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ON

FUNCTIONAL FLUIDS -

APPLICATION RESEARCH FOR 1954-55

- -

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I. INTRODUCTION

Monsanto has been actively interested in the field of functional fluids since 1948. Two lines of products, Skydrol fire resistant aircraft hydraulic fluids and Pydraul fire resistant industrial hydraulic fluids, have been introduced and several individual fluids have reached commercial status. Research has continued on both the new fluids and those in the research and development stages. This report covers work on functional fluid application research principally in the industrial field and includes formulation studies, property determinations, and sample preparations. The period covered by this report is from August, 1954 through December, 1955.

II. SUMMARY

The Pydraul series of fire resistant industrial fluids was extended to include Pydraul 150, a low viscosity, low temperature fluid, Pydraul 600, a high viscosity fluid, and Pydraul AC, an air compressor lubricant, as well as Pydraul F9, a medium viscosity fluid. Formulation studies were carried out and tentative processes developed. Acryloid 710 was adopted as the viscosity index improver for this series wherever needed replacing Santodex which was withdrawn from the market. Physical and chemical properties were studied for these Pydraul fluids and for several development fluids.

Cooperation was given in the Navy's search for fire resistant shipboard hydraulic fluids by provision of new fluids.

Samples of a fire resistant steam turbine lubricant, an adhesion drive fluid, and a high specific gravity torque converter fluid were supplied to prospective customers.

Three phosphate esters were sent to Douglas at their request for additive solubility studies.

III. REFERENCES

1. Final Report No. 620, "Hydraulic Fluids and Synthetic Lubricants", 117-2080 by R. E. Hatton, May 15, 1952.

2. Final Report No. 728, "Functional Fluids", 117-2380 by R. E. Hatton, May 21, 1953.

3. Final Report No. 986, "Functional Fluids - Application Research, 1952-54", 117-2502 by R. E. Hatton, L. W. Bannister, W. E. Koerner, O. B. Cecil, August 4, 1954.

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4. Tentative Process P-553, "Blending of Pydraul 600", 117-2815 by R. E. Hatton, Sept. 24, 1954.

5. Tentative Process P-607, "Blending of Pydraul 150 (Fluid OS-57)", 117-2815 by R. E. Hatton, May 20, 1955.

6. Tentative Process P-628, "Blending of Fluid OS-67", 2-02-750.01-2815 by R. E. Hatton, August 18, 1955.

7. Final Report No. 1333, "Navy Shipboard Fluid - Process Development of OS-70, Part I", 2-02-750.01-3011 by R. S. Mitchell, November 11, 1955.

IV. EXPERIMENTAL WORK AND DISCUSSION

A. Pydraul F9

1. Viscosity Index Improvers

Pydraul F9, Monsanto's medium viscosity industrial fire resistant hydraulic fluid and lubricant, consists of a base stock and additives, one of which is a viscosity index improver. Monsanto's Santodex was used for this purpose. It was decided for business reasons to suspend the manufacture of Santodex and it therefore became necessary to find a replacement. It appeared that Acryloid 794 was the least expensive purchasable replacement possible and its use in Pydraul F9 was studied.

Solubility characteristics of Acryloid 794 were found to be similar to those of Santodex, being very miscible with Aroclor 1248 and essentially insoluble in tricresyl phosphate. However, it was quite readily soluble in Pydraul Base, the mixture of Aroclor 1248 and tricresyl phosphate normally used. Efforts to induce separation from the Base were unsuccessful.

It was found that 2.5% Acryloid 794 in Pydraul Base gave about the same properties as 4.2% Santodex. A series of fluids were prepared and their properties determined. The data are as follows:

Sample	1	A	B	C	D	E
Viscosity,cs.210°F.	5.91	6.02	5.89	5.96	5.97	5.83
Viscosity,cs.100°F.	53.51	54.83	53.53	53.79	54.61	53.82
Viscosity index	+ 34	+ 36	+ 32	+ 36	+ 34	+ 26
Pour Point,°F.	+ 5	0	0	0	0	0
Flash Point,°F.	410	410	400	390	380	385
Fire Point,°F.	>680				>670	>670
Sp. Gr. 25/25°C.	1.2857				1.2851	1.2760

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Samples 1, A, B, C, and D were prepared from 45.0% tricresyl phosphate, 52.5% Aroclor 1248 and 2.5% Acryloid 794 using various lots of raw materials. The values obtained give some indication of variation in property to be expected in normal formulation. These samples met regular Pydraul F9 specifications for viscosity. The specific gravity was slightly greater than the 1.26-1.28 range normally allowed and sample 1 had a pour point higher than the specification value of 0°F. maximum. However, this was not considered serious and had previously been observed as a normal variation between batches.

Sample E was prepared from the same tricresyl phosphate and Aroclor 1248 as sample D. Santodex was used in sample E and Acryloid 794 in sample D. Thus these two samples give an exact comparison of changes resulting from change in viscosity index improver.

The data thus far discussed indicated that Santodex could be replaced by Acryloid 794 in Pydraul F9. Therefore, a five gallon sample was prepared and sent to Douglas for evaluation and comparison to Pydraul F9 in certain functional tests. The properties of this sample, called FH-103, are as follows:

Viscosity, 210°F.	5.96 c.s.
Viscosity, 100°F.	54.6 c.s.
Viscosity Index	+ 32
Specific Gravity, 25/25°C.	1.2694
Acidity	0.03 NN
Pour Point	0°F.
Flash Point	400°F.
Fire Point	700°F.

The thermal stability of regular Pydraul F9 was compared to that of FH-103. Beakers of both fluids were placed in the oven and samples removed periodically. The oven temperature was 150°C. throughout the test. Data are as follows:

Time in Days	Acidity in NN	
	Pydraul F9	FH-103
3	0.21	0.20
7	0.39	0.48
14	1.16	0.78
21	1.7	1.46
28	3.6	3.6
35	7.9	7.5
42	9.4	6.6

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Weight losses were quite similar during this test for each material. These observations indicate that the change in viscosity index improver from Santodex to Acryloid 794 will have little effect on thermal stability.

Pump testing at Douglas showed that FH-103 was less shear stable than Pydraul F9 made from Santodex. It was felt that, if possible, a product of better shear characteristics should be found.

A series of viscosity index improvers were evaluated in Pydraul type formulations for shear stability. The Diesel Injector Shear Test was used. The test involved passing the fluid through a Diesel injector five times and measuring viscosity before and after the test. The fluid was then again passed through the injector five more times giving a total of ten passes and viscosity again determined. Shear was measured in viscosity change.

This test was carried out on a series of samples and the data obtained are as follows:

Sample	A	B	C	D	E	F
Composition, wt. %						
Aroclor 1248	53.8	51.6	52.5	52.5	52.5	52.5
Tricresyl phosphate	46.2	44.2	45.0	45.0	45.0	45.0
VI Improver	None					
Santodex		4.2				
Acryloid 794			2.5			
Acryloid 763				2.5		
Acryloid 710					2.5	
Acryloid HF855						2.5
Shear Data						
Original viscosity	3.80	5.77	5.99	5.74	5.67	5.25
210°F.	39.19	53.55	54.96	54.10	54.13	50.95
V.I.	-258	+22	+33	+17	+9	-24
After 5 passes						
210°F.	3.98	4.28	4.26	4.52	4.67	4.80
100°F.	39.21	42.59	41.89	44.58	46.17	47.22
V.I.	-258	-134	-159	-120	-98	-77
% loss in visc. at 100°F.	0	76%	83%	64%	53%	32%
After 10 passes						
210°F.	3.78	4.27	4.15	4.41	4.54	4.77
100°F.	38.38	41.56	40.90	43.38	45.03	46.25
V.I.	-250	-149	-177	-136	-119	-75
% loss in visc. at 100°F.	0	85%	89%	72%	60%	40%

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The composition of the samples is listed in the table. One batch of Pydraul base (Aroclor 1248, tricresyl phosphate, silicone defoamer) was used for all samples to eliminate variation in base stock viscosity. The data indicate that Santodex and Acryloid 794 are comparable in shear with Acryloid 794 being slightly poorer. Shear stability increased in order of Acryloids 794, 763, 710, and HF855. It should be noted that insufficient Acryloid HF855 was used in Sample F to give a fluid meeting Pydraul F9 specifications. Three weight percent should be sufficient. Probably slightly more shear would have been experienced at that viscosity index improver level than given in the table but certainly not much.

Based upon these data and economic considerations, it was decided to use Acryloid 710. Five gallons of a Pydraul F9 formulation was sent to Douglas for pump tests. The material was labelled FH-105 and consisted of 52.5% Aroclor 1248, 45.0% tricresyl phosphate, 2.5% Acryloid 710 and 50 ppm. DC 200-350 cs. at 25°C. In studying this formulation it was noted that the Acryloid 710 does not seem as potent as either Santodex or Acryloid 794 in that less viscosity index improvement is given for the same thickening (as indicated by 100°F. viscosity). Specifications stated that Pydraul F9 should have a minimum viscosity index of 15 and a viscosity at 100°F. of about 240 SUS (52 c.s.). Fluid FH-105 was a compromise since it was desired to stay as close as possible to present Pydraul F9 properties. The properties of FH-105 are given in the following tabulation. Included are data on Pydraul F9 containing 2.75% Acryloid 710 (A) and 3.00% Acryloid 710 (B) which indicate the effects of increased concentration.

Sample	FH-105	A	B
Viscosity, 210°F.	5.80 cs.	6.05 cs.	6.28 cs.
Viscosity, 100°F.	56.20 cs.	58.03 cs.	59.94 cs.
Viscosity index	+ 11	+ 24	+ 33
Acidity	0.05 NN		
Sp. Gr. 25/25°C.	1.285	1.283	1.282
Pour Point	0°F.		+ 5°F.
Flash Point	395 F.		
Fire Point	680°F.		

After testing by Douglas, a formulation change was approved and an amendment made to the manufacturing process for Pydraul F9 (amendment dated June 2, 1955). Pydraul F9 produced after this date had the composition listed for FH-105 above. Specifications for Pydraul F9 were amended to increase the specific gravity range to be from 1.275 to 1.295. Complete specifications for Pydraul F9 are as follows:

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Appearance	Cloudy liquid, free of sediment
Moisture	0.20%, maximum
Acidity	0.15 NN, maximum
Pour Point	0°F., maximum
Sp. Gr. 25/25°C.	1.275 to 1.295
Viscosity at 100°F.	45 to 60 cs.
Viscosity at 210°F.	5.2 to 6.1 cs.
Viscosity Index	5 minimum

2. Thermal Stability

The thermal stability of Pydraul F9 was studied at 150°C. in conjunction with a series of tests on other fluids. The data are recorded under part C-4 of this section of the report.

3. Lubricity Additives

The Navy was faced with the problem of selecting a fire resistant hydraulic fluid for shipboard use. During their evaluations, it was found that Pydraul F9 did not perform as well as certain competitive triaryl phosphate fluids in a special bearing test.

One approach to the problem involved the use of additives which might be expected to reduce wear. A series of samples were prepared containing one percent of the following materials in Pydraul F9 and in a triaryl phosphate (Cellulube 220): Santolube 393, RT-53A, RD 18-588, and Duomeen T Dioleate. These samples were labeled FH-108 for untreated Pydraul F9; FH-109, FH-110, FH-111 and FH-112 represented the additive solutions in Pydraul F9 in the order listed above. Code numbers FH-113, FH-114, FH-115, FH-116, and FH-117 represented the same series using Cellulube 220 as the base material. Douglas tested these materials and found that only Duomeen T Dioleate reduced wear in the Falex Wear Test. This additive was only soluble at the one percent level on heating the mixture to about 60°C.

In view of these results, an additive treated Pydraul F9 was submitted to the Navy for bearing tests. However, in this test, no advantage was found for the additive-treated Pydraul F9. It would appear that little correlation exists between wear as measured by the Falex machine and bearing fatigue life as measured by the Navy test.

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4. Other Tricresyl Phosphates

An appreciable savings in the cost of Pydraul F9 would result if gasoline grade tricresyl phosphate (G grade TCP) could be used in the formulation instead of plasticizer grade tricresyl phosphate.

Using the established formulation, a Pydraul type sample was prepared from G grade TCP made from Shell cresylic acid 2000AA. A control batch was also prepared from regular A grade tricresyl phosphate using the same lots of additives used to prepare the evaluation sample. The analyses of these batches, as well as of the tricresyl phosphate base stocks are as follows:

	Pydraul, Control Batch	Pydraul, Evaluation Batch	Tricresyl phosphate, A grade (for control)	TCP, G grade from 2000AA (for evaluation)
Viscosity, cs.				
+ 210°F.	5.99	6.43	4.26	4.84
+ 100°F.	54.6	68.5	32.4	45.9
Pour Point	0°F.	+10°F.	-20°F.	-10°F.

The differences in viscosity between the two batches would not rule out the use of this phosphate ester. However, the high pour point of the formulation using G grade TCP would be too high to be satisfactory. Using the established formulation, the G grade TCP is not satisfactory for use in Pydraul F9.

Another sample of G grade TCP was examined. This material was made from Productol cresylic acid in Dept. 50 of the J.F. Queeny plant. Data are as follows:

Viscosity, cs.	
+ 210°F.	4.57
+ 100°F.	39.74
Viscosity Index	+ 19
Sp. Gr. 25/25°C.	1.1539

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B. Pydraul 600

1. Formulation Studies

Pydraul F9 can be classed as a medium viscosity hydraulic fluid, its viscosity at 100°F. being 250-275 Saybolt Universal Seconds (SUS). Although Pydraul F9 had found wide usage in a variety of hydraulic systems, it appeared that certain pumps require 600 to 900 SUS fluids. The Sales Department indicated that a real need exists for Pydraul-type fluids having these viscosity properties. Some interest had also been expressed in a 150 SUS Pydraul-type fluid.

Laboratory work was undertaken to formulate fluids from Aroclor-tricresyl phosphate base stocks. Satisfactory fluids having 100°F. viscosities of 900, 600, and 150 SUS were developed. All these fluids are derived from the same chemical type compounds as Pydraul F9, all being based on tricresyl phosphate and Aroclor mixtures. Therefore, it is felt that these fluids would be very similar to Pydraul F9 in stability, flammability, and general utility.

Two general types of base stocks were studied for each viscosity desired, one consisting of a 50:50 blend of tricresyl phosphate and an Aroclor and the other consisting of a 25:75 blend. The composition and the properties of the selected formulations are given in the following table. Fluids A and B are in the 600 SUS class, C and D are in the 900 SUS class, and E and F are in the 150 SUS class. Fluids B, C, and F are the fluids of choice based upon property and economic considerations.

Fluid Designation	A	B	C	D	E	F
Code Number	HV-5.5	HV-1-4	HV-2-4	HV-3-2	HV-7-2	HV-6-2
Composition, weight %						
Tricresyl phosphate	47.25	24.0	48.0	24.5	49.0	24.5
Aroclor 1242					49.0	73.5
Aroclor 1248		36.0				
Aroclor 1254	47.25	36.0		[illegible]		
Aroclor 1260			[illegible]			
Acryloid 794	5.5	4.0	4.0	2.0	2.0	2.0
Properties						
Viscosity, 100°F, SUS	609	630	924	900	159	154
cs.	131	136	199	194	34.1	32.8
Viscosity, 210°F, SUS	65.4	59.0	65.8	53.7	41.6	40.7
cs.	11.8	9.9	11.8	8.4	4.67	4.41
Viscosity Index	+83	+33	+17	-153	+25	- 5
Pour Point, °F.	+15	+15	[illegible]	+ 25	-10	-10
Sp. Gr. 25/25°C.	1.2902	1.3632	1.3279	1.4080	1.2537	1.3099
Flash Point, °F.	430	465	430	415	375	350
Fire Point, °F.	>680	>680	>690	>680	640	>670

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Silicone defoamer was added to each fluid at a concentration of fifty parts per million. Viscosity at 50°F. was found to be 2250 cs. for fluid A and 4025 cs. for fluid B. Cloud point for fluid A was +40°F. Fluid B did not cloud to its pour point.

It was decided that Fluid B would be developed as Pydraul 600. A Tentative Process (Report No. P-628, August 18,1955) was written. A one thousand gallon batch was prepared in the Interim Production Facilities. Properties of this material are as follows:

Viscosity, 210°F.	9.67 cs.
Viscosity, 100°F.	135.8 cs.
Viscosity Index	+26
Specific Gravity, 25/25°C.	1.364
Pour Point	+15°F.
Moisture	0.01%

The product was sent to several prospective customers for evaluation.

During the development of the fluids described in this section, a series of formulations were prepared and studied. Data for these formulations are as follows:

Fluid Designation	Composition, % by weight						Viscosity					
		Aroclor					210°F.		100°F.		Vis.	PP
	TCP	1242	1248	1254	1260	*	cs.	SUS	cs.	SUS	Index	°F.
HV Base	50			50			4.84	42.1	71.1	330	- 282	+10
HV-3	48.5			48.5		3	8.07	52.7	99.5	461	+ 24	
HV-4	48			48		4	9.44	57.4	111.1	515	+ 55	
HV-5	47.5			47.5		5	10.36	62.4	122.8	569	+ 74	
HV-6	47			47		6	12.50	68.4	136.3	631	+ 89	
HV-1- Base	25		37.5	37.5			4.30	40.4	71.3	330	- 525	+20
HV-1-4	24		36	36		4	9.91	59.8	135.9	630	+ 33	+15
HV-1-6	23.5		35.25	35.25		6	13.53	72.5	174.9	810	+ 74	
HV-2- Base	50				50		6.04	46.0	131.8	611	- 309	+10
HV-2-3	48.5				48.5	3	9.91	59.0	175.2	812	- 21	
HV-2-4	48				48	4	11.81	65.8	199.4	924	+ 17	+20
HV-2-6	47				47	6	15.69	80.7	234.3	1090	+ 67	+20
HV-3- Base	25			75			5.34	43.8	145.9	676	- 620	+25
HV-3-2	24.5			73.5		2	8.95	53.7	194.2	900	- 153	+25
HV-3-3	24.25			72.75		3	10.33	60.5	224.2	1040	- 66	
HV-3-6	23.5			70.5		6	13.95	73.9	316.5	1470	- 18	+20

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Fluid Designation	Composition, % by weight						Viscosity					
		Aroclor					210°F.		100°F.		Vis.	PP
	TCP	1242	1248	1254	1260	*	cs.	SUS	cs.	SUS	Index	°F.
HV-4-												
Base	25			37.5	37.5		6.60	47.8	298.5	1390	- 814	+35
HV-4-3	24.25			36.38	36.38	3	12.41	68.0	419.8	1945	- 160	
HV-4-6	23.5			35.25	35.25	6	20.88	102.3	573	2650	+ 7	+30
HV-5-												
Base	25				75		8.43	53.9	713	3300	-1165	+40
HV-5-3	24.25			72.75		3	15.83	81.2	900	4170	- 288	
HV-5-6	23.5			70.5		6	25.16	121.0	1082	5020	- 51	+35
HV-6-												
Base	25	75					2.80	35.6	21.2	103	- 208	- 5
HV-6-2	24.5	73.5				2	4.41	40.7	32.8	154	- 5	-10
HV-6-3	24.25	72.75				3	5.39	43.9	37.5	175	+ 79	
HV-6-6	23.5	70.5				6	8.84	55.3	59.4	276	+ 133	- 5
HV-7-												
Base	50	50					3.28	37.2	25.6	122	- 153	-10
HV-7-2	49	49				2	4.67	41.6	34.1	159	+ 25	-10
HV-7-3	48.5	48.5				3	5.44	44.1	36.9	172	+ 87	
HV-7-6	47	47				6	8.53	54.3	53.7	249	+ 131	- 5
HV-8-												
Base	42.1			57.9			4.99	42.6	88.8	412	- 372	+15
HV-8-3	40			55		3	8.75	55.0	130.6	605	- 4	
HV-8-5	40			55		5	12.14	67.0	166	769	+ 57	+15

* Acryloid 794

In order to make the Pydraul series consistent and to prevent the stocking of a large number of Acryloids, it was decided to change from Acryloid 794 to Acryloid 710 in Pydraul 600. A sample of Pydraul 600 from Acryloid 710 (FH-107) was prepared and sent to Douglas for evaluation. Properties are as follows:

Sample	FH-107
Viscosity, 210°F.	9.24 cs.
Viscosity, 100°F.	134.5 cs.
Viscosity Index	+11
Acidity	0.06 NN
Sp. Gr. 25/25°C.	1.352
Pour Point	-15°F.
Flash Point	415°F.
Fire Point	490°F.

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The composition of FH-107 is as follows: 36% Aroclor 1248, 36% Aroclor 1254, 24% tricresyl phosphate, 4% Acryloid 710 and 50 ppm DC 200-350 cs. at 25°C. An amendment was made to the Tentative Process on Sept. 12, 1955 and Pydraul 600 made after that date had the same composition as FH-107.

2. Viscosity Data

Viscosity data over a wide temperature range were determined for Pydraul 600 and are as follows:

Viscosity, cs.	
210°F.	9.83
130°F.	46.0
100°F.	135
50°F.	3910

3. Solubility of Water in Pydraul 600

The solubility of water in various fluids was determined at room temperature and at 210°F.

The procedure for the determinations at room temperature was as follows: A sample of the fluid was stirred from 1-1/2 to 2 hours with an equal volume of water by bubbling an air stream through the mixture to insure intimate contact. The layers were allowed to separate about an hour. The ester layer was then centrifuged for 30 minutes to free it from occluded water. Samples of the ester were weighed in duplicate into tared stoppered flasks containing a mixture of benzene and methanol blanked with Karl Fischer reagent. The samples were then titrated with Karl Fischer reagent.

The procedure for the determinations at 210°F. was as follows: A sample of the fluid was stirred for 1-1/2 to 2 hours with a large maintained excess of water by bubbling an air stream through the mixture contained in a large tube placed in a 210°F. constant temperature bath. The layers were then allowed to separate for about 4 hours. The ester layer was clear, showing no occluded water to be present in it. Using a warmed pipette, samples of the ester layer were weighed in duplicate into tared stoppered flasks containing a mixture of benzene and methanol blanked with Karl Fischer reagent. The samples were then titrated with Karl Fischer reagent. The results are listed in the following table:

	Pydraul 150	OS-58-1	OS-63	Pydraul 600
Solubility of H_2O at room temperature (ca. 75°F.)	0.52%	0.11%	0.26%	0.12%
	0.48%	0.12%	0.22%	0.12%
Solubility of H_2O at 210°F.	1.16%	0.39%	0.62%	0.31%
	1.13%	0.39%	0.62%	0.31%

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C. Pydraul 150

1. Formulation Studies

Many applications require the use of fire resistant hydraulic fluids possessing better low temperature properties than Pydraul F9. To fill such needs, OS-57 was developed. Details of the formulation study are reported in Final Report No. 988, "Functional Fluids - Application Research, 1952-54", Job No. 117-2508. A Tentative Process (Report No. P-607, May 20, 1955) was written under this job number and the name of the fluid changed to Pydraul 150.

In order to make the Pydraul series consistent, it was decided to change from Acryloid 794 to Acryloid 710 in Pydraul 150. A sample of Pydraul 150 from Acryloid 710 (labeled FH-106) was prepared and submitted to Douglas for evaluation. Properties of the sample are as follows:

Sample	FH-106
Viscosity, 210°F.	7.55 c.s.
Viscosity, 100°F.	31.06 c.s.
Viscosity Index	+169
Acidity	0.07 NN
Sp. Gr. 25/25°C.	1.125
Pour Point	-55°F.
Flash Point	390°F.
Fire Point	470°F.

The composition of FH-106 is as follows: 69% 2-ethylhexyl diphenyl phosphate, 23% Aroclor 1242, 8% Acryloid 710 and 50 ppm DC 200-350 cs. at 25°C. It was necessary to use 8% Acryloid 710 to obtain the desired properties for Pydraul 150 as compared to the 7.5% Acryloid 794 previously used. An amendment was made to the Tentative Process on Sept. 12, 1955 and Pydraul 150 subsequently produced was formulated by this process.

2. Viscosity Data

Viscosities over a wide temperature range were determined for a sample of Pydraul 150 and are as follows:

Viscosity, cs.	
210°F.	7.73
130°F.	18.5
100°F.	30.5
0°F.	650

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3. Solubility of Water in Pydraul 150

The solubility of water in Pydraul 150 was found to be 0.50% at room temperature and 1.2% at 210°F. Details of these determinations are given under section B-3 of this report.

4. Thermal Stability

Previous work on the thermal stability of Pydraul 150 was conducted at 125°C. or above. It was felt that such studies should be extended to temperatures in the range of 110°C. and comparative data for fluids such as Skydrol 7000, Skydrol 500, and OS-54 should be collected. Even this temperature is somewhat above normal operating temperatures in hydraulic systems.

The method used was as follows: One hundred gram samples of the fluid were placed in beakers and the beakers placed in an electrically heated oven at 110°C. After the desired time had elapsed the samples were removed and examined.

The data for this series are as follows:

Time in Days	0	3	7	14	21	28	35	42	49	56	63
Pydraul 150											
Acidity, NN	0.08	0.36	0.61	1.11	1.66	2.96	3.9	8.3	11.7	20.6	27.4
Viscosity, cs., 210°F.	7.73		7.58		7.58		7.79		8.06		
100°F.	30.45		29.99		30.27		30.96		31.09		
Skydrol 500											
Acidity, NN	0.03	0.11	1.21	5.7	11.0	18.2	27.8	28.7	40.9	43.1	53.7
Viscosity, cs., 210°F.	4.02		4.11		4.45		4.96				
100°F.	11.94		12.44		13.41		16.26				
Skydrol 7000											
Acidity, NN	0.13	0.87	1.75	4.4	7.0	11.6	16.9	29.2	43.7	138	152
Viscosity, cs., 210°F.	4.05		4.10		4.22		4.51				
100°F.	15.90		16.35		17.26		19.00				
Fluid OS-54											
Acidity, NN	0.09	0.20	0.31	0.66	0.85	1.04	0.98	1.00	2.49	2.90	5.2
Viscosity, cs., 210°F.	7.40		7.70		8.06		8.24		8.26		
100°F.	39.91		43.14		46.17		47.04		46.16		

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Weight losses after 63 days were about 12% for Pydraul 150, 23% for Skydrol 500, 21% for Skydrol 7000, and 11% for Fluid OS-54. Skydrol 7000 separated into two layers after 49 days. All fluids darkened on heating, the amount of darkening being greater with greater acidity development.

Considerable differences in thermal stability may be noted. Fluids OS-54 and Pydraul 150 are more stable to heat than either Skydrol. All fluids appear to decompose in the normal manner for alkyl aryl phosphates, liberating a volatile material and developing acidity.

These data together with previous data can be used to determine safe maximum temperature-time operating limits. For comparative purposes, the time required to develop 1.0 NN acidity may be used. At 110°C. these times would be about 3 days for Skydrol 7000, 6 days for Skydrol 500, 12 days for Pydraul 150 and 25 days for Fluid OS-54. Similar times for Pydraul 150 are about 4 days at 125°C., one day at 150°C. and about 6 hours at 175°C., illustrating the time-temperature relationship.

Similar data were obtained for Pydraul F9 at 150°C. and are as follows:

Time in Days	Acidity, NN	Viscosity, cs. 210°F.	Viscosity, cs. 100°F.
0	0.17	5.62	45.08
3	0.27		
7	0.33	5.24	47.72
14	0.82		
21	2.81	5.23	48.22
28	4.1		
35	7.0	5.38	52.62
49	18.9		
56	37.4		
63	48.1		

The weight loss was about 30% in 63 days. These data demonstrate the increased thermal stability of the Pydraul F9 fluid containing tricresyl phosphate as compared to those reported above which contain alkyl aryl phosphates.

D. Navy Fluids

As a result of several shipboard hydraulic fluid fires, the Navy began a thorough evaluation of the problems involved and a search for suitable fire resistant fluids. Monsanto cooperated with this program by furnishing samples and formulating special fluids. This section details part of this work.

DSW 620941

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1. OS-54

OS-54 was originally developed as a fire resistant power steering fluid and became of interest to the Navy. Details are recorded in Final Report 988, job number 117-2508. The thermal stability of OS-54 was studied and detailed data are given under section C-4 of this report.

2. OS-63

After a thorough examination of all shipboard hydraulic systems, the Navy had concluded that the low temperature properties of Pydraul F9 were not completely satisfactory. Pydraul F9 had previously passed flammability, pump, and bearing tests.

A fluid somewhat similar to Pydraul F9 was selected from our back-log of formulations and a rust inhibitor added. Such a material, called Fluid OS-63, should meet the low temperature and the antirust requirements of the Navy. A one pound sample (A) was prepared and submitted for evaluation. Properties were as follows:

Sample	A	B
Viscosity, cs., 210°F.	5.41	5.46
100°F.	37.4	37.6
20°F.	3560	-----
Viscosity Index	82	84
Sp. Gr. 25/25°C.	1.246	1.246
Flash Point, °F.	360	385
Fire Point, °F.	660	650
Pour Point, °F.	-10	-10
Acidity, NN	---	0.11

Fluid OS-63 consisted of 48.4% tricresyl phosphate, 48.4% Aroclor 1242, 3.0% Acryloid 794, 0.2% Santolube 70 and 50 ppm DC 200-350 cs.

Satisfactory results obtained in preliminary tests led to a request for more fluid and several gallons (Sample B) were prepared.

The solubility of water in OS-63 was found to be 0.24% at room temperature and 0.62% at 210°F. Details of the determination are given in section B-3 of this report.

DSW 620942

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3. OS-66

The Navy requested a Pydraul 600 type fluid possessing improved shear characteristics. Accordingly, a gallon of Fluid OS-66, which was Pydraul 600 containing Acryloid HF855M, was prepared. The properties of this batch were as follows:

Viscosity,cs., 210°F.	9.24
Viscosity,cs., 100°F.	128.8
Viscosity Index	+20
Acidity	0.05 NN
Sp. Gr. 25/25°C.	1.3596

This material was sent to the Navy under Lot Number Y-2175.

4. OS-70 (Triaryl Phosphates)

The Navy's evaluation of many fire resistant fluids led to the adoption of Cellulube 220 because of its performance in a special bearing test. Cellulube 220 is a triaryl phosphate fluid produced by the Celanese Corporation of America. In order to participate in sale of fluid to the Navy, two approaches were taken. The first approach involved the examination of Pydraul F9 failure in the particular bearing test as contrasted to satisfactory operation in the field for many years. (See Section A-3.) The second approach concerned the preparation of a product equivalent to Cellulube 220. Studies along this line were started under this job number. However, the major portion of the work was done under job number 2-02-750.01-3011 and all data will be reported under the latter job number.

E. Pydraul AC (OS-67)

A need existed for a fire resistant air compressor lubricant. Work was started between Mr. Moreton of Douglas and Standard Oil of California personnel to develop a fire resistant air compressor lubricant. Fluid OS-67 which consists of 43% tricresyl phosphate and 57% Aroclor 1254 resulted. A sample was prepared in our laboratory and physical properties were determined and compared with the Douglas sample (LHD). Data are as follows:

Sample	OS-67	LHD
Viscosity, cs., 210°F.	5.28	5.18
Viscosity, cs., 100°F.	85.64	98.10
Viscosity Index	351	368
Sp. Gr. 25/25°C.	1.552	1.549
Pour Point, °F.	-20	-20

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Variation is as would be expected from normal variations in raw material.

Larger quantities were needed for development work and a tentative process (Report No. P-628, August 18, 1956) was written.

Satisfactory large scale tests resulted in the wide spread adoption of OS-67. Its name was changed to Pydraul AC.

F. Steam Turbine Fluids

A steam turbine fire resistant lubricant was developed under job number 117-2508. Four gallons of this fluid, OS-58-1, were prepared for submission to prospective customers. Its properties were as follows:

Viscosity at 210°F.	5.43 cs.
Viscosity at 100°F.	39.5 cs.
Sp. Gr. 25/25°C.	1.304
Pour Point	-5°F.
Acidity	0.05 NN

This further quantity was required because of promising results in preliminary studies.

The solubility of water in OS-58-1 was found to be 0.12% at room temperature and 0.39% at 210°F. Details of this determination may be found in Section B-3 of this report.

Work on steam turbine fire resistant lubricants was continued under job number 2-02-750.01-2949.

G. L-3A Fluid

A sample of used Fluid L-3A from Axelson Manufacturing Co. was examined. This material had been used 200 hours in their Alternator Drive unit at 180°F. to 210°F. Problems concerning improved lubricity with decreased traction properties through possible contamination had been experienced.

The properties of the sample as compared to those of the fluid originally sent are as follows:

Sample	Used	New
Viscosity, cs., 210°F.	3.24	3.19
Viscosity, cs., 100°F.	16.11	15.53
Viscosity Index	59	63
Acidity, NN	1.45	1.21
Sp. Gr. 25/25°C.	1.069	1.065
Flash Point, °F.	300	340
Fire Point, °F.	400	425
Moisture, %	0.25	---

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The sample of used fluid was quite cloudy and normal filtration techniques would not produce a clear material.

The acidity of the used fluid seemed abnormally high. Changes in other properties indicate possible contamination.

A reserve sample of new fluid was sent to Douglas who plan to run comparative lubricity tests.

Larger quantities of fluid were desired by Axelson for further test work and 20 gallons were prepared. The properties of this were as follows:

Viscosity, 210°F.	3.91 cs.
Viscosity, 100°F.	15.02 cs.
Viscosity Index	+ 76
Acidity	0.38 NN
Sp. Gr. 25/25°C.	1.062

L-3A fluid consists of 60% tricresyl phosphate and 40% Ucon DLB 50-E. It has also been known as OS-22.

H. OS-41

The Ford Motor Company expressed interest in OS-41, a proposed synthetic high specific gravity torque converter fluid. Three gallons were prepared and submitted for tests. The material met specifications in all respects. OS-41 consists of 48% 2-ethylhexyl diphenyl phosphate, 48% Aroclor 1248, 4% Acryloid HF855 and 50 ppm DC 200-350 cs. at 25°C.

I. Phosphate Esters for Douglas

Douglas requested samples of a low molecular weight dialkyl aryl phosphate and a high molecular weight alkyl diaryl phosphate for test work concerning additive solubilities. Samples of n-decyl diphenyl phosphate and 2-butyloctyl dicresyl phosphate were taken from reserve supplies and sent to Douglas as FH-122 and FH-123, respectively. Dimethyl phenyl phosphate was prepared and submitted to Douglas as FH-121. Details of preparation are as follows:

In general accordance with U.S. Patent 2,426,691, dimethyl phosphoryl chloride was prepared as follows: Phosphorus trichloride (262 ml., 3 moles) was added dropwise to a cooled solution of 372 ml. (9.2 moles) of methanol and 500 ml. of benzene, the addition requiring 2 hours at 5-12°C. During the next hour, while the reaction vessel was still immersed in an ice-bath, vacuum was gradually applied to the system until a pressure of 220 mm. was reached.

DSW 620945

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Then chlorine gas was bubbled in at -2 to +12°C. (140-220 mm.) until the reaction mixture turned yellow and the temperature began to fall; 3.5 hours were required for the chlorination and the chlorine uptake was 213.5 g., just 0.8 g. over the theoretical. The cooling bath was then lowered and the pressure in the system was reduced to 50 mm. where it was held as the reaction product warmed to room temperature during the next three hours.

The crude dimethyl phosphoryl chloride was added dropwise with stirring at 0-5°C. to a sodium phenate solution, which had been prepared from 252 g. (3.15 moles) of plant lye, 420 ml. of water, and 296.4 g. (3.15 moles) of phenol. The addition required 5 hours, after which the reaction mixture was stirred for 4 hours without cooling. During the latter period, the alkalinity of the mixture was maintained by additions of lye as needed.

Layers were separated, and the organic layer was washed with two 900-ml. portions of 2% lye solution, three 900-ml. portions of 1% lye solution, and four 1000-ml. portions of water. The last two water washes were treated with a few drops of sulfuric acid to get them to separate. After washing, the product was dehydrated under vacuum until essentially all benzene had been removed. At this point 50 ml. of water was added and the dehydration was finished at full water pump vacuum to 110°C. The dry ester was stirred with 3 g. of Nuchar C-145-N as it cooled, then was filtered through Attapulgus earth. The finished dimethyl phenyl phosphate had the following properties: n_D^{25} 1.4862, sp. gr. 25/25°C. 1.2262, NN 0.30, and APHA 300. The yield was 322 g. (53.1%).

V. CONCLUSIONS

A new viscosity index improver was accepted for use in Pydraul F9. The substitution was necessary because of the end of manufacture of Santodex. Acryloid 710 was chosen because of resistance to shear, ability to produce a satisfactory Pydraul F9, and economic considerations. Acryloid 794 was rejected because of poor shear stability. Amendment was made to the Manufacturing Process for this formulation change.

It was shown that gasoline grade tricresyl phosphate cannot be used as a direct replacement for plasticizer grade in Pydraul F9.

A high viscosity fire resistant industrial hydraulic fluid was developed and introduced to the market as Pydraul 600. Various properties were determined to assist in its utilization. A Tentative Process was written.

DSW 620946

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Pydraul 150, a low temperature, low viscosity fire resistant industrial hydraulic fluid, had previously been proposed for certain applications. Further formulation studies were carried out and a Tentative Process written. Thermal stability tests indicated that Pydraul 150 was similar to Skydrol 7000 in resistance to thermal breakdown. The rate of breakdown was shown to be dependent upon composition and temperature (Pydraul 150, OS-54, Skydrol 500, Skydrol 7000, and Pydraul F9 were run in this series of tests). The data obtained assist in determining safe maximum operating temperature-time limits. Various physical properties were determined for Pydraul 150.

The solubility of water in Pydraul 150, Pydraul 600, OS-58-1, and OS-63 was determined at room temperature and at 210°F. These data are of particular value in the design of recovery systems for wet fluids.

During the Navy's evaluation program of fire resistant shipboard hydraulic fluids, two distinct plans were followed by Monsanto. The first plan involved emphasis on Pydraul type fluids. A number of fluids such as OS-54, OS-63, and OS-66 were submitted for evaluation. An additive was found through cooperative testing with Douglas that reduced the wear characteristics of Pydraul F9 in the Falex Wear Test. However, such improvement did not carry over to bearing fatigue life as measured by the Navy bearing test. The second plan involved the development of a triaryl phosphate fluid similar to an approved material (Cellulube 220). This program was started and further work done under job number 3011.

A fire resistant air compressor lubricant, Pydraul AC (OS-67) was developed by Douglas. Considerable promise was shown in large scale tests. A Tentative Process was prepared.

Further samples of a proposed fire resistant steam turbine lubricant, OS-58-1, were prepared for evaluation by interested groups. Preliminary results were quite promising and the work was continued under job number 2949.

Samples of used L-3A fluid were examined. Contamination was suspected and found. Larger quantities of L-3A were prepared and supplied for further test work in an adhesion drive.

Three gallons of OS-41 were prepared and submitted to Ford Motor Co. for study as a torque converter fluid.

n-Decyl diphenyl phosphate, 2-butyloctyl dicresyl phosphate, and dimethyl phenyl phosphate were submitted to Douglas for test for solvent powers on certain additives. Dimethyl phenyl phosphate was prepared by reaction of methanol with phosphorus trichloride, chlorination of the intermediate dimethyl phosphite to dimethyl phosphoryl chloride, and Schotten-Baumann condensation of the latter with sodium phenate solution.

DSW 620947

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VI. APPENDIX

During the period of this work, other studies in the field of functional fluids were in progress. A listing of job numbers is as follows:

2813 - Skydrol 500 Investigations

2814 - Preliminary Screening Evaluations - Functional Fluids

2816 - Silicate Ester Fluid Investigations

2919 - Application Research on Silicate Ester Fluids

2921 - Exploratory Research on Functional Fluids - 1955,56

2922 - Minor Plant Investigations and Consultations on Functional Fluids - 1955,56

2949 - Synthetic Steam Turbine Lubricants

3011 - Navy Shipboard Fluid

3012 - High Temperature Fluids

Notebook page numbers are as follows:

L.W.B.:

A-66915, 16

R.S.M.:

A-54559, 62, 72, 74
A-59342, 44, 46, 49, 50
A-60191
A-63426, 40
A-67454, 58, 74, 500

R.E.H./A.J.B.:

A-52233, 36, 37, 38, 40, 41, 42, 43, 44, 48, 49
A-65051, 52, 53, 54, 62, 65, 67, 68, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80

Roger E. Hatton

rmd
7-30-56

DSW 620948

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