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DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

BUREAU OF SHIPS
Department of the Navy
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DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

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FOREWORD

This report was prepared by the Research and Development Department of the American Oil Company under U.S. Navy, Bureau of Ships Contract Nobs-90267, Project Serial No. SR001-03-01, Task 606. Covered is work done from December 1, 1964 to February 1, 1965. The work was administered under the direction of the Chief. Bureau of Ships, Code 534A, with Mr. E. C. Davis as technical monitor.

ABSTRACT

The object of this study is the development of a water-base hydraulic fluid which (1) yields a fire-resistant non-aqueous residue, (2) is compatible with materials of construction and sea-water contamination, (3) satisfactorily lubricates shipboard pumps, (4) presents no unusual storage or handling problems, and (5) exhibits no toxicological hazards under conditions of use.

Low-density polyethylene can be chlorophosphonated by reaction with phosphorus trichloride and oxygen. Hydrolysis and neutralization produces products which show considerable promise as thickeners. Fluids prepared from products from 21,000-molecular-weight polyethylene have been found to exhibit undesirable viscosity instability and high wear in Vickers Vane pumps. Viscosity instability is much less pronounced when 12,000-molecular-weight polymer is used to prepare the thickeners and 18% of potassium ethane phosphonate, added as a pour depressor, is present. High pump wear, however, is still a problem. Work on the development of an antiwear additive has begun. Flammability characteristics and compatibility with materials of construction and 10% sea water do not appear to be problems with these fluids.

Attempts to prepare polymers of unsaturated organic acids of phosphorus having molecular weights sufficiently high to thicken water have been discontinued.

DEVELOPMENT OF NONFLAMMABLE HYDRAULIC FLUID

INTRODUCTION

Two types of fire-resistant hydraulic fluids are being used in aircraft-carrier systems. The fluid used in hydraulic catapults is a mixture of water, glycol, polyglycols, and additives. An aromatic phosphate ester fluid is used in aircraft elevators. Because of the complexity of submarine hydraulic systems, both of these fluids have serious shortcomings. The water-glycol fluids are incompatible with sea water, are relatively poor lubricants for heavily loaded bearings, and are corrosive to aluminum. In addition, loss of water results in the formation of flammable residues. Because of fluid-leakage problems, phosphate esters cannot be used in submarines.

A satisfactory water-base fluid for shipboard hydraulic-system use is needed. For the uses envisioned, fire resistance in both the finished fluid and the non-aqueous residue is of prime importance. In addition, the fluid must be capable of lubricating shipboard hydraulic pumps, be compatible with materials of construction and with 10% sea-water contamination, and present no unusual handling and storage problems. The fluid should be formulated to minimize toxicity hazards under conditions involving long periods of continuous exposure. Fluid residues should be removable by flushing with water.

In this study, the general approach consists of the synthesis and evaluation of water-soluble thickening agents which exhibit satisfactory fire-resistant properties. Development of thickening agents which allow formulation of a fluid having the desired fire-resistance, viscosity, and shear-stability characteristics will be followed by development of additives where necessary to impart satisfactory lubricating ability, oxidation and corrosion resistance, pour point, resistance to stable foam formation, and compatibility with sea water. When success, or near-success in the development of an appropriate thickening agent is indicated, it will be necessary to determine the toxicological hazards which may result from use of the fluid.

EXPERIMENTAL

The current program on non-flammable hydraulic fluids is aimed primarily at the development and evaluation of a suitable water-soluble thickener which contains sufficient phosphorus to impart fire resistance to the non-aqueous residue. Work on the polymerization of unsaturated acids of phosphorus has been discontinued because molecular weights have consistently been too low to result in satisfactory thickening of water. Work on the products from the chlorophosphonation of polyethylene continues. In addition, a suitable pour-point depressor having the desired flammability characteristics is being sought.

Chlorophosphonation of Polyethylene - Numerous chlorophosphonations of 12,000 m.w. and 21,000 m.w. polyethylene have been carried out using the procedure presented in Bimonthly Report No. 2. After hydrolysis and aging of the reaction products, fluids were prepared for testing in a Vickers Vane pump and for other studies.

Viscosity Stability - In Bimonthly Report #4, a small number of data was presented which indicated that viscosity stability of water solutions of polyethylene phosphonates may be a problem. Further data are:

Sample No.	Sample Description	Viscosity, SSU at 150°F
1	Freshly prepared from 21,000 m.w. polyethylene and NaOH (pH-8.0)	184
2	#1 after standing for 4 days	200
3	#1 after standing for 9 days	217
4	#1 after 1/2 hour in sonic shear test	165
5	#4 after standing for 9 days	205
6	#5 sucked back up viscosimeter tube and rerun immediately	195
7	#6 rerun in same way	191

Thus the viscosity of the fluid is dependent on its previous history, possibly because of varying degrees of loose bonding between thickener molecules because of attractive forces between the large number of sodium phosphonate groups. Similar viscosity properties are not uncommon in solutions of polyelectrolytes.

Potassium Ethanephosphonate - Several pounds of ethanephosphonic acid were prepared by hydrolysis of diethyl ethanephosphonate using aqueous hydrochloric acid in the usual manner. Water and hydrochloric acid were removed by vacuum distillation followed by azeotropic distillation from benzene. Ethanephosphoric acid was separated from the benzene by filtration.

Varying amounts of ethanephosphonic acid were added to the acid solution obtained from 12,000 m.w. polyethylene by chlorophosphonation, hydrolysis, and aging at 150°F. These solutions were neutralized to a pH of 8-8.5 by the addition of solid KOH. In every case it was necessary to boil off water to obtain the desired viscosity (about 140 SSU at 150°F). Calculated from the amount of polyethylene chlorophosphonated, the thickener content of these solutions was about 20%. Pour point data are:

% Potassium Ethanephosphonate	Pour Point, °F
0	+40
13	-15
18	-40
23	-26
25	-25
30	-18

Potassium ethanephosphonate appears to be a satisfactory pour point depressor.

Pump-test Fluid - A large batch of fluid was prepared which contained about 20% of the potassium thickener from 12,000 m.w. polyethylene, 18% of potassium ethanephosphonate, 1.4% of potassium chromate, and 5 p.p.m. of L530 silicone. Viscosity data obtained on this fluid are:

Viscosity at					
150°F		100°F		25°F	
SSU	C.S.	SSU	C.S.	SSU	C.S.
144	30.4	377	81.4	9768	2118

The viscosity of this batch of fluid is at the upper end of the desired range (25-31 c.s.) at 150°F and considerably higher than the desired maximum (850 c.s.) at 25°F. The measured viscosity at 25°F is also considerably higher than would be expected by extrapolation from data at 150°F and 100°F.

Data obtained in the sonic shear test are:

	Viscosity, SSU at 150°F	
	Immediately	10 days later
Unsheared Fluid	144.9	150.2
Sheared Fluid*	134.3	137.4

* in Raytheon Sonic Oscillator at 10,000 cycles, 0.7 R.F. Amperes at 100°F for 30 minutes.

Although some viscosity loss occurred in the shear test and some increase in viscosity occurred on standing, the viscosity-stability properties are improved over those fluids containing higher-molecular weight thickener and no potassium ethanephosphonate.

A static corrosion test was carried out on the fluid. Copper, steel, aluminum, and zinc strip were immersed in the same sample of the fluid for ten days at 150°F. Weight-losses data are:

	Weight Loss, mg/cm^2
Copper	nil
Steel	nil
Aluminum	0.02 (gain)
Zinc	0.09

Other data obtained on this fluid are:

Pour Point, °F	-20
Specific Gravity, g/cc.	1.28

Pump Test - Two gallons of the fluid described above were charged to the sump of a Vickers Vane pump. After ninety hours of operation at 1000 p.s.i. and 150°F, excessive water loss had occurred because of evaporation resulting from a poorly fitted sump cover. At this time, the fluid was examined and was found to have a viscosity at 150°F of 605 SSU. Sufficient water was added to bring the viscosity down to about that of the original fluid. Total volume of the fluid which resulted was about 2.75 gallons. Thus shearing in the vane pump resulted in a substantial increase in effectiveness of the thickening.

New pump parts were installed and the test was continued for an additional 150 hours. Because of evaporation loss, it was necessary to add about 1 1/2 pints of water every twenty-four hours. No apparent increase in volume occurred and the viscosity returned to about that of the original fluid after each water addition. Thus no further change in the thickener occurred.

Weight-loss data obtained after the test are:

Part	Weight Loss, gms.
End Plates	.0027 (gain)
Rotor	0.1366
Ring	18.86
Vanes	0.0489

These weight-loss data are similar to those obtained on a fluid prepared from 21,000 m.w. polyethylene thickener and containing no potassium ethanephosphonate (reported in Bimonthly Report No. 4).

Antiwear Agents - A search for an additive to minimize pump wear has begun. Data obtained in the Shell Four Ball test after one hour at 1800 r.p.m., room temperature, and 15 kg. load are:

Base Fluid: Water +20% Thickener (12,000 m.w. polymer)
+20% Potassium Ethanephosphonate
+1.4% Potassium Chromate
+5 p.p.m. L530 Silicone

Additive	Wear Scar Diameter (mm)
None	1.12
2% Triethanolammonium dilaurylphosphate	1.20
2% Potassium dialkyldithiophosphate	1.19
1% Chlorendic acid	1.15
1% Dimercaptothiadiazole	1.14
1% Perfluroheptamide	1.11
1% Carbowox dialeate (1500)	1.17
1% Polyoxyethylene oleylammonium chloride	1.20
1% LP 700*	1.24
1% LS 500*	1.15
1% LE 600*	1.11
5% LE 600*	1.13
5% LE 500*	1.10

* General Analine and Film products.

No additives tested has shown any effect on the results obtained in this test.

FUTURE PROGRAM

1. The effect of shear on the viscosity-stability properties of fluids containing polyethylene phosphonate thickeners will be studied.

2. A Four-Ball Friction Pendulum and a modified NASA Pin and Disk Friction Machine will be used for screening additives. Any promising additives will be tested in the Vickers Vane pump.

3. The sump cover of the pump now being used will be modified to minimize water evaporation.

4. Preparation of thickeners and ethanephosphonic acid will continue so that sufficient fluid is available for pump tests.