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Report

St. Louis Research Report No. 2176

FINAL REPORT

ON

FUNCTIONAL FLUIDS - APPLICATION RESEARCH (1956-57)

JOB NO. 2-02-750.01-3132

DSW 621643

STLCOPCB4095674

MONSANTO CHEMICAL COMPANY
Organic Chemicals Division
St. Louis Research Department

St. Louis Research Report No. 2176

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October 14, 1958

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INTRODUCTION

Since Monsanto's entry into the field of functional fluids in 1948, their marketed fluids have been divided into two lines. One group consists of Skydrol fire-resistant aircraft hydraulic fluids, the other includes the Pydraul fire-resistant industrial hydraulic fluids. This report covers work on functional fluid application research for 1956 - 1957, principally in the industrial field, including the formulations and property determinations of new fluids, a study of extended applications for current Pydrauls, evaluation of potential base stocks and production of new fluids.

SUMMARY

Since consistency of viscosity is considered more important than low change of viscosity with temperature, the current trend in functional fluids is toward shear stable formulations. For this reason, shear stable Pydraul 625 replaced Pydraul 600, Fluid OS-16 was marketed as Pydraul 60 and Pilot Plant blends of OS-90 and OS-91, as well as Aroclor 1248RI, were submitted to potential customers for large scale evaluations. Further formulation problems, brought under study, were the selection of a shear stable thickening agent for tricresyl phosphate and the utilization of OS-70 (a triaryl phosphate) in Pydraul fluids.

In a search for new base stocks, viscosity evaluations were made on various substituted biphenyls, polyesters, phosphonates, propionates and phosphates. Heat stabilities and storage tests were run on the more promising base stocks and formulations. Coefficients of thermal expansion and compatibilities were determined on a series of Pydrauls fluids in an effort to meet the requirements of new industrial applications.

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2. Final Report No. 728, "Functional Fluids", 117-2380 by R.E. Hatton, May 21, 1953.
3. Final Report No. 988, "Functional Fluids - Application Research 1952-54", 117-2508 by R.E. Hatton, L.W. Bannister, W.E. Koerner and O.B. Cecil, August 4, 1954.
4. Final Report No. 1562, "Functional Fluids - Application Research for 1954-55", Job No. 2-02-750.01-2815 by R.E. Hatton, July 6, 1956.
5. Tentative Process, Report No. P-707 "Preparation of OS-16", Job No. 2-02-750.01-3132 by J.D. Sullivan, July 13, 1956.
6. Tentative Process, Report No. P-740, "Blending of OS-83", Job No. 2-02-750.01-3132 by J.D. Sullivan, December 27, 1956.
7. Tentative Process, Report No. P-810, "Blending of Aroclor 1248RI", Job No. 2-02-750.01-3132 by R.E. Hatton, November 19, 1957.

EXPERIMENTAL WORK AND DISCUSSION

I. Formulations

1. Thickening Agents for Tricresyl Phosphate (TCP)

a. TCP Formulations as Transition Fluid

The purposes of this investigation were: -

General - To market a new phosphate ester based functional fluid.

Specific - Formulate a transition fluid for "changing over" from hydrocarbon oil to Pydraul F-9 without closing down a large hydraulic installation, since some hydrocarbon oils are insoluble in phosphate esters.

Since Pydraul F-9 is soluble in naphthenic and paraffinic base oils, various Acryloids were tested as a thickening agent for tricresyl phosphate in an effort to formulate a transition fluid for "changing over" from hydrocarbon oil to Pydraul F-9 without closing down a large hydraulic installation. The following table lists the various Acryloids and polyacrylates tested along with the amounts required to attain the desired viscosity of the transition fluid.

<u>Additive</u>	<u>Code</u>	<u>in TCP</u>	<u>Required Amount</u>	<u>Reference</u>
70/30 2EHAc/EAc 30% in OS-69*	P-72	insoluble	----	A-99268
Skydrol 500 Acryloid	50020	soluble	5.9%	A-99266
Oil Free N-5262A	L-1301	insoluble	----	A-99268
N-5262A-pure quill	PC-1344	insoluble	----	A-99267
Skydrol 7000 Acryloid	734	insoluble	----	A-99266
duPont's V.I. Improver	PL-172	soluble	4.2%	A-99266
Special Acryloid	G-5573X	soluble	4.5%	A-99266

* OS-69 = 10% TCP in Aroclor 1242

b. Compatibility with Hydrocarbon Oils

The more promising additives, as well as several Ucon fluids, were formulated with tricresyl phosphate (TCP) to a desired viscosity and each formulation was mixed with an equal volume of paraffinic oil, as well as an equal volume of naphthenic oil. The mixtures were allowed to settle before careful separation and analysis of each layer. Table I identifies the TCP formulations in combination with the hydrocarbon oils and lists some of the physical properties of each component before mixing, along with the corresponding changes in these properties as a result of the mixing operation.

PL-272 is an experimental duPont additive, 50020 is the Acryloid used in Skydrol 500 and 50-HB-660, as well as 75-H-90,000, are water soluble Ucons.

TABLE II

Fluid No.	Composition of Pydraul					Physical Properties			
	Triaryl Phosphate					Viscosity (c.s.)			
	80-70	80F	S-140	P-II	Arclor 125H	100°F.	210°F.	Pour Point	Sp. Gr. 25°/25°C.
# 1	45%	45%			52.5%	45-60	5.2-6.1	5 0°F.	1.275-1.295
# 2	45%	45%			52.5%	75.2			
# 3	45%	45%			52.5%	73.2			
# 4	45%	45%			52.5%	54.8	4.4	-280 + 5°F.	
# 5	45%	45%			52.5%	57.7	5.3	-61	
# 6	43%	43%			57%	85-95	5.0-5.2	+20°F.	1.348-1.352
# 7	43%	43%			57%	127.5	5.6	+25°F.	
# 8	24%	24%			36%	125-140	8.8-9.6	+15°F.	1.35-1.37
# 9	24%	24%			36%	91.7		+25°F.	
# 10	24%	24%			36%	102.6			
# 11	24%	24%			36%	133.1	7.8		
# 12	50%	50%			52.5%	29.8	4.2	-20°F.	
# 13	55%	55%			52.5%	31.0	4.3	-25°F.	
# 14	70%	70%			52.5%	55	5.7	-20°F.	
# 15	24.8%	24.8%			52.5%	49.4	5.8	0°F.	1.2898
# 16	21.5%	21.5%			52.5%	50.6	5.77	0°F.	1.2890
# 17									

1 Regular Pydraul F-9 Formulation
 # 15 Typical Pydraul F-9 Formulation
 # 6 Regular Pydraul AC Formulation
 # 8 Regular Pydraul 600 Formulation

Essentially no interchange of layer volume resulted in mixing the phosphate ester formulations with paraffinic oil, whereas measurable amounts of naphthenic oil was dissolved in the phosphate ester layers. Cellulube 220 experienced the largest take-up of naphthenic oil. All of the additives tested were essentially retained in the TCP layer after the mixing operation. The phosphate ester extracted colored material from both of the hydrocarbon oils. The paraffinic oil caused the TCP layer, containing Ucon's 75-H-90,000, to turn coal black upon mixing. The TCP extracted additives from the paraffinic oil which resulted in increased viscosities and viscosity indices of all of the TCP formulations tested but the mixing caused a decrease in the specific gravities of the phosphate ester layers due to equally mutual solubilities. The specific gravities of the paraffin base oil layers were correspondingly increased. On the other hand, the naphthenic oil caused a decrease in the specific gravities, the viscosities and the viscosity indices of all of the phosphate ester layers by straight dilution, which in turn caused a substantial increase in the specific gravities of the naphthenic oil layers.

c. Shear Stabilities of TCP Formulations

The shear stability of various tricresyl phosphate (TCP) formulations were evaluated in the Functional Fluid Testing Laboratories. Ucon 75-H-90,000 was shear resistant at a 1.58% concentration of TCP. The following table lists the shear characteristics along with the concentration of various polymers required to convert TCP into fluids with viscosities comparable to Cellulube 220.

<u>% Polymer in TCP</u>	<u>Initial</u>	<u>Sheared*</u>	<u>% Shear</u>	<u>Initial</u>	<u>Sheared*</u>	<u>% Shear</u>
5.9% 50020	49.36	41.40	16.1	6.84	5.41	20.9
10% HB-660	44.38	43.62	1.7	5.75	5.39	0.6
8% 75H-90,000	105.60	101.71	3.7	--	12.40	---
1.58% 75H-90,000	47.80	47.80	0	5.38	5.38	0
4% PL-272	48.00	40.20	16.3	6.26	4.98	20.4
Cellulube 220	47.02	46.52	1.1	4.77	4.70	1.5
TCP	33.30	---	---	4.34	--	---

* 12 passes through a Diesel Injector Shear machine.

d. Hydrolytic Stabilities of TCP Formulations

Continuing the investigation of thickening agents for tricresyl phosphate, the following formulations were submitted by the Functional Fluid Application Research Laboratories for hydrolytic stability determinations.

Formulation #1 - 1.55% Ucon 75-H-90,000; 200 ppm RI-150
 Formulation #2 - 1.55% Ucon 75-H-90,000; 0.2% RI-150
 Formulation #3 - 4% HF-825
 Formulation #4 - 1.55% Ucon 75-H-90,000; 50 ppm Tretolite AD-9

The following results were obtained from the standard "coke-bottle" method for hydrolytic stability on these formulations:

	Weight Loss (Cu) mg./sq. cm.	Appearance of Copper Test Strips
Formulation #1	0.39	brown w/ black streaks
Formulation #2	0.69	reddish-bronze color
Formulation #3	0.71	gray-black cast
Formulation #4	0.29	lt. tan w/ gray cast

The appearance of the copper strips #1 and #4 are borderline and all of the above copper strips show more copper staining than a similar test on Cellulube 220. The maximum allowable copper weight loss in this test is 0.30 mg. per sq. cm. according to military specifications MIL-H-19457 and Cellulube 220 ranges between 0.06 and 0.12 mg. per sq. cm. These formulations are not considered satisfactory for submission to the Navy under the above specification.

2. Utilization of OS-70 in Pydraul Fluids

a. Preparation of FH-127, FH-128 and FH-129

OS-70, a triaryl phosphate from Productol's "Special B Grade" cresylic acid, proved to be unsatisfactory for use as a substitute for tricresyl phosphate (TCP) in Pydraul F-9 (A-79808), Pydraul 600 (A-79809) and Pydraul AC (A-79807). As a result of viscosity, pour point and specific gravity determinations, 45% Santicizer 140 in OS-70 proved to be a suitable substitute for the 45% TCP component of Pydraul F-9 (A-79821). Substituting a mixture of OS-70 and triphenyl phosphate (D-11) (70% to 30%) for the TCP component of Pydraul F-9 gave a comparable fluid from the standpoint of physical properties (A-79822). Table II shows the scope of this study. Varying the amounts of Acryloid 710 used in conjunction with OS-70 in the Pydraul F-9 formulation gave poor VI's. Substituting OS-70 for TCP in the regular Pydraul AC formulation gave high viscosities and pour points. Using OS-70 in the Pydraul 600 formulation and reducing the concentration of Acryloid 710 gave a fluid with satisfactory viscosities but high pour points.

The formulations for Pydraul F-9 and Pydraul AC in which 55% OS-70 and 45% Santicizer 140 were substituted for the TCP component were designed as FH-127 and FH-128 respectively (A-79850). A sample representing a mixture of fifty percent regular Pydraul F-9 in FH-127 was labeled FH-129. Table III lists the physical properties of these fluids which were sent to Douglas Aircraft Company for evaluation and for approval of formulation changes.

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TABLE I

Combinations of Immiscible Oils	Sp. Grav. at 25/25°	BEFORE MIXING			Layer Volume	AFTER SEPARATION			Sp. Grav. at 25/25°
		100°F.	Viscosity 210°F.	VI		100°F.	Viscosity 210°F.	VI	
Paraffinic Base TCP contg. 4.2% PL272	0.8687 1.1600	48.00 cs.	6.26 cs.	+ 81	50 cc 50 cc	49.03 cs.	6.42 cs.	+ 85	0.8839 1.1459
Naphthenic Base TCP contg. 4.2% PL272	0.9047 1.1600	48.00 cs.	6.26 cs.	+ 81	50 cc 50 cc	47.04 cs.	6.06 cs.	+ 75	0.9266 1.1056
Paraffinic Base TCP contg. 5.9% 50020	0.8687 1.1546	49.36 cs.	6.84 cs.	+102	50 cc 50 cc	51.27 cs.	7.05 cs.	+104	0.8846 1.1406
Naphthenic Base TCP contg. 5.9% 50020	0.9047 1.1546	49.36 cs.	6.84 cs.	+102	50 cc 50 cc	49.49 cs.	6.67 cs.	+ 94	0.9205 1.0990
Paraffinic Base TCP contg. 10% 50-HB-660	0.8687 1.1488	44.38 cs.	5.75 cs.	+ 68	50 cc 50 cc	44.51 cs.	--	--	0.8836 1.1365
Naphthenic Base TCP contg. 10% 50-HB-660	0.9047 1.1488	44.38 cs.	5.75 cs.	+ 68	50 cc 50 cc	42.59 cs.	--	--	0.9243 --
Paraffinic Base TCP contg. 8% 75-H-90,000	0.8687 1.1560	105.6 cs.	--	--	50 cc 50 cc	106.0 cs.	--	--	0.8845 1.1434
Naphthenic Base TCP contg. 8% 75-H-90,000	0.9047 1.1560	105.6 cs.	--	--	50 cc 50 cc	95.1 cs.	--	--	0.9307 --
Paraffinic Base Tricresyl Phosphate	0.8687 1.16	33.30 cs.	4.34 cs.	- 26	50 cc 50 cc	33.39 cs.	4.32 cs.	- 31	0.8844
Naphthenic Base Tricresyl Phosphate	0.9047 1.16	33.30 cs.	4.34 cs.	- 26	50 cc 50 cc	32.76 cs.	4.23 cs.	- 41	0.9275
Paraffinic Base Cellulube 220	0.8687	47.68 cs.	--	--	50 cc 50 cc	46.44 cs.	--	--	0.8886
Naphthenic Base Cellulube 220	0.9047	47.68 cs.	--	--	50 cc 50 cc	40.49 cs.	--	--	0.9447

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TABLE III

<u>Sample</u>	<u>FH-127</u>	<u>FH-128</u>	<u>FH-129</u>
Acidity, NN	0.05	0.03	0.05
Moisture, %	0.06	0.05	0.05
Sp. Gr. at 25/25°C.	1.289	1.355	1.282
Pour Point, °F.	0	+20	0
Viscosity, cs. at 210°F.	5.54	4.78	5.66
Viscosity, cs. at 100°F.	49.0	75.2	51.0

The Douglas Aircraft test results on these fluids are listed in the Appendix of this report.

3. Pilot Plant Production of OS-90 and OS-91

Fifteen gallons of OS-90 and 15 gallons of OS-91, high viscosity Aroclor formulations, were prepared in the pilot plant for shipment to the Chrysler Corporation. OS-90 contains 55% Aroclor 1254 and 45% Aroclor 1248, whereas OS-91 contains 20% Aroclor 1260 and 80% Aroclor 1254. These formulations will be tested as high density torque converter fluids. The following table lists the analyses of these formulations.

Viscosity at 100°F.	118.3 cs.	917.7 cs.
at 210°F.	4.32 cs.	7.11 cs.
	6.11 cps.	
Acidity	0.02 NN	0.02 NN
Moisture	0.01%	0.03%
Sp. Gr. at 25/25°C.	1.4994	1.5659
Pour Point	+35°F.	+60°F.

4. Pydraul 150 Defoamer Concentrate

A supply of Pydraul 150 defoamer concentrate (A-79828) containing 50 ppm D.C. 200 was prepared for the U.S. Steel Gary Plant.

5. Production of Fluid OS-16 (Pydraul 60)

OS-16 is 2-ethylhexyl diphenyl phosphate (Santicizer 141) containing a sufficient amount of dye to impart to the fluid a characteristic blue color. OS-16 was introduced by Monsanto in 1949 as a low viscosity, non-toxic, fire-resistant hydraulic fluid and underwent extensive testing in various applications of the coal mining industry. This product was very satisfactory as a hydraulic fluid for coal mining machinery but a demand for OS-16 did not materialize because the price was considered prohibitive. In 1955, the Aluminum Company of America found OS-16 to be an excellent hydraulic fluid in a control mechanism because of its shear stable viscosity index in addition to its fire-resistant characteristics. The increased demand for OS-16 in this application warranted the large scale production of this fluid. A tentative process for the production of OS-16 was published in Report No. P-707, July 13, 1956 by J.D. Sullivan under Job No. 2-02-750.01-3132. This fluid is being marketed under the name of Pydraul 60.

a. Screening of Blue Dyes

Because the production of "Blue Mist" dye was discontinued, a search for a suitable substitute was undertaken to provide the characteristic color for OS-16. Traffic Blue, Blue 3, Blue 2, Blue TX from the Patent Chemical Co. (A-79810) and duPont Oil Blue A (A-79805) were evaluated for this application. DuPont Blue A was far superior from the standpoint of solubility and concentration. A color comparable to 28 ppm Blue Mist dye in Santicizer 141 was obtained with a similar solution containing 7 ppm duPont Oil Blue A and the resulting dye concentrate did not require filtration before formulation when the latter was used. Thus, duPont Oil Blue A was adopted for the OS-16 formulation and sufficient dye concentrate was prepared in the laboratory to supply the production requirements of OS-16 in Department 50 (A-79810-11).

b. Storage Stability of OS-16

A sample of OS-16 (Lot R-3156) was removed from the Packing Room after five years of drum storage. The blue dye had faded to a light purple and the acidity increased to 0.85 NN (A-79837).

6. Production of Fluid OS-83 (Pydraul 625)

OS-83, a shear-stable version of Pydraul 600, is the most recent addition to the Pydraul line of fire-resistant industrial fluids. Several gallons of OS-83 were prepared in the laboratory and submitted for customer evaluations in particular applications where consistency of viscosity appears to be more important than low change of viscosity with temperature. This new functional fluid has a specific gravity of 1.3566 at 25°/25°C. (A-89452) and a viscosity of about 625 SUS at 100°F. The viscosity of OS-83 varied from 6.0 cs. at 210°F. to 6800 cs. at 50°F.

<u>Temperature</u>	<u>Viscosity in cs.</u>
210°F.	6.02
130°F.	36.65
100°F.	135.5
75°F.	644.
50°F.	6810.

A tentative process for the production of OS-83 was published in Report No. P-740, December 27, 1956 by J.D. Sullivan under Job No. 2-02-750.01-3132. OS-83 has been officially transferred to the Sales Department and this fluid is being marketed under the name of Pydraul 625.

7. Viscosity Spread of Pydraul AC

Proposed applications of Pydraul AC required determining viscosities of Pydraul AC in order to predict the pumpability of the fluid at various temperatures. The viscosity of Pydraul AC varied from 5.00 cs. at 210°F. to 3200 cs. at 50°F.

<u>Temperature</u>	<u>Viscosity in cs.</u>
210°F.	5.00
130°F.	26.7
108°F.	84.5
75°F.	356.0
58°F.	3210

8. Blending of Aroclor 1248RI

Aroclor 1248RI is a rust inhibited version of Aroclor 1248 proposed for use as a fire resistant hydraulic fluid. Some trouble has been experienced with deposits and rust in certain hydraulic systems using Aroclor fluid. The addition of a small amount of rust inhibitor, Santolube 70, should decrease this tendency. A tentative process for the blending of Aroclor 1248RI was published in Report No. P-810, November 19, 1957 by R.E. Hatton under the Job No. 2-02-750.01-3132.

II. Applications

1. Heat Stabilities of MCDP and Santicizer 141

1-Methylcyclohexylmethyl diphenyl phosphate (MCDP) was prepared for comparison in thermal stability with Santicizer 141 (2-ethylhexyldiphenyl phosphate). The former compound was considerably more stable at 150°C. but about equivalent at 175°C. Viscosity characteristics were poorer than those of Santicizer 141. The following table lists the weight losses and acid formations at various temperatures for Santicizer 141 and MCDP.

<u>Material</u>	<u>Temp.°</u>	<u>Hours</u>	<u>Wt. Loss</u>	<u>NN</u>
Santicizer 141	150	12	0.23%	1.25
MCDP	150	12	0.13	0.27
Santicizer 141	150	24	1.16	7.0
MCDP	150	24	0.16	0.56
Santicizer 141	175	24	31.4	213
MCDP	175	24	26.2	209

In the evaluation as plasticizers, 1-methylcyclohexylmethyl diphenyl phosphate was considerably poorer in flex but slightly better in volatility and kerosene extraction than Santicizer 141.

2. Heat Stabilities of Pydraul F-9 and FH-127

Samples of Pydraul F-9 and FH-127 were heated in beakers in a 150°C. oven for 32 days. Samples were taken at intervals and examined. Little difference was noted. FH-127 is a Pydraul type fluid made from OS-70. The following table lists the results of these tests.

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Time in Oven 150°C.	Acidity, (NN)		Weight Loss ^x		Sp. Gr. at 25/25°C.	
	PF9	FH-127	PF9 g.	FH-127 g.	PF9	FH-127
0	.082	.082	---	---	1.275	1.289
27 hr.	.082	.082	1.6	1.8	1.275	1.290
74 hr.	.112	.112	3.9	4.2	1.275	1.289
1 wk.	.122	.122	6.1	5.9	1.275	1.291
11 da.	.243	.243	9.2	8.8	1.275	1.288
18 da.	.467	.467	14.4	14.9	1.269	1.284
25 da.	.841	.841	19.4	19.9	1.261	1.277
32 da.	1.12	1.12	23.5	25.3	1.272	1.283

x 900 grams of each fluid was used in this test.

Time in Oven 150°C.	Viscosity 100°F.		Viscosity 210°F.	
	PF9 cs.	FH-127 cs.	PF9 cs.	FH-127 cs.
0	52.9	48.5	5.91	5.54
27 hr.	51.7	50.0	5.50	5.35
74 hr.	51.6	50.0	5.37	5.61
1 wk.	51.0	51.1	5.30	5.63
11 da.	51.2	51.0	5.32	5.67
18 da.	52.1	52.0	5.40	5.82
25 da.	54.4	54.0	5.51	6.07
32 da.	53.6	54.9	5.32	6.01

3. Compatibility of Pydraul AC with Fluorochemical 101

A liquid was required having a higher specific gravity than, and incompatible with Pydraul AC for use in certain air compressor lubricating devices. Shaking equal amounts of Pydraul AC or tricresyl phosphate in Fluorochemical 101 formed a white liquid which immediately separated into two phases. Aroclor 1254 - Fluorochemical 101 mixtures did not entirely separate after standing for several days.

4. Coefficients of Thermal Expansion (WEK and WDW)

A Vycor pycnometer was used to measure the densities of the four Pydraul samples over the temperature range 0°-200°C. These data are tabulated below:

Pydraul 150

Temperature (°C.)	Density (g./ml.)	Volume (ml./g.)
0.1	1.1428	0.8752
24.9	1.1223	0.8910
60.1	1.0935	0.9145
88.8	1.0707	0.9340
117.5	1.0467	0.9554
149.9	1.0198	0.9805

Pydraul AC-OS-67

<u>Temperature (°C.)</u>	<u>Density (g./ml.)</u>	<u>Volume (ml./g.)</u>
24.9	1.3475	0.7421
64.4	1.3119	0.7623
100.3	1.2813	0.7805
133.0	1.2472	0.8017
162.0	1.2230	0.8176
191.6	1.1958	0.8363

Pydraul 600

24.9	1.3598	0.7354
69.3	1.3181	0.7587
98.0	1.2936	0.7730
128.5	1.2631	0.7917
165.0	1.2317	0.8119
198.5	1.2015	0.8323

Fluid OS-79

0.2	1.4231	0.7027
24.9	1.3992	0.7147
59.9	1.3655	0.7323
98.6	1.3289	0.7525
145.3	1.2836	0.7791
191.0	1.2392	0.8070

The equations of the straight lines which result when density is plotted as a function of temperature are:

$$\begin{array}{ll}
 \text{Pydraul 150} & \text{--- } d_t = 1.1428 - (8.17 \times 10^{-4})_t \\
 \text{Pydraul AC-OS-67} & \text{--- } d_t = 1.3703 - (9.07 \times 10^{-4})_t \\
 \text{Pydraul 600} & \text{--- } d_t = 1.3823 - (9.12 \times 10^{-4})_t \\
 \text{Fluid OS-79} & \text{--- } d_t = 1.4232 - (9.67 \times 10^{-4})_t
 \end{array}$$

Where d_t is the density in g./ml. at $t^\circ\text{C}$. These equations can be used to calculate exact densities within the experimental range, and may also be used to obtain approximate densities outside the experimental range. Calculated values differ from experimentally observed values by less than 0.1%. To obtain volumes in ml./g. at any temperature, calculate the density at that temperature and then take the reciprocal of this value.

The coefficients of thermal expansion were calculated from the equation;

$$\text{coefficient} = \frac{2 (V_2 - V_1)}{(V_2 + V_1) (T_2 - T_1)}$$

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Where V_2 is the volume at temperature T_2 and V_1 is the volume at temperature T_1 . These coefficients, as calculated from the experimental points of widest separation, are listed below:

Pydraul 150	---	$7.576 \times 10^{-4}/^{\circ}\text{C.}$
Pydraul AC-OS-67	---	$7.160 \times 10^{-4}/^{\circ}\text{C.}$
Pydraul 600	---	$7.121 \times 10^{-4}/^{\circ}\text{C.}$
Fluid OS-79	---	$7.242 \times 10^{-4}/^{\circ}\text{C.}$

These values may be converted to engineering units (value/ $^{\circ}\text{F.}$) by dividing by 1.8.

5. Ice-Box Storage Stability Tests

The following table lists the results of ice-box stability tests on various formulations along with the date on which these tests were started.

a. Pydraul F-9 in which the TCP (tricresyl phosphate) component of the fluid was substituted by 30% triphenyl phosphate and 70% OS-70 was compatible (5-15-56 to 2-57).

b. Pydraul F-9 in which the TCP component of the fluid was substituted by 45% Santicizer 140 and 55% OS-70 was compatible (5-15-56 to 2-57).

c. Aroclor 1242 (70.2 grams) and Acryloid 794 (22.5 grams) was compatible (7-2-54 to 2-57).

d. Pydraul 150, Batch #2, W-Bldg., was compatible (7-9-54).

e. Santicizer 141 (90 grams) and 10 grams HF-855 was compatible (7-9-54 to 2-57).

f. FH-87 (90 grams) and 10 grams of R-3876X was compatible (7-6-54 to 2-57).

g. Santicizer 141 (90 grams) and Acryloid 710 (10 grams) separated on storage (7-6-54).

h. Santicizer 141 (69.1 grams) and Acryloid 794 (7.5 grams) separated on storage (7-2-54).

6. Applications of Pydraul Fluids

(a) Pydraul 600 in Dept. A-9 (St. Louis)

An earlier analysis of Pydraul 600 used as a bearing lubricant in a speed reducer of Department A-9 showed a moisture content of 0.02%, but the acidity had increased to 18 NN. The system was cleaned out and recharged with fresh Pydraul 600 (A-71050). The following table lists the acid build-up at the indicated operating temperatures during the second run.

	<u>Operating Temperature</u>	<u>Acidity</u>
After 4 days	138.2°F.	2.47 NN
After 5 days	147.2°F.	2.75 NN

It would appear that conditions experienced in this unit are too severe for Pydraul 600.

(b) Pydraul F-9 in W-Bldg. (St. Louis)

Pydraul F-9 was successfully demonstrated as a gear lubricant in an Oilgear Hydraulic Pump in the W-Bldg. The following table lists the analytical results of this used Pydraul F-9.

	<u>Z-898</u>	<u>Specifications</u>
Viscosity at 100°F.	40.06 cs.	45-60 cs.
at 210°F.	4.34 cs.	5.2-6.1 cs.
Moisture	0.30%	0.25%, max.
Acidity	0.1 NN	0.15, max.
Sp. Gr. at 25/25°C.	1.2711	1.275-1.295

The drop in viscosities of the fluid indicates the usual shear experienced in the operation but is quite satisfactory for used fluid. The moisture content is a little above specification but the acidity is excellent for used fluid.

(c) Pydraul AC at Nitro

An oil found in instrument air line drops at Monsanto (Nitro) was shown to contain chlorine and phosphorus in approximately the same ratio these occur in Pydraul AC. Therefore, it appears certain that leakage of Pydraul AC from the air compressor had occurred.

(d) Pydraul F-9 at Mobay

Two samples of Pydraul F-9 containing phosgene and isocyanate along with varied percentages of orthene were prepared to test the resulting formulations for lubricity.

The following table identifies these formulations and lists the corresponding physical properties (A-75727).

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	FH-125	FH-126
	Pydraul F-9 containing: 0.05% (wt.) phosgene 0.10% (wt.) isocyanate 6.5% orthene	Pydraul F-9 containing: 0.05% (wt.) phosgene 0.10% (wt.) isocyanate 20.0% (wt.) orthene
Sp. Gr. at 25/25°C.	1.2764	1.2802
Acidity	0.49 NN	0.49 NN
Viscosity at 100°F.	31.51 cs.	13.29 cs.
at 210°F.	4.70 cs.	3.08 cs.

The following table lists viscosity data on Pydraul F-9 containing varying percentages of orthene.

Formulations	Viscosities	
	at 100°F.	at 210°F.
95% F-9 + 5% orthene	35.65 cs.	4.98 cs.
90% F-9 + 10% orthene	24.73 cs.	4.25 cs.
80% F-9 + 20% orthene	13.57 cs.	3.24 cs.

Samples of these contaminated fluids and of the original Pydraul F-9 were sent to Douglas Aircraft Co. for Shell Four-Ball Wear Tests. Results are as follows:

	Steel on Steel			Steel on Bronze		
Loadings:	1 kg.	10 kg.	40 kg.	1 kg.	10 kg.	40 kg.
FH-125	.39	.53	.88	.62	1.00	1.23
FH-126	.42	.53	.87	.63	1.10	1.32
Pydraul F-9, Lot Y-76	.14	.24	.70	.55	1.18	1.27
Previous Samples of Pydraul F-9	.20	---	.70	.40	----	1.27

Notes: Bronze balls tarnished in FH-125 and FH-126.
Bronze balls did not tarnish in Pydraul F-9.
Steel balls were also slightly discolored in FH-125 and FH-126 but not in Pydraul F-9.

Although the bronze balls tarnished with the contaminated samples, the wear values in our opinion do not reflect any significant change. In the case of the steel balls, the wear values do reflect a somewhat significant difference, perhaps even more so for the 40 Kg. load than for the somewhat larger spread by lower reproducibility results obtained at one Kg.

We think it would be safe to say that some increase in chemical wear attack could be expected for the two contaminated samples run under boundary layer conditions with steel bearing on steel.

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All the data seem to indicate that the contamination expected in this application degrades the Pydraul F-9. It is impossible to relate exactly such results to actual experience in a vacuum pump in terms of life of equipment, satisfactory operation, and so on. Only an actual test can provide such information. If Pydraul F-9 as such is satisfactory, then these results indicate that contaminated Pydraul F-9 will not be as good a lubricant and that corrosive attack is possible.

III. Evaluations

(1) Various Substituted Biphenyls

The unexpected viscosity properties of various isopropylated triphenyl phosphates prompted viscosity evaluations of isopropyl biphenyl, isopropyl Aroclors and butyl Aroclors. These results were compared with viscosity determinations on TCP formulations containing these compounds.

The following table indicates that the various substituents lowers the viscosity index of the resulting biphenyls and that the isopropyl group is no exception.

	<u>Viscosities (cs.)</u>		<u>Viscosity Index</u>
	<u>at 100°F.</u>	<u>at 210°F.</u>	
Isopropyl biphenyl	5.26	1.57	--
(Aroclor 1232)-Dichlorobiphenyl	6.75	1.58	--
Isopropyl Dichlorobiphenyl	19.14	2.65	-203
Butyl Dichlorobiphenyl	278.26	9.20	-224
(Aroclor 1242)-Trichlorobiphenyl	15.58	2.26	-250
Isopropyl Trichlorobiphenyl	131.35	5.54	-447

The viscosity effects resulting from formulating these substituted biphenyls in TCP are additive and the isopropyl derivatives in contact with the phosphate ester grouping shows no improvement in viscosity properties.

50% Isopropylbiphenyl	9.99	2.21	- 8
50% Dichlorobiphenyl	15.06	2.61	- 76
50% Isopropyl Dichlorophenyl	25.65	3.38	-123
50% Butyl Dichlorobiphenyl	72.65	5.60	-101
50% Isopropyl Trichlorobiphenyl	56.39	4.76	-173

(2) Polyester Permanent-Type Plasticizers

Viscosities were determined on polyester permanent-type plasticizers submitted by Dr. T.M. Patrick. The sample labeled Santicizer 404 had viscosities of 785 cs. at 130° and 113 cs. at 210°F. The viscosities for Santicizer 408 were 730 cs. at 130°F. and 123 cs. at 210°F.

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(3) Viscosities of Various Phosphonates

The following table lists the viscosity characteristics of di-2-ethylhexyl chloromethyl phosphonate and dibutylchloromethyl phosphonate which are currently being tested as additives and/or base stocks for functional fluids.

	<u>Viscosity</u>	
	<u>at 100°F.</u>	<u>at 210°F.</u>
Di 2-ethylhexylchloromethyl phosphonate	9.56 cs.	2.28 cs.
Dibutylchloromethyl phosphonate	4.11 cs.	1.32 cs.

(4) Viscosity of Tri (o-Benzylphenyl) Phosphate

Continuing the study of structural effects on the viscosity indices of phosphate esters, tri (o-benzylphenyl) phosphate (RSM-A96232) has a viscosity at 100°F. of 681.6 cs. and 18.47 cs. at 210°F. to give a viscosity index of -80. Viscosity determinations on the above compound illustrates the reduction in viscosity index resulting from the addition of aromatic side chains on the phenyl groups of triphenyl phosphate even through the media of methylene linkages.

(5) Dayton's Fluids

Octyl 3-(octyloxy)propionate (CP-15074) and 2-ethylbutyl 3-(2-ethylbutoxy)propionate (CP-15075) were submitted for primary evaluations as functional fluids by Central Research, Dayton, Ohio. The following table lists various physical properties of these compounds.

	<u>CP-15074</u>	<u>CP-15075</u>
Viscosity at 100°F.	6.25 cs.	2.94 cs.
at 210°F.	1.93 cs.	1.17 cs.
Pour Point	-78°F.	-90°F.
Flash Point	335°F.	290°F.
Fire Point	355°F.	305°F.

These compounds are not promising as high temperature functional fluid base stocks.

(6) Various Phosphates from Carbide Coal Xylenols

Various trixylenyl phosphates were evaluated as possible functional fluids. The triaryl phosphate prepared from Carbide Coal Hydrogenation xylenols gave a higher viscosity index than similar phosphate esters made from other xylenols.

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<u>Source of Raw Material</u>	<u>V.I.</u>	<u>Viscosity (cs.)</u>		<u>Notebook</u>
		<u>at 100°F.</u>	<u>at 210°F.</u>	
Productol's D-2 Xylenol	-34	69.11	5.97	A-79802
Productol's D-3 Xylenol	- 3	64.50	6.07	A-79803
Carbide Coal Hydrogenation Xylenol	+17	41.34	5.06	A-84116

ACKNOWLEDGMENT

We appreciate the work of the production departments in the successful large scale formulating of Pydraul 60 and Pydraul 625. The assistance rendered by the Functional Fluids Application Laboratories, the Research Physical Chemical Group, the JFQ Analytical Section, the Pilot Plant personnel, and Douglas Aircraft Physical Testing Laboratories is gratefully acknowledged.

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APPENDIX

The following table lists the Shell 4-Ball scar diameters in mm. for Pydraul 600, FH-127 and FH-128 as reported by Douglas Aircraft Company.

Fluid	Lot Number	Steel On Steel			Steel On Bronze		
		1 Kg.	10 Kg.	40Kg.	1 Kg.	10Kg.	40 Kg.
Pydraul 600	Y-541	0.13	0.39;0.46	0.53	0.43	0.92	1.15;1.49
Pydraul 600	Y-541	0.14	0.49	0.55	0.50	0.70	1.48;1.39
FH-127	Z-2457	0.17	0.22	0.77	0.56	1.06	1.23
FH-127	Z-2457	0.17	0.26	0.73	0.52	0.92	1.17
FH-128	Z-2458	0.13	0.24	0.75	0.47	1.17	1.18
FH-128	Z-2458	0.23	0.23	0.73	0.60	1.09	1.18

The following table lists the results of the oxidation-corrosion tests on FH-127, Pydraul F-9 and Pydraul 600 as reported by Douglas Aircraft Company.

Fluid	Lot No.	Viscosity at 130°F.(cs.)			Neut. No. mg.KOH/gm.		
		Initial	Final	% Change	Initial	Final	% Change
FH-127	Z2457	20.5	20.8	+1.5	.00	.06	--
FH-127	Z2457	20.5	21.1	+2.9	.00	.04	--
Pyd. F-9	---	20.2	20.2	0.0	.00	.06	--
Pyd. 600	Y-541	43.9	44.0	+0.2	.00	.03	--
Pyd. 600	Y-541	43.9	45.8	+4.1	.00	.00	--

Fluid	Wt. Change mg./cm. ²				
	Cu	Fe	Al	Mg	Cd/Fe
FH-127	-.09	+.01	+.03	+.08	+.04
FH-127	-.16	.00	+.02	+.08	+.04
Pyd. F-9	-.09	-.03	+.09	+.06	+.08
Pyd. 600	-.13	+.02	-.01	-.01	+.07
Pyd. 600	-.07	+.05	+.05	+.10	+.05

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Further tests run on FH-127, Lot Z-2457 at Douglas Aircraft Company are as follows:

KVCs at 210°F.	5.48
KVCs at 100°F.	49.2
Pour Point	-1°F.

Hot Manifold Flammability - No ignition at 1410°, maximum attainable temperature.

High Pressure Spray Flammability - No ignition.

AIT (Quartz in iron) 1-1150° -3 (Drops - °F. - Secs.)

Foaming Tendency -

Sequence:

	<u>Ml. of foam at end of 5 min. blowing period</u>	<u>Ml. foam after 10 min. settling period</u>	<u>Foam half life in secs.</u>	<u>Foam life in secs.</u>
75°F.	60	None	20	80
200°F.	15	None	5	25
75°F. (After 200°F. test)	90	None	35	160

Rubber Swell (7 days at 158°F.)

<u>Material</u>	<u>% Swell</u>	<u>Hardness</u>	
		<u>Int.</u>	<u>Final</u>
Butyl (P & RP Compd. 805-70)	13.1	81	69
Nitrile (P & RP Compd. 479-70)	109.3	70	48

On the Pydraul 600, Lot Y-541, the following results were obtained:

High Pressure Spray Flammability - No ignition.

Hot Manifold Flammability - No ignition at 1445°, the highest attainable temperature.

AIT (Quartz in iron) 1-1138° -3 (drops - °F. - Secs.)

(continued on next page)

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Foaming tendency -

Sequence:

	<u>Ml. of foam at end of 5 min. blowing period</u>	<u>Ml. foam after 10 min. settling period</u>	<u>Foam half life in secs.</u>	<u>Foam life in secs.</u>
75°F.	270	70	360	600
200°F.	140	None	25	50
75°F. (after 200°F. test)	140	30	200	600

Rubber Swell

<u>Material</u>	<u>% Swell</u>	<u>Hardness</u>	
		<u>Int.</u>	<u>Final</u>
Butyl (P & RP Cmpd. 805-70)	39.2	81	52
Nitrile (P & RP Cmpd. 479-70)	121.8	68	43

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