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# INVESTIGATION OF RHEOLOGICAL PROPERTIES OF DILUTE SOLUTIONS OF POLYMERIC ANTIMIT AGENTS IN HYDROCARBON FUELS

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Interim Report  
AFLRL No. 59

by  
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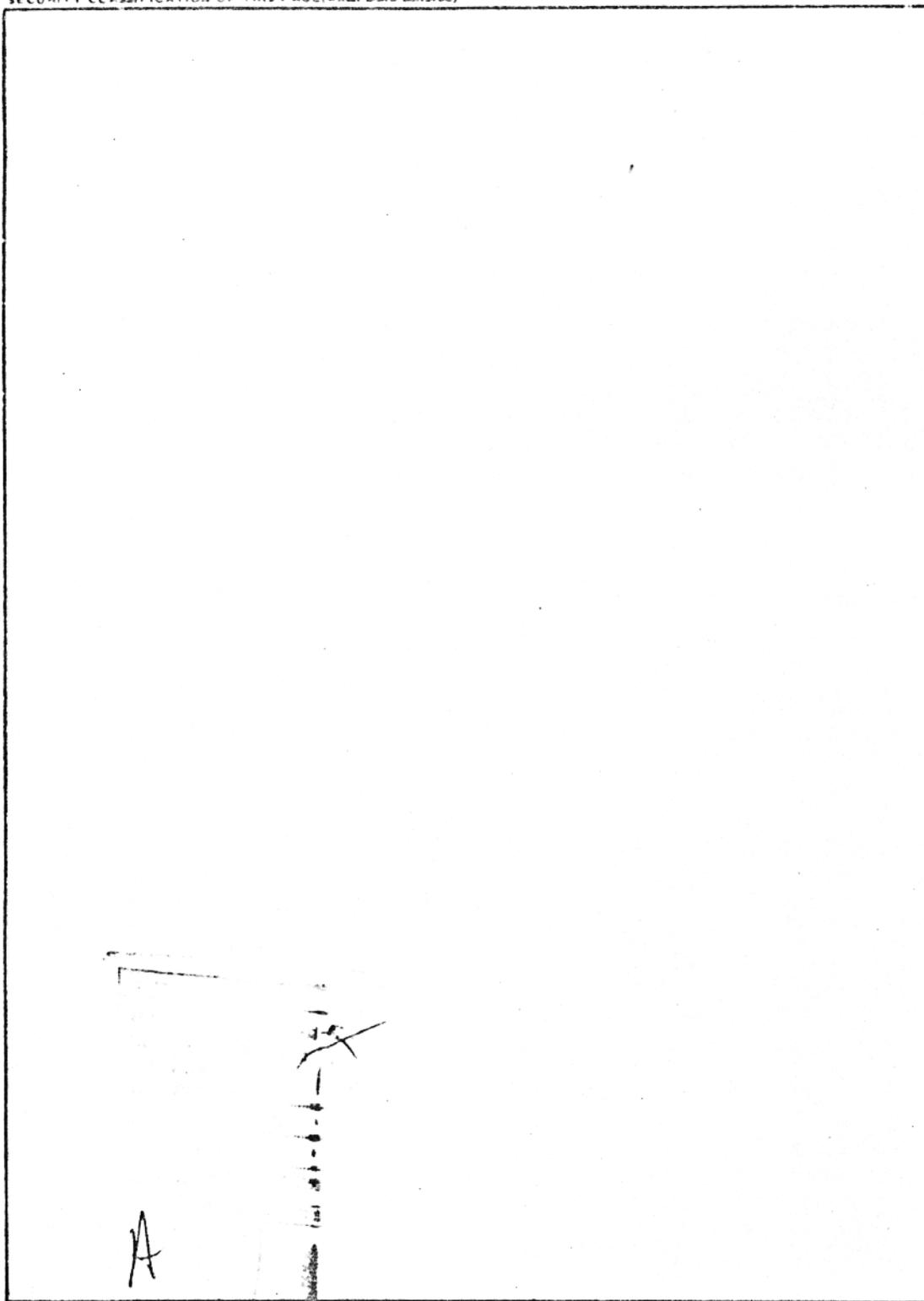
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## FOREWORD

This report was prepared at the U.S. Army Fuels and Lubricants Research Laboratory, Southwest Research Institute, under DOD Contract No. DAAK02-73-C-0221. The project was administered by the Fuels, Lubricants, and Coatings Division, Petroleum and Materials Department, U. S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Virginia, with Mr. F. W. Schaeckel serving as Project Monitor. The AF-LRL project has been conducted under the consecutive cognizance of Dr. James Bryant and Major R. Stryjewski, U. S. Army Deputy Chief of Staff, Research and Development and Acquisition.

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## INTRODUCTION

This report on the rheological properties of dilute polymer solutions constitutes a small part of a larger program currently under investigation by the U.S. Army Fuels and Lubricants Research Laboratory (AFRL) to determine the fire safety and physical properties of fuels containing polymeric antimist additives. An overview of the results obtained by this laboratory and various U.S. organizations has been presented at the 45th meeting of the AGARD NATO Propulsion and Energetics Panel on Aircraft Fire Safety in Rome, Italy, 7-11 April, 1975.<sup>(1)</sup>

One of the most important properties of a liquid that determines its relative resistance to atomization is the viscosity. Even with most non-Newtonian liquids there is usually a good correlation between the stability of a liquid jet and the apparent viscosity, provided that it is measured at the appropriate rate of shear and provided that the fluid is essentially inelastic.<sup>(2)</sup> On the other hand, viscoelastic liquids such as dilute polymer solutions may have very low viscosities and still be highly resistant to atomization! This phenomenon is even more perplexing in light of stability analyses that predict that jets of viscoelastic liquids will be less stable than purely viscous liquids! Some recent studies of jet breakup have verified that, with dilute polymer solutions, the initial instability of the jet occurred sooner than would be expected for a purely viscous liquid (as is predicted by theory); however, the ensuing breakup proceeds by an altogether different mechanism.<sup>(3)</sup> Specifically, the breakup of a viscous jet is characterized by the exponential growth of surface waves and, consequently, is rather abrupt. On the other hand, the breakup of a viscoelastic liquid is much more gradual and is characterized by the formation of a series of droplets held together by thin threads much like a string of beads. The important point is that the formation of a thin thread from a larger jet is associated with an elongational or stretching flow rather than the more familiar shear flow. Furthermore, it has been predicted that viscoelastic fluids should exhibit a much higher resistance when stretched than when sheared. For example, in the model of a rubber-like liquid, the viscosity is independent of the shear rate, i.e., it would appear to be Newtonian from shear experiments, but is an increasing function of the rate of elongation.<sup>(4)</sup>

Some physical insight as to the mechanism for this behavior can be provided by the micro-rheology of a dilute polymer solution. It is generally accepted that a typical linear polymer exists in a dilute solution in the form of a highly flexible coil<sup>(5)</sup> (Figure 1a). If a fluid element of this solution is subjected to a simple shearing flow, as is produced in a typical viscometer, the primary response of the polymer to the impressed velocity gradient is a clockwise rotation. At low rates of shear and with a low viscosity liquid such as JP-8, the solvent will offer very little resistance to this rotational motion; consequently, the polymer molecule will remain in a relatively undeformed state and the viscosity of the solution will be low and essentially independent of the shear rate. An altogether different situation arises if a filament of fluid is subjected to a simple elongation (Figure 1b). In this case, the hydrodynamic forces are much more efficient in being able to orient and deform the polymer molecule.<sup>(6)</sup> Thus, the elongational flow is resisted primarily by the mechanical properties of the polymer, while the shear flow is resisted primarily by the mechanical properties of the solvent.

While several rheological models predict that a viscoelastic liquid can exhibit a much higher resistance to elongation than to shear, experimental verification of these predictions has been conspicuously absent due to the difficulty of producing a rapid elongational flow; however, recently it has been shown that an elongation flow field can be produced by utilizing a porous bed.<sup>(7)</sup> While this geometry is too complex for precise analysis, an approximate analysis has shown that the

\*Superscript numbers in parentheses refer to references at the end of the report.

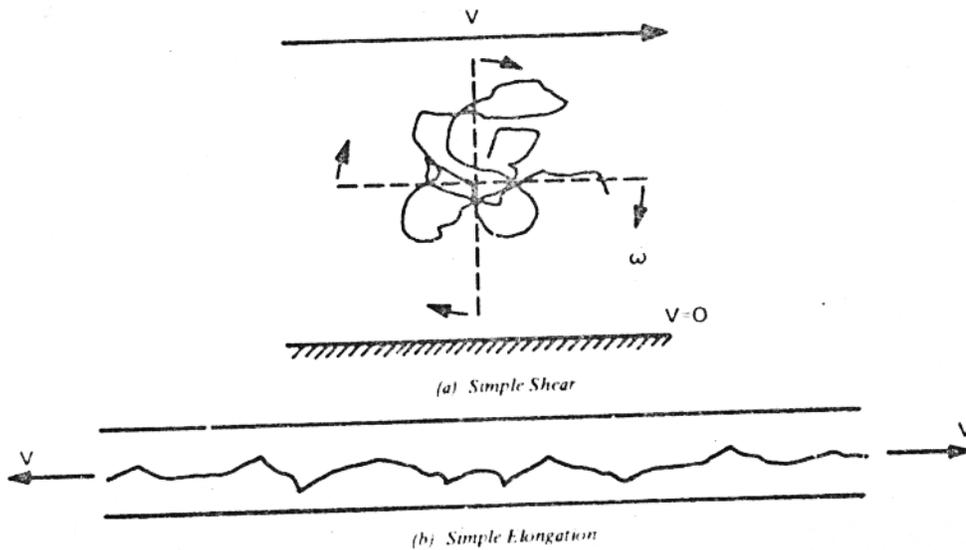


FIGURE 1. MICRORHEOLOGY OF FLEXIBLE POLYMER MOLECULE IN DILUTE SOLUTION

primary mode of deformation will be elongation when the length-to-width ratio of the pore is close to unity. This would be the case for a porous bed made of uniform spheres. On the other hand, the primary mode of deformation will be shear when the length-to-width ratio of the pore approaches infinity, e.g., a porous bed formed by a bundle of capillary tubes. Experimental flow measurements through porous media have confirmed that viscoelastic liquids require much higher pressure drops (sometimes two orders of magnitude higher) than a purely viscous liquid of equivalent viscosity.<sup>(7)</sup>

### OBJECTIVES

The primary objectives of this investigation are as follows:

- (1) Establish that dilute solutions of polymer antimist agents in JP-8 exhibit an abnormally high resistance to steady flow through porous media that is in no way due to adsorption or filtration of the additive.
- (2) Determine the effects of physical properties of the porous media such as particle size and permeability on the relative resistance of these solutions.
- (3) Determine if the resistance to flow in porous media can be related to antimist effectiveness.

### APPROACH

It has been shown that the anomalous behavior of viscoelastic liquids in porous media can be predicted by the Deborah Number<sup>(5)</sup> (defined as the ratio of the characteristic fluid relaxation time to the characteristic time scale of the deformation process). Unfortunately, the normal stress

differences that are required to calculate the fluid relaxation time are difficult to measure for low viscosity solutions, consequently, we will take a less basic approach.

At low Reynolds' numbers\*, the flow of Newtonian liquids through a porous bed is governed by the Darcy equation:

$$Q = \frac{KA\Delta P}{\mu L} \quad (1)$$

where  $Q$  is the volumetric flow rate,  $A$  is the cross-sectional area of the bed,  $L$  is the length of the bed,  $K$  is the permeability,  $\Delta P$  is the pressure drop, and  $\mu$  is the viscosity. Since dilute solutions (0.2 percent) of AM-1† in JP-8‡ appears to be Newtonian in steady flow through capillary tubes, deviations from Equation 1 can be used to detect viscoelastic behavior, provided it can be established that adsorption or filtration effects are not significant. This can be accomplished by measuring the permeability of the porous media with Newtonian (inelastic) liquids of known viscosity (i.e., mineral oil and JP-8) before and after the use of the polymer solutions and also by showing that the flow of these solutions does not exhibit any time dependency or hysteresis effects.

In order to investigate the effect of pore size and permeability on the relative resistance of viscoelastic liquids, we will assume that the porous bed can be approximated by a bundle of capillary tubes.<sup>(8)</sup> While it is realized that this oversimplified model neglects the pore entrance effects that are probably the primary reason for the anomalous behavior of viscoelastic liquids, it might at least be able to serve as a basis for comparing porous beds consisting of similarly shaped particles. Using this approach, we can define consistency variables:

$$\tau_c = \frac{2D_p \epsilon \Delta P}{25(1 - \epsilon)L} \quad (2)$$

$$F(\tau_c) = \frac{3(1 - \epsilon)Q}{AD_p \epsilon^2} = \frac{1}{\tau_c^3} \int_0^{\tau_c} \tau^2 f(\tau) d\tau \quad (3)$$

Where  $\tau_c$  is an average shear stress scaled to the porous media and  $4F(\tau_c)$  is an average shear rate. Accordingly, a "Darcy Viscosity" can be defined as:

$$\eta_c = \frac{\tau_c}{4F(\tau_c)} \quad (4)$$

When  $\eta_c$  is Newtonian, Equation 4 reduces to the Darcy Equation in which

$$K = \frac{D_p^2 \epsilon^3}{150(1 - \epsilon)^2} \quad (5)$$

is the predicted permeability. In the following experiments we will measure the permeability and particle size and then use Equation 5 to calculate the porosity. If the analog to capillary tube

\*  $N_{Re} = \frac{D_p Q \rho}{150 \mu (1 - \epsilon) A} < 0.05$ ,  $\rho$  is the density,  $\epsilon$  is the porosity, and  $D_p$  is the particle diameter.

† Rheological studies have initially been confined to an antimist agent designated by AFRL as AM-1. This is a proprietary product of Continental Oil Co.; hence, little can be said about its chemical constitution except that it is a long-chain hydrocarbon polymer with a molecular weight in excess of one million.

‡ Tentative Military Specification (equivalent to Jet A-1).

experiments is correct, flow data of viscoelastic solutions in different porous media should result in the same Darcy Viscosities when expressed in terms of  $\tau_c$  and  $F(\tau_c)$ .

A second and equivalent approach is to assume a rheological model for the fluid and then to calculate the flow curve. Since the behavior of viscoelastic solutions in porous media is similar to that of a shear thickening fluid (it is important to note that this is just an apparent effect) one could express such behavior in terms of a power law model, i.e.,

$$\tau = mf(\dot{\tau})^n \quad (6)$$

Where  $\tau$  is the shear stress,  $f(\dot{\tau})$  is the shear rate, and  $m$  and  $n$  are rheological parameters. Using Equation 6 with Equations 2 and 3, the predicted pressure drop for the flow of a power law fluid becomes<sup>(8)</sup>:

$$\frac{\Delta P}{L} = \frac{150m \left(9 + \frac{3}{n}\right)^n (1 - \epsilon)^{n+1} Q^n}{12D_p^{n+1} \epsilon^{2n+1} A^n} \quad (7)$$

The rheological parameters  $m$  and  $n$  will be obtained by curve fitting the experimental data with Equation 7.

The equivalence of the two approaches is readily apparent by the fact that we can also define a Darcy Viscosity from the Power Law Parameters:

$$\eta_c = m^{1/n} \tau_c^{1 - (1/n)} \quad (8)$$

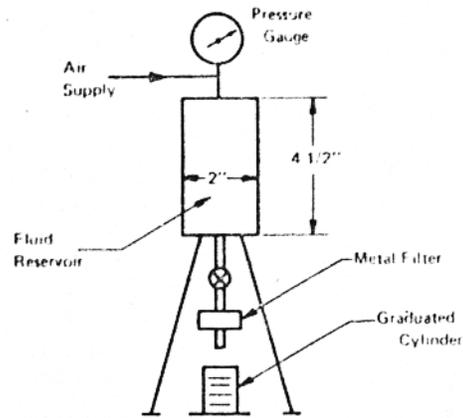
Both methods have their advantages and disadvantages. For example, analysis of flow data by consistency variables is simple and direct, and the resulting Darcy Viscosity is measured in familiar units of poise; however, it is generally a complex function of the shear stress or shear rate. On the other hand, while the Power Law Parameters are slightly more difficult to obtain and have less physical meaning to us, they are able to correlate the flow over a wide range of conditions, thereby making it easier to quantitatively compare two experiments. Since the rheological behavior in capillary tubes indicate that the dilute AM-1 solutions are Newtonian, Equation 7 will not be able to predict viscoelastic behavior; however, it may be possible to determine  $m$  and  $n$  in a particular porous bed and then predict the flow in a bed of similar pore geometry but different pore size and permeability.

In order to determine whether the resistance of AM-1 solutions is related to fire safety, we will compare the effect of AM-1 on the mist flammability and the Darcy Viscosity. The mist flammability will be determined by the Mist Flashback Test<sup>(9)</sup>, which has been used to simulate the air shear encountered in a full-scale helicopter crash.

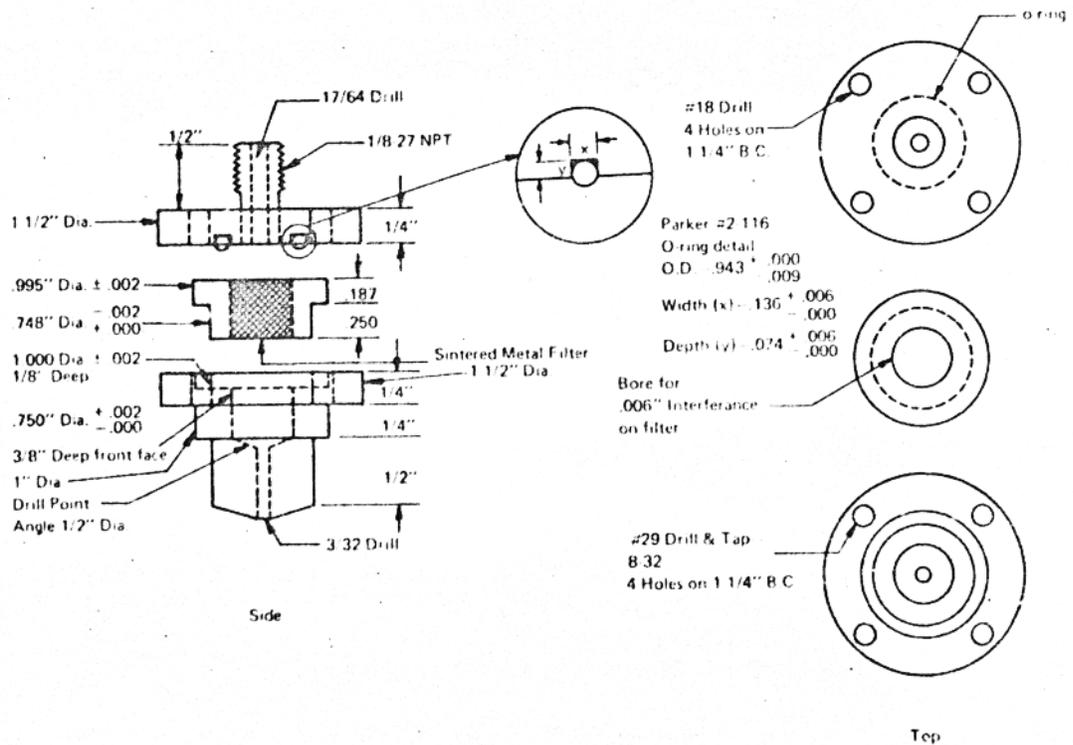
## EXPERIMENTAL

### Description of Apparatus and Procedure

Flow data were obtained with the simple apparatus illustrated in Figure 2a. This device is essentially a scaled-down version of the capillary tube viscometer used in the rheological studies of



(a) Diagram of Apparatus



(b) Detail Drawing of Filter Holder

FIGURE 2. DIAGRAM OF APPARATUS AND FILTER HOLDER

emulsified fuels<sup>(10)</sup> in which the capillary tube has been replaced by a metal filter (details of the filter holder assembly are shown in Figure 2b). In a typical experiment, one would set the pressure and then measure the mass or volumetric flow rate by collecting a sample over a particular time interval. It was found that determining the weight of mineral oil was more accurate than determining its volume; however, with low viscosity liquids, both methods worked equally well.

Measurements were made at both increasing and decreasing pressures and over different time intervals so as to detect changes in permeability due to adsorption or filtration effects.

### Physical Properties of Porous Media

The porous media used in this investigation were in the form of sintered bronze filters.\* Two different grades (460 and 230) corresponding to two different particle sizes, and two different filter sizes (1/8 X 5/8 in. and 7/16 X 7/16 in.) were used in the investigation. Eight of the 1/8-in. filters were pressed into a single holder to form a composite filter having a thickness of approximately 1 inch. With the 7/16-in. filters, only a single element was used.

The dimensions of the metal particles in the 460- and 230-grade filters were determined with a microscope and calibrated eyepiece. Each particle was characterized by two length dimensions  $x_1$  and  $x_2$ . The mean and standard deviation of these measurements are presented in Table I. The ratios of these average dimensions were 0.78 and 0.81 for the 460 and 230 grades, respectively. These ratios show that the particles are not truly spherical, but that both grades have essentially the same characteristic shape. An average particle diameter was calculated by taking the arithmetic average of the two length dimensions, and was found to be 0.038 cm and 0.076 cm for the 460 and 230 grades, respectively.

TABLE I. PHYSICAL PROPERTIES OF SINTERED BRONZE FILTERS

Grade	Particle Dimensions				$X_1/X_2$	$D_p$ (cm)	Filter Dimensions		Permeability (Darcies)	Porosity*
	Mean $X_1$ (cm)	Std. Dev. $\sigma_1$ (cm)	Mean $X_2$ (cm)	Std. Dev. $\sigma_2$ (cm)			Length (cm)	Area (cm <sup>2</sup> )		
460	0.0328	0.003	0.0422	0.003	0.78	0.038	1.11	1.0	70 to 89	0.324 to 0.342
230	0.0670	0.004	0.0840	0.005	0.81	0.076	1.13	1.0	310 to 322	0.323 to 0.332
460	—	—	—	—	—	—	2.51†	1.92	85	0.330
230	—	—	—	—	—	—	2.57†	1.92	300	0.323

\*Calculated from Equation 5

†Eight 1/8 in. elements.

Permeabilities were determined from the slope of the flow curves for both mineral oil (133 cp at 78°F) and a JP-8/mineral oil blend (8.0 cp at 78°F). Five different single-filter elements exhibited a range in permeabilities of 72 to 89 Darcies for the 460 grade and 310 to 322 Darcies for the 230 grade. The two composite filters were very close to these values.

### Preparation and Properties of Blends of Antimist Agent in JP-8 Fuel

The antimist agent, AM-1, is normally received as a 5-percent concentrate (approximately) in low-volatility kerosene. Laboratory batches (less than 5 gallons) of dilute solutions of this additive are routinely prepared by adding a predetermined volume of the concentrate to a measured volume of base fuel with continuous stirring, using a small propeller-type blade. The solution is stirred at a slow rate until it becomes clear and free of undissolved aggregates of concentrate. Stirring is continued for about one hour after dissolution appears to be complete.

\*Perth Metal Industries, Ltd., P.O. Box 572, Monteith Avenue, Stratford, Ontario.

Following preparation of a new batch of AM-1 antimist fuel, the concentration of polymeric antimist agent is routinely checked by measuring the existent gum content (ASTM D-381) of the blend and of its base fuel. In addition, the flash point (Penske-Martens, D-93) is determined to confirm that the blending procedure has not caused significant evaporation losses. Since capillary tube data of AM-1 solutions produced linear graphs up to wall shear rates of  $1300 \text{ sec}^{-1}$  and concentrations up to 0.2 percent, the simpler ASTM D-445 viscosity method was used routinely to check the viscosity of each newly prepared blend. The data presented in Table 2 illustrate the influence of additive content on viscosity (ASTM D-445) for several different concentrations of AM-1 in JP-8R.

TABLE 2. VISCOSITY FOR NEAT AND ANTI-MIST JP-8R FUEL BLENDS

AM-1 Content (wt%)	Viscosity [ $\text{cS}$ (ASTM D-445) @ 24 C]
0.0	2.1
0.05 AM-1	3.0
0.07 AM-1	3.3
0.1 AM-1	3.9
0.2 AM-1	6.5
0.3 AM-1	9.0

### Discussion of Results

Flow data for triplicate experiments with a 0.2-percent AM-1 solution through two different grade (460 and 230) filters are presented in Figure 3. Since the dashed lines are the expected results

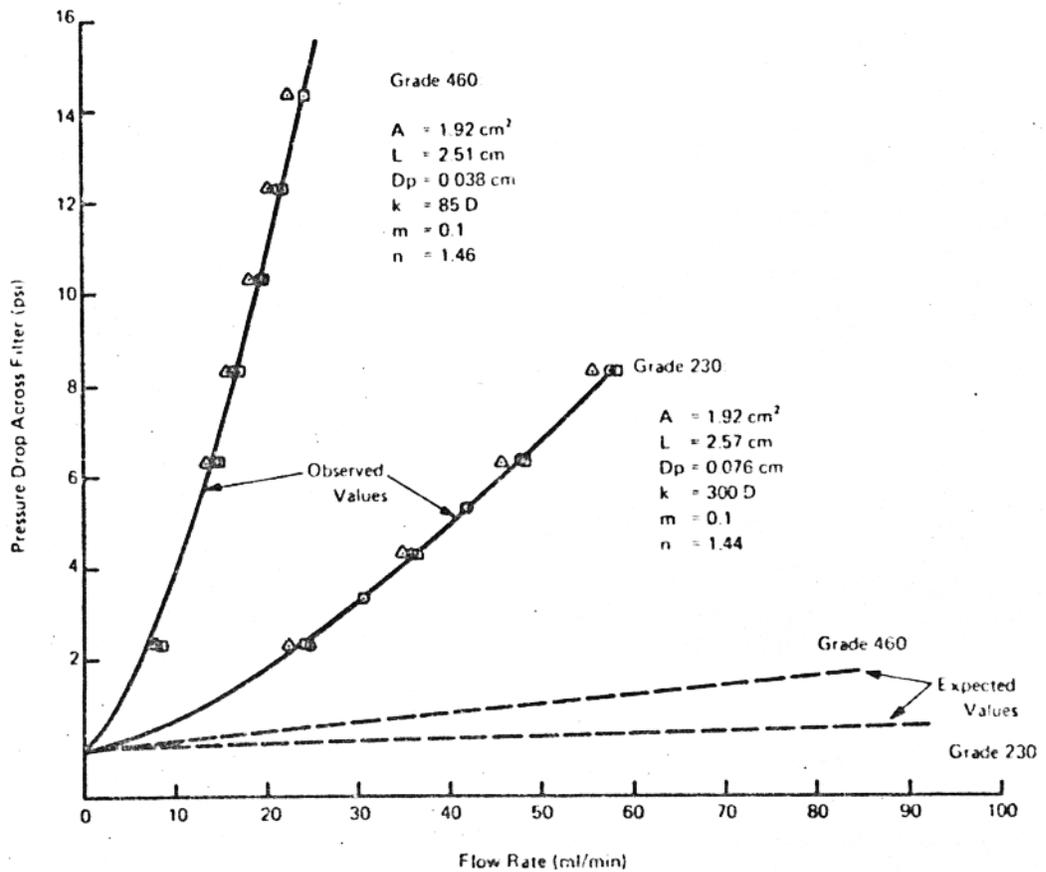


FIGURE 3. FLOW CHARACTERISTICS OF A 0.2-PERCENT AM-1 SOLUTION IN TWO DIFFERENT GRADE FILTERS

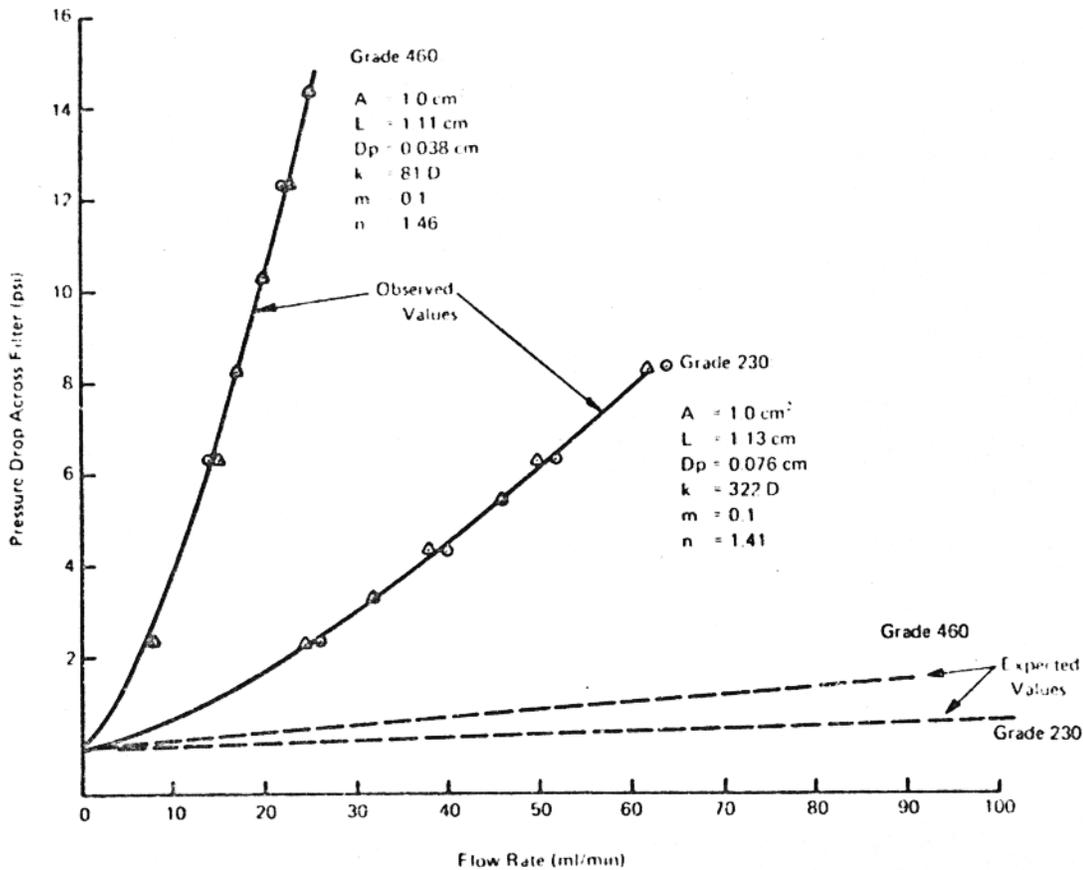


FIGURE 4. FLOW CHARACTERISTICS OF A 0.2-PERCENT AM-1 SOLUTION IN TWO DIFFERENT GRADE FILTERS

for a Newtonian liquid having the same shear viscosity as the polymer solution, the ratio of the observed to the expected pressure to produce a specified flow demonstrates the abnormally high resistance that these solutions exhibit in porous media. The curves drawn through these data were calculated by Equation 7 using the measured physical properties of the filters and assuming values for the Power Law Parameters. The best fit was obtained with  $m = 0.15$  and  $n = 1.46$  and  $1.44$  for the 460 and 230 grades, respectively. The higher  $n$  value indicates a slightly higher specific resistance in the smaller pores. Flow data were also obtained with filters having essentially the same permeabilities but different dimensions from those used in the first series of experiments. The results shown in Figure 4 yield very close to the same Power Law Parameters ( $m = 0.15$  and  $n = 1.46$  and  $n = 1.41$ ). Thus, the anomalous resistance appears to be essentially independent of end effects.

In Figure 5 we have expressed the data in terms of the consistency variables defined by Equations 2 and 3. This approach shows that the Darcy Viscosity (Equation 4) or the resistance to flow is higher in the finer (460) grade filter but is essentially independent of the filter dimensions. While this is in agreement with our interpretation of the Power Law Model approach, we can make a quantitative comparison by choosing a particular shear stress or shear rate and calculating the Darcy Viscosity from Equations 4 and 8. Thus, from Figure 5 at a stress of  $1000 \text{ dynes/cm}^2$ , the Darcy

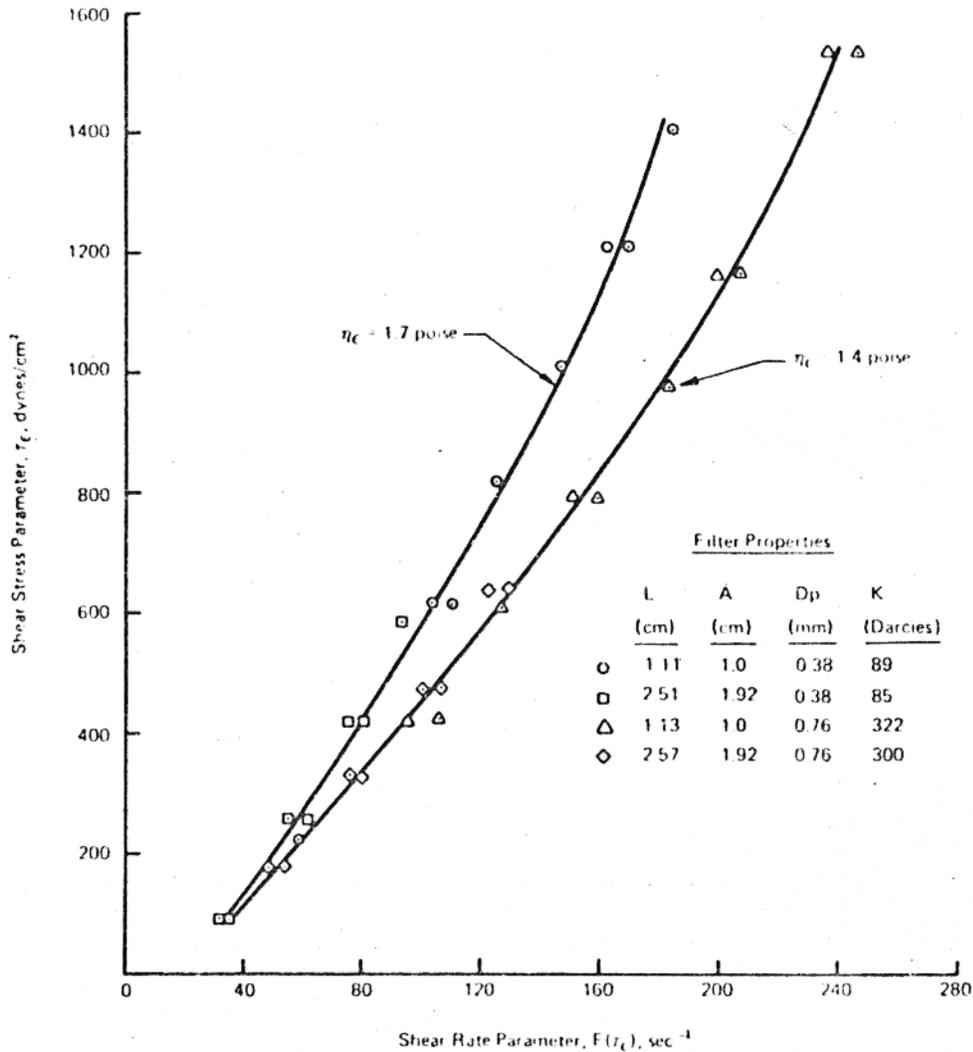


FIGURE 5. USE OF CONSISTENCY PARAMETERS FOR FLOW DATA IN DIFFERENT FILTERS

Viscosity is 1.7 and 1.4 poise for the 460- and 230-grade filters, respectively, whereas the Power Law Model calculates 1.8 and 1.5 poise. This small difference is very close to the experimental repeatability and can be attributed to the accuracy to which the Power Law Parameters were fit to the data.

In order to gain more confidence as to the repeatability of these results, additional data were obtained with several different filters. In the analysis of these results it has been assumed that filters within a given grade have the same average particle size. The results of these experiments, which are summarized in Table 3, confirm that the average Darcy Viscosity (at 1000 dynes/cm<sup>2</sup>) is 1.7 and 1.4 poise with a standard deviation of 0.05 and 0.07 poise for a 0.2-percent AM-1 solution in the 460- and 230-grade filters. When one considers that the shear viscosity of this solution is only 0.056 poise, it is evident that the elastic resistance of this solution in these porous media is from 25 to 30 times the viscous resistance.

TABLE 3. FLOW PROPERTIES OF A 0.2-PERCENT AM-1 SOLUTION  
IN DIFFERENT FILTERS

Filter Properties				Power Law Parameters		Darcy Viscosity
<i>L</i> (cm)	<i>A</i> (cm <sup>2</sup> )	<i>D<sub>p</sub></i> (cm)	<i>K</i> (Darcies)	<i>m</i>	<i>n</i>	<i>N</i> @ 1000 dynes/cm <sup>2</sup> (poise)
<i>Grade 460</i>						
2.51	1.92	0.038	85	0.10	1.46	1.69
1.11	1.0	0.038	70	0.10	1.45	1.70
1.11	1.0	0.038	72	0.10	1.48	1.74
1.11	1.0	0.038	82	0.10	1.46	1.66
1.11	1.0	0.038	88	0.09	1.46	1.58
1.11	1.0	0.038	89	0.10	1.46	1.69
				0.10	1.46	1.68 Std. Dev. = 0.05
<i>Grade 230</i>						
2.57	1.92	0.076	300	0.10	1.44	1.36
1.13	1.0	0.076	310	0.10	1.40	1.32
1.13	1.0	0.076	313	0.10	1.41	1.38
1.13	1.0	0.076	317	0.10	1.41	1.34
1.13	1.0	0.076	318	0.10	1.43	1.51
1.13	1.0	0.076	322	0.10	1.41	1.36
				0.10	1.42	1.38 Std. Dev. = 0.07

TABLE 4. POWER LAW PARAMETERS FOR TWO 0.2-PERCENT AM-1  
SOLUTIONS HAVING THE SAME SHEAR VISCOSITY  
AND GUM CONTENT

Filter Properties				0.2% AM-1		Power Law Parameters	
<i>L</i> (cm)	<i>A</i> (cm <sup>2</sup> )	<i>D<sub>p</sub></i> (cm)	<i>K</i> (Darcies)	Viscosity (cp)	Gum (mg)	<i>m</i>	<i>n</i>
1.11	1.0	0.038	89	5.43	170.0	0.10	1.45
1.11	1.0	0.038	89	5.44	169.2	0.15	1.48
1.13	1.0	0.076	322	5.43	170.0	0.10	1.41
1.13	1.0	0.076	322	5.44	169.2	0.15	1.41

It is important to point out that while excellent repeatability (5 percent of the mean) was obtained when flow measurements were made in different filters with a given solution of AM-1, in some instances solutions made from different batches of AM-1 but having the same amount of AM-1 (as indicated by the gum content and shear viscosity) exhibited significantly different rheological behavior with the same filter (see Table 4). While the exact causes of these differences have not been established, it is known that this additive has a rather wide molecular weight distribution. Consequently, trace amounts of a very high molecular weight species could have little or no effect on gum content or shear viscosity and yet have a significant effect on elasticity. In any event, it is interesting to note that this simple experiment is able to detect differences in rheological behavior that would not have been expected from any other measurements. Whether or not these differences are important to fuel safety is not presently known.

The effect of additive content was studied by diluting a 0.2-percent AM-1 solution with JP-8 to make 0.1-percent, 0.05-percent and 0.025-percent solutions. As expected, the Darcy Viscosity

decreased with each dilution and in each instance the resistance was still slightly higher in the finer filter. By expressing these results in terms of a relative fluidity (i.e., the resistance of JP-8 relative to the resistance of the polymer solution), we can compare the effects of additive content on Darcy Viscosity and mist flammability by means of the Mist Flashback Test.<sup>(8)</sup> In Figure 6 the relative Darcy

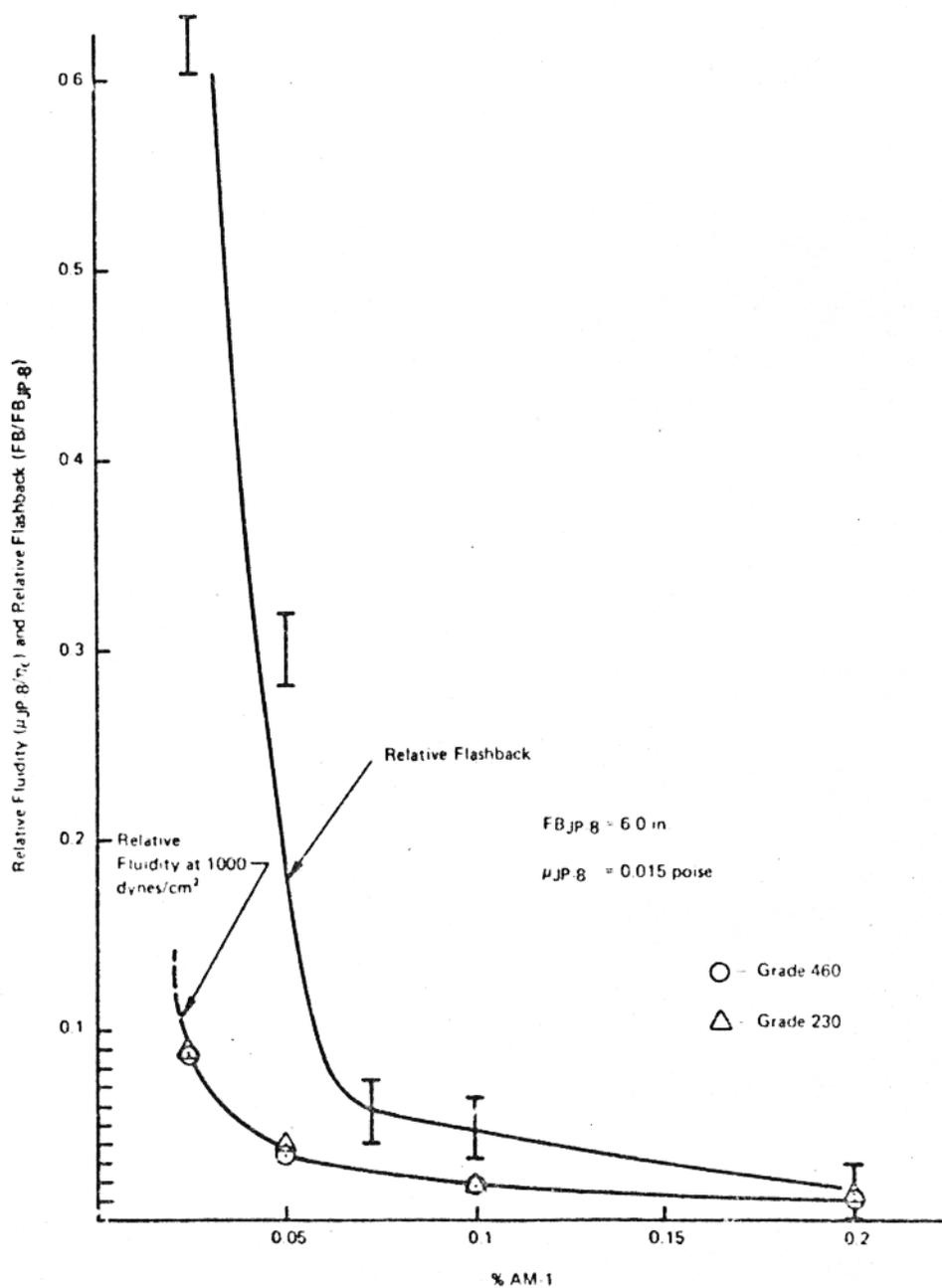


FIGURE 6. EFFECT OF AM-1 CONTENT ON RELATIVE FLUIDITY AND RELATIVE FLASHBACK

fluidity (at a shear stress of 1000 dynes/cm<sup>2</sup>) and the relative flashback (i.e., the flashback of the solution relative to JP-8) data are compared as a function of AM-1 content. These results show that there is a close correspondence between the relative flashback and relative fluidity particularly in the range of 0.07 to 0.2 percent. Below 0.07 percent the relative flashback increases rapidly, while this critical concentration appears to be slightly lower (0.05 percent) for the relative fluidity. This difference could possibly be explained by the fact that the mist flashback test has been optimized to produce maximum sensitivity. Since the relative resistance is a function of the shear stress, it is quite possible it would be more sensitive to this critical concentration if measurements were compared at different stress levels. Nevertheless, in the region of interest (0.07 to 0.2 percent AM-1), the two measurements appear to be related.

### SUMMARY AND CONCLUSIONS

It has been found that the addition of 0.2-percent AM-1 to JP-8 produces a solution that exhibits a relatively low and essentially shear independent viscosity; however, this same solution offers an unusually high resistance (25 to 30 times higher than we would expect from the viscosity) to flow through metal filters consisting of nearly spherical particles. These results are in agreement with rheological theories that predict that a viscoelastic liquid may appear to have a low Newtonian viscosity in steady shear experiments and to have a high elongational viscosity that increases with the rate of elongation. With particle shape held approximately constant, the specific resistance (or Darcy Viscosity) appears to be slightly higher in the finer pores; however, the high degree of repeatability and the absence of hysteresis or time effects in the flow data essentially rule out filter plugging as the reason for the anomalous resistance. Furthermore, viscosity measurements in different capillary tubes, intermediate in size between the fine and coarse pore size filters used in these experiments, gave no indication that adsorption of the polymer could be a significant factor in changing the pore size. The use of either Power Law Parameters or consistency variables produces equivalent results, and while they are not capable of predicting the high resistance, a priori, they do serve as a means for comparing data from different filters.

The effect of additive content on the relative fluidity of AM-1 solutions is very similar to the effect on mist flammability. The primary difference appears to be in the exact location of the critical concentration, i.e., the concentration below which these measurements show a disproportionately large increase. For mist flammability, this occurs at 0.07-percent AM-1 while for relative fluidity, the critical concentration is about 0.05 percent. It is possible that closer agreement could be obtained if the relative fluidity were compared over a wide range of stresses rather than at the value of 1000 dynes/cm<sup>2</sup> that was used here.

The results of this study suggest that it may be feasible to develop a nondestructive (i.e., nonburning) fluid flammability evaluation technique. In other words, antimist effectiveness of dilute solutions of high molecular weight polymers may be evaluated by simple measurements of the solution's resistance to flow through a porous medium.

### REFERENCES

1. Weatherford, W.D., Jr. and Wright, B.R., 45th Meeting of the AGARD/NATO Propulsion and Energetics Panel, Aircraft Fire Safety, Rome, Italy, 7-11 April, 1975. CP-1566
2. Goldin, M., et al, *Chem. Engr. J.*, 4, 8 (1972).

3. Goldin, M., et al, *J. Fluid Mech.*, **38**, 689 (1969).
4. Lodge, "Elastic Liquids," 116, Academic Press, London and New York (1964).
5. Bueche, F., "Physical Properties of Polymers," 71, Interscience Publishers (1962).
6. Hassager, O., *J. Chem. Phys.*, **60**, 2111 (1974).
7. Marshall, R.J., and Metzner, A.B., *Ind. Engr. Chem. Fund.*, **5-6**, 393 (1967).
8. Christopher, R.J. and Middleman, S., *I&EC Fundamentals*, **4**, 422 (1965).
9. Wright, B.R., et al, Interim Report, AFLRL No. 25 (1973).
10. Mannheimer, R.J., Final Report AFLRL No. 18 (1973).

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