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THE EFFECT OF THE MOLECULAR WEIGHT OF ADDITIVE ON THE PROPERTIES OF ANTIMISTING FUELS

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INTRODUCTION

Antimisting aircraft fuels, when ignited, do not produce the roaring fireball which often accompanies aircraft crashes (1). This result is attributable to the suppression of the aerosolization of the fuel by added macromolecules which alter the structure of the droplets of fuel emanating from rent fuel tanks after the crash.

The first studies of the antimisting effect of macromolecules on aviation fuel were carried out in Great Britain in 1968 (2). In that early work it was established that there was a qualitative relationship between the suppression of the atomization of the fuel and the molecular weight of the additive above a certain critical concentration; the latter being inverse to the molecular weight of the additive. Subsequent investigations have demonstrated a dependence of the antimisting effectiveness of polyisobutylene in diesel fuel on the viscosity average molecular weight to a power exceeding 2 (3), and in jet-A fuel to the $2\alpha + 1$ power (4), where α is the exponent in the Mark-Houwink equation.

In their study Chao et al. were able to demonstrate a strong correlation between the extent of antimisting effectiveness and flammability reduction with the maximum ductless siphon height supported by the solution. They introduced the ductless siphon to the study of antimisting fuels as a measure of the elongational viscosity imparted by the macromolecules to the fuel. The apparatus does not provide a uniform elongational flow field but there is no device, at present, for determining the true elongational viscosity of these solutions and the ductless siphon has the advantage of being easy to assemble and use. The precision of the measurements can be improved by drawing the liquid column in a controlled environment, reading the height optically or with a strain gauge, etc. The principal factor of interest with respect to antimisting fuels, however, is that it has been demonstrated that the ductless siphon is a tool for rapidly screening macromolecules for their effectiveness as antimisting agents.

In this work it is suggested that the ductless siphon might also be used for the rapid estimation of the molecular weight of megadalton macromolecules.

EXPERIMENTAL

Three samples of polyisobutylene (BASF: B-100, B-200, B-200-246) were dissolved in isooctane at room temperature with occasional gentle swirling over several days. The viscosity average molecular weights were determined with an Ostwald viscometer from the Mark-Houwink equation (5):

$$[n] = 3.06 \times 10^{-4} \overline{M}_v \; 0.65 \qquad 1)$$

The values are given in Table I.

The height-at-break of serial dilutions of the stock solutions of the three samples was measured in the apparatus of Figure 1. Six measurements were made on each solution and the measurements were averaged. The averaged heights were plotted against the concentration and the slope of each line, h/c, was determined by linear regression analysis. The slope values, along with the correlation coefficients, r, are entered in Table I.

The effect of the molecular weight on the height-at-break property and, by extension, the antimisting effectiveness and the flammability suppression potential of polyisobutylene in isooctane is dramatic.

In a 1975 paper Williams (6) proposed a theory which explains why high molecular weight macromolecules in dilute solution exhibit quite large extensional viscosities relative to lower molecular

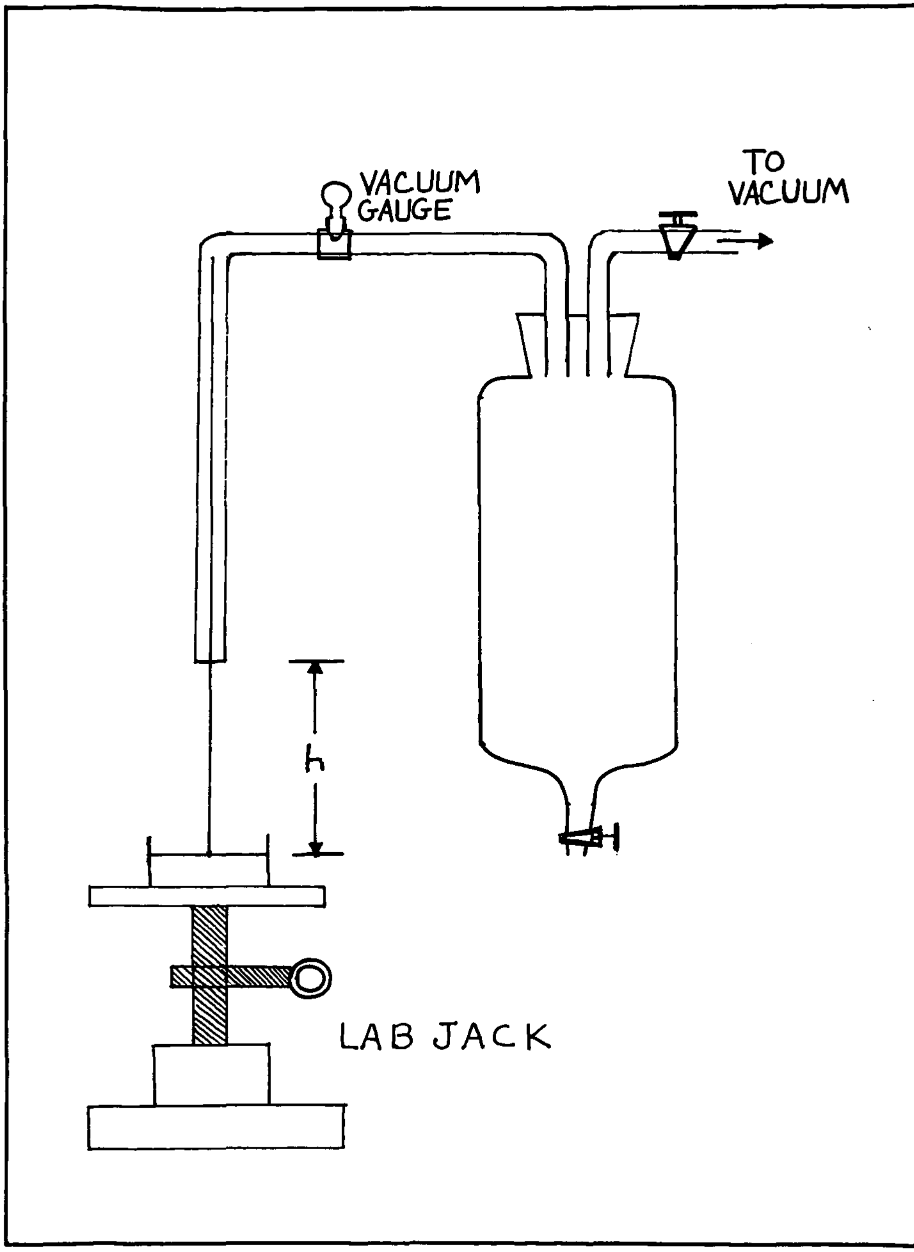

Fig. 1. Ductless siphon apparatus.

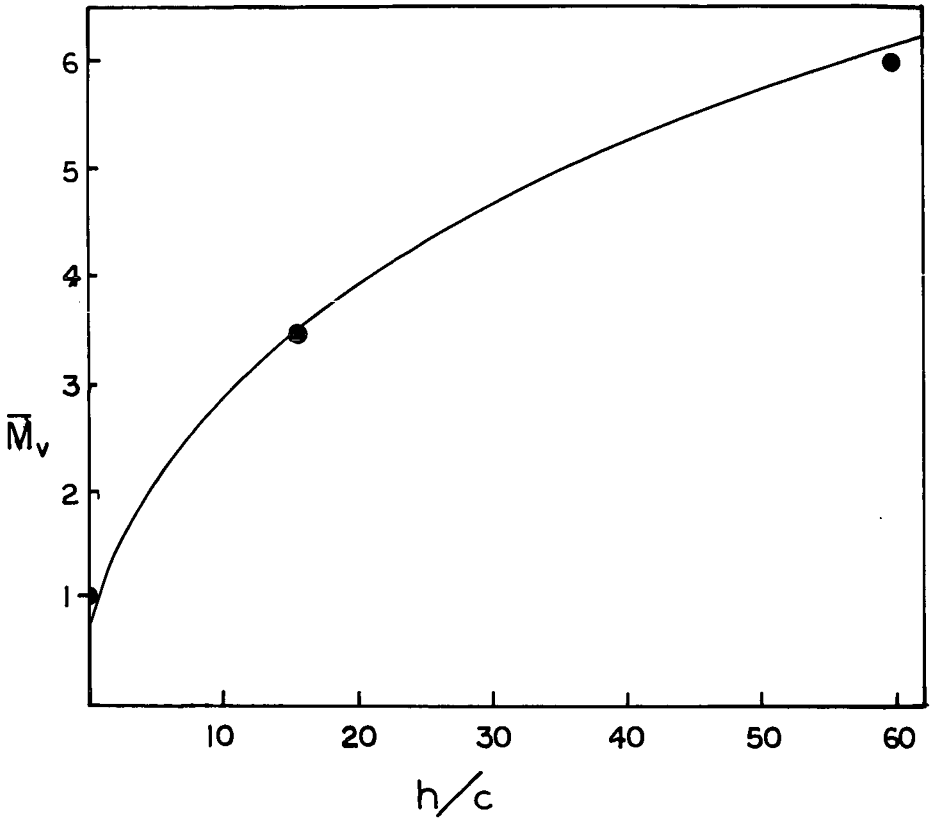

FIG. 2. MOLECULAR WEIGHT VS. SLOPE OF PLOTS OF HEIGHT-AT-BREAK VS. CONCENTRATION OF POLYISOBUTYLENE IN ISO-OCTANE AT 20 °C.

weight species. An extension of the theory applied to the use of the ductless siphon for estimating the extensional viscosity of samples of antimisting fuels was completed last year (7). The working equation is:

$$\frac{\bar{n}}{n_o} = 3\ (1 + \dot{\varepsilon}\ \ c\ n_s\ K^2\ M_v^{(2\alpha + 1)} / \ RT + \text{---}) \qquad 2)$$

where $\bar{n}$ is the extensional viscosity
n_o is the shear viscosity of the solution
$\dot{\varepsilon}$ is the elongation rate in pure extensional flow
c is the concentration in g/dl
n_s is the shear viscosity of the solvent
K and α are the constants of the Mark-Houwink equation.

TABLE I

VISCOSITY AVERAGE MOLECULAR WEIGHT AND SLOPES OF HEIGHT-AT-BREAK VS. CONCENTRATION PLOTS FOR SAMPLES OF POLYISOBUTYLENE MEASURED IN ISOOCTANE AT 20°C

Sample	$M_v \cdot x\ 10^{-6}$ (g/mol)	$\frac{h}{c}$ (cm/g/dl)	r
B-100	1.00	0	0.951
B-200	3.46	15.7	0.999
B-200-246	5.96	59.7	0.999

For a given polymer/solvent, for megadalton samples with the ductless siphon height-at-break measured at the same temperature at which the exponential term in the Mark-Houwink equation is evaluated, we propose the relation:

$$\frac{h}{c} = k\overline{M}_v^{(2\alpha + 1)} \qquad 3)$$

where k is a constant. For the polyisobutylene/isooctane system at 20°C, $\alpha = 0.65$. A plot of $\overline{M}_v$ vs h/c appears in Figure 2, where the theoretical curve, evaluated from the measured height-at-break values, is given by:

$$\overline{M}_v = 1.05 \times 10^6 \left(\frac{h}{c}\right)^{0.44} \qquad 4)$$

Inasmuch as interest in antimisting fuels is growing and ultra high molecular weight macromolecules are markedly superior in their performance in antimisting fuels, this method may be used for rapid estimation of molecular weights when the Mark-Houwink exponential term is known.

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