil Crankcase	Gear
0.0	36.41	6.07	110.0	10	—
1.0	57.29	8.78	116.5	20W/20	—
2.0	76.56	11.63	122.0	20W/30	—
3.0	119.70	16.72	124.0	20W/50	80
4.0	166.94	21.87	125.5	20W/50	80/90
5.0	233.04	29.00	127.5	—	80/90/140
6.0	301.17	35.99	129.0	—	80/90/140
7.0	387.94	44.21	130.0	—	—

Table 4(d). Viscosity-Temperature Characteristics of Pale Oil-70/PBS(1) Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil Crankcase	Gear
0.0	13.97	2.79	16.0	—	—
1.0	24.92	4.98	116.0	—	—
2.0	36.41	7.05	127.5	10W/20	—
3.0	51.31	10.17	138.0	10W/20	—
4.0	73.36	13.94	138.0	20W/30	—
5.0	106.30	19.13	140.5	20W/50	80
6.0	144.23	24.77	141.5	20W/60	80
7.0	190.56	31.13	142.0	—	80/140

Table 5(a). Viscosity-Temperature Characteristics of Spindle Oil/PBS(1) Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil Crankcase	Gear
0.0	15.37	3.51	107.5	—	—
1.0	23.34	5.14	127.0	—	—
2.0	32.86	7.26	139.5	10W/20	—
3.0	49.49	10.75	145.5	10W/20	—
4.0	64.96	13.83	147.0	10W/30	—
5.0	94.48	18.95	147.0	10W/50	80
6.0	132.19	24.94	147.0	10W/60	80
7.0	168.99	30.12	147.0	—	80/140

Table 5(b). Viscosity-Temperature Characteristics of Pale Oil-70/PBS(L) Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil Crankcase	Gear
0.0	13.97	2.79	16.0	—	—
1.0	21.54	4.50	114.5	—	—
2.0	31.13	6.52	131.5	10W/10	—
3.0	46.85	9.28	136.0	10W/20	—
4.0	63.58	12.03	137.0	20W/30	—
5.0	95.62	16.79	137.5	20W/50	80
6.0	132.64	21.91	138.0	20W/60	80
7.0	172.62	27.28	138.5	—	80/140

Table 5(c). Viscosity-Temperature Characteristics of Spindle Oil/PBS(L) Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil Crankcase	Gear
0.0	15.37	3.51	107.5	—	—
1.0	22.24	4.99	127.5	—	—
2.0	30.12	6.75	138.5	10W/10	—
3.0	39.24	8.91	146.5	10W/20	—
4.0	53.95	11.78	147.0	10W/20	—
5.0	70.86	15.00	147.5	10W/30	80
6.0	102.66	20.59	148.0	10W/50	80
7.0	134.45	25.70	148.0	10W/60	80/140

Table 5(d). Viscosity-Temperature Characteristics of Pale Oil-70/PPS Blends.

Additive % by vol.	Viscosity 100°F	Viscosity 210°F	Viscosity Index	Blended Oil Crankcase	Gear
0.0	13.97	2.79	16.0	—	—
1.0	22.90	4.75	117.0	—	—
2.0	36.81	7.26	130.0	10W/20	—
3.0	51.21	9.99	136.5	10W/20	—
4.0	79.72	15.22	141.0	20W/30	80
5.0	104.71	19.24	142.0	20W/50	80
6.0	139.91	24.44	142.5	20W/60	80
7.0	188.52	31.13	142.5	—	80/140

مزج زيت التزليق باستعمال البولمر مادة مضافة

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من الممكن مزج أجزاء ثقيلة من النفط مع مواد محايدة للحصول على مزيج ذي مؤشر للزوجة أعلى نوعاً من الوسط الحسابي للزوجة الخامات الأولية. إلا أن استعمال المواد البوليدية (المركبات المتضاعفة الأصل) التي تدعى بمحسنات مؤشر اللزوجة، يؤدي إلى قيم عالية لمؤشر اللزوجة. وفي هذه الدراسة، لوحظ أن بوليمتاكرايليت أكثر تأثيراً كمحسن مؤشر لزوجة الزيت من البولمر الاسهامي لمادتي الايثلين والبروبيلين. كذلك فإن مبلمر الستايرين الايثلين والبروبيلين. كذلك فإن مبلمر الستايرين المقلون ملائم أيضاً لاستعمال كمحسن مؤشر لزوجة زيوت التزليق. وكلما زادت درجة القلونة فإن البولمر يغدو أكثر انحلالاً في الزيت، ونتيجة لذلك فإن إداء تحسين مؤشر اللزوجة للبولمر يزداد.