Alkylated polymers as lube oil additives

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It is proposed that alkylated polystyrene is suitable for use as a viscosity index improver for lubricating oils. It can be prepared by alkylating polystyrene with tertiary alkyl chlorides or bromides from 4 to 8 carbon atoms in the presence of aluminium chloride or bromide as catalyst while having the polystyrene dissolved in an inert solvent. It was observed that as the degree of alkylation increases the polymer becomes more soluble in oil, consequently the viscosity index improving performance of the polymer increases. It was also seen that as the size of the alkyl group attached to the polystyrene ring increases, the viscosity index, VI, improving performance of the polymer decreases. Molecular weight of a polymer has a great influence upon the VI improving effect of the polymer. As it is increased the thickening performance also increases. The experimental data showed that the thickening effect of a polymeric viscosity index improver decreases with increasing viscosity of the base oil.

1. Introduction

The mixing of relatively high molecular weight materials in various solvents to obtain fluids of superior viscosity temperature properties has long been known [1]. Application of this principle in the preparation of lubricating oils is becoming a matter of increasing importance and usefulness.

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 and 210° F* [2–4].

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, called viscosity index improvers, yields higher viscosity index values [5].

Some additives such as VI improver, 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 in the hope of obtaining the selection of an ideal one.

2. Methods and experiments

For the purpose of this study, domestically produced polystyrenes were alkylated with different tertiary alkylchlorides in the presence of anhydrous aluminium chloride catalyst while having the polystyrene dissolved in an inert solvent which was cyclohexane.

Polystyrene, K-500, which has 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, by varying the amount of alkylating agent, and thus obtaining products of two different degrees of alkylation. Another polystyrene which had a molecular weight of 140 000 was alkylated with tertiary butyl chloride. Table I gives the materials and product labels.

The various blends were prepared by using basically two types of base stock lubricating oils; namely parafinic and napthenic. The properties of base stock oils are given in Table II. In order to determine the effectiveness of the polymer in

TABLE I Raw materials and product labels

Product label	Polystyrene used	Alkylating agent
PBS(1)	K-500	t-butyl chloride
PBS(2)	K-500	t-butyl chloride
PBS(L)	625	t-butyl chloride
PPS	K-500	t-pentyl chloride

*1° F = (9/5)° C + 32.

0022–2461/83 $03.00 + .12

TABLE II 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	36.4	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
Colour	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

question, binary mixtures of different polymer concentration were prepared for each oil class.

After blending, viscosities and viscosity indices of these oils were calculated to ASTM methods [6].

3. Results and discussions

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

Tertiary alkyl groups were attached to the polystyrene rings in *para* form without disturbing the structure of the main polymer chain. Poly-

TABLE IIIA Viscosity–temperature characteristics of pale oil-70/PBS(2) blends

Additive (wt %)	Viscosity		Viscosity index	Blended oil	
	100° F	210° F		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	80
6.0	133.33	24.73	146.0	10W/60	80
7.0	173.98	30.73	146.0	–	80/140

TABLE IIIB Viscosity–temperature characteristics of spindle oil/PBS(2) blends

Additive (wt %)	Viscosity		Viscosity index	Blended oil	
	100° F	210° F		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/30/50	80
6.0	110.39	22.82	151.0	10W/60	80
7.0	136.51	26.97	150.5	70	80/140

TABLE IIIC Viscosity–temperature characteristics of SAE 10/PBS(2) blends

Additive (wt %)	Viscosity		Viscosity index	Blended oil	
	100° F	210° F		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 IVA Viscosity–temperature characteristics of pale oil-70/PBS(1) blends

Additive (wt %)	Viscosity		Viscosity index	Blended oil	
	100° F	210° F		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	139.5	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 IVB Viscosity–temperature characteristics of spindle oil/PBS(1) blends

Additive (wt %)	Viscosity		Viscosity index	Blended oil	
	100° F	210° F		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

styrene is insoluble in oil, but the attached alkyl groups make it soluble in oil thus providing 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 Tables III to VI and Figs. 1 to 4.

Another product, PBS(1), was obtained by using an amount of alkylating agent that was half of that used in the formulation of the product, PBS(2). It was observed that the VI improving

TABLE VA Viscosity–temperature characteristics of pale oil-70/PBS(L) blends

Additive (wt %)	Viscosity		Viscosity index	Blended oil	
	100° F	210° F		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 VB Viscosity–temperature characteristics of spindle oil/PBS(L) blends

Additive (wt %)	Viscosity		Viscosity index	Blended oil	
	100° F	210° F		Crankcase	Gear
0.0	15.37	3.51	107.0	–	–
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 VI Viscosity–temperature characteristics of pale oil-70/PPS blends

Additive (wt %)	Viscosity		Viscosity index	Blended oil	
	100° F	210° F		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	80/140
7.0	188.52	31.13	142.5	–	–

performance of this product was 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 the 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 than to high temperature viscosity resulting in a decreased thickening performance compared to the one which has the higher degree of alkylation.

Another product, PBS(L), can be obtained by using a lower molecular weight polystyrene in alkylation. It was 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.

However, as the length of the molecular 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 a lower molecular weight polymer can.

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

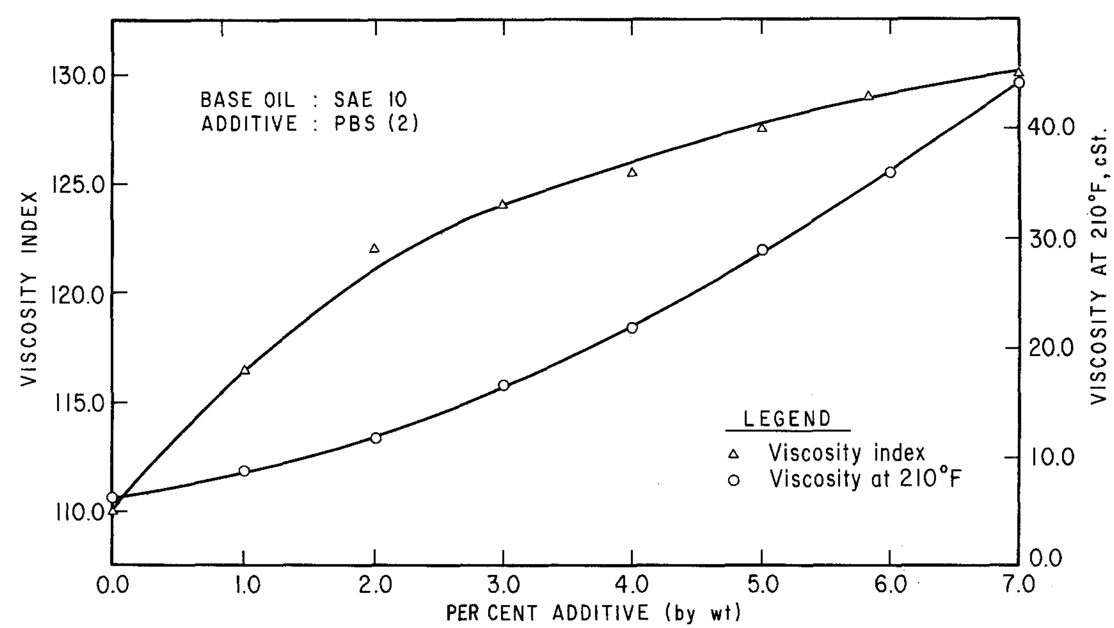

Figure 1 Viscosity–temperature behaviour of SAE 10/PBS(2) blends.

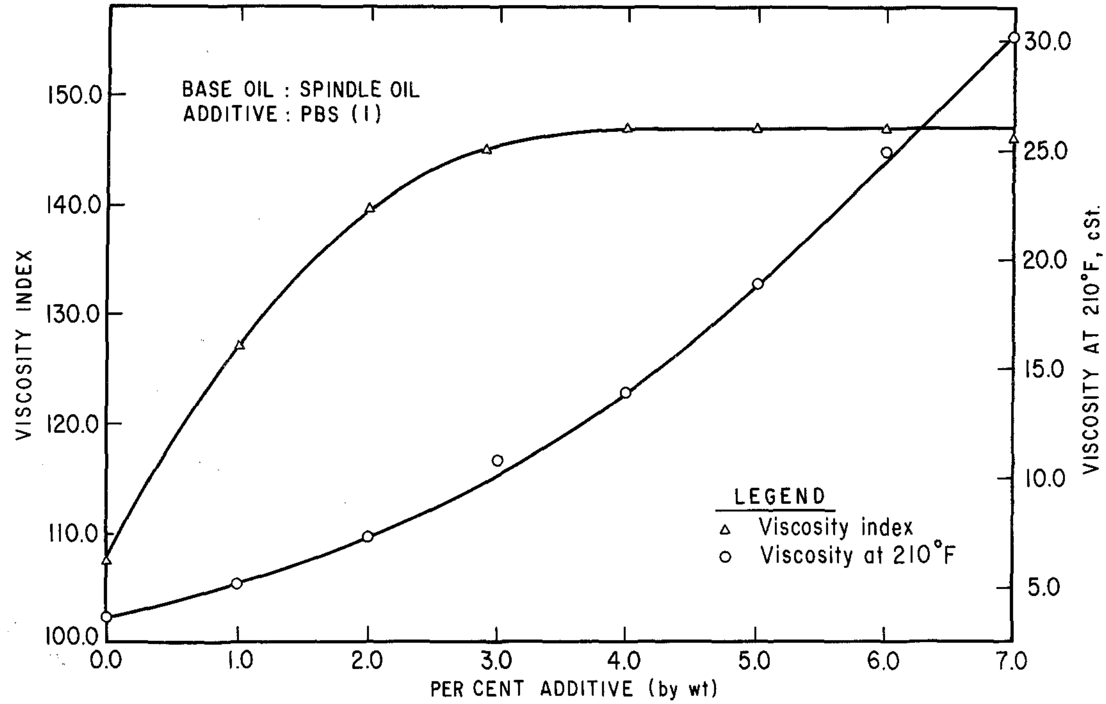

Figure 2 Viscosity–temperature behaviour of Spindle oil/PBS(1) blends.

the base oil viscosity while having a smaller viscosity index increasing effect compared to the *p*-tertiary butyl polystyrene. The increase in viscosity may be attributed to the increased molecular weight due to the pentyl group and 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

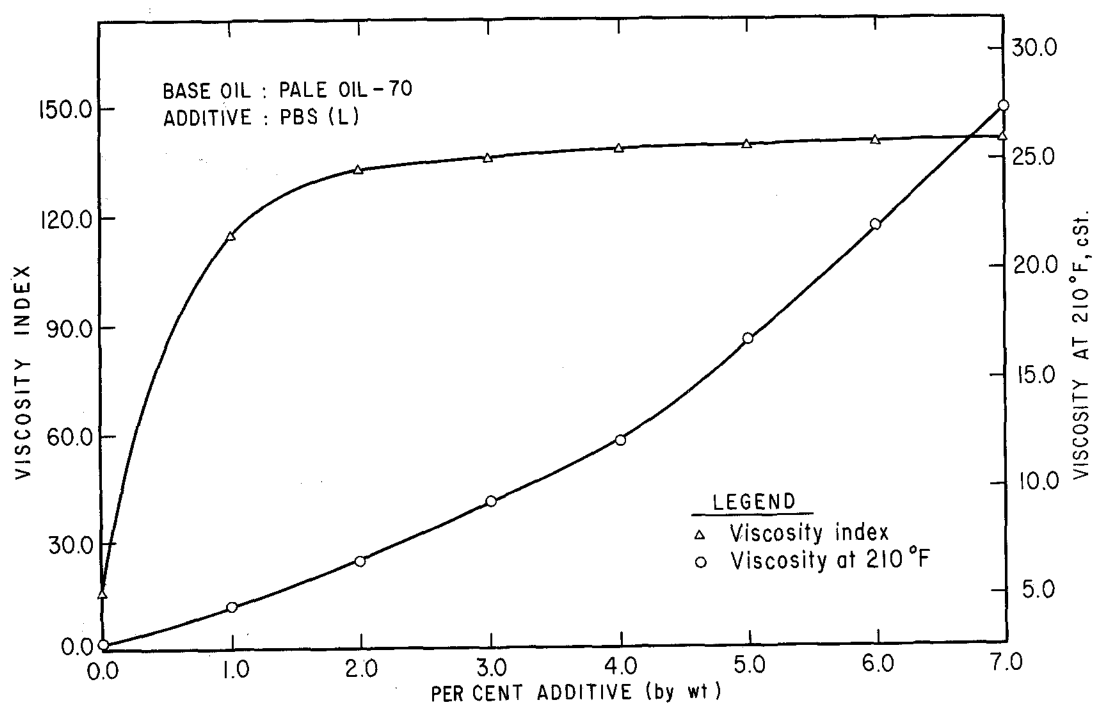

Figure 3 Viscosity–temperature behaviour of Pale oil-70/PBS(L) blends.

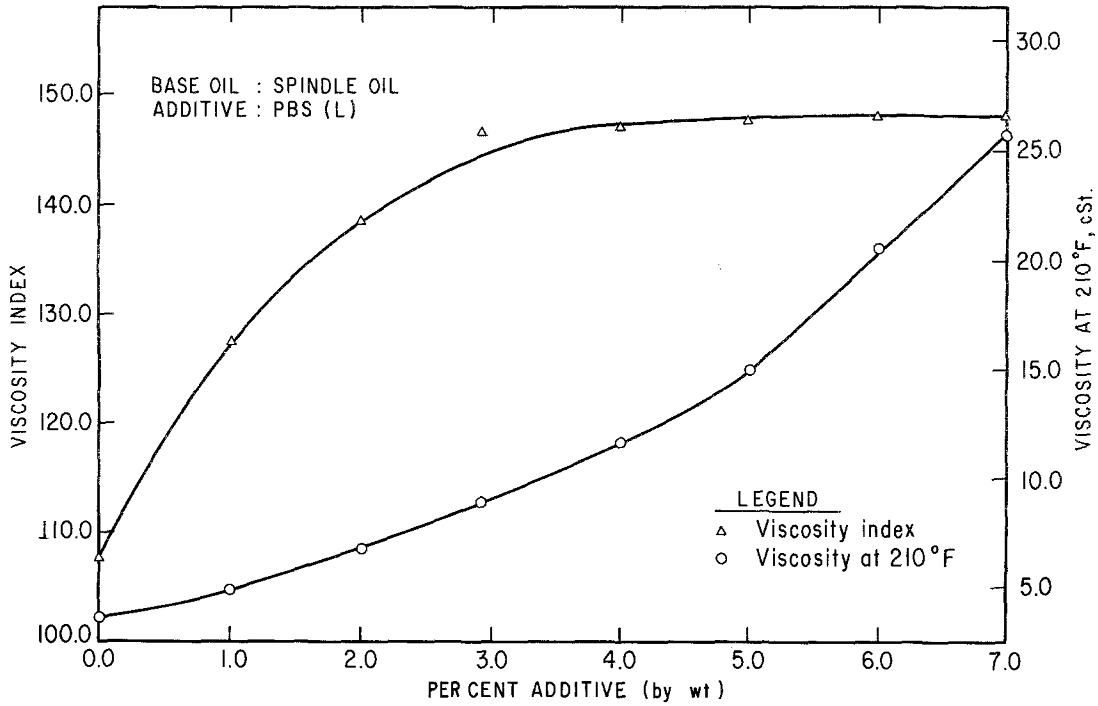

Figure 4 Viscosity–temperature behaviour of Spindle oil/PBS(L) blends.

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 parafinic oils then napthenic stocks. But even with the latter type a 70 pale oil can be brought to 100 VI with 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 concentrations 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 the viscosity.

The trend in VI improvement of the polymers used agreed well with the ones studied in literature [7].

4. Conclusion

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

The degree of alkylation is an important parameter in the formulation of *p*-tertiary alkyl polystyrene VI improver. As the degree of alkylation increases the polymer solubility in oil increases, and 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, the selection of the polymer–base oil couple is of particular importance in the formulation of a desired grade of oil.

The thickening effect of a polymer increases with concentration in oil up to a certain limit, and addition of additive beyond this concentration has less effect on the VI of the oil, e.g. the VI of the oil remains almost constant but the viscosity of the oil increases.

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