

## Solutions of Drag-Reducing Polymers—Diameter Effect and Rheological Properties

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### Synopsis

Solutions (0.5% by weight) of two high molecular weight drag-reducing polymers, a polyethylene oxide and an acrylamide copolymer having anionic functionality, were prepared under low and high shear conditions. Rheological measurements demonstrated that high shear preparation causes a decrease in the size of the polymer units, the effect being markedly greater for the polyethylene oxide.

These solutions were diluted to 25 ppm and drag reduction measured in 0.047-in. and 0.93-in. diameter test sections. The method of solution preparation showed no significant effect in the small tube measurements. In the large tube, however, low shear solution preparation led to drag reductions comparable to those found in the small tube, while high shear preparation gave markedly lower drag reductions. These results are discussed in terms of polymer supermolecular structure.

### INTRODUCTION

Drag reduction caused by the addition of small quantities of a high molecular weight polymer to a liquid in turbulent flow is often determined by pressure drop measurements in tubes or pipes, from which per cent drag reductions are calculated. Interpretation of such results and their extrapolation to the larger pipes involved in the practical use of drag-reducing polymers are often difficult because of the uncertainty of the diameter effect. In some cases, the per cent drag reduction observed in larger tubes is only slightly less than that in small ones, while in other cases it is strikingly lower. Ellis<sup>1</sup> has recently shown that unsheared Polyox WSR 301 solutions (10 ppm) gave essentially the same per cent drag reduction in 0.115- and 1.43-cm diameter tubes, but after recirculating in an impeller pump, the solutions showed the original drag reduction in the smaller tube but essentially none in the larger. This clearly demonstrated the dependence of drag reduction on larger tubes on previous shear history of the solution. He pointed out the possibility of the existence of supermolecular structure or aggregates in solutions of drag-reducing polymers which may be reduced by shearing and suggested that pitiuity or "stringiness" at higher concentrations may be an important parameter in characterizing previous shear history. On the basis of the observations of Corino and Brodkey,<sup>2</sup> other workers<sup>3-7</sup> have also suggested that pitiuity may be a general characteristic of drag-reducing polymer solutions.

When the Ellis paper appeared, we were in the midst of an aging study of stock solutions (0.5 or 1.0% concentration) of friction-reducing polymers. These included acrylamide copolymers having either anionic or cationic functionality, hydroxyethyl cellulose, and Polyox FRA. The rheological properties of these stock solutions were measured periodically using the Weissenberg rheogoniometer, and concurrently the drag-reducing efficiency of suitable dilutions was determined. The latter measurements were made in a modified Hoyt<sup>8</sup> turbulent flow rheometer at a Reynolds number ( $Re$ ) of about 20,000. This instrument employs a test section having a diameter of 0.047 in., or 0.119 cm, which is very similar to Ellis's smaller tube. Despite large changes in the rheological properties of certain of the stock solutions, particularly those which were stored at 35°–40°C, no difference in friction-reducing efficiency on aging was observed when measurements were made in the 0.047-in. test section. However, when drag reduction was determined in an 0.93-in.-diameter test section, which was operated at  $Re = 116,500$ , those stock solutions which had shown a marked decrease in the lower Newtonian viscosity,  $\eta_0$ , and in the first normal stress difference,  $P_{11} - P_{22}$  (a measure of the elastic properties of the solution), gave much lower drag reductions in the larger tube than those showing no change in  $\eta_0$  and  $P_{11} - P_{22}$ , thus confirming Ellis's observations.

These results and the fact that the pituities of moderately concentrated solutions of friction-reducing polymers are much higher if the solutions are prepared under very mild shearing conditions<sup>9</sup> prompted the following experiments.

## EXPERIMENTAL

The drag-reducing polymers studied were: Polyox FRA (Union Carbide) polyethylene oxide; Reten 423 (Hercules Incorporated), a high molecular weight acrylamide copolymer having anionic functionality.

Solutions (0.5% by weight) of these polymers were prepared by adding the polymer to about 3 liters of water, stirring gently with a propeller stirrer for 2 hr, then slowly tumbling the container end-over-end for 6 hr. This is referred to as low shear preparation (LSP). A portion of this solution was then subjected to approximately 16 hr of stirring at approximately 2500 rpm by a 1-in.-diameter propeller. This is referred to as high shear preparation (HSP).

The intrinsic viscosities,  $[\eta]$ , of the Polyox solutions were determined in water by the conventional dilution technique, using the Martin equation to extrapolate to zero concentration; those of the Reten were determined in 0.1M KCl. Viscosities and  $P_{11} - P_{22}$  versus shear rate curves for the stock solutions were determined using the Weissenberg rheogoniometer with a 10-cm-diameter cone and plate. Pituities were measured using an apparatus developed in this laboratory, in which a rod is dipped into the solution and then withdrawn at a constant rate.<sup>9</sup> The length of the "string" at break, in cm, is taken as a measure of pituity. Small-diameter (0.047 in.)

drag reduction measurements were made using the Hoyt rheometer, modified to cover a wide range of Reynolds numbers and to permit recycling, in order to follow shear degradation. Recycling of the whole charge of solution in this instrument required three measurement cycles, or 70–75 sec. Large-diameter (0.93 in.) drag reduction was determined in a circulating loop driven by a Moyno pump. Here, the time to cycle the complete charge was 80–85 sec.

## RESULTS AND DISCUSSION

The experimental results are given in Table I. It is immediately apparent that the  $[\eta]$  and the rheological properties of the 0.5% stock solutions are markedly influenced by the method of solution preparation and that Polyox is much more sensitive to high shear preparation than the Reten 423. In the case of the LSP Polyox solution, it still showed non-Newtonian behavior at a shear rate of  $7 \times 10^{-3} \text{ sec}^{-1}$ , while the HSP was essentially Newtonian up to a shear rate of  $20 \text{ sec}^{-1}$ . The latter solution had an  $\eta_0$  which was less than 1% that of the LSP. This is also reflected in the marked difference in  $[\eta]$  between the different preparations. High shear preparation also caused complete loss in pitivity and a drastic reduction in  $P_{11} - P_{22}$ . In contrast, the differences between low and high shear solution preparation were far less for the Reten 423 solutions. These changes in rheological properties strongly suggest that high shear preparation causes a decrease in size of the polymer units which are present in the LSP cases. This hypothesis is further confirmed by the fact that at shear rates of  $0.2 \text{ sec}^{-1}$  and above, all of the solutions except the HSP Polyox showed a marked "stress overshoot" or maximum in shear stress-versus-time curves at constant shear rate, which is an indication of supermolecular structure breakdown.<sup>10</sup> This may be due to either disentanglement, chain scission, or both. At this point, we are inclined to believe that disentanglement is the more important process. Experiments are planned to test this hypothesis.

Consideration of the drag reduction results given in Table I and Figures 1 and 2 shows clearly that the method of solution preparation has no significant effect on either the initial drag reduction or its decrease in the small tube after recycling for 1 hr. In contrast, while the LSP solutions give very similar results in both the 0.047-in.- and 0.93-in.-diameter test sections, the HSP solutions give significantly lower per cent drag reductions in the larger-diameter test section. For further confirmation, samples of solutions which had been recycled in the larger apparatus for 1 hr were then measured in the turbulent flow rheometer. Markedly higher drag reductions were again observed in the smaller-diameter instrument.

These results confirm the often proposed hypothesis (see refs. 3–7 and 11, for example) that to achieve drag reduction there must be a matching between the size of the polymer unit and that of the energy dissipating eddies in the turbulent flow, which are larger in larger tubes. They also support

TABLE I  
Rheological Properties of Stock Solutions and Drag Reduction Results

Stock solutions	$\eta_0$ , poises	$[\eta]$ , dl/g	Pituity, cm	$P_{11} - P_{22}$ <sup>a</sup> , dynes/ cm <sup>2</sup>	Stress over- shoot	0.93-in. Pipe (Re 116,500)		0.047-in. Pipe (Re 20,000) turbulent flow rheometer	
						Initial	After 1 hr	Initial	After 1 hr
						Drag reduction at 25 ppm, %			
Polyox FFA Lot W-8218-R Low shear solution prepn.	>50	21.8	>50	580	yes	67	14	73	27
High shear solution prepn.	0.52	11.7	0	16	no	36	8	68	28
Reten 423 Lot 6144 Low shear solution prepn.	330	23.7	13.6	600	yes	64	38	72	29
High shear solution prepn.	162	19.0	9.1	600	yes	48	39	36	39

<sup>a</sup> At a shear rate of 40 sec<sup>-1</sup>

the hypothesis that "stringiness" or pitness is an important parameter in drag reduction. They suggest that, for a given type of polymer, those rheological properties of concentrated solutions which are indicative of supermolecular structure can be correlated with drag reduction efficiency in larger

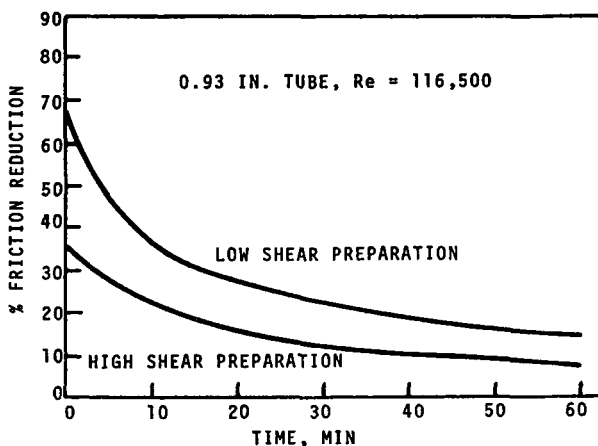


Fig. 1. Effect of preparation conditions of 0.5% Polyox stock solutions on friction reduction at 25 ppm.

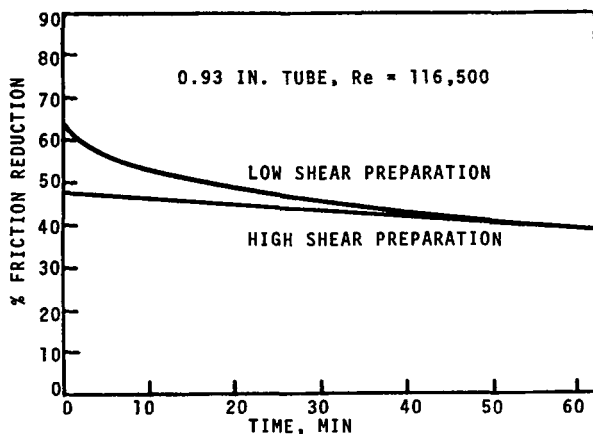


Fig. 2. Effect of preparation conditions of 0.5% Reten 423 stock solutions on friction reduction at 25 ppm.

pipes and that the "diameter effect," which has been so troublesome in drag reduction studies, may really be a measure of aggregation or supermolecular structure of the polymer molecules in the test solution.

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