

The Drag Reduction of Chrysotile Asbestos Dispersions

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Synopsis

The drag reduction (DR) of dispersions of Chrysotile asbestos fibers in aqueous solutions of Aerosol OT and in ethylene glycol, and of glass microfibers in water at a pH of 3 were studied as a function of concentration and temperature with a rotating disc apparatus. Only the dispersions of asbestos in aqueous Aerosol OT showed DR comparable to poly(ethylene oxide) WSR 35 (~500,000 MW), and these dispersions were more fully studied. As was the case with Polyox WSR 35, the asbestos dispersions achieved maximum DR at a concentration of about 200 ppm. They showed no DR temperature dependence at constant Reynolds number at high concentrations but displayed a decreasing DR with increasing temperatures at low concentrations. However, the temperature effect was much smaller for the asbestos dispersions than for Polyox. The asbestos dispersions also showed a much smaller decrease of DR with time at a given disc rotation than was previously measured for poly(ethylene oxide). Electron microscope evidence indicated that less than 10% of the fibers were fully separated, and it is probable that these were the fibers which were primarily active in DR. Hence, if complete separation and dispersion could be accomplished without breaking the fibers, Chrysotile asbestos would be a most potent, not very shear-degradable DR species.

INTRODUCTION

It is possible to suppress and/or delay the initiation of turbulence in a flow system by the addition of trace amounts of certain additives, and this phenomenon is popularly known as drag reduction (DR). The most effective additives to date are long, linear polymers dissolved in a good thermodynamic solvent. In particular, the most effective and most studied systems are aqueous solutions of poly(ethylene oxide) (Polyox) and of polyacrylamide in the 1,000,000 or greater molecular weight range. However, since these highly effective drag-reducing agents are shear degraded by the turbulent flow, the DR decreases with time of flow. It might be expected, however, that fibers having high aspect ratios might be less subject to shear degradation than the more fragile polymer molecules. Although solid additives have long been known to show limited drag-reducing capabilities,^{1,2} Ellis³ has recently demonstrated that dispersions of Chrysotile asbestos fibers (ultimate fiber diameters of ~250 Å) are effective drag reducers at low concentrations, approaching the performance of the better polymer additives. Fragmentary evidence was also presented which indi-

cated that asbestos fibers might be less subject to shear degradation than Polyox. Since the preparation of asbestos dispersions was not described in Ellis' paper, the technique will be fully described in this report.

While most DR theories have tried to relate the phenomenon with a relaxation time of the additive, additional experimental evidence has recently been submitted⁴ which suggests that a relaxation time is involved in the mechanism underlying DR. These data show that at sufficiently low concentrations, the DR of polymer solutions is significantly altered by changes in the temperature, solvent power, and viscosity of the solvent. Since long fibers surely have shorter relaxation times than do the longest DR polymers, they would be expected to be less sensitive to variations in temperature and viscosity of solvent. A further objective of this study was to check this point.

EXPERIMENTAL

Materials

Long-grade asbestos Chrysotile fibers (manufacturer's specification, 3T12) and borosilicate glass microfibers (manufacturers specification, Code 100) were obtained from the Johns Manville Co. The manufacturer specified the glass fibers to have an average diameter of 0.05–0.1 microns. Aerosol OT was obtained as a 25% water dispersion from the Fisher Co. Technical-grade ethylene glycol was obtained from Union Carbide. Distilled water was used in all aqueous preparations.

Method of Dispersion

Asbestos fibers were dispersed in aqueous solutions of 0.25% Aerosol OT and in ethylene glycol. The glass fibers were dispersed in water adjusted (in the presence of fiber) to pH 3 with HCl. Dispersion of these materials was accomplished by stirring with a magnetic stirrer for a period of at least one week. The black magnetic particles which separated from the asbestos fiber bundles adhered to the Teflon-coated magnet of the stirrer and were easily removed. Coarse fibers were removed by filtering through a Buchner funnel with no funnel paper. The concentration of the dispersion was then measured by filtering (using filter paper), then washing a weighted aliquot of the dispersion with methanol, and finally weighing the dried (100°C) filtrate.

Apparatus

The rotating disc apparatus used to measure DR has previously been described.⁴ In brief, a Teflon-coated disc was rotated at a series of constant speeds (0–3000 rpm) and the torque (millivolt output of instrument. Manufacturers calibration was 36.6 mV/in.-lb) on the disc recorded as a function of time via a recorder. The disc and its shaft were placed in a Pyrex cell which contained the solvent, or drag-reducing liquid. The entire assembly was then placed in a temperature-controlled liquid bath.

DR was measured at a given rpm by comparing the torque obtained with the drag-reducing dispersion to that of solvent alone, namely,

$$\text{per cent DR} = \frac{(MV)_s - (MV)_D}{(MV)_s} \times 100$$

where $(MV)_s$ = millivolt output for solvent (corrected when possible for solution viscosity), and $(MV)_D$ = millivolt output for dispersion.

The Reynolds number (a measure of the extent of turbulence) was defined as

$$\text{Re} = \frac{r^2 w}{\nu}$$

where r = radius of disc, in cm; w = speed of rotation, in rad/sec; and ν = kinematic viscosity.

Whenever possible, the per cent DR and the Re were calculated on the basis of a solvent which would have a viscosity equal to that of the dispersion at shear rates comparable to the DR measurements.

Viscosity Measurements

The viscosity of the aqueous asbestos dispersions was measured at 25°C as a function of shear rate with a Haake Rotovisco viscometer using a double gas cup and bob. Figure 1 is a typical log-log plot of the data, where U is a viscometer setting that is inversely proportional to the rpm of the viscometer bob, and S is the instrument meter reading which is directly proportional to the stress on the bob. Since these plots indicated that the dispersions were non-Newtonian, the method described by Van

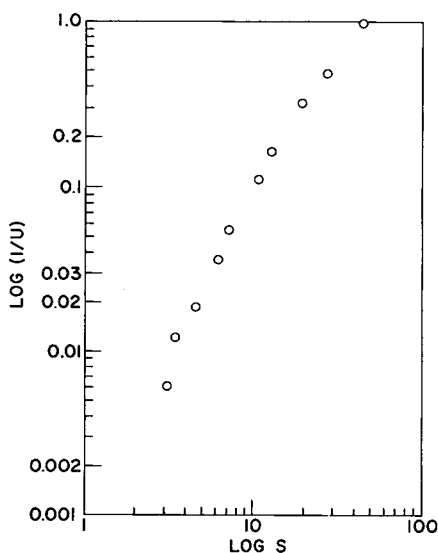


Fig. 1. Shear rate vs. shear stress of 2502 ppm aqueous asbestos dispersions at 25°C.

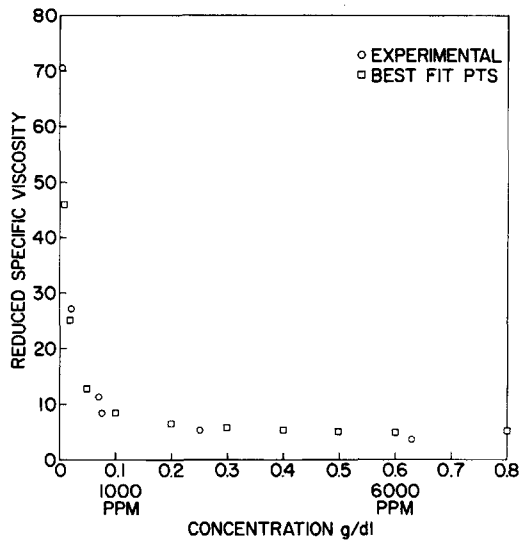


Fig. 2. Reduced specific viscosity vs. concentration of aqueous aerosol OT asbestos dispersions at 25°C.

Wazer and co-workers⁵ was used to determine the true shear rates. The slope of the apparent log shear rate-versus-log shear stress plot was obtained by first fitting the data for each concentration by the method of least squares to a parabolic equation and then differentiating the best-fit equation. At the highest concentration tested, the dispersions seemed to be approaching a second Newtonian behavior for the highest shear rate (in analogy to the behavior of polymer solutions). Hence, the reduced specific viscosity for the highest shear rate was plotted versus concentration (see Fig. 2). A hyperbolic least-squares fit of the data was then used to correct for the viscosity of the aqueous asbestos dispersions in the DR measurements. It was assumed that the relative viscosity of the dispersion was temperature independent. (Note: If η is the viscosity of a solution or a dispersion of concentration C (g/dl) and η_0 is the viscosity of the solvent, then relative viscosity = η/η_0 and reduced specific viscosity = $(\eta - \eta_0)/\eta_0 C$.) No viscosity measurements were performed for the asbestos-ethylene glycol or the glass fiber-water dispersions.

RESULTS AND DISCUSSION

Asbestos-Aerosol OT-Water Systems

Table I is a listing of the concentration dependence of the drag reduction at 30°C of the aqueous asbestos dispersion stabilized with Aerosol OT. If the effect of viscosity is not properly accounted for in the calculation of per cent DR and of the Re, an anomalous maximum appears in the concentration dependence of the drag reduction. Maximum DR, based upon solution

TABLE I
Concentration Dependence of the Drag Reduction Effect
for Aqueous Asbestos Dispersions (30°C)

Concentration, ppm	Based upon solvent viscosity		Based upon dispersion viscosity	
	Reynolds number $\times 10^{-5}$	Drag reduction, %	Reynolds number $\times 10^{-5}$	Drag reduction, %
1552	10.8	39	5.2	45
741	10.8	41	6.2	45
417	10.8	42	6.8	45
390	10.8	43	6.8	46
390	10.1	40	6.3	44
390	9.2	40	5.8	43
390	8.4	39	5.3	42
390	7.5	37	4.7	40
150	6.6	42	7.3	45
125	7.5	21	5.1	25

viscosity, was achieved at a concentration of about 200 ppm. Previously,⁴ a similar value was reported for Polyox WSR 35 in water ($MW \sim 5 \times 10^5$) for the maximum concentration needed to achieve maximum DR. Figure 3 is a plot of per cent DR versus $1/Re$ for the 390-ppm asbestos dispersion for various temperatures ranging from 10° to 90°C. This plot differs from the previous one⁴ where per cent DR was plotted versus Re . The rationale

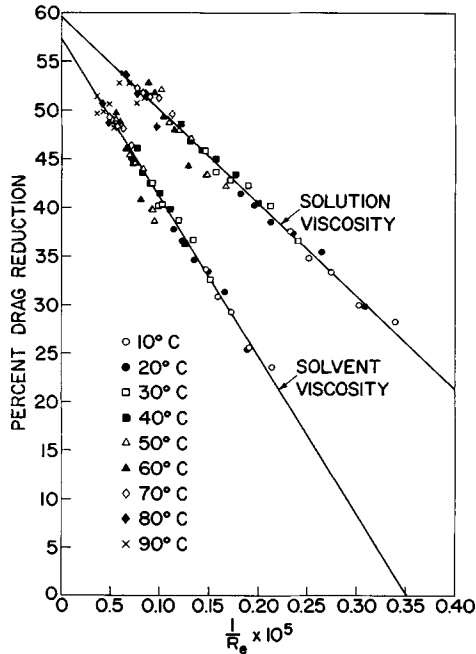


Fig. 3. Per cent drag reduction vs. $1/Re$ for 390 ppm aqueous asbestos dispersions at various temperatures.

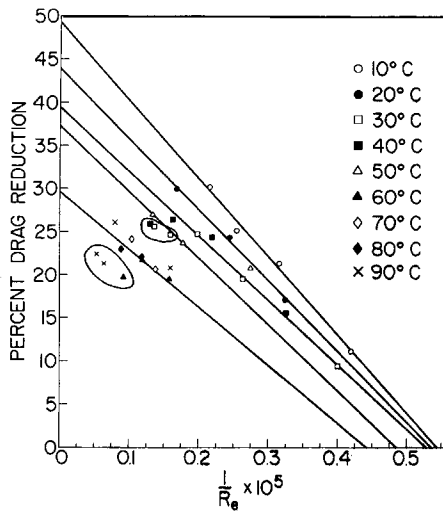


Fig. 4. Per cent drag reduction vs. $1/Re$ for 125 ppm aqueous asbestos dispersions at various temperatures.

behind the $1/Re$ plot is based upon a correlation function previously suggested⁴ namely,

$$\text{per cent DR} = K De \frac{(Re - Re_c)}{(Re)}$$

where Re_c = critical Reynolds number = Reynolds number where DR begins, De = Deborah number = a ratio of a relaxation time of additive to that of flow system, and K = constant (perhaps equal to the maximum DR).

In previous work⁴ it was found that when a large excess of additive above that needed to achieve maximum DR was present, the dependence of DR upon De was eliminated, i.e., $De = 1$. The goodness of the fit suggests the absence of any relaxation time effect at 390 ppm. Such was not the case, however, at a lower concentration of 125 ppm, as seen in Figure 4. Here, the measurements were frequently complicated by a large decrease in per cent DR with time of shear. As was the case for the previously studied polymer solutions, shear degradation increased with increasing rpm, temperature, and Reynolds number. This systematic change allows certain conclusions to be drawn. In Figure 4, the circled points indicate measurements where the indicated DR is low due to degradation effects. On the other hand, at rpm's of 1000 and 1500, no change in per cent DR with time of rotation (at least 1 min) was detected even at 90°C. Moreover, at the two lowest temperatures (10° and 20°C), no excessive degradation was indicated even at 3000 rpm, the data fitting a straight line for each temperature in a $1/Re$ plot. Hence, it would seem that at a concentration of 125 ppm, a small temperature effect exists. These results are similar to those

previously obtained for WSR 35 solutions, where no temperature effect was observed at 571 ppm but did occur at 125 ppm. However, the effect for the asbestos dispersion is much smaller. For example, for a 125 ppm of WSR 35 at 90°C, no DR was measured at 1000 rpm, while a 21% DR was obtained at similar conditions with the asbestos dispersion.

The rate of decrease of DR with time of rotation of the asbestos dispersion, of Polyox FRA solutions ($MW \sim 6 \times 10^6$), and of WSR 35 water solutions are compared in Table II. In making comparisons between agents, it must be recognized that shear degradation will increase with increasing Re and torque on the disc. Table II therefore lists the Re and a relative measure of the millivolt output of the measurement (before DR). It

TABLE II
Comparison of Shear Degradation Effects Between Polyox and Asbestos (90°C)

Substance	Time min	Based upon solvent viscosity			Based upon solution (dispersion) viscosity		
		Reynolds		Drag re- duction, %	Reynolds		Drag re- duction, %
		number $\times 10^{-5}$	Relative torque		number $\times 10^{-5}$	Relative torque	
Polyox FRA (31 ppm, 3000 rpm)	0	27	1	50	27	1	50
	1/2	↑	↑	14	↑	↑	14
	1	↓	↓	7	↓	↓	7
	1 1/2	27	1	5	27	1	5
Polyox FRA (31 ppm, 1500 rpm)	0	14	0.3	36	14	0.3	36
	1/2	14	0.3	26	14	0.3	26
	1	14	0.3	16	14	0.3	16
WSR 35 (571 ppm, 2000 rpm)	0	18	0.5	36	16	0.46	37
	1/2	18	0.5	24	16	0.46	25
	1	18	0.5	15	16	0.46	17
Asbestos (390 ppm, 3000 rpm)	0	27	1	50	17	0.9	53
	1/2	↓	↑	49	↑	↑	52
	1	↓	↑	48	↑	↑	51
	1 1/2	↓	↑	47	↑	↑	50
	2	↓	↑	46	↑	↑	49
	2 1/2	↓	↑	45	↑	↑	48
	3	↓	↑	44.5	↑	↑	48
3 1/2	27	1	43	17	0.9	47	

should also be recognized that degradation may decrease with an increasing excess of additive above that which is needed to achieve maximum DR. If one compared, for example, a 390 ppm of Polyox FRA (a more than 300% excess of polymer) with a similar concentration of asbestos, then FRA would seemingly not degrade for many hours of rotation while the asbestos dispersion would show an immediate but small degradation. On the other hand, if a 390 ppm of the asbestos dispersion is compared (see Table II) with 571 ppm WSR 35 (both at 90°C), then the asbestos dispersion shows significantly less degradation than the polymer, despite the fact that the asbestos dispersion not only has a lower excess of additive but a higher Re and torque.

Asbestos-Ethylene Glycol System

DR could not be obtained for asbestos dispersions in ethylene glycol (see Table III) comparable to that obtained in the surfactant-stabilized aqueous dispersions for temperatures ranging from 70° to 130°C. However, at temperatures of 70°–90°C, the measured DR is relatively high if the low (solvent-based) Re of the system is taken into account. An unusual phenomenon occurred in that per cent DR increased with time of rotation. Visually, the dispersions prepared in ethylene glycol did not seem to be as well dispersed as those prepared in the aqueous surfactant solutions. It may well be that at the low Re 's involved, the shear stresses tended to aid dispersion of the asbestos fibers without producing significant degradation. At the higher temperatures where the Re 's were higher and comparable to those of water at the lower temperatures, the expected high DR's were not obtained. It is possible that the higher temperatures tended to either quickly degrade the dispersion or partially coagulate it.

TABLE III
Drag Reduction of Asbestos Fiber Dispersions in Ethylene Glycol

Concentration, ppm	Temp., °C	Reynolds number $\times 10^{-6}$ ^a	Drag reduction, % ^a	Time, min		
1463	70	2.4	1.0	0		
			7.1	6		
617	70	2.4	1.8	0		
			4.9	4		
	80	3.1	5	9	11	150
	90	3.6	17.2	150	900	0
	100	4.6	10	0	0	0
130	7.4	12.1	0	0	0	

^a Based upon solvent viscosity.

Glass-Water-HCl System

This system (Table IV) was not as efficient as the aqueous asbestos dispersions in regard to both the measured DR's and the concentrations needed to achieve DR. This may be due to either the smaller aspect ratio (the glass fiber is about five times thicker than asbestos) or less successful dispersibility of the glass fibers.

Electron Microscopy

An attempt was made to characterize these dispersions with respect to the degree of dispersion, aspect ratio, and thickness of the fibers by electron microscopy. Samples for the electron microscopy (Philips Model 200)

TABLE IV
Concentration Dependence of the Drag Reduction Effect
for Aqueous Glass Fiber Dispersions (40°C, pH 3)

Concentration, ppm	Reynolds number $\times 10^{-5a}$	Drag reduction, % ^a
80	13.1	0
2218	13.1	15
6728	13.1	23

^a Based upon solvent viscosity.

were prepared by vacuum filtering a few drops of the dispersion through a 300-mesh nickel screen, thus catching the fibers on the screen. It was hoped that this method of preparation would not contribute to coagulation of the fibers. The screen was then cut with a razor blade to fit the stage of the electron microscope. Figures 5 to 7 are typical pictures obtained. It was found that those fibers were, for the most part, not fully dispersed and were also much longer than the field of the microscope. In general, the fibers presented a somewhat entangled appearance. The ultimate diameter of a fully separated asbestos fiber is 200–300 Å. It was estimated that less than 10% of the fibers were of this size. No differences could be detected between asbestos fibers dispersed in Aerosol OT water solutions and those dispersed in ethylene glycol. Photomicrograph comparisons of samples

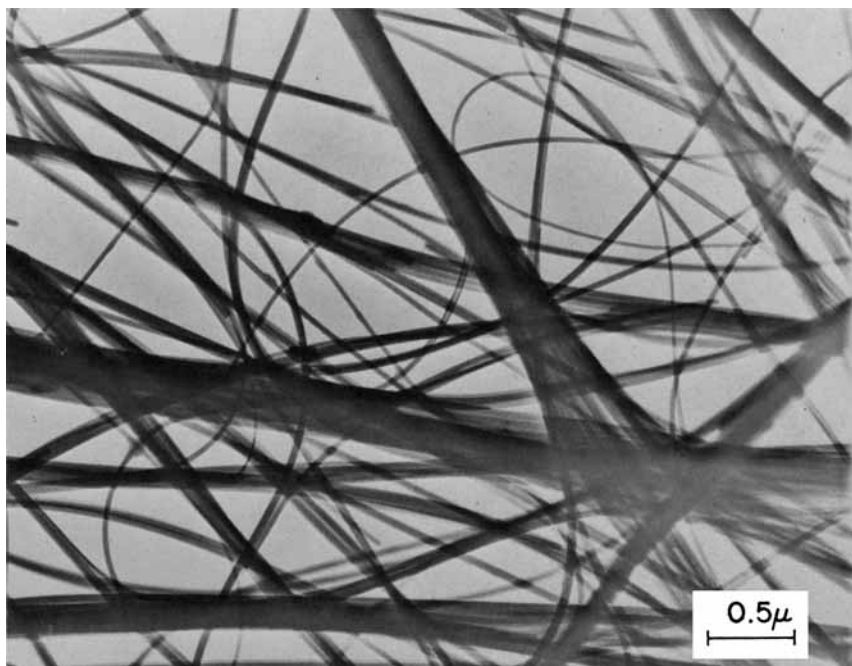


Fig. 5. Electron microscope picture of asbestos fibers (the thin fibers are approximately 200 Å thick).

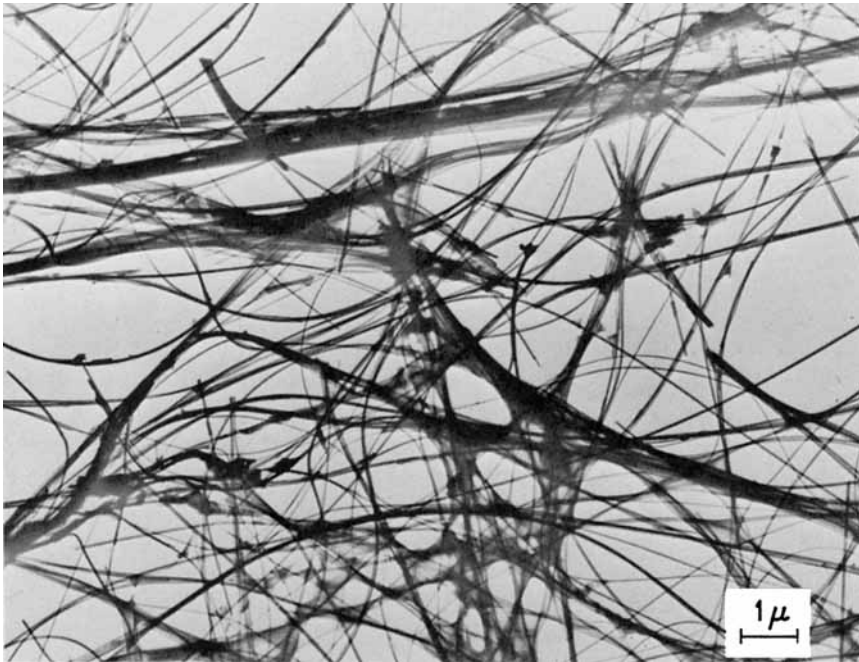


Fig. 6. Electron microscope picture of asbestos fibers at lower magnification.

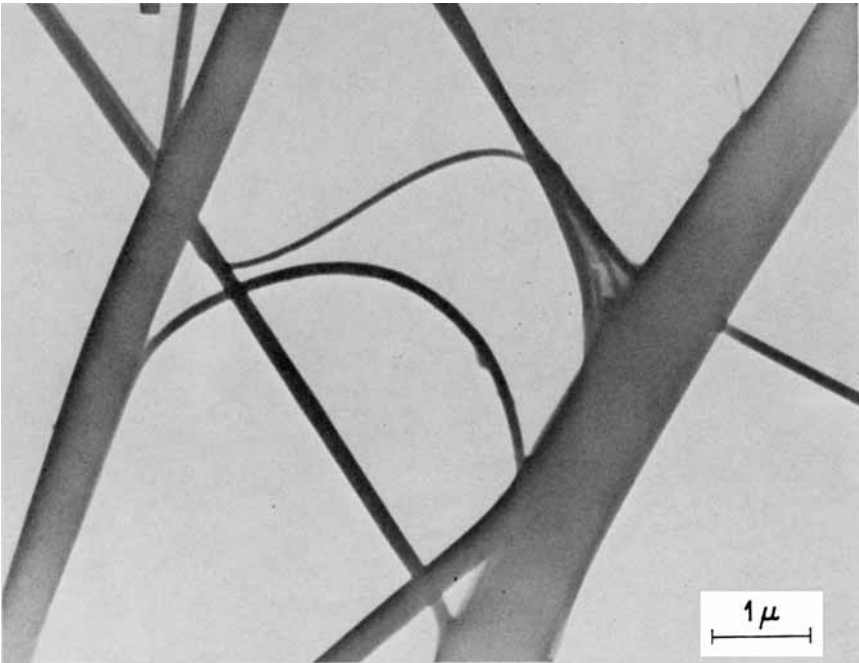


Fig. 7. Electron microscope photograph of glass microfibers (the thin fiber in the center of picture is about 1000 Å thick).

made from Aerosol OT asbestos dispersions which had been sheared in the rotating disc apparatus at 30000 for $\frac{1}{2}$ min and 5 min showed virtually no difference in appearance from that of the unsheared samples. The similar appearance of the sheared and unsheared dispersions (which, however, displayed marked differences in DR capabilities) might possibly be explained by postulating that the very thin, long fibers play the major role in DR. Hence, differences between dispersions might be masked by the large majority of lesser dispersed, entangled fibers. It would seem, then, that if complete dispersion of the asbestos fibers had been obtained, an even more impressive result would have been obtained.

CONCLUSIONS

1. Drag-reducing dispersions of Chrysotile asbestos fibers in aqueous Aerosol OT solutions can be prepared which are fully as effective as Polyox WSR-35 on a weight-for-weight basis.

2. As with aqueous Polyox WSR-35 solutions, the DR of these dispersions decreased with increasing temperature at concentrations below that concentration needed to achieve a maximum DR. The effect, however, was much smaller for the aqueous asbestos dispersions, as expected.

3. When comparisons are properly made, these dispersions show a much smaller decrease in DR with time of rotation than does Polyox.

4. Dispersions of asbestos in ethylene glycol or of glass microfiber in water were not as effective as the aqueous asbestos dispersions stabilized with Aerosol OT.

5. Electron microscope photographs indicated that less than 10% of the asbestos fibers were fully separated and dispersed. No differences, however, were detected between the various dispersions, even though they showed marked differences in DR. It was therefore concluded that only a small fraction of the fibers were active in DR.

6. A long, thin fiber such as Chrysotile asbestos, if fully dispersed and separated, would not only be a highly effective DR agent but would also be less shear degradable than a polymer molecule.

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