

Enhancement of viscosity index of mineral base oils

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Multigrade engine oils of high viscosity index (VI) are required for modern internal-combustion engines. Such a high VI is difficult to achieve by the conventional processing of petroleum fractions. Therefore, VI improvers are added in the mineral base oils to achieve the desired VI. The enhancement of VI of mineral base oils (100 N, 150 N and 500 N) by the addition of VI improvers [polyisobutylene(PIB), polybutadiene rubber (PBR)] has been studied. VI of blended oils, made from the mineral base oils 100 N, 150 N and 500 N by the addition of PIB and PBR, is found to pass through maximum. It was observed that the occurrence of maximum depends on the mineral base oil used and the type and concentration of VI improver.

Keywords: Viscosity index, Mineral base oil, Polyisobutylene, Polybutadiene rubber, VI improver

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Base oil is the major component of an automotive lubricant/industrial lubricant. It provides desirable tribological characteristics. There are two major sources of base oils: (a) mineral base oils and (b) synthetic base oils. The quality of base oils used worldwide is changing rapidly due to stringent environmental regulation and the pressing need to perform in severe operating conditions. The present day demand of lubricating oil is for excellent oxidation stability, superior low temperature performance, low volatility, low carbon forming tendency, viscosity stability and improved additive response. Many methods have been proposed to express the changes in viscosity with temperature for lubricating oils. Viscosity index (VI), with its advantages and disadvantages, is widely used to define oil quality. A high VI indicates a relatively small change of viscosity with temperature and vice versa. The quality base oils are free from reactive hydrocarbons and other impurities that contribute to the degradation of lubricants in service¹. The current requirement of high performance base oils can conveniently be met by hydroprocessing route. Commercial oils for internal combustion engines are generally multigrade engine oils with VI between 150 and 200. Therefore, VI improvers are added in base oils for improving viscometric and rheological properties. These chemical additives modify the rate of change of viscosity with temperature.

VI improvers are polymers of unsaturated hydrocarbons or unsaturated esters whose structure must be selected to achieve good compatibility with the mineral base oils, selective thickening effect as a function of temperature, sufficient stability under oxidation and mechanical shear stresses, and possibly some anti-wear, anticongel and dispersant effectiveness with respect to pollutants conveyed by the oil²⁻³. Some types of polymers generally used commercially as VI improvers and known to possess certain inherent advantages and disadvantages in performance are (i) polyisobutylenes (PIB), (ii) hydrogenated styrene-isoprene copolymers, (iii) olefin copolymers, e.g. ethylene-propylene copolymer, (iv) esters of styrene-maleic anhydride copolymers and (v) polyalkyl methacrylates (PMA). VI improvers are commercially available in the form of solutions in oil, in concentrations ranging between 5 and 70% depending on the actual viscosity of the polymer, so that they can be pumped in blending plants. Certain polymers are also commercialized in powder or granular form. Polymers commercialized today are classed in two main categories, non-dispersant and dispersant hydrocarbon polymers, and non-dispersant and dispersant ester polymers.

Viscosity index is an index designed to emphasize the degree of refinement or chemical composition of the base oil. Dean and Davis⁴ proposed VI for industrial characterization of automotive lubricants. It

is an indication of viscosity-temperature characteristic of oils in terms of its Saybolt viscosities at 311 and 372 K. Two series of reference lubricating oil fractions (H and L) were used for comparison. Series H and L oils were assigned a VI of 100 and 0, respectively. The VI of an oil under test was calculated from the equation.

$$VI = 100(v_L - v_U)/(v_L - v_H) \quad \dots (1)$$

where v_U is the kinematic viscosity of oil at 311 K, v_L and v_H are the kinematic viscosities at 311 K of the series L and H having the same kinematic viscosity at 372 K. Thus, the viscosity of an oil of higher VI is less affected by temperature and therefore, it is a better oil. Subsequently, Hardiman and Nissan⁵ proposed revision to the VI system. They found that VI system failed for VI greater than 130, and comparison became meaningless. They sought to make the VI applicable at any two temperatures and to wider range of oils. They reported the following empirical equations for the VI:

$$VI = 3.63 (60 - 10^n) \quad \dots (2)$$

where n is given by

$$n = (\ln v_1 - \ln k) / \ln v_2 \quad \dots (3)$$

v_1 is the kinematic viscosity in cSt at the lower temperature, v_2 is the kinematic viscosity in cSt at the higher temperature, k is a function of the temperature range alone and is independent of the nature of the oil and n , a constant characteristic for each oil, depends on the temperature range chosen. For the temperature range 311-372 K, they determined k to be 2.714. They found good correlation between their suggested VI and that of Dean and Davis⁴, their suggested one having the advantage of applicability to a wider range of oils.

Moore *et al.*⁶ reported the calculation of the VI of squalane from non-equilibrium molecular dynamics simulations. This computational approach offers the possibility of predicting the performance of potential multigrade engine oils prior to synthesis. VI calculation for a blend of two lubricating oils by the ASTM D341 method is not always precise⁷. The VI established by direct viscosity measurements of the blend usually is found to be higher than the blend VI calculated by the method ASTM D341.

Capillary viscometer has been employed by LaRiviere *et al.*⁸ to measure the viscosities of dilute polymer solutions over the temperature range of -10 - 150°C. The thickening effects of the olefin copolymer and the hydrogenated diene copolymer are found to be higher at low temperatures (e.g. 40°C) than at higher ones (e.g. 100°C), phenomenon for which was attributed to stronger intermolecular hydrodynamic interactions at low temperatures. Hedrich *et al.*⁹ reported the effects of VI improvers on low temperature pumpability of engine oil and fuel consumption. The effect of VI improvers on viscosity of engine oils was investigated by Wu *et al.*¹⁰. They proposed a model that describes the changes of final oil viscosity with the viscosity of base oil which is a linear equation with an intercept. Their model does not agree with the equations developed by Kraemer or Huggins.

It has been reported in the literature that lubricating oils for increased fuel efficiency of automobiles contain hydrocarbons with viscosity more than 4 cSt at 100°C, VI more than 100 and pour point less than -10°C and VI improver consisting of 17-20 wt.% of polymethacrylate (average molecular weight of 500000 to 1500000) and 3-5 wt.% of ethylene-propylene copolymer (average molecular weight of 100000 to 250000). Chen *et al.*¹¹ reported the results of an experimental study on the influence of VI improver on performance of gasoline engine fuel and oil. They found that the dispersant type polymethacrylate and olefin copolymer with high molecular weight are helpful to improve the fuel economy performance of the aero engines.

The potential for use of copolymers of iso-decyl methacrylate and 1-decene as VI improver in multigrade engine oils has been investigated by Ghosh *et al.*¹². They found that copolymers of this category can serve as better VI improver than usual PMAs. Four sets of copolymeric additives were synthesized via copolymerization of dialkyl fumarates and dialkyl maleates with vinyl acetate and vinylpyrrolidone monomers¹³. They investigated the efficiency of these copolymers as VI improver and found that dialkyl ester/vinyl pyrrolidone copolymers are more efficient as VI improvers than the dialkyl ester/vinyl acetate copolymers. Mohamed *et al.*¹⁴ synthesized styrene alkylmethacrylate succinimide phosphoric acid additives at different styrene/methacrylate mole ratios and evaluated for use in multigrade engine oil formulations as

multifunctional VI improvers having both antioxidant and dispersant properties. They found the optimum performance properties of the synthesized products that were obtained by using styrene/methacrylate mole ratio of 0.35 and a temperature of 140-145°C for 4-5 h.

The shear stability of polymers used as VI improvers has been investigated at varied polymer concentrations (0.5-4 wt.%) in mineral base oils by Ghosh *et al.*¹⁵. They studied the effects of mineral base oil viscosity, composition of the base oil and polymer concentration on shear stability index (SSI). They found that the magnitude of SSI is dependent on polymer chemistry and the nature of base oil. Bartz¹⁶ formulated some SAE 15W-40 multigrade oils, using polymethacrylate of different molecular weights with a mixture of base oils 150 N and 500 N. They found that viscometric properties as well as shear stability depended strongly on the polymer concentration and molecular weight of the VI improver. However, the evaporation losses were strongly dominated by the volatility properties of the base oil.

Experimental Procedure

Materials

The mineral base oils (100 N, 150 N and 500 N) were obtained from Mineral Oil Corporation Ltd, Kanpur and VI improvers (PIB, PBR) were obtained from Paras Lubricant, New Delhi.

Method

The mineral base oil (200 mL) was taken in a glass beaker. The electrically operated stirrer was run to agitate the oil at the desired speed to avoid foaming. The VI improver was added in the impeller region, about 1 cm below the liquid surface near the shaft and at a radial distance of about 1 cm at different concentrations, where the drop is discontinued. The average shear rate in the impeller region is of the order of 10 rotations per second. Visual observations were made at every 15 min and it has been found that the blending is completed in about 45 min. The stirrer blade is set at three regions at time intervals of 15 min, so that the chances of surfacing or clinging to the vessel walls are minimized. After blending, the resulting samples were tested for the kinematic viscosities at 40 and 100°C which were determined by Redwood viscometer [IS: 1448 (P:25)-1976]¹⁷. When the temperature reaches the test level, the orifice of the viscometer is unsealed and the efflux time for 50 mL of sample is observed. The result was reported in

terms of the efflux time. This efflux time was inserted into Eq. (4) to give the kinematic viscosity, v , in mm^2/s .

$$v = At - B/t \quad \dots(4)$$

where A = instrument calibration constant, B = instrument type constant, depending on the capillary diameter, and t = efflux time in s.

Viscosity index is calculated by [IS: 1448 (P: 56) 1980] using the experimental values of kinematic viscosities at 40 and 100°C. When the kinematic viscosity was above 70 mm^2/s at 100°C, the values of v_L , v_D and v_H were calculated as follows:

$$v_L = 0.8353 v_Y^2 + 14.67 v_Y - 216 \quad \dots (5)$$

$$v_D = 0.6669 v_Y^2 + 2.82 v_Y - 119 \quad \dots (6)$$

$$v_H = 0.1684 v_Y^2 + 11.85 v_Y - 97 \quad \dots (7)$$

where v_L is the kinematic viscosity, in mm^2/s , at 40°C of a petroleum product of VI 0 having the same kinematic viscosity at 100°C as the petroleum product whose VI is to be calculated, v_Y is the kinematic viscosity, in mm^2/s , at 100°C of the petroleum product whose VI is to be calculated,

$$v_D = v_L - v_H \quad \dots (8)$$

where v_H is the kinematic viscosity, in mm^2/s , at 40°C of a petroleum product of VI 100 having the same kinematic viscosity at 100°C as the petroleum product whose VI is to be calculated.

From the above values of v_L , v_D and v_H , the VI of the petroleum product was calculated as follows:

$$VI = 100(v_L - v_U)/(v_L - v_H) \quad \dots (9)$$

$$VI = 100(v_L - v_U)/v_D \quad \dots (10)$$

where v_U is the kinematic viscosity, in mm^2/s , at 40°C of the petroleum product whose VI is to be calculated

For petroleum products of VI 100 or greater, VI was calculated from the following equations:

$$VI = [(\text{antilog } N) - 1]/0.00715 + 100 \quad \dots (11)$$

$$N = (\log v_H - \log v_U)/\log v_Y \quad \dots (12)$$

where N = power required to raise the kinematic viscosity of the oil at 100°C to equal the ratio of the v_H and v_U kinematic viscosities at 40°C and v_U and v_Y are the measured kinematic viscosities at 40 and

100°C, respectively of the liquid whose VI has to be found, while ν_H is the kinematic viscosity at 40°C of a liquid of VI 100 which has the same kinematic viscosity at 100°C as the liquid whose VI has to be found. The value of ν_H is read from table.

Experiments were carried out to investigate the effect of type and concentration of polymers (PIB, PBR), used as VI improver in the mineral base oils 100 N (VI=90), 150 N (VI=96), and 500 N (VI=97) [19]. A definite quantity of mineral base oil was blended in the laboratory with a known amount of VI improver (PIB, PBR). The blending was carried out at a room temperature of 38°C and an average shear rate of 10 rotations per second. The concentration of VI improver was varied from 0.2 to 4 volume percent.

VI of the blended oil was determined to obtain the enhancement of VI of the mineral base oil by the addition of VI improver. For this the kinematic viscosities of the blended oil at 40 and 100°C were determined experimentally by Redwood viscometer number 1. From the VI values of the blended oil and mineral base oil, the enhancement of VI of mineral base oil is obtained as a function of concentration of VI improver.

Results and Discussion

Effect of concentration of VI improver on VI of blended oil

Figures 1 and 2 show the variation of VI of blended oils, made from mineral base oils 100 N, 150 N and 500 N by the addition of PIB and PBR, respectively, with the concentration of PIB/PBR expressed as vol.%. These figures depicts the effectiveness of PIB/PBR on different mineral base oils. The concentration of PIB/PBR was varied in the range of 0 to 4 vol.%. From this figure it can be seen that VI of the blended oil made from mineral base oil 100 N and PIB/PBR passes through maximum with increase in the concentration of PIB/PBR. The similar curves are obtained for mineral base oils 150 N and 500 N. It can be seen from these figures that the maximum VI is obtained at different concentrations of PIB/PBR. These concentrations of PIB are 3, 1 and 0.5 vol.% whereas for PBR are 3.5, 3 and 1 vol.% for mineral base oils 100 N, 150 N and 500 N, respectively. The maximum possible VI of blended oils, made from mineral base oils 100 N, 150 N and 500 N by addition of PIB and PBR are 180, 147 and 143 and 183, 158 and 147, respectively. These figures are helpful in selecting the mineral base oil for producing multigrade engine oils of desired VI by the addition of PIB and PBR.

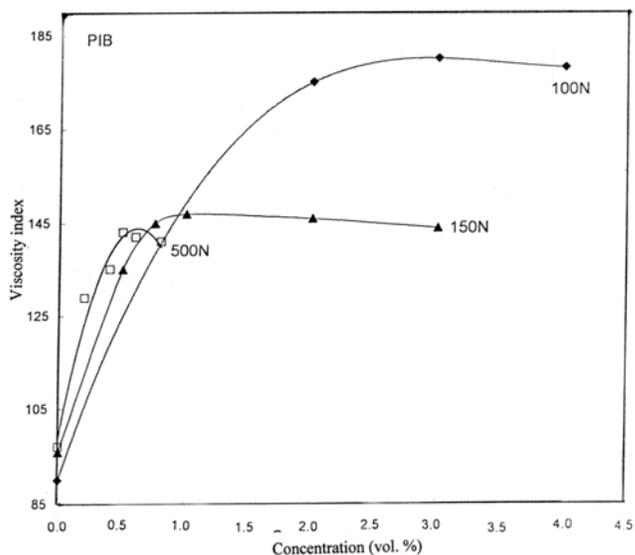


Fig. 1—Variation of viscosity index of mineral base oils 100 N, 150 N and 500 N with concentration of PIB.

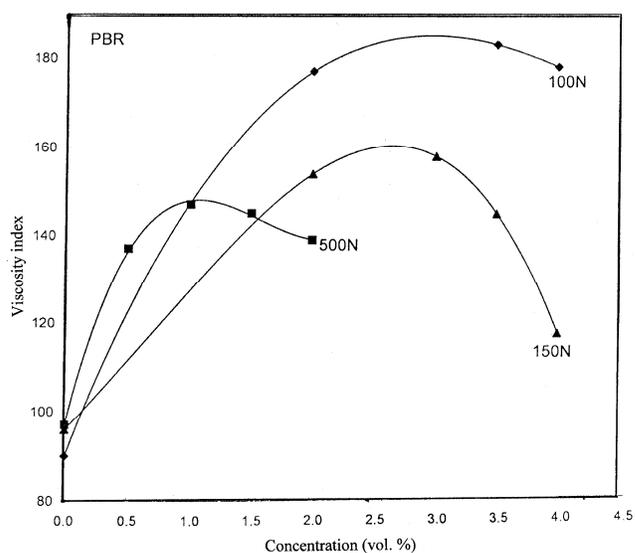


Fig. 2—Variation of viscosity index of mineral base oils 100 N, 150 N and 500 N with concentration of PBR

Figure 3 is a plot of VI, ν_{L-VU} and ν_{L-VH} for mineral base oil 150 N versus concentration of PBR. It can be seen from this figure that, with increase in the concentration of VI improver, ν_{L-VU} first increases and then decreases, but ν_{L-VH} increases monotonically. By definition, VI is the ratio of ν_{L-VU} and ν_{L-VH} . Therefore, VI of blended oils passes through maxima with increase in the concentration of VI improver

Figure 4 shows the variation of VI of blended oil with the concentration of VI improvers PIB and PBR.

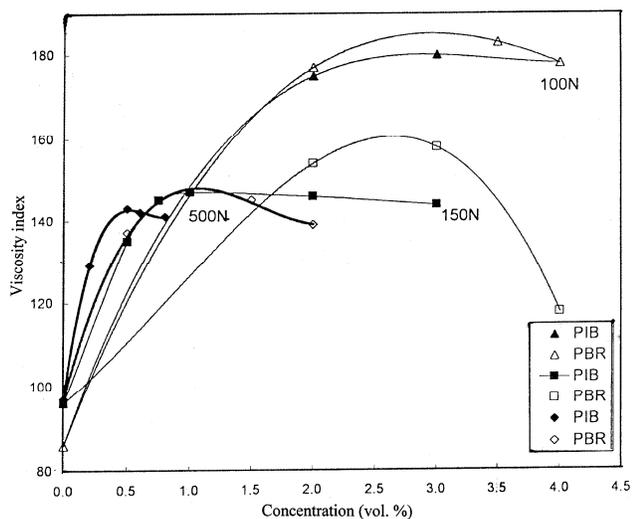


Fig. 3—Variation of viscosity index of mineral base oils 100 N, 150 N and 500 N with concentration of PIB and PBR

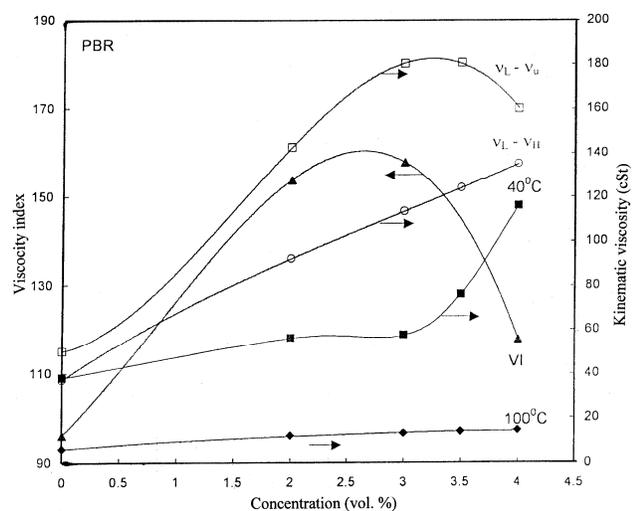


Fig. 4—Variation of viscosity index and kinematic viscosity of mineral base oil 150 N with concentration of PBR

It can be seen that for the concentration of VI improver higher than about 1.6 vol.%, the VI of blended oil is slightly higher when PBR is used as VI improver compared to PIB at the same concentration level. Therefore, for the concentration of VI improver higher than about 1.6 vol.%, the enhancement of VI of mineral base oil 100 N by the addition of PBR is slightly more for the same level of concentration of PIB and PBR. For the concentration of VI improver lower than about 1.6 vol.%, the enhancement of VI of mineral base oil 100 N by the addition of PIB is expected to be slightly more for the same level of concentration of PIB and PBR. For the mineral base oil 150 N, the maximum VI of the blended oil is

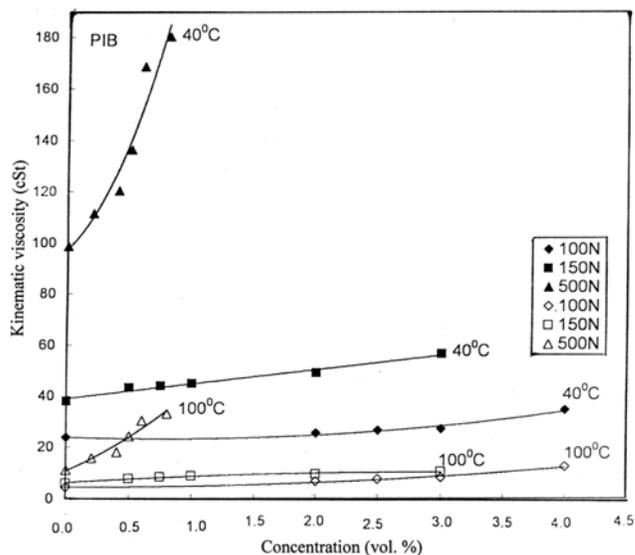


Fig. 5—Variation of kinematic viscosity of mineral base oils 100 N, 150 N and 500 N with concentration of PIB at 40 and 100°C

obtained at the concentration of 1 vol.% of PIB and 3 vol.% of PBR. For the concentration of VI improver higher than about 1.6 vol.%, the enhancement of VI of mineral base oil 150 N by the addition of PBR is slightly more for the same level of concentration of PIB and PBR. For the concentration of VI improver lower than about 1.6 vol.%, the enhancement of VI of mineral base oil 150 N by addition of PIB is expected to be slightly more for the same level of concentration of PIB and PBR. For the mineral base oil 500 N, the maximum VI of the blended oil is obtained at the concentration of 0.5 vol.% of PIB and 1 vol.% of PBR. For the concentration of VI improver higher than about 0.6 vol.%, the enhancement of VI of mineral base oil 500 N by the addition of PBR is slightly more for the same level of concentration of PIB and PBR. For the concentration of VI improver lower than about 0.6 vol.%, the enhancement of VI of mineral base oil 500 N by addition of PIB is expected to be slightly more for the same level of concentration of PIB and PBR.

Effect of concentration of VI improver on kinematic viscosity of blended oil

Figure 5 is a plot of kinematic viscosity of blended oils, made from mineral base oils 100 N, 150 N and 500 N by addition of PIB, at 40°C and 100°C versus concentration of PIB. This figure indicates that the kinematic viscosity of blended oils increases with increase in the concentration of PIB. It also indicates that the rate of change of kinematic viscosity of a

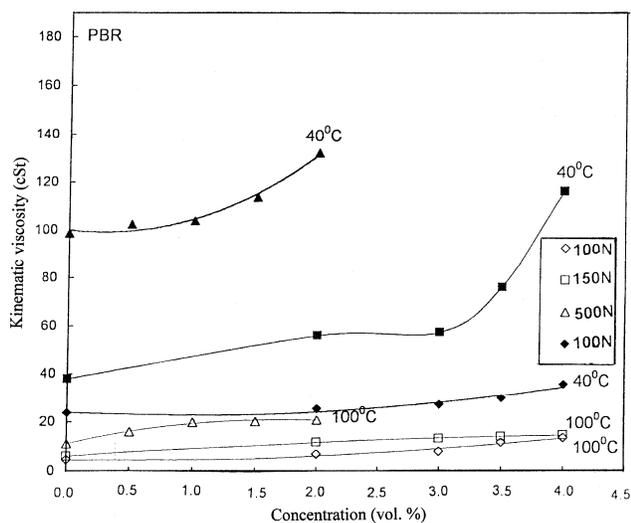


Fig. 6—Variation of kinematic viscosity of mineral base oils 100 N, 150 N and 500 N with concentration of PBR at 40 and 100°C

blended oil, made from a mineral base oil by addition of PIB, at 40°C with concentration of PIB is higher than the value at 100°C. Therefore, the difference in the kinematic viscosities of a blended oil at 40 and 100°C increases with increase in the concentration of PIB for all mineral base oils.

Figure 6 is a plot of kinematic viscosities of blended oils, made from mineral base oils 100 N, 150 N and 500 N by addition of PBR, at 40 and 100°C versus concentration of PBR. This figure indicates that the kinematic viscosity of blended oils increases with increase in the concentration of PBR and decreases with increase in temperature. It also indicates that the rate of change of kinematic viscosity of a blended oil, made from a mineral base oil by the addition of PBR, at 40°C with increase in concentration of PBR is higher than the value at 100°C. Therefore, the difference in the kinematic viscosities of blended oil at 40 and 100°C increases with increase in the concentration of PBR for all mineral base oils. The variation of the kinematic viscosity at 100°C should be considered in the formulation of desired engine oil.

Conclusions

The following conclusions were drawn from the present study:

- 1 The maximum VI of blended oils made from 100 N, 150 N and 500 N were found to be 180, 147 and 143 at 3.0, 1.0 and 0.5 vol.% of PIB, respectively.
- 2 The maximum VI of blended oils made from 100 N, 150 N and 500 N were found to be 183, 158 and

147 at 3.5, 3.0 and 1.0 vol.% of PBR, respectively.

- 3 For the mineral base oils 100 N and 150 N, PIB is found to be more effective for the enhancement of VI for the concentration of VI improver lower than about 1.6 vol.%. For the concentration of VI improver higher than about 1.6 vol.%, PBR is found to be more effective for these mineral base oils.
- 4 For the mineral base oil 500 N, PIB is found to be more effective for the concentration of VI improver lower than about 0.5 vol.% and PBR is more effective above the concentration of VI improver higher than about 0.5 vol.%.
- 5 The difference in the kinematic viscosities of a blended oil at 40 and 100°C is found to increase with increase in the concentration of PIB and PBR for all mineral base oils.

References

- 1 *Base Oils: Quality Trends and Technology Options for their Production*, edited by Srivastava S P, Int Symp Fuels Lubr (Allied Publishers, New Delhi), 2000, 69.
- 2 Kobe K A & McKetta J J (Eds), *Advances in Petroleum Chemistry and Refining (Lubricating Oil Additives)*, Vol VI (John-Wiley & Sons, New York), 1959.
- 3 Briant J, Denis J & Parc G, *Rheological Properties of Lubricants* (Editions Technip, Paris), 1989.
- 4 Dean E W & Davis G H B, *Chem Met Eng*, 36(3) (1929) 618.
- 5 Hardiman E W & Nissan A H, *J Ins Pet*, 31(451) (1945) 255.
- 6 Moore J D, Cui S T, Cummings P T & Cochran H D, *AIChE J*, 43(12) (1997) 3260.
- 7 Kyriakopoulos G B, *Hydrocarbon Processing*, 54(9) (1975) 137.
- 8 LaRiviere D, Asfour A -F A, Hage A & Gao J Z, *Lubr Sci*, 12(2) (2000) 133.
- 9 Hedrich K, Renner G & Dardin A, *Mineraloeltechnik*, 45(11) (2000) 13.
- 10 Wu Z, Lu Z, Li H & Wang L, *Shiyou Xuebao, Shiyou Jiagong*, 18(2) (2002) 87.
- 11 Chen Z, Jiao Y & Chen M, *Harbin Gongye Daxue Xuebao*, 34(1) (2002) 31.
- 12 Ghosh P, Pantar A V & Sarma A S, *Indian J Chem Technol*, 5 (1998) 371.
- 13 Abdel-Azim A & Abdel-Azim R M, *J Polym Res*, 8(2) (2001) 111.
- 14 Mohamed M M, Abou El Naga H H & Meneir M F ET, *J Chem Technol Biotechnol*, 60(3) (1994) 283.
- 15 Ghosh P, Pantar A V, Rao U S & Sarma A S, *Indian J Chem Technol*, 5 (1998) 309.
- 16 Bartz W J, *Lubr Sci*, 12(3) (2000) 215.
- 17 IS:1448[P:25]-1976 (Indian Standard on kinematic viscosity by Redwood Viscometer).
- 18 IS:1448[P:56]-1980 (Indian Standard on Viscosity Index Calculation).
- 19 Tanveer S, *Rheology of Multigrade Engine Oils*, Ph.D. Thesis, CSJM University, Kanpur, (2005).