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Final Technical Report

VISCOMETRIC AND MISTING PROPERTIES
OF POLYMER-MODIFIED JET FUEL

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SUMMARY

Solutions of polyisobutylenes L160, L200, E200, and E230 in Jet-A were prepared at concentrations up to 3000 ppm. These polymers have molecular weights in the range 5 to 9×10^6 and have previously been shown to induce anti-misting properties in Jet-A. In connection with the pumpability of such solutions, especially at low temperatures, the shear viscosity η of these solutions was measured at temperatures 25°C, 0°C, and -25°C.

Concentration-dependence of η was very similar for all four polymer solutes, the increase of $\eta(c)$ at 3000 ppm being roughly four-fold (relative to Jet-A) for the L-series and five-fold for the B-series. This behavior prevailed at all temperatures, and there was no evidence of phase separation or other chemical instability at -25°C at any concentration. In the more practical c-range for anti-misting applications, say within 1000 ppm, the increase of $\eta(c)$ was only twofold.

BACKGROUND

It has been amply demonstrated¹⁻⁴ that a small amount of polymeric solute dissolved in a kerosene-based jet fuel reduces the ignition and flammability of fuel sprays. Interest in this phenomenon stems from its potential for suppressing fires in aircraft suffering crash landings that are otherwise survivable. The mechanism for fire suppression involves polymer-induced alteration of fuel rheology, so that crash impacts at normal speeds will produce sprays having very few of the fine droplets ($D_p < 10 \mu\text{m}$) which are needed to propagate an ignition event.

There remain a number of practical problems, however. One of these is the question of fuel pumpability. Rheological alterations in the fuel include an increase of viscosity and the appearance of elasticity, both of which can make the liquid more difficult to pump from fuel tank through fuel lines and filters to the engines. Even without the induced elasticity, which retards stretching motions (e.g., in droplet formation), the viscosity enhancement is potentially a source of concern because of the additional pressure needed to produce shear flows within the fuel delivery system.

The latter concern was the one addressed in the present work. There is general acknowledgement that easily-dissolved linear polymers (e.g., polyisobutylenes, PIB) function effectively as antimisting agents,⁴ but the extent to which they increase fuel viscosity—especially at low temperatures—was not known. Our project objective was therefore to determine the Newtonian viscosity η of PIB solutions in Jet-A fuel over a range of practical polymer concentrations and realistically low temperatures.

EXPERIMENTS

Materials. Four linear PIB's of commercial origin were used here; these and others were characterized by GPC in our previous work,⁴ so their molecular weight distributions and averages are well known. These four samples were L160 and L200 "Vistanex" from Exxon, and E200 and E230 "Oppanol" from BASF. Values of M_w and M_w/M_n obtained from GPC traces were: 5.0×10^6 , 3.6 for L160; 5.4×10^6 , 4.9 for L200; 6.0×10^6 , 4.3 for E200; and 9.0×10^6 , 8.2 for E230. Values of M_v obtained from viscosity data on solutions (extrapolated to

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$c = 0$ to obtain intrinsic viscosity $[\eta]$ that is correlated with \bar{M}_v were always slightly smaller than the cited \bar{M}_v values, as must be so.

Jet-A was obtained from Shell Oil Co. at Oakland Airport. Solutions were prepared with extreme care, to prevent mechanical degradation of the polymer solute. Finely divided chunks of the rubbery polymer were placed in a flask, covered with Jet-A, and the flask slowly rotated (by motor drive) at an angle in a warm water bath. In this way, stock solutions of 3000 ppm by weight were prepared over a period of several days, and solutions of lower concentration were obtained by successive dilution. At all times during preparation and storage, solutions were covered to prevent vaporization of the lighter components of Jet-A and inadvertent concentration change.

Apparatus. The original intent was to test viscosities down to -45.6°C (-50.0°F). However, with the modified budget (\$11,451 in direct costs) and less than a year to work, this objective could not be achieved. The necessary refrigeration system was designed, components ordered, and assembly begun. When it was noted that the system could not be ready by the Agreement termination date, an alternate strategy was devised and a simpler system built that could be used to acquire data down to -25.0°C (-13.0°F).

This latter system was a "phase change" thermostat, consisting of a constant-temperature bath (in which viscometers were immersed) filled with a liquid undergoing a slow freezing/melting process at temperature T_f . Thus, $T = 0^\circ\text{C}$ was achieved with a bath medium consisting of ice and water in equilibrium, and $T = -25.0^\circ\text{C}$ was achieved in a bath of carbon tetrachloride ($T_f = -25^\circ\text{C}$) that was cooled by a jacket of dry ice ($T_f = -44^\circ\text{C}$). Measurements at room temperature (24°C) were made as usual.

Viscosities were measured with U-tube Ubbelohde capillary viscometers. The time t needed for fluid to flow through the capillary from one level to another by gravity is proportional to η/ρ , where ρ is density, but since ρ was not affected by the presence of trace polymer we have $\eta \propto t$ (neglecting correction factors that were always small).

RESULTS

Viscosity of the Jet-A at 20°C was $1.78 \text{ mPa}\cdot\text{s}$ (cp), as determined from $\eta = Bt$ where B was determined by calibration with water at this temperature. At other temperatures, the same B was used because capillary performance is only slightly affected by thermal changes in this range.

Results are displayed as $\eta(c)$ for the Vistanex polymers in Fig. 1 and for the Oppanol polymers in Fig. 2. In each case, data correspond to the three temperatures -25°C , 0°C , and $+25^\circ\text{C}$. Sensitivity of viscosities explicitly to temperature is given in Figs. 3 and 4 for polymers with $c = 500 \text{ ppm}$ and 3000 ppm , respectively. In each case $\eta(T)$ for Jet-A is given for comparison.

There was no evidence with any of the PIB solutions that chemical instability occurred. Fluids even at -25°C were found not to gel and not to produce visible cloudiness, as might be expected for cases of colloidal precipitation. Thus, even for the highest molecular weight (B230 with $\bar{M}_w = 9 \times 10^6$) at the highest concentration ($c = 3000 \text{ ppm}$) and the lowest temperature achieved here ($T = -25^\circ\text{C}$), PIB solutions in Jet-A appear to be

short of saturation and chemically stable. This desirable situation is not matched by all polymers being considered as antimisting candidates.

DISCUSSION

Figures 1 and 2 (note the logarithmic ordinate scale) show the expected monotonically increasing behavior of $\eta(c)$. At each temperature, the two Vistanex polymers (Fig. 1) achieve viscosities at 3000 ppm roughly four-fold larger than Jet-A, while the two Oppanols (Fig. 2) increase roughly five-fold. It is likely that aircraft fuel pumps would be able to handle viscosities that are only four or five times that of Jet-A.

It is also true that concentrations as high as 3000 ppm should not be necessary. Using sparks of 0.5 J, Chao et al.⁴ showed that $c \cong 10$ to 100 ppm should suffice for B230 under circumstances of spark ignition. Furthermore, Kapelke⁵ found with a large-scale flame-ignition device (adopted by the Federal Aviation Administration) that $c = 1000$ ppm of B230 was at least as effective there as 3000 ppm of FM9. It is significant that $\eta(c)$ -increases with B230 in this practical and effective range--100 to 1000 ppm--are only two-fold (Fig. 2) at most.

It should also be noted that the other PIB's have η -increases comparable to that of B230--i.e., two-fold at $c = 1000$ ppm. Dilute-solution shear viscosities are rather insensitive functions of polymer molecular weight. In view of the clear superiority of B230 as a flame suppressant/antimisting agent,^{4,5} it seems reasonable to focus attention on polymers only of the highest possible molecular weight--actually, $[\eta] = KM^a$ seems to be the best correlating parameter⁴--and thus on the production or extraction of PIB's with \bar{M} still higher than that of commercial B230. The penalty in terms of increased η is trivial in comparison with major improvements in AM behavior as \bar{M} (or $[\eta]$) increases.

The very modest polymer-induced increase in viscosity is reflected also in Fig. 3 ($c = 500$ ppm) where curves for all PIB solutions are quite close to the Jet-A curve. The T -dependence of $\eta(T)$ for all solutions follows closely the solvent behavior, as expected, and this fact is likely to prevail down to -45.6°C (-50°F) as well. Thus, if $\eta(T)$ for Jet A were known at -50°A , the viscosities of PIB solutions at 500 ppm could be estimated with some accuracy--provided that saturation limits were not exceeded at the lower temperatures.

Figure 4 shows this same T -dependence to be manifested at 3000 ppm as well, although the upturn for L160 at -25°C (suggested by one point) would seem to violate this. While this higher-than-expected η at 3000 ppm might be explained at -25°C as due to colloidal precipitation, no such event was actually observed and seems unlikely in view of the normal behavior of $\eta(T)$ for the higher- \bar{M} polymers (B200, B230) which seem better candidates for having limited solubility. It is more likely that the single high point in Fig. 4 for L160 (at -25°C) is spurious, representing data scatter. This view is reinforced by Fig. 1, wherein the same point is seen to be inconsistent with the trend of all data shown there as well.

Even though magnitudes of $\eta(c, T)$ for PIB's in Jet-A seem small enough, it is good to bear in mind that fuel pumpability depends on other factors as well. In particular, fluid elasticity enhances greatly the elongational

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viscosity $\bar{\eta}$ that may play a major role in pump and filter performance.

CONCLUSION

Increases in the shear viscosity $\eta(c, T)$ for PIB solutions in Jet-A are quite modest, down to -25°C , and no signs of chemical instability are found. The highest value recorded here was for B230 at 3000 ppm at -25°C , for which $\eta = 24$ cp. It is expected that viscosities for the range -46° to -25°C will exhibit the same trends as found in the present data, but measurements of these must await further funding.

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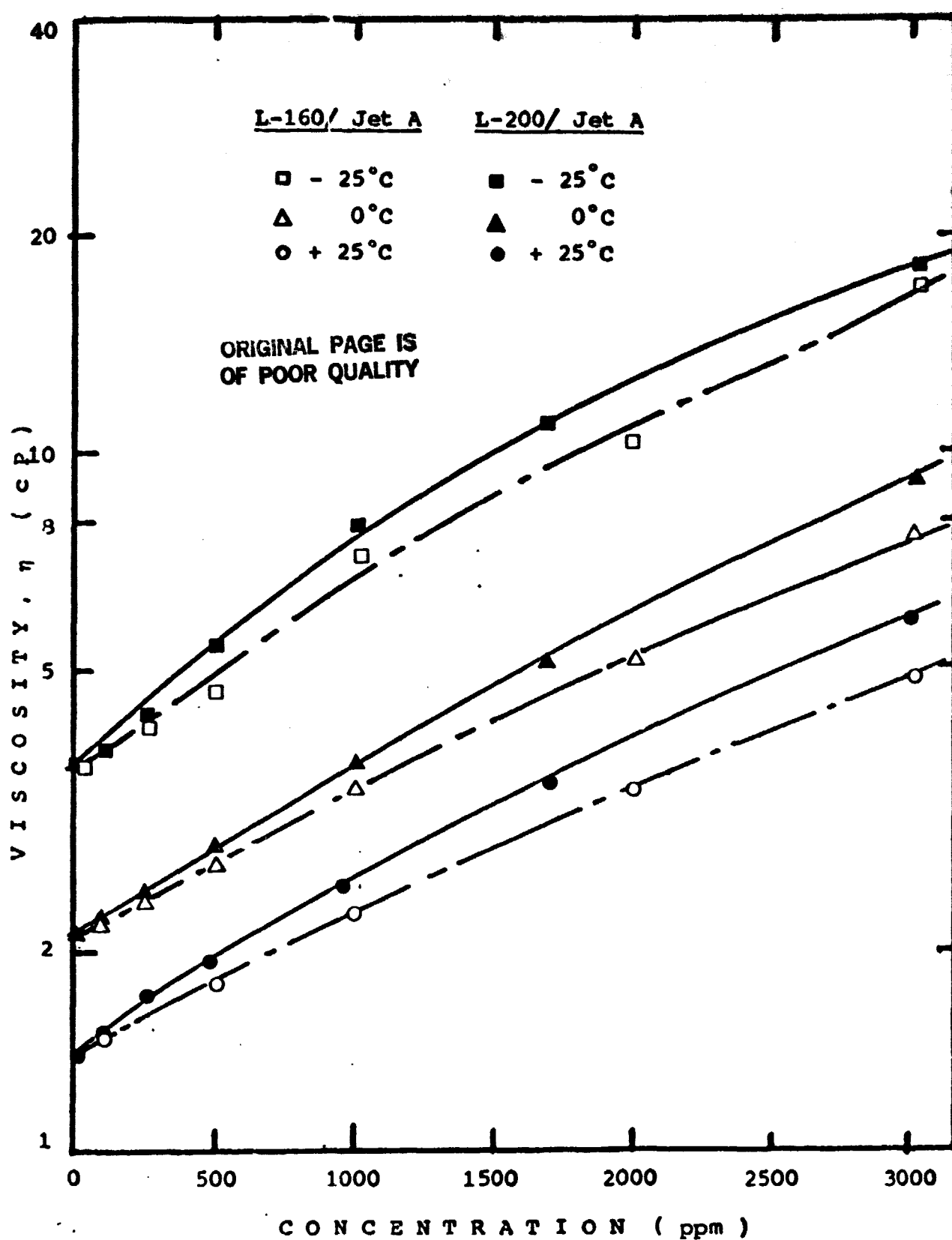


Fig. 1. Viscosity dependence on concentration for two PIB polymers (L160, L200) dissolved in Jet-A. The polymers are compared at -25°C (top two curves), 0°C, and +25°C (bottom two curves).

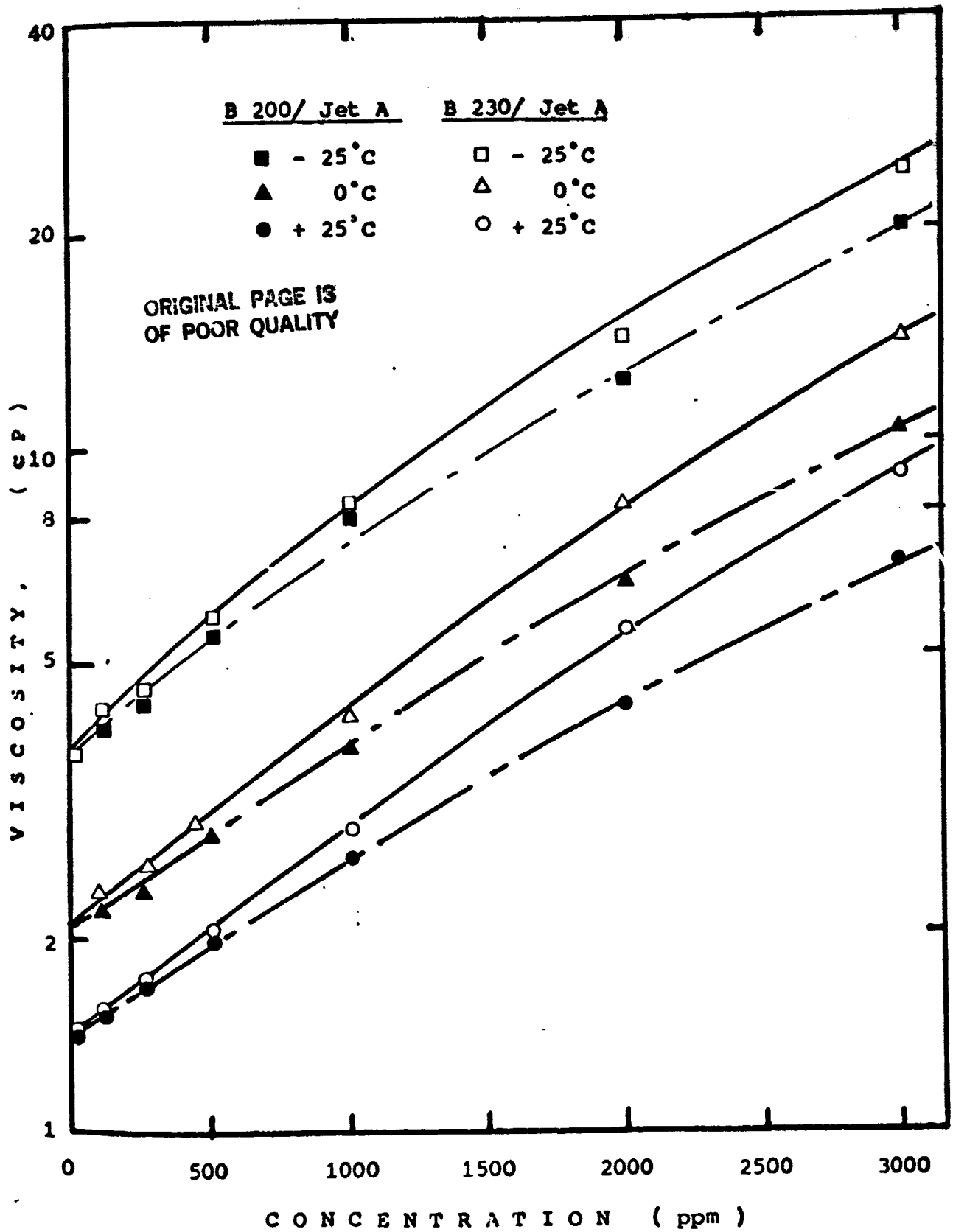


Fig. 2. Like Fig. 1, except that the two polymers are B200 and B230.

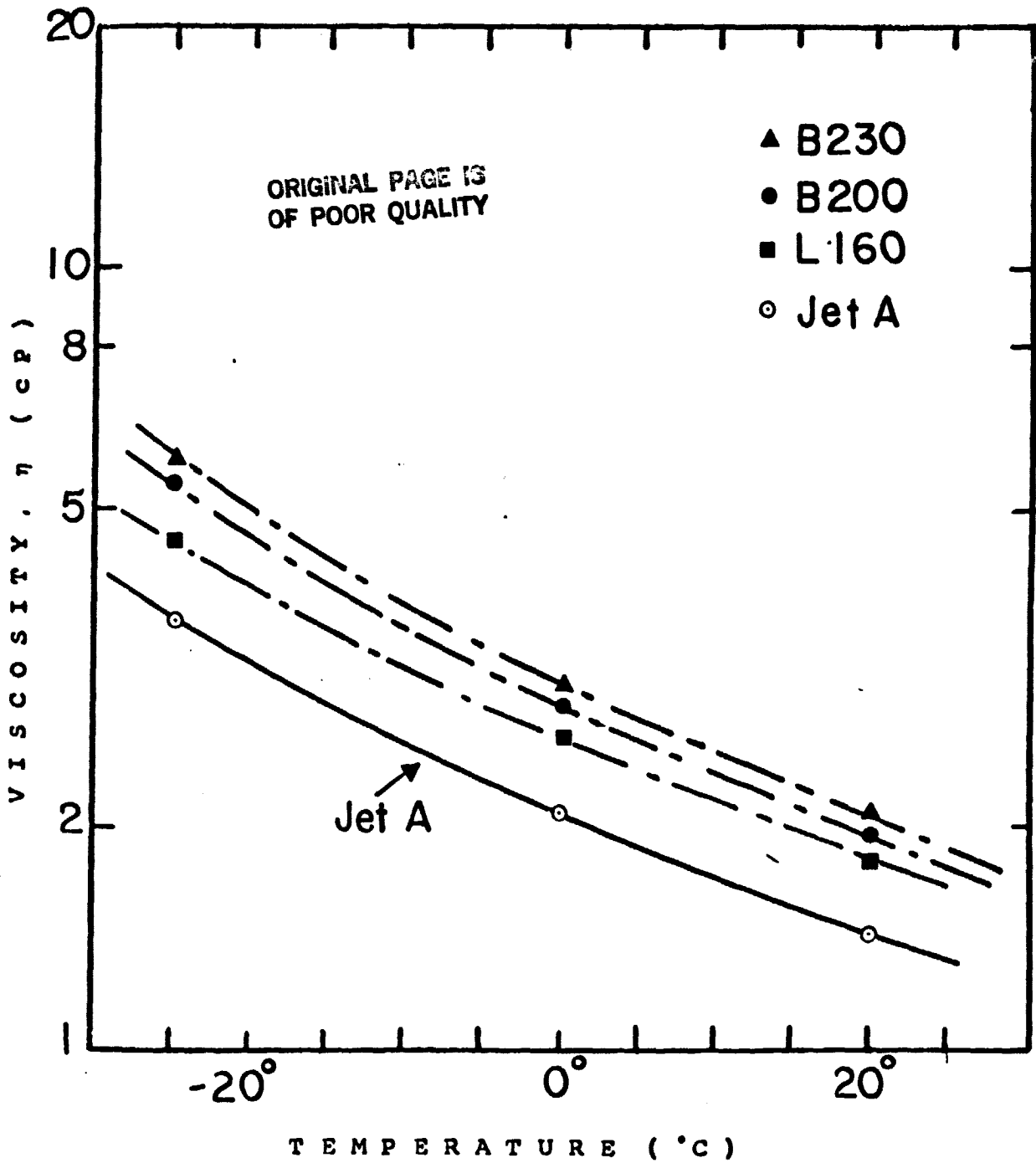


Fig. 3. Viscosity dependence on temperature for three PIB polymers (L160, B200, B230) dissolved in Jet-A, and also for Jet-A itself. Polymer concentration is 500 ppm.

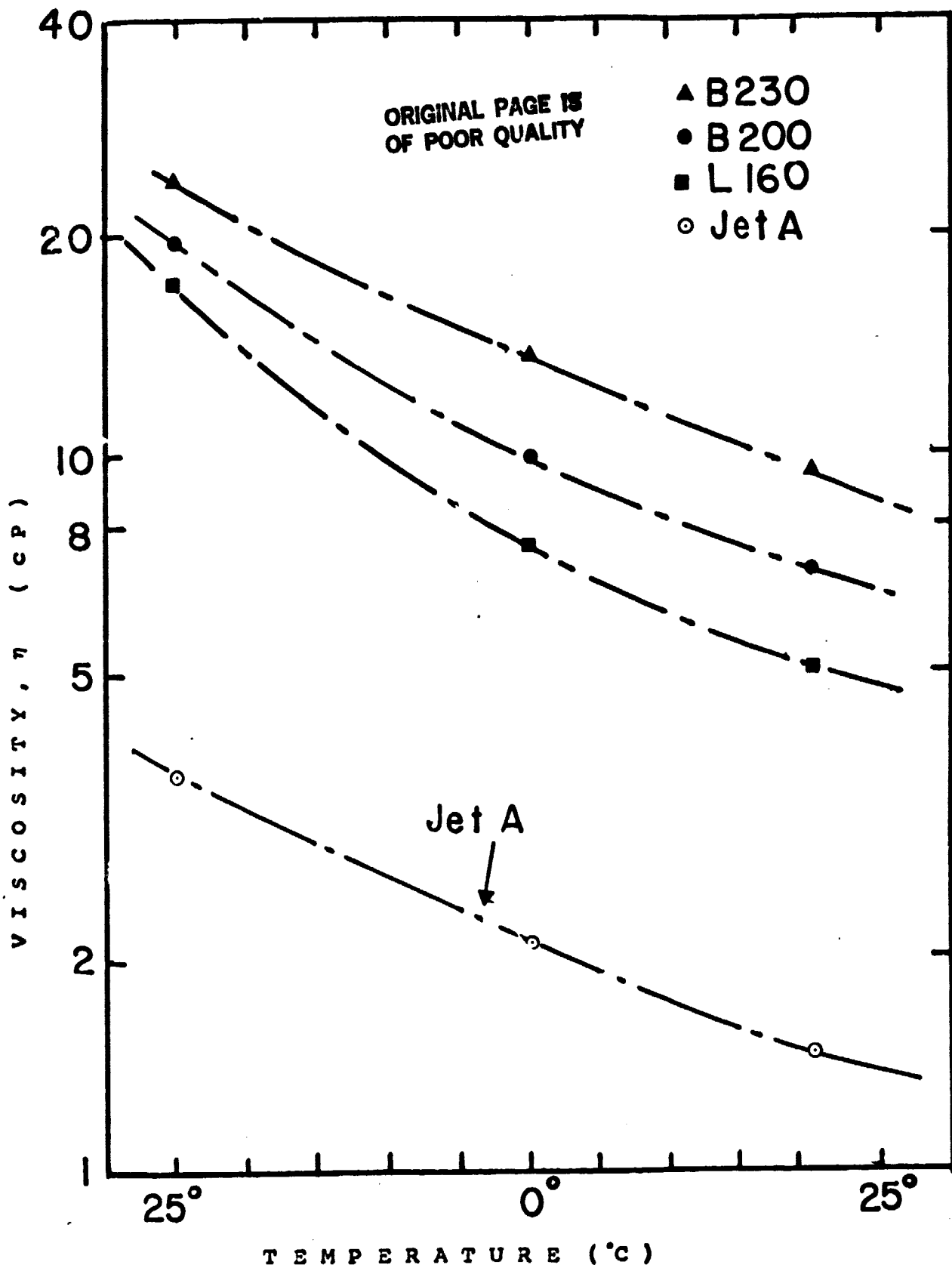


Fig. 4. Like Fig. 3, except that the concentration is 3000 ppm.