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Influenced of EPDM viscosity index improvers on Kurdistan manufacturing oils

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Abstract— Effects of different types of EPDM (ethylene-propylene-dine monomer) improvers in manufacturing of engine oil grades (SAE-30, SAE-40, and SAE-50) on thermal properties of these oils have been investigated. The additives type (KEP270, DE3071, K 4802, DCR3 and PA 6205) were used to prepare grades (SAE-30, SAE-40 and SAE-50). The solutions were characterized by determination specific gravity, viscosity index, flash point and pour point. The effect of temperature (from40 oC to 100 oC) and concentration (from 0.5 to 3.5 w/v %) have been also studied.

Index Terms— Activation energy, Arhhinues, Base oil, EPDM, SAE-grade, Viscosity improver, viscosity index.

1 Introduction

Lubricants and lubrication techniques are an indispensable feature of all machinery, ranging from applications which enable the manipulation of very small parts to the movement of very heavy masses. The general move towards more severe operating conditions in a drive for greater economics and overall efficiency has led to an increase in the significance of lubricant viscosity, and more specifically lubricant behaviour with changing temperatures. Although viscosity is only one of many factors taken into account in the characterization of lubricant performance, it is essential that a lubricant has a sufficiently high viscosity at normal operating temperatures. The ideal lubricant would be one whose viscosity was minimally affected by the range of operating temperatures encountered though in reality viscosity changes substantially with temperature, depending on the chemical and physical properties of the lubricant. In the past, numerous methods have been suggested for expressing the variation of viscosity with temperature [1]. Perhaps the most common is the viscosity index (VI) proposed by Dean and Davis [2]. The Viscosity Index is an empirical number that indicates the effect of change of temperature on the viscosity of oil. A low Viscosity Index signifies relatively large change of viscosity with temperature [3]. Therefore the VI improvers are added in base oils for improving to modify the rate of change of viscosity with temperature [4]. These additives are polymers of unsaturated hydrocarbons or unsaturated esters whose structure must be selected to achieve excellence compatibility with the mineral base oils. Because EPDM (ethylene-propylene-diene monomere) is a highly versatile rubber which does not contain any unsaturated structure in its main chain it has excellent weather resistance, ozone resistance and heat resistance as well as very good dielectric performance and low temperature flexibility so it has excellent filler loading characteristic [5]. Its propensity to absorb oil, makes it advantageous to be used in oil viscosity improver application. Globally, EPDM demand was an estimated 935000 tons in 2004. Demand in forecast to increase at an average annual rate of 3.5% for 2004-2009, reaching 1110 tons in 2009. A break-down of global EPDM demand by end use segment is illustrated in figure (1). The importance of the "automotive" sector is apparent, as this sector accounts for 42% of EPDM demand [6]. The problems of temperature, viscosity instability are solved in multigrade luboils by the addition of viscosity index improvers, made from various types of polymers including Ethylene propylene copolymers. Polymers is available in liquid, crumb. Pellet and solid bale form. The mechanism of VII operation has been postulated by various researchers i.e (Selby and Muler). These viscosity modifiers improve the viscosity index (VI). This function depends not only on particular polymer chemistry and constitution but also on shear rate and temperature.

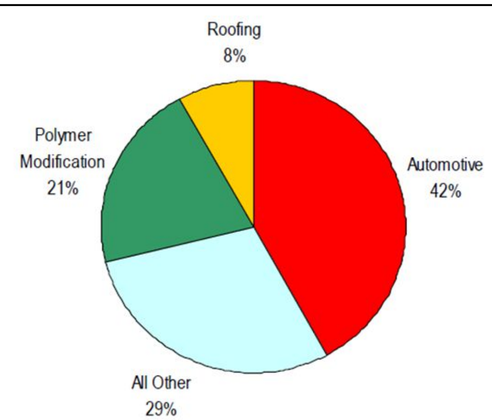

Fig. 1. Demand for EPDM

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Understanding the effect of temperature on the viscosity of the fluid is very important. In engines the lubricant oil is heated to very high temperatures due to combustion of the fuel, hence it is vital to know whether the lubricating oil, which is a fluid, will be viscous enough to be able to carry out the lubrication of the moving parts of the engine at those high temperatures. Therefor the aim of this work is to characterize the grade (SAE-30, SAE-40 and SAE-50) with different VI improver additives with the effect of temperature and concentration on the viscosity of manufacturing base oil.

2 EXPERMENTAL

2.1 Materials

The lubricant base oil and all viscosity improvers were provided by Asia oil factory from Kurdistan Region with the general characteristics were shown in Table (1) and Table (2).

TABLE 1
GENERAL CHARACTRESTICS OF VISCOSITY IMPROVERS

Properties	KEP270	DE3071	K4802	PA6205
Mooney viscosity [ML 1+4, 125 °C]	71.00	51.00	77.00	67.00
ENB Content [wt %]	4.50	-	4.30	2.80
Ethylene content [wt %]	57.00	49.00	52.00	65.00
Volatile content [wt %]	0.40	0.50	0.50	0.45
Specific gravity	0.86	0.86	0.86	0.86

TABLE 2
GENERAL PROPERTIES OF BASE OIL

Properties	Standard method	Units	Results
Specific gravity at 15.6 °C	ASTM D-1298	-	0.8915
API Gravity	ASTM D-1298	degree	27.22
Viscosity @100 °C	ASTM D-445	Cst	11.00
Viscosity @40 °C	ASTM D-445	Cst	95.80
Viscosity Index	ASTM D-2270	-	99.00
Flash Point (C.O.C)Pour Point	ASTM D-ASTM D-92	°C	240.00
Pour Point	ASTM D-97	°C	-6.00
Colour	ASTM D-1500	-	2.50

2.2 Method

A series of base oil solutions were prepared as a stock solutions by dissolving 3g of different co-polymer additives in 97 g base oil to prepare 3% W/W of base oil. Each mixture was prepared by stirring and heating to about 70 °C at the same time to ensure homogenize thorough mixing. The viscosity grades SAE-30, SAE-40 and SAE-50 were prepared by diluting the stock solution with base oil for each improver. The percentage V/V% of SAE viscosity grade for each improver was determined according to the kinematic viscosity range (9-12 for SAE-30, 14-16 for SAE-40 and 17-21 for SAE-50).
The kinematic viscosity for each stock solution was measured at 100 oC using Ostwald viscometer then the specific volume for each grade was determined from the ASTM blending chart by V/V% to mix with base oil in the grade viscosities rang [SAE-30 (9-12), SAE-40 (14-16) and SAE-50 (17-21) cst]. The specific gravity for each grade was measured by hydrometer and the kinematic viscosity at 40 oC and 100 °C also were measured.
Lower viscosity component of manufacturing Kurdistan base oil was measured and given 11 Cst. To improve the viscosity of the base oil 3 g of each improver was added to 97 g of base oil as a stock solution. The higher viscosity components for solutions were determined at100°C.

3 RESULT AND DISSCUSION

The SAE viscosity grades constitute a classification for engine lubricating oils in rheological terms only and are intended for use by engine manufacturers in determining the engine oil viscosity grades to be recommended for use in their engines and by oil marketers in formulating and labeling their products. Addition of polymers, which have viscosity improving behaviour increases the viscosity of the base oil to the required level indicated intestinally for grades SAE-30(Viscosity @100 °C / Cst, 9- 12), SAE-40 (Viscosity @100 °C / Cst, 14- 16), SAE-50 (Viscosity @100 °C / Cst, 17- 21).Table (3) shows %v/v of each viscosity improvers, stock solution which must be added to reach such SAE- grades. Another essential requirements of engine lubricating oil is that it must have a low enough viscosity at low temperature to assist in cold starting and a high enough viscosity at high temperature to maintains its load-bearing characteristics. It is therefore desirable to have a fluid whose viscosity- temperature dependence is small. There are many ways of expressing the variation of viscosity with temperature. One of the most widely used in the lubricating field is viscosity index [7]. The viscosity is the property of the fluid that resists the flow of the fluids like liquids and gases. The viscosity index of oil is calculated from its viscosities at 40 and 100°C. The procedure for the calculation is given in ASTM Method D 2270-74 for Calculating Viscosity Index from Kinematic Viscosity at 40 and 100°C [8].

International Journal of Scientific & Engineering Research Volume 6, Issue 8, August -2015
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TABLE 3
VOLUME RATIOS OF VISCOSITY IMPROVER BY PERCENTAGE OF VOLUME BASE OIL FOR PREPARING SAE-30, SAE-40 AND SAE-50.

Stock Solution of improver 3% W/W	Viscosity @ 100 oC. Cst	V/V% for SAE-30	V/V% for SAE-40	V/V% for SAE-50
KEP 270	325	4	13	24
DE3071	244	5	15	26
K4802	116	6	17	31
DCR3	109	7	18	32
PA 6205	55	8	24	42

Table (4) shows viscosity index of lubricating oils of all the three SAE- grades prepared by addition of all used types of viscosity improver in this work, among other general characterization of different improvers with the base oil. The importance of viscosity index as a measure of base oil quality has been established by the American Petroleum Institute (API)by establishing a group classification system that different base oils by saturates content, sulphur content, and viscosity index[9].The widely repeated mechanism of how polymers improves viscosity index is that polymers raise the viscosity of the fluid proportionality more at higher temperatures than at lower temperatures due to expansion of the polymer coil with increasing temperature[10].

TABLE4
CHARACTERIZATION OF DIFFERENT IMPROVERS WITH BASE OIL

Type of improver		SP.Gr	API	Vis. @ 40 °C Cst	Vis. @ 100 °C. Cst	VI	FP	PP*
DE3071	SAE30	0.887	28.03	120.4	12.8	98.20	241	-12
	SAE40	0.888	27.85	142.4	14.6	101.26		-12
	SAE50	0.890	27.40	194.4	20.6	124.34		-12
KED270	SAE30	0.881	29.11	125	12.2	85.24	240	-12
	SAE40	0.881	29.11	210	17.8	91.79		-12
	SAE50	0.882	28.93	265.8	22.2	101.07		-12
K4802	SAE30	0.881	29.11	127.6	11.7	78.72	242	-12
	SAE40	0.888	27.85	131.2	14.4	109.10		-12
	SAE50	0.891	27.31	220.2	21.8	119.12		-12
DCR3	SAE30	0.890	27.49	102	11.7	91.33	244	-12
	SAE40	0.882	28.93	131.4	14.4	108.82		-12
	SAE50	0.890	27.49	188.2	19.2	115.82		-12

With addition of 0.1% w/w of PPD.

Tables (5-9) shows the effect of temperature on different ratios of all types of polymers used on the base oil viscosity, and they show that all viscosity improves used are effective as viscosity index improves as they elevate the viscosity index of the base oil. The improver KEP270 gives the higher viscosity at 100 oC (325 Cst) on addition of 3% w/w to the base oil, while the improver PA 6205 gives the lower viscosity (55 Cst) at same temperature and same concentration of the additive. The different between viscosities at high temperature (100 oC) and low temperature (40 oC) is highest for DE3071 (575 Cst) and lowest for DCR3 (398 cst) at concentration of 3% w/v of stock solution of 3% w/w of the improver.

TABLE5
EFFECT OF TEMPERATURE ON DIFFERENT RATIOS OF POLYMER PA6205 ON BASE OIL

PA 6205	0.5 % W/V	1 % W/V	1.5 % W/V	2 % W/V	2.5 % W/V	3 % W/V	3.5 % W/V
Temp.	η	η	η	η	η	η	η
40	115.2	128	219.2	252.8	344	496	604.8
50	68.8	83.2	137.6	148.8	208	289.6	420.8
60	44.8	52.8	86.4	102.4	132.8	182.4	249.6
70	30.4	35.2	59.2	64	89.6	124.8	172.8
80	20.8	25.6	41.6	46.4	62.4	88	112
90	16	17.6	30.4	35.2	49.6	62.4	76.8
100	12.2	14.4	21.8	27.2	33.6	44.6	51.8

TABLE6
EFFECT OF TEMPERATURE ON DIFFERENT RATIOS OF POLYMER PA6205 ON BASE OIL

PA 6205	0.5 % W/V	1 % W/V	1.5 % W/V	2 % W/V	2.5 % W/V	3 % W/V	3.5 % W/V
Temp.	η	η	η	η	η	η	η
40	115.2	128	219.2	252.8	344	496	604.8
50	68.8	83.2	137.6	148.8	208	289.6	420.8
60	44.8	52.8	86.4	102.4	132.8	182.4	249.6
70	30.4	35.2	59.2	64	89.6	124.8	172.8
80	20.8	25.6	41.6	46.4	62.4	88	112
90	16	17.6	30.4	35.2	49.6	62.4	76.8
100	12.2	14.4	21.8	27.2	33.6	44.6	51.8

TABLE7
EFFECT OF TEMPERATURE ON DIFFERENT RATIOS OF POLYMER DR 3071 ON BASE OIL

DE 3071	0.5 %W/V	1 % W/V	1.5 % W/V	2 % W/V	2.5 % W/V	3 % W/V	3.5 % W/V
Temp.	η	η	η	η	η	η	η
40	120.2	140.2	190.4	308.8	371.2	451.2	627.2
50	70.4	94.4	120	198.4	297.2	324.8	419.2
60	49.6	67.2	76.8	128	211.2	241.6	337.6
70	33.6	40	52.8	84.8	161.6	172.8	260.8
80	22.4	28.8	36.8	59.2	131.2	115.2	158.4
90	17.6	20.8	27.2	43.2	99.2	89.6	97.6
100	12.8	14.5	18.8	28.6	33.6	40.5	51.6

International Journal of Scientific & Engineering Research Volume 6, Issue 8, August -2015
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TABLE8
EFFECT OF TEMPERATURE ON DIFFERENT RATIOS OF POLYMER KEP 270 ON BASE OIL

KEP 270	0.5 % W/V	1 % W/V	1.5 % W/V	2 % W/V	2.5 % W/V	3 % W/V	3.5 % W/V
Temp.	η	η	η	η	η	η	η
40	96	142.4	180.8	299.2	369.6	443.2	460.8
50	65.6	86.4	107.2	188.8	286.4	313.6	388.8
60	44.8	44.8	65.6	113.6	209.6	228.8	203.2
70	36.8	32	43.2	75.2	155.2	147.2	180.8
80	16	20.8	33.6	56	148.2	102.4	124.8
90	12.8	16	24	40	110.4	81.6	108.8
100	11.2	14.8	17.6	27.2	41.2	50.2	58.8

TABLE9
EFFECT OF TEMPERATURE ON DIFFERENT RATIOS OF POLYMER DCR3 ON BASE OIL

DCR3	0.5 % W/V	1 % W/V	1.5 % W/V	2 % W/V	2.5 % W/V	3 % W/V	3.5 % W/V
Temp.	η	η	η	η	η	η	η
40	94.4	131.2	187.2	305.6	374.4	444.8	467.2
50	64	81.6	113.6	188.8	284.8	308.8	404.8
60	41.6	64	70.4	110.4	206.4	222.4	241.6
70	30.4	36.8	48	68.8	150.4	158.4	179.2
80	22.4	28.8	35.2	52.8	118.4	121.6	132.8
90	16	16	25.6	41.6	100.8	102.4	113.6
100	11	14.4	19.2	28.6	50.8	60.8	69.2

The relation between viscosity and temperature is gives by an Arhhinues like equation

$$\eta = A\, e^{Ea/RT} \qquad (1)$$

Where η = viscosity, Ea= activation energy, T is temperature, R is gas constant and A is constant. The logarstmatic form of the equation

$$[\log \eta = \log A + \frac{Ea}{RT}\,] \qquad (2)$$

And it gives a clear linear linear relation between viscosity and activation energy, and reverse relation between viscosity and temperature. A plot log η vs 1/T for all improvers at all used temperature (40, 50, 60, 70, 80, 90, and100 oC) are shown in fig (2-6), with slope =Ea/R and intercept = log A.
The equation parameters for different percentage of the improvers are shown in Table (10).

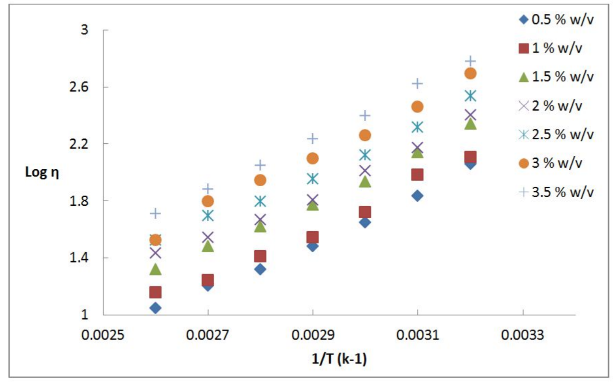

Fig. 2. Plot log η vis 1/T a stock solution of PA6205 shows effect of temperatures with different concentration at range (0.5% - 3.5%).

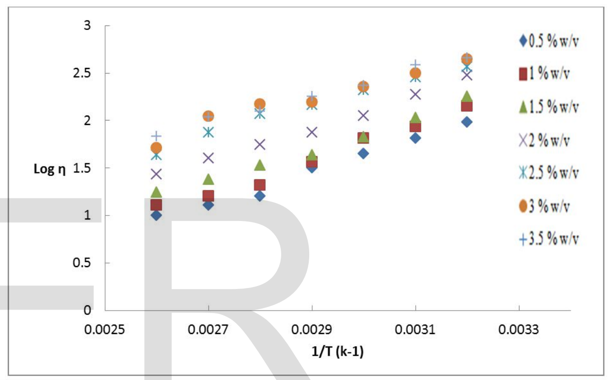

Fig. 3. Plot log η vis 1/T a stock solution of KEP270 shows effect of temperatures with different concentration at range (0.5% - 3.5%).

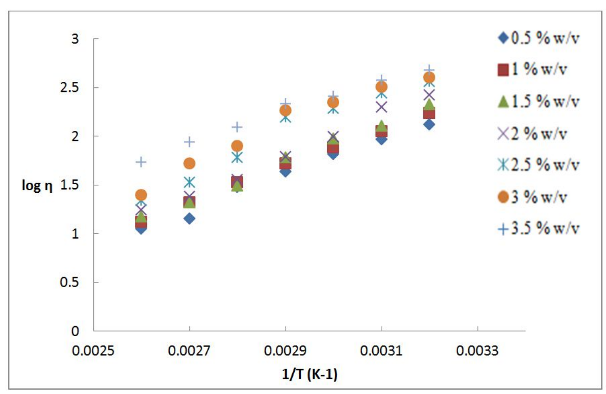

Fig. 4. Plot log η vis 1/T a stock solution of K4802 shows effect of temperatures with different concentration at range (0.5% - 3.5%).

International Journal of Scientific & Engineering Research Volume 6, Issue 8, August -2015
ISSN 2229-5518

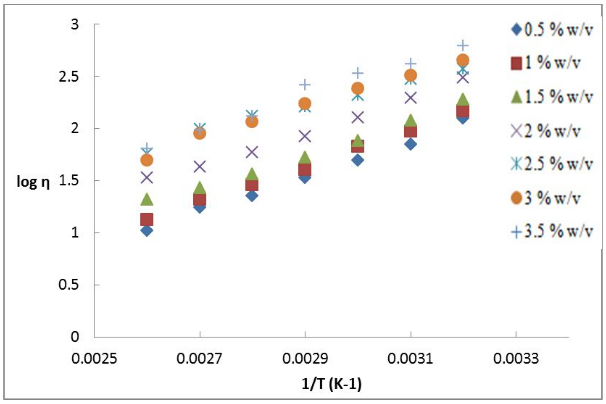

Fig. 5. Plot log η vis 1/T a stock solution of DE 3071 shows effect of temperatures with different concentration at range (0.5% - 3.5%).

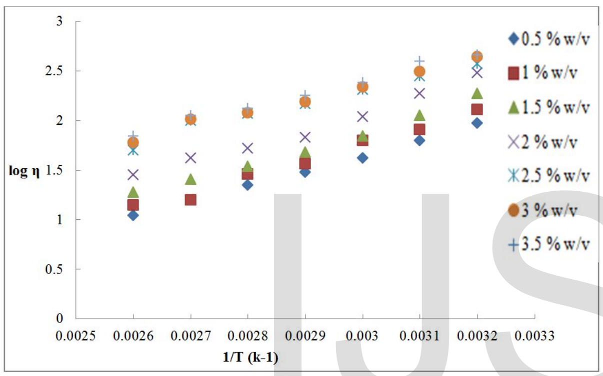

Fig. 6. Plot log η vis 1/T a stock solution of DCR3 shows effect of temperatures with different concentration at range (0.5% - 3.5%).

TABLE10
ARHHINUES PARAMETERS FOR THE DIFFERENT PERCENTAGE OF IMPROVERS IN BASE OIL AT DIFFERENT TEMPERATURES

Improvers	Parameters	0.5% W/V	1 % W/V	1.5 % W/V	2 % W/V	2.5 % W/V	3 % W/V	3.5 % W/V
	A	1*10-4	1.3*10-4	6.3*10-4	2.9*10-5	3.9*10-5	1.7*10-4	4.6*10-3
K4802	Ea	37.3	36.8	39.1	41.8	42.3	38.7	30.2
	R2	0.9843	0.9929	0.9939	0.9951	0.9604	0.9582	0.984
	A	3.9*10-4	4.5*10-4	1.2*10-3	1.7*10-3	3.1*10-2	5.5*10-3	3.2*10-3
DE3071	Ea	32.6	32.8	30.7	31.1	24.5	29.5	31.8
	R2	0.9926	0.9971	0.9907	0.9913	0.9826	0.99	0.9829
	A	5.1*10-4	6.2*10-4	8.6*10-4	1.5*10-3	1.6*10-3	5.9*10-4	1.1*10-3
PA 6205	Ea	31.6	31.7	32.1	30.7	31.4	35.2	34.4
	R2	0.9912	0.9851	0.9948	0.985	0.9894	0.9929	0.9985
	A	3.1*10-4	2*10-4	7.9*10-4	9.5*10-4	6.1*10-3	1.5*10 -2	1.8*10-2
KEP270	Ea	32.8	34.8	31.6	32.6	28.8	26.6	26.3
	R2	0.9849	0.9836	0.9856	0.9921	0.9824	0.9518	0.9864
	A	12*10-4	6.2*10-4	10*10-4	11*10-4	19*10-3	19*10-3	20*10-3
DCR3	Ea	29.1	31.7	31.02	32.19	25.6	25.9	26.1
	R2	0.9978	0.9859	0.9867	0.9789	0.9717	0.9882	0.9846

TABLE11
VISCOSITY INDEX FOR BLENDED LUBE OIL USING DE3071 AT DIFFERENT CONCENTRATIONS

Concentration W/V%	Viscosity @ 40 °C. Cst	Viscosity @ 100 °C. Cst	Viscosity index
0.5	120.2	12.8	99
1	140.2	14.5	102
1.5	190.4	18.8	111
2	308.8	28.6	125
2.5	371.2	33.6	130
3	451.2	40.5	138
3.5	627.2	51.6	140

TABLE12
VISCOSITY INDEX FOR BLENDED LUBE OIL USING PA6205 AT DIFFERENT CONCENTRATIONS

Concentration W/V%	Viscosity @ 40 °C. Cst	Viscosity @ 100 °C. Cst	Viscosity index
0.5	115.2	12.2	95
1	128	14.4	112
1.5	219.2	21.8	120
2	152.8	27.2	140
2.5	344	33.6	139
3	496	44.6	143
3.5	614.8	51.8	143

TABLE13
VISCOSITY INDEX FOR BLENDED LUBE OIL USING K4802 AT DIFFERENT CONCENTRATIONS

Concentration W/V%	Viscosity @ 40 °C. Cst	Viscosity @ 100 °C. Cst	Viscosity index
0.5	131.2	13.4	96
1	172.8	16.4	99
1.5	212	19	100
2	265.6	22.8	105
2.5	364.8	29.2	110
3	442.4	38.4	132
3.5	564	51.2	150

International Journal of Scientific & Engineering Research Volume 6, Issue 8, August -2015
ISSN 2229-5518

TABLE14
VISCOSITY INDEX FOR BLENDED LUBE OIL USING KEP270 AT DIFFERENT CONCENTRATIONS

Concentration W/V%	Viscosity @ 40 °C. Cst	Viscosity @ 100 °C. Cst	Viscosity index
0.5	96	11.2	102
1	142.4	14.8	103
1.5	180.8	17.6	106
2	299.2	27.2	121
2.5	369.6	41.2	164
3	443.2	50.2	176
3.5	460.8	58.8	198

TABLE15
VISCOSITY INDEX FOR BLENDED LUBE OIL USING DCR3 AT DIFFERENT CONCENTRATIONS

Concentration W/V%	Viscosity @ 40 °C. Cst	Viscosity @ 100 °C. Cst	Viscosity index
0.5	94.4	11	101
1	131.2	14.4	109
1.5	187.2	19.2	117
2	305.6	28.6	126
2.5	374.4	50.8	200
3	444.8	60.8	209
3.5	467.2	69.2	227

Tables (11-15) show estimation of viscosity index using ASTM D-2770 standard method for all viscosity improvers at all concentration and, Fig. (7) Shows the variation of viscosity index of the blended oils made from the mineral base oil SN500 by the addition of the improvers (PA 6205, DE 3071, K4802, KEP270 and DCR3), with concentration of the improvers expressed as w/v%. The figure depicts the effectiveness of the viscosity improvers on mineral base oil. The concentrations of the improvers were varied in the range of 0.5 to 3.5 w/v %. From this figure it can be seen that viscosity index of the blended oil passes through maximum with increase in the concentration of all improvers except the improver K4802 which is nearly constant till 3 w/v% then increases sharply at 3.5 w/v%. The maximum possible viscosity index of the blended oils, made from the mineral base oil SN500 by the addition of the improvers are 140,143,150,198 and 227. These figures are helped in selecting the viscosity improver for producing multi-grade engine oils of desired viscosity index.

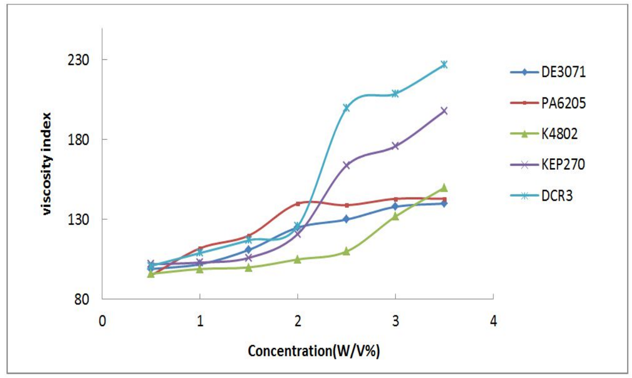

Fig. 7.Variation of viscosity index of mineral base oil with concentration of various viscosity improvers

4 CONCLUSION

1. All viscosity index improvers used in this work are effective as viscosity index improvers as they increase the viscosity index of the base oil.
2.The viscosity index improver type KEP270 gives the higher viscosity at 100 °C (325 Cst on addition of 3% w/w to the base oil, while the improver type PA6205 give the lower viscosity (55 Cst) of the same temperature and the same concentration of the additive.
3. Order of increasing viscosities of the base oil on addition of 3% is as follow:-
KEP270 (325 Cst) > DE 3071 (Cst) > K4802 (116 Cst) > DCR (109 Cst) > PA 6205(55 Cst).
4. The difference between viscosity @100 °C and @40 °C is the highest for DE 3071 (375 Cst and lowest for DCR3 (398 Cst) at concentration 3.5 % W/v of the stock solution of 3% W/w of the improver.

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