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ON

FUNCTIONAL FLUIDS -- APPLICATION RESEARCH, 1952-54

Job No. 117-2508

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D I S T R I B U T I O N S H E E T

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I. INTRODUCTION

During 1948 Monsanto became interested in the field of functional fluids and with the introduction of Skydrol and the signing of a joint agreement with the Douglas Aircraft Co., Inc., started research in the general field of fluids which were principally synthetic in nature. Functional fluids have been defined as fluids without which a machine cannot perform its designed function -- for example, hydraulic fluids, lubricants, heat transfer fluids, etc. Early work resulted in Pydraul P-9, a non-flammable type industrial hydraulic fluid and the development of background information. Many other fluids have been proposed and are in various stages of development. This report covers the period of August, 1952 through July, 1954. The scope of the work was large including formulation studies, property determinations, application research, sample preparation, and sales service.

II. SUMMARY

Pydraul P-9 and Skydrol 7000 are Monsanto's commercial fluids in the functional fluid field. Skydrol 7000 is a non-flammable type hydraulic fluid for aircraft and Pydraul P-9 is a non-flammable type fluid especially designed for stationary hydraulic machinery. Both fluids have enjoyed considerable success in sales.

Efforts were expended to improve the competitive position of Pydraul P-9 by a change in formulation to reduce raw material costs, by examination of competitive fluids and by investigation of new sources of raw materials. Many properties were determined for Pydraul P-9. These included such things as compatibility with other materials, hydrolytic stability, solubility of water in the fluid, specific heat, electrical properties, thermal conductivity, variation of density with temperature, and flammability characteristics under specified conditions. As a customer service, samples of used Pydraul P-9 were examined for condition and reusability.

Similar but less extensive work was done with Skydrol 7000. Several samples were examined as a customer service and properties such as compatibility with various materials and hydrolytic stability studied.

Skydrol 500 was developed to meet the low temperature requirements of military specifications for non-flammable-type aircraft hydraulic fluids. It was necessary to change certain additives and a satisfactory formulation was developed with Douglas. Test procedures for examination of this fluid were studied and causes of disagreement between our tests and Douglas tests were elucidated. Cooperative testing was undertaken with the Navy by the thin film corrosion test and resulted in the test being discarded as a Skydrol-type test.

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fluids are concerned. The hydrolytic stability of Skydrol 500 was studied. It was shown that results of the recommended test do not correlate with actual use data. The overall result of such work has been a strengthening of the competitive position of Skydrol 500.

Further work on Fluid OS-41, which was designed as a torque converter fluid, has shown that corrosion is not a problem. Various properties were determined to aid in evaluation of the fluid by prospective customers.

Leakage in hydraulic steering systems on automobiles led to fires. A non-flammable type fluid (Fluid OS-54) was developed for this use and is under test. The same fluid is of interest for shipboard use and is under consideration by the Navy.

A definite need exists for a fire resistant, steam turbine lubricant. A fluid (Fluid OS-58) has been developed and after examination by the Engine Test Laboratory for rusting characteristics and the addition of anti-rust additives it was sent to various groups for further evaluation.

A formulation for a lower temperature industrial fire resistant hydraulic fluid was devised (Fluid OS-57). Such a fluid has been reported as needed in applications where hydraulic P-9 is too viscous at low temperatures. Tests on this fluid are in progress by several interested people. Heat stability studies were started and indicated the fluid to be similar to Skydrol in this characteristic.

Samples of many compounds were given preliminary screening for evaluation as functional fluids. Certain materials were of sufficient interest to warrant further testing.

III. REFERENCES

1. Final Report, "Hydraulic Fluids and Synthetic Lubricants", 117-2030, by R. E. Hatton, May 15, 1952.
2. Final Report, "Functional Fluids", 117-2380, May 21, 1953, by R. E. Hatton.
3. Final Report, "Formulation of OS-40 and OS-45", 117-2534, by L. J. Breuklander.
4. Final Report, "Dibutyl Phenyl Phosphate -- Pilot Plant Preparation", 117-2555.

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IV. EXPERIMENTAL WORK AND DISCUSSION

A. Pydraul F-9

1. Formulation Change

In an effort to reduce the raw material costs of Pydraul F-9, Mr. H. K. Nason suggested that the Aroclor 1248 concentration be increased about five per cent. The effects of such changes were investigated. Formulations were prepared using the following proportions:

Regular: 47.9% tricresyl phosphate
47.9% Aroclor 1248
4.2% Santodex

Special: 44.2% tricresyl phosphate
51.6% Aroclor 1248
4.2% Santodex

Raw materials vary somewhat in properties and therefore two formulations of the regular and special type were made. Those numbered one were from one set of raw materials and those numbered two were from another set. Therefore, the properties of the "ones" should be compared and those of the "twos" should be compared to determine the effects of formulation changes. The data are as follows:

Sample	Regular 1	Special 1	Regular 2	Special 2
Viscosity, cs, 210°F.	5.68	5.71	5.67	5.77
100°F.	50.60	52.25	50.20	52.56
Viscosity Index	29	23	30	27
Sp. Gr., 25/25°C.	1.2659	1.2760	1.2661	1.2763
Pour Point, °F.	-5	0	0	+5
Flash Point, °F.	410	405	405	410
Pire Point, °F.	680	680	680	680

Our specifications for Pydraul F-9 include a 0°F. maximum pour point, 15 minimum viscosity index, and specific gravity of 1.26 to 1.28 at 25/25°C. Other specification properties such as appearance, color, moisture, and acidity would be unchanged by such a formulation change as that proposed. Not included in our formal specifications but listed in the general section are viscosity characteristics, being 40.0 to 60.0 cs. at 100°F. and 4.51 to 6.51 cs. at 210°F. The data indicate that the change in formulation increases viscosity, specific gravity, and pour point, decreases viscosity index, and does little to anything to flash.

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and fire point. The only property which does not pass our regular specifications is pour point, being about 5°F. higher for the special formulation.

Before such a change in formulation could be adopted, approval by Douglas Aircraft Co. of its utility was required. Five gallons of the formulation were prepared in the laboratory. The properties of this batch were as follows:

Viscosity, 210°F.	5.72 cs.
100°F.	51.91 cs.
Viscosity Index	+26
Specific Gravity, 25/25°C.	1.2756
Four Point	+5°F.
Flash Point	405°F.
Fire Point	680°F.
Acidity	0.06 NN

The sample was sent to Douglas under the code number PH-98 for their evaluation.

Tests by the personnel at Douglas indicated that the new formulation was essentially functionally equivalent to regular Pydraul F-9. The formulation of Pydraul F-9 was changed in June, 1954 by amendment to the manufacturing process. The formulation for Pydraul F-9 is therefore 44.2% tricresyl phosphate, 51.6% Aroclor 1248, 4.2% Santodex, and 50 ppm of silicone defoamer, DC 200 - 350 cs. at 25°C.

2. Use of Petroleum Derived Tricresyl Phosphate

Only tricresyl phosphate (TCP) derived from coal tar cresols had been used in Pydraul F-9 production. In view of the increased use of TCP and the shortage of coal tar cresols, TCP has been made from petroleum cresols in the plant. Samples of Pydraul F9 were prepared using TCP from petroleum cresols and using a purchased TCP (Kronitex AA from Chio-Apex). The physical properties of these samples as compared to specifications for Pydraul F9 are as follows:

	Petroleum	Kronitex AA	Specifications
Viscosity, cs, 210°F.	5.64	5.51	4.51-6.51
100°F.	51.9	49.1	40 - 60
Viscosity index	18	20	15 minimum
Sp. gr. 25/25°C.	1.263	1.266	1.26-1.28
Acidity, NN	0.07	0.08	0.15 maximum
Four point, °F.	0	0	+5 maximum
Moisture, %	0.12	0.12	0.20 maximum
Bohm Test, 10 min	7	7	Report ml.

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The data for the two samples are essentially similar to those for regular Pydraul P9. The petroleum grease used for the TCP was Productol, 210° out. Samples of these Pydrauls were sent to Douglas for lubricity tests. It was reported by Douglas that no significant difference was found in the Shell Four Ball Wear Test. The use of Productol derived TCP or "Kronitex AA" TCP alone for Pydraul P9 was approved, thus increasing the types of TCP available for this use to three.

3. Solubility of Water in Pydraul P9

The solubility of water in various functional fluids was determined at room temperature and at 210°F. by the following procedures.

In the determination at room temperature, 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 one hour. The ester layer was then centrifuged for one hour at 1300 rpm to free 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.

In the determination at 210°F. a sample of the fluid was stirred from 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 four hours at 210°F. The ester layer was clear showing no occluded water to be present in it. Using a warmed pipet, samples of the fluid layer were weighed in duplicate into tared stoppered flasks containing a mixture of benzene and methanol blanked with Karl Fisher reagent. The samples were then titrated with Karl Fisher reagent.

The results using Pydraul P9 were as follows:

Solubility of water at 75°F. 0.17%; 0.18%
Solubility of water at 210°F. 0.54%; 0.55%

4. Hydrolytic Stability

A regular "coke bottle" hydrolytic stability test (from MIL-R-7100; see Skydrol 500 section of this report) was run on Pydraul P9 and a series of other proposed fluids. Results are as follows:

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Sample	Pydraul F9	Fluid OS-41	Fluid OS-54	Fluid ST-3
Acidity, NN:				
Initial	0.08	0.17	0.16	0.03
Oil layer	0.03	0.16	0.19	0.02
Water layer	0.08	0.12	0.11	0.05
Total	0.11	0.28	0.30	0.07
Viscosity, cs, 130°F.				
Initial	20.91	13.94	22.05	17.43
Final	20.13	13.75	21.93	17.31
% Change	-3.7	-1.4	-0.5	-0.7
Effect on copper				
Wt. change, mg./cm ²	-0.05	-0.22	-0.20	-0.06
Sludge wt., grams	0.002	0.014	0.021	0.009

The data for the other materials are included for comparative purposes. All four samples are well within limits for this test. Such limits are usually total acidity development of 0.67 NN maximum, viscosity change of -5 to +15% at 130°F., copper loss of 0.05 mg. per sq. cm. maximum and sludge formation of less than 0.5% (or .375 grams).

5. Compatibility with Skydrol

Some interest had been expressed in the compatibility of Skydrol and Pydraul F9 by various customers. Mixtures were prepared using ratios of 75:25, 50:50, and 25:75. After several days at room temperature, no evidence of separation was noted. Storage at 0°C. for 24 hours did not result in separation. It can be concluded that Skydrol and Pydraul F9 are mutually compatible at temperatures to 0°C.

6. Flammability in Contact with Molten Nitrates

A series of experiments were performed in an attempt to determine the flammability characteristics of Pydraul F9 in contact with molten metal nitrates. A 50:50 mixture of sodium and potassium nitrates was heated to at least 1000°F. Iron, porcelain, and nickel crucibles were used. On heating the mixture of nitrates, gas was evolved after the mass had melted. Pydraul F9 was dropped and sprayed onto the surface of the molten nitrates at temperatures of 1000°-1050°F. When iron or porcelain crucibles were used, the Pydraul F9 vaporized and did not spontaneously ignite. In the molten nitrates were in nickel and the evolution of gas was quite vigorous, spontaneous ignition did occur. This was not true if gas evolution was slow. The

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Pydraul formed dense white fumes on vaporization from the molten nitrate and these fumes could be ignited by a spark or a flame. The experiment using the nickel crucible was repeated several days later with the same mixture of nitrates. The evolution of gas was much less at 1000°F. and spontaneous ignition did not occur. It appears from these data that Pydraul will not spontaneously ignite in contact with a 50:50 mixture of sodium and potassium nitrates at 1000°F. except under certain specialized conditions, that is a rapid evolution of gas and in the presence of nickel. The vapors of Pydraul can be ignited. These results are similar to those previously obtained for Pydraul F9 and molten aluminum. The work with the molten nitrates was undertaken to answer questions concerning the use of Pydraul as the hydraulic fluid in machinery used to heat treat aluminum by immersion of the aluminum in a molten nitrate bath.

7. Flammability on Spraying into Open Flames

The behavior of Pydraul F9 on spraying into open flames in an incinerator was examined. This work was done to provide data for insurance personnel as requested by the Sales Department.

The spray outfit supplied by Douglas Aircraft Company was used. The equipment was designed so that nitrogen pressure could be placed upon a reservoir containing the fluid under test and the fluid forced through a small orifice and formed into a fine spray. The pressure used in the tests was 1000 psi. The fluid was drawn up into the reservoir by the use of a suction pump. This equipment was set up in front of the plant incinerator in which a wood fire had been built and after the entire incinerator had become hot because of the burning of waste paper. Temperatures of 1100 to 1400°F. were measured in the incinerator by means of optical pyrometry.

Three fluids were used, Pydraul F9, DTE Medium (mineral oil), and Houghto-Safe 271 (water base fluid). Spraying the DTE Medium into the incinerator resulted in vigorous burning as the fluid contacted the flames and hot surfaces. Spraying Pydraul F9 tended to increase the flame slightly, the fluid vaporizing and burning. There was no flash back. Spraying Houghto-Safe 271 resulted in no increase in flames. These results demonstrate Pydraul F9's fire resistant properties under the test conditions. The good results obtained on the water base fluid indicate the effectiveness of water as a snuffer when the entire fluid is vaporized. Pydraul F9 was decidedly better than the mineral oil.

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8. Relative Evaporation Rates

The relative evaporation of several fluids was determined in response to a Sales Department request. The procedure used is as follows: 250 ml. beakers were filled approximately 3/4 full with the fluid under study, weighed, covered with ribbed type watch glasses, and allowed to stand in the laboratory at room temperature. The fluids examined were Pydraul F9, DTE Medium (mineral oil) and Houghto-Safe 271 (water base fluid). A similar volume was used in each case, being about 180-190 ml. The fluid weights were about 230, 160, and 185 grams, respectively. The beakers were weighed periodically and the weight losses observed were as follows:

Total Days	Total Loss in Weight, Grams		
	Pydraul F9	DTE Medium	Houghto-Safe 271
0	0.0	0.0	0.0
15	0.1	0.1	23.1
34	0.1	0.1	50.1
45	0.1	0.1	69.6
65	0.1	0.1	80.4

These data show that the Pydraul F9 and the mineral oil, DTE Medium, had lost no appreciable amount while the water base fluid, Houghto-Safe 271, had lost about 40% by weight in 65 days. Both Pydraul F9 and DTE Medium were unchanged in appearance. The Houghto-Safe 271 sample decreased greatly in volume and the solids which are normally present seemed to increase slightly in amount. These data point up the problems involved in maintaining the proper concentration of water in water base fluids and the greater permanence of Pydraul F9.

9. Screening New Components

A Monsanto defoamer, N5262A from Nitro was examined in Pydraul F9 and in Skydrol. No foam suppression was found in Pydraul F9 at a concentration of 0.01%. A slight tendency toward more stable foam was noted. The material appeared to set as a defoamer in Skydrol but was no more effective than the presently used material.

Several different types of cresylic acid had been converted to tricresyl phosphate and the products and processing examined (see Progress Reports on 117-246 and 117-258). Two of the esters were screened for functional fluid uses and are compared in the following table with tricresyl phosphate.

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of our regular plant manufacture. Shell 2000AA refers to the triaryl phosphate ester made from Shell petroleum cresylic acid (2000AA grade) and Midland refers to the ester made from Midland Tar's cresylic acid.

Sample	Shell 2000AA	Midland	A-11
Viscosity, cs., 210°F.	5.28	4.76	4.37
100°F.	55.6	39.2	35.1
Viscosity index	-50	-10	-42
Sp. Gr., 25/25°C.	1.1535	1.1459	1.161
Flash Point	455°F.	465°F.	465°F.
Fire Point	700°F.	665°F.	655°F.
Pour Point	+10°F.	0°F.	-15°F.

The data reflect the higher content of xylenols in the cresylic acid, in specific gravity, viscosity, and pour point of the esters.

The tricresyl phosphate from Midland Tar cresylic acid was converted to Pydraul F9 (called sample M-F9). Tricresyl phosphate (regular plant A-11) was used to prepare Pydraul F9 using the same other ingredients (called sample A-11-F9). The data are as follows:

Sample	A-11-F9	M-F9
Viscosity, cs., 210°F.	5.76	6.11
100°F.	52.2	58.6
Viscosity index	+28	+26
Sp. Gr., 25/25°C.	1.2634	1.2543
Flash point	405°F.	405°F.
Fire point	over 675°F.	over 675°F.
Pour point	+5°F.	+10°F.

The data for the two samples reflect the higher content of xylenols in the Midland Tar cresylic acid, the F9 type fluid made from the triaryl phosphate having higher viscosity and pour point and lower specific gravity. It does not appear that such tricresyl phosphate would be of value for Pydraul F9 production.

10. Testing System Accessories

Samples of "O" rings made of butyl and Neoprene rubber were soaked in Pydraul F9 for 7 days at 150°F. Visual observation showed that the "O" ring immersed in Pydraul F9 became larger in diameter, thicker, and considerably softer and more pliable. These data indicate that these packings, identified as Parker 624-6, would not be useable with Pydraul F9.

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A sample of durable flat gasket, thought to be made of asbestos and some kind of binder, was immersed in Skydrol and Pydraul F9 and the fluid held at 150°F. for fifteen days. No visible changes in fluid or gasket occurred.

11. Competitive Fluids

Competitive fluids for Pydraul F9 are Lindol HF and Houghto-Safe 271. Samples of these fluids were obtained and comparative tests have been run. Lindol HF is reported to be tricresyl phosphate. Houghto-Safe 271 is reported to be a water base type fluid. Data obtained thus far and compared to Pydraul F9 specifications as typical properties are as follows:

Property	Pydraul F9	Lindol HF	Houghto-Safe
Viscosity, cs, 210°F.	4.51-6.51	4.20	8.80
130°F.	-----	14.60	-----
100°F.	40.0-60.0	31.0	43.2
Viscosity index	15 min.	-23	154
Sp. Gr., 25/25°F.	1.26-1.28	1.169	1.053
Flash point, °F.	420 - 450	450	280
Fire point, °F.	650 - 725	645	280
Pour point, °F.	+5 max.	-10	+5

The Houghto-Safe 271 fluid was medium yellow in color and a flocculent material separated on standing. Shaking dispersed the solid temporarily. Considerable boiling was found while running the flash point. The volume had decreased about 50 per cent before a flash was obtained. The Lindol HF fluid appears to have properties similar to tricresyl phosphate as normally prepared.

Viscosity characteristics were determined for another sample of Houghto-Safe 271. The data are as follows:

Viscosity, 210°F.	3.56 cs.
170°F.	13.46 cs.
130°F.	24.10 cs.
100°F.	41.9 cs.
77°F.	70.4 cs.
68°F.	88.3 cs.
50°F.	149.4 cs.
25°F.	375 cs.
Viscosity index	+155

A sample of used Houghto-Safe 271 was received from Pickers. The material came from a pump test and had been used 1016 hours at 120-150°F. Viscosity data were found to be 9.09 cs. at 210°F. and 45.61 cs. at 100°F.

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100°F. indicating some thickening. The sample was sent to Douglas for further study.

12. Customer Service Samples

During part of the time covered by this report samples of Pydraul F9 were submitted by various customers for study. Each sample will be handled separately in this section of the report. The work was continued under job number 117-2633 which covers the second year of this report.

A sample of Pydraul F9 removed from a pump test by the Hydraulic Press Manufacturing Co. was submitted for analysis. The sample contained a so-called "scum". Examination of the fluid indicated no change in physical properties except for loss of viscosity index. This is normal for Pydraul F9. Analysis of the fluid indicated less than 0.01% copper and no water soluble chlorides. The amount of zinc present was estimated to be about 0.05%. It might be surmised that the zinc came from the brass bearings in the pump, the copper being effectively removed by plating on the steel parts. Some copper plating was reported by H.P.M. The scum layer showed freedom from more than traces of the common metals but more than one per cent silica. It had the appearance and behavior on heating of a silicone grease or rubber.

Pydraul F9 in use at the Trico Products Company had become emulsified with water and was separated by centrifugation. An examination of the separated, used Pydraul indicated that fluid was within specification limits on moisture and foaming characteristics. Viscosities were as expected for used Pydraul. The acidity was 0.34 NN, considerably above our specification maximum of 0.15 NN. This high acidity was probably due to hydrolysis during emulsification.

A sample of used Pydraul F9 was received from Alloy Die Casting Company who indicated that the fluid had been used for over a year. Analysis showed that the fluid was quite dark and had the following physical properties: viscosity, 4.26 cs. at 210°F., 37.91 cs. at 100°F. for a viscosity index of -105; and acidity of 0.13 NN; and a specific gravity at 25/25°C. of 1.256. The viscosity was as would be expected for used Pydraul F9. The very low acidity was somewhat unexpected and indicates the long service life of Pydraul F9.

A sample of used Pydraul F9 was received from Johnson Motors and examined. Since the sample appeared dark

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In color, it was filtered through paper. The resulting material was black and nearly opaque, being clear in very thin layers with no visible suspended matter (Sample A). A small amount of dirt was present on the filter paper. Part of this liquid was then filtered through a layer of Attapulugus earth. The resulting material (Sample B) was dark yellow in color and completely clear. No trouble was experienced in the filtration. However, as would be expected, the filtration through Attapulugus earth was somewhat slower than through paper alone.

The physical data for these two samples as compared to specifications for new Pydraul F9 are as follows:

Pydraul F9	Sample A	Sample B	Specifications
Viscosity, cs., 210°F.	4.27	4.25	4.51-6.51
100°F.	37.60	36.91	40.0-60.0
Viscosity index	-98	-94	15 min.
Acidity, NN	0.15	0.04	0.15 max.
Sp. Gr., 25/25°C.	1.2521	1.2525	1.26-1.28

These physical properties indicate that the Attapulugus earth does remove acidic materials as well as colored bodies. The viscosity data show normal wear and are as expected for used Pydraul F9. The material should be satisfactory for use after filtration, especially if Attapulugus earth is used.

Two samples of Pydraul F9 were received which had been submitted by the Eaton Manufacturing Co. of Battle Creek, Michigan and have been examined.

The first sample was marked as follows: "Put in pump 11-1-51. Sample taken 2-16-53." This sample (called No. 1) was dark in color and had dark colored particles floating in it. It was allowed to stand several days and the solids tended to accumulate on the surface. The entire mixture was filtered using filter paper only and a dark yellow very slightly hazy filtrate resulted. The residue on the paper was black in color. This filtration was very slow. The filtrate was examined for physical properties with the results shown (sample No. 1):

Sample	No. 1	No. 2	Specifications
Viscosity, cs., 210°F.	4.50	4.57	4.51-6.51
100°F.	41.12	40.34	40.0-60.0
Viscosity index	85	86	15 min.
Acidity, NN	0.11	0.10	0.15 max.
Sp. Gr., 25/25°C.	1.265	1.235	1.26-1.28

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These data indicate that the Pydraul F9 should be satisfactory for further use provided the solids are removed. The filtered material meets specifications on acidity and specific gravity and viscosity data are as would be expected for used Pydraul F9.

The second sample was marked as follows: "Put in machine 11-28-51. Pydraul added February, 1953. Sample withdrawn 4-2-53. Machine No. 246481." This sample (called No. 2) was quite milky and full of solids. Some of the solids tended to accumulate in an upper layer on standing. However, the fluid still appeared milky. This sample was filtered through filter paper only and the filtration was extremely slow. The resulting filtrate was dark yellow and clear with no evidence of separation of layers. The residue on the filter paper was black and slightly sticky. The physical data for the filtrate are given above under sample No. 2. It appears that the Pydraul F9 has been contaminated as evidenced by the low specific gravity.

Two samples of Pydraul F9 were submitted by the Trico Products Corp. These samples represented used Pydraul F9 that had been centrifuged to remove water. Questions concerning its reuse and flammability were raised. Both samples contained a certain amount of sludge which could be removed by filtration through filter paper. Both samples were also dark in color and this color and sludge could be completely removed by filtration through Attapulugus earth. Analytical data for the two samples as received are as follows: (Viscosity was determined on a filtered sample).

Sample	Trico #1	Trico #2	Specs.
Viscosity, cs., 210°F.	4.46	4.41	4.51-6.51
100°F.	39.7	39.1	40-60
Viscosity index	-79	-84	15 min.
Sp. Gr., 25/25°C.	1.261	1.260	1.26-1.28
Acidity, NN	0.15	0.12	0.15 max.
Moisture, %	0.45	0.46	0.20 max.
Flash point, °F.	445	435	---
Fire point, °F.	730	760	---

The viscosity data are as would be expected for used Pydraul F9 and indicate normal shear. The specific gravity is high and indicates negligible contamination. The moisture content is quite high and represents entrained water probably held up by the sludge. This used Pydraul F9 would probably be reuseable if the sludge were removed.

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The question of inflammability was also examined. Fresh Pydraul F9 had a flash point of 415°F. and a fire point of 690°F. using the micro technique required in this investigation because of the limited amount of samples from Trico. Since the accuracy of this micro technique is about $\pm 15^\circ\text{F}$. it would appear that all samples are approximately equivalent in these properties. Samples of fresh Pydraul F9 and the Trico samples placed in watch glasses would flash when matches were laid at the edge of the liquid. Undoubtedly the small amount of liquid involved was raised to the flash point. This test was used by the customer and reported by him only for the used Pydraul F9.

Trico Products Corp. have been recovering used Pydraul F9 which has been contaminated with water. A sample was received and found to have the following properties:

Viscosity, 210°F.	4.65 cs.
100°F.	41.62 cs.
Viscosity index	-56
Acidity	0.42 NN
Specific Gravity, 25/25°C.	1.2391
Flash point	415°F.
Fire point	690°F.
Moisture	0.20%

The sample appears to be somewhat high in acidity (specification maximum is 0.15 NN). The specific gravity is slightly low indicating some contamination probably with petroleum oils. The moisture content is satisfactorily low.

Two samples of Pydraul F9 were received from Delco Radio Division of General Motors Corporation for analysis to determine if they were contaminated with petroleum oils. The regular tests were run on these materials and the following data obtained:

Sample	Reed Prentice No. 5	Cleveland No.
Viscosity, cs., 210°F.	4.36	3.84
100°F.	36.97	37.46
Viscosity index	-68	-215
Acidity, NN	0.09	0.13
Sp. Gr., 25/25°C.	1.257	1.247
Flash point, °F.	420	400
Fire point, °F.	645	645

It would appear that both samples were very slightly contaminated since the specific gravity is slightly

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15.
lower than the 1.26 to 1.28 specification range for Pydraul F9. This is also reflected by the slightly lower flash point. All other characteristics are as expected for used Pydraul F9.

13. Physical Measurements

Data concerning specific heat, variation of density with temperature, electrical properties and thermal conductivity of Pydraul F9 are given in section M of this report.

B. Skydrol 7000

1. Compatibility Studies

American Airlines had requested data concerning compatibility of Skydrol 7000 and aviation gasoline. Five samples were prepared using Grade 100/130 gasoline. These samples contained 0.1%, 0.3%, 1.0%, 10% and 25% Skydrol. There was no evidence of separation of liquids or sediment at room temperature or at temperatures as low as -15°F. Evaporation of the gasoline from the 1%, 10%, and 25% solutions mentioned above left a clear residue which appeared to be Skydrol. Skydrol is completely compatible with Grade 100/130 gasoline under the conditions tested.

The compatibility of Skydrol 7000 and Skydrol 500 in the ratio of 1:9 was examined at room temperature and at 32°F. At both temperatures there was evidence of separation into liquid layers, the upper layer being less than one per cent of the mixture. There was no evidence of separation of viscosity index improver at these temperatures. However storage of the mixture at -40°F. resulted in the separation of a resinous material. This material went back into solution on warming.

Because of the wide differences between specific gravity of Skydrol and hydraulic fluid MIL-O-5606 (petroleum fluid), it should be possible to determine the approximate amount of contamination of Skydrol by this fluid. The specific gravity of various mixtures of Skydrol and MIL-O-5606 fluid was determined. Results are as follows:

<u>Composition</u>	<u>Sp. Gr., 25/25°C.</u>
100% Skydrol	1.0819
95% Skydrol - 5% MIL-O-5606	1.0670
90% Skydrol - 10% MIL-O-5606	1.0530
85% Skydrol - 15% MIL-O-5606	1.0391
100% MIL-O-5606	0.8547

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2. Hydrolytic Stability

During an extensive study of the hydrolytic stability of Skydrol 500, Skydrol 7000 was used as a reference fluid. The data for these various tests are best presented with the work on Skydrol 500 and can be found in the appropriate section of this report.

3. Solubility of Water in Skydrol 7000

The procedures given in the section on Pydraul F9 were used to determine the solubility of water in Skydrol 7000. The results were as follows:

Solubility of water at 75°F. 0.54%; 0.54%
Solubility of water at 210°F. 1.73%; 1.75%

The acidity of the fluid was measured before and after exposure to conditions similar to the water solubility determination at 210°F. for an extended period. The initial acidity was 0.12 NN; after 4-1/2 hours exposure, 0.13 NN; and after 7-1/2 hours, 0.22 NN.

4. Customer Service Samples

Vickers Incorporated had run a pump test at 225°F. using Skydrol and had reported extremely high corrosion and fluid decomposition. It was suspected that these phenomena were caused by local overheating from the electric heaters used in the reservoir of their system to maintain a fluid temperature of 225°F. resulting in thermal decomposition of the Skydrol with subsequent corrosion of metal parts by the decomposition products (principally organic phosphoric acids). A sample of Skydrol from the pump test was found to have an acidity of 114 NN while other samples of Skydrol maintained at 250°F. in an oven for 7 days had acidities ranging from 3.0 NN to 7.1 NN. These data indicate that the Skydrol in the pump test had been exposed to unusually high temperatures.

A sample of Skydrol-water mixture from Pan American Airways was examined. It was freed from rust by filtration and separated into two layers. The oil layer was examined and found to contain 0.69% moisture and 0.05 NN acidity. Shaking the Skydrol layer with Drierite and allowing to stand followed by filtration gave a product analyzing 0.24% moisture and meeting new material specifications. The data indicated that water can be removed by drying with a solid absorbent. Dangers due to incomplete removal of solids should be recognized. The best way to remove water from Skydrol is dehydration by heating under reduced pressure as has been demonstrated many times.

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5. Physical Measurements

Data concerning the thermal conductivity of Skydrol 7000 are given in section M of this report.

C. Skydrol 500 (Fluid OS-40)

A fluid was developed in cooperation with Douglas Aircraft to meet military specification MIL-F-7100 for a non-flammable type aircraft hydraulic fluid. This fluid was called Fluid OS-40 and was based on dibutyl phenyl phosphate. Work leading to this fluid is described in the final reports on job numbers 117-2080 and 117-2380. It was decided during the period covered by this report to call this fluid Skydrol 500. Therefore, all references in this report will be to Skydrol 500.

1. Formulation of Skydrol 500

Skydrol 500 formulation first used consisted of 87.0% dibutyl phenyl phosphate, 12.0% Acryloid U, 0.9% phenyl glycidyl ether (PGE) and 0.1% wax disulfide (WDS). Several batches were made up using this formulation. Since the PGE-WDS combination was added as inhibitor and copper deactivator and since new lots of these additives had been received preparatory to making a pilot plant run, oxidation and corrosion tests were run at 250°F. using the standard procedure. Data are as follows:

Sample	A	A	B	B
Viscosity, cs., 130°F.				
Initial	7.33	7.33	7.79	7.79
Final	7.16	7.21	8.20	8.15
Acidity, NN				
Initial	0.15	0.15	0.03	0.03
Final	0.21	0.21	1.5	1.4
Effect on metals, wt. change, mg./cm. ²				
Copper	-1.36	-1.55	-0.69	-0.47
Iron	0	+0.01	0	-0.01
Aluminum	0	0	0	+0.01
Magnesium	0	-0.01	+0.01	0
Cadmium plated steel	-0.05	-0.03	-0.03	-0.02

Sample A was Skydrol 500 prepared several months ago and Sample B was made from the new lots of additives. Although there are some differences between the two samples in oxidation and corrosion characteristics,

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these variations appear to be normal based on previous data. A 45-gallon batch of Skydrol 500 was prepared in the Pilot Plant under job number 117-2438. The fluid had properties similar to those of the laboratory prepared material.

Several different lots of Acryloid had been supplied by Rohm and Haas as viscosity index improver for Skydrol 500. In order to suggest specifications for this additive solutions of their material were prepared in dibutyl phenyl phosphate at 12 weight per cent concentration. The data are as follows:

Sample	U	R3823X5	R3876X
Viscosity, cs., 210°F.	3.59	3.96	3.92
100°F.	10.88	11.67	11.54
-40°F.	580	520	530

The latter two samples would give Skydrol 500 of satisfactory properties. Specifications were suggested based on these latter two samples.

2. Oxidation and Corrosion Tests

Skydrol 500 consisted of dibutyl phenyl phosphate (FH-87), a viscosity index improver, and an inhibitor pair which included a copper deactivator. The formulation first studied contained wax disulfide (WDS) from Shell as the copper deactivator and was cloudy because of the limited solubility of the WDS. Work at Douglas had indicated that ethylene bis tolyl sulfide (EBTS) was more satisfactory as a copper deactivator from the standpoint of less copper attack and complete solubility. A larger amount of the EBTS was prepared by Shell and sent to Monsanto for use in preparing Skydrol 500. This particular sample was not checked by Douglas; therefore a sample of Skydrol 500 was prepared and placed in the Oxidation and Corrosion Test at 250°F. The results are as follows:

Sample	Skydrol 500					FH-87
	EBTS	EBTS	WDS*	WDS**		
Viscosity, cs., 130°F.						
Initial	8.01	8.01	7.79	7.90	2193	
Final	8.33	8.33	8.06	8.08	2.95	
Acidity, MN						
Initial	0.02	0.02	0.01	0.01	0.02	
Final	0.03	0.03	0.13	0.23	0.60	
Effect on metals, wt. changes in mg./cm. ²						
Copper	-0.57	-0.54	-0.92	-0.90	-1.30	
Iron	+0.08	+0.01	+0.01	+0.01		
Aluminum	0	+0.01	+0.01	0		
Magnesium	-0.01	0	+0.01	0		
Cadmium plated steel	-0.02	-0.01	0	0		
	Filtered		Unfiltered			

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Skydrol 500 (EBTS) is the material which was made from the larger sample of copper deactivator. Copper losses were about 0.5 to 0.6 mg. per sq. cm. as contrasted to the losses reported by Douglas of about 0.2. A sample of the EBTS they used was requested and further testing was to be done to determine, if possible, reasons for the different results obtained.

Two samples of Skydrol 500 from wax disulfide (Skydrol 500 WDS) were also run, one clarified by filtration and one used as is (very cloudy, solids present). The latter material gave a greater viscosity increase and acidity increase than the filtered material. Attack on metals was similar. A sample of FH-87 was also included in the test as a standard. Normal results were obtained.

The formulation used for the Skydrol 500 was 86.75% dibutyl phenyl phosphate, 11.75% Acryloid R3876X, 1.0% phenyl glycidyl ether, and 0.5% ethylene bis (tolyl sulfide).

A sample of EBTS was obtained from Douglas (labeled WWJ, lot LR-1864-40) and samples of Skydrol 500 were prepared from our lot of EBTS (lot P-4221) and from the Douglas sample. Both lots of EBTS came originally from the Shell Chemical Company.

Results of an Oxidation and Corrosion Test at 250°F. are as follows:

Sample	EBTS	Skydrol 500				WWJ	FH-87
		EBTS	EBTS	WWJ			
Wt. change, mg./cm. ²							
Copper	-0.573	-0.542	-0.612	-0.488	-0.427	-2.85	
Cadmium/ steel	-0.031	-0.039	-0.008	-0.008	-0.008	-0.016	
Iron	0	0	-0.023	-0.023	-0.008	0	
Magnesium	0	-0.008	-0.016	0	0	0	
Aluminum	0	+0.008	+0.008	0	0	0	
Initial NN	0.05	0.04	0.04	0.04	0.04	0.02	
Final NN	0.20	0.16	0.19	0.19	0.15	0.66	

The identity of samples is as follows: Skydrol 500-EBTS was made using our sample of EBTS (lot P-4221), Skydrol 500-WWJ was made using Douglas sample of EBTS (lot LR-1846-40) and FH-87 was the standard dibutyl phenyl phosphate. Two separate preparations of Skydrol 500-EBTS were made. The results indicated considerable discrepancy between Douglas results and ours and that our results were consistent from test to test. It is interesting to note that the results

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using our sample of EBTs show higher copper losses than those using the Douglas sample. Douglas reported copper losses of 0.14 to 0.19 mg. per sq. cm. with their sample of EBTs and 0.23 with our sample. The results shown for dibutyl phenyl phosphate (FH-87) are normal. Work was continued to determine the causes of different results in the Oxidation and Corrosion Test obtained by the two laboratories.

As a part of this investigation the two samples of EBTs were comparatively evaluated. Results are as follows:

	% S	% C	% H	n_D^{25}	Sp.Gr. at 25/25°C.
Calculated for ethylene bis (tolyl sulfide) ($C_{16}H_{18}S_2$)	23.37	70.04	6.61	---	---
Ethylene bis(tolyl sulfide) Lot No. P-4221, Shell Development Co. Emeryville, Calif.	23.71	69.57	6.53	1.6196	1.121
	23.53	69.48	6.50		
WWJ-Base Lot Bt. LR-1846-10, Douglas Aircraft Co., Inc. Santa Monica	22.90	69.66	6.49	1.6192	1.122
	22.97	69.85	6.44		

Because of the differences in copper attack in the oxidation and corrosion test with Skydrol 500 experienced by our laboratory and by the Douglas laboratory, further work was undertaken to study the test. It was found that moisture in the air used for the test was at least partially responsible for the differences. The air used came from the regular plant compressors and passed through a commercial drier and pressure reducer before use. However, it appears that this equipment did not sufficiently remove moisture. The data obtained in two tests using Skydrol 500 are as tabulated on the following page.

The Skydrol 500 samples are as follows: V-2178 was the oldest sample of Skydrol 500 available containing ethylene bis tolyl sulfide as a copper deactivator, WWJ was made from Douglas' sample of ethylene bis tolyl sulfide, EBTs was made from our sample and P.H. Skydrol 500 was made in the pilot plant. The "dye" in all cases was 10 ppm Alizarine Irisol. The term "Reg" means that the air used was that normally available from the commercial drier. "Dry" means that

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21.

Skydrol 500 Sample	Weight change, mg. per sq. cm.					Acidity, NN	
	Cu	Fe	Al	Mg	Cd/Fe	Initial	Final
V-2178 (Reg)	- 0.92	-0.01	0	+0.01	-0.02	0.05	0.29
V-2178 (Reg) + dye	- 1.15	0	0	0	-0.01	0.04	0.30
WWJ (Reg)	- 0.66	0	0	+0.01	-0.01	0.03	0.35
WWJ (Dry)	- 0.19	+0.01	-0.01	+0.01	-0.02	0.03	0.28
EBTS (Reg)	- 0.91	0	0	-0.02	-0.02	0.03	0.35
EBTS (Dry)	- 0.25	+0.01	0	0	-0.02	0.03	0.29
P.P. (Reg)	- 0.54	0	-0.01	-0.02	0	0.04	0.28
P.P. (Dry)	- 0.40	-0.02	-0.01	0	-0.01	0.04	0.05
P.P. (Dry)	- 0.44	-0.02	-0.01	0	-0.02	0.04	0.08
P.P. (Dry) + dye	- 0.49	-0.02	-0.01	0	-0.01	0.03	0.06
V-2178 (Dry) + dye	- 0.33	0	-0.01	0	-0.02	0.04	0.04
P.P. (Wet)	-11.63	0	0	-5.35	+2.40*	0.04	4.64

*Cd actually stripped in spots, weight gain due to surface coating.

the air was specially dried by passage through Drierite, and (Wet) means that the air was saturated with water at 25-30°C. by bubbling the air through water.

These data definitely indicate that the moisture content of the air influences the corrosive effects of Skydrol 500, the (Wet) sample showing extreme copper, magnesium, and cadmium attack. In all cases drying the air lessened the corrosive action. Two tests are represented in these data, the first six samples being from the first test and the remainder from the second. The results in the second test are still somewhat high even with drying and further work will be required to elucidate all factors involved in the test. All future tests will be run using bottled air to be sure of freedom from contamination and the air will be thoroughly dry. These results again indicate the relatively poor hydrolytic stability of dibutyl phenyl phosphate, the base stock used for Skydrol 500.

3. Selection of Dye

For identification purposes, it was proposed to dye Skydrol 500 a distinctive purple. Several oil soluble purple dyes as well as mixtures of red and blue dyes were added to Skydrol 500. The resulting solutions containing 10 ppm dye were heated at 150°C. for various periods of time. Only Alizarine Irisol N, from General Dyestuffs, was color-stable for five days. Skydrol under similar conditions changed from green to dark yellow.

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The effects of Alizarine Irisol N on the oxidation and corrosion test results were studied as indicated in the previous section. The data indicated that the presence of the dye resulted in slightly greater copper attack. However, it was felt that this increase is not significant. Therefore, the addition of 10 parts per million of Alizarine Irisol N was used as the colorant in Skydrol 500.

4. New Formulation of Skydrol 500

The formulation of Skydrol 500 was finalized as follows:

86.75% dibutyl phenyl phosphate
 11.75% Acryloid R3876X
 1.00% phenyl glycidyl ether
 0.50% ethylene bis(tolyl sulfide)
 10 parts per million Alizarine Irisol N

Several batches of Skydrol 500 were prepared in the Pilot Plant. The physical data for these are as follows and give some indication of ranges expected in formulation:

Property:

Viscosity, cs., 210°F.	3.98	3.96	3.97	3.95
100°F.	11.84	11.70	11.73	11.69
-40°F.	550	550	530	530
-65°F.	2600	2270	2230	2280
Acidity, NN	0.04	0.06	0.08	0.07
Sp. Gr., 25/25°C.	1.063	1.063	1.062	1.063

Based upon these data and similar data from laboratory batches, the following tentative specifications were proposed for Skydrol 500:

Appearance	Clear, purple, oily liquid, free of sediment
Viscosity at 210°F.	3.95 ± 0.05 cs.
100°F.	11.7 ± 0.5 cs.
Sp. Gr. at 25/25°C.	1.063 ± 0.003
Acidity	0.15 NN maximum
Moisture	0.25% maximum

5. Screening Inhibitors

The inhibitor pair, wax disulfide and phenyl glycidyl ether, used originally in Skydrol 500 gave satisfactory oxidation and corrosion characteristics. However, the use of the wax disulfide led to a lubrication problem. Furthermore, wax disulfide was not readily available. Efforts were made to find other inhibitors.

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A series of fluids were prepared and examined in the Oxidation and Corrosion Test at 250°F. Results are as follows:

Sample No.	1	2	3	4	5	6
Viscosity, cs, 130°F.						
Initial	2.91	8.16	8.33	8.09	8.09	7.79
Final	2.93	8.36	8.53	8.57	8.29	8.20
Acidity, NN						
Initial	0.03	0.04	0.96	0.08	0.07	0.03
Final	0.63	0.85	1.76	2.83	0.26	1.50
Wt. change, mg/cm ²						
Copper	-3.27	-3.00	-2.66	-7.08	-1.88	-0.69
Iron	+0.01	+0.02	0.00	+0.02	+0.02	0.00
Aluminum	+0.01	+0.02	+0.02	+0.02	+0.05	0.00
Magnesium	+0.02	+0.01	+0.02	+0.01	+0.01	+0.01
Cadmium plated steel	+0.02	+0.02	+0.02	+0.02	+0.05	+0.03

These samples are as follows: No. 1 is dibutyl phenyl phosphate (FH-87); No. 2 is FH-87 and 12% Acryloid R-3876X; No. 3 is sample No. 2 and 0.5% dimer acid; No. 4 is sample No. 2 and 0.1% sulfurized terpene and 0.9% phenyl glycidyl ether; No. 5 is sample No. 2 and 0.5% dibenzyl sulfide and 1.0% phenyl glycidyl ether; and No. 6 is Skydrol 500. Several conclusions may be drawn. None of the inhibitors studied performed as well as those used in Skydrol 500. The Acryloid viscosity index improver used for Skydrol 500 had little effect on the oxidation and corrosion characteristics of the base stock.

Douglas Aircraft personnel found that ethylene bis (tolyl sulfide) functioned very satisfactorily in Skydrol 500 and the search for other new materials was not pressed. However, the ethylene bis (tolyl sulfide) was not readily available and was quite expensive.

A number of materials were screened by Douglas and by our laboratory but none were found to be nearly as satisfactory as that presently used. Samples of sulfur containing materials were requested from Nitro and together with several others were used to prepare Skydrol 500 like formulations which were run in the regular Oxidation and Corrosion Test (MIL-F-710C specification). The data obtained may be summarized as tabulated on the following page.

The identity of samples is as follows: Sample 1, Skydrol 500 Base is the phosphate ester and viscosity index improver. This material was used for formulate all other samples in the test. Sample 2, Skydrol 500

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Sample	Acidity, NN		Fluid Loss %	Effect on metals, wt. change in mg. per sq. cm.				
	Initial	Final		Cu	Cd/Fe	Fe	Mg	Al
1. Skydrol 500 Base	0.04	0.85	0.5	- 3.00	+0.02	+0.02	+0.01	+0.02
2. Skydrol 500	0.07	0.09	0.9	- 0.30	0	+0.01	-0.01	0
3. Base + J-1362	0.09	0.68	0.9	- 0.72	-0.03	-0.02	-0.01	-0.02
4. Base + J-1363	0.09	0.73	0.9	- 0.96	-0.01	-0.02	0	0
5. Base + M-2	0.06	2.42	1.1	- 9.89	-0.16	-0.01	0	-0.66
6. Base + N-4713	0.10	2.40	1.1	-13.7	0	-0.01	0	+0.01
7. Base + N-3337	0.07	0.21	0.9	- 0.92	-0.16	+0.02	-0.02	0
8. Base + N-5520	0.09	3.98	1.1	-18.3	0	0	-0.21	0
9. Base + N-125	0.08	0.15	1.1	- 0.52	0	0	+0.05	+0.02
10. Base + Rosin Amine D	0.20	2.25	0.8	-21.0	-0.12	+0.04	-1.45	+0.02

contains the regularly used copper deactivator (0.5%) and inhibitor (phenyl glycidyl ether, 1.0%). Materials J-1362 (1,2-di(t-butylmercapto)ethylene) and J-1363 (1,2-di(t-octylmercapto)ethylene) from Dayton and N-4713 (di-o-ethylphenylthiourea), N-3337 (β , β' -thiodipropionitrile), N-5520 (diphenylthiourea) and N-125 (bis[2-(2-benzothiazolylmercapto)ethyl]ether) from Nitro were examined as copper deactivators at 0.5% concentration with 1% phenyl glycidyl ether and 98.5% Skydrol 500 Base. Materials M-2 (benzo(c)cinnoline 5 oxide) and Rosin Amine D were examined as combination deactivator-inhibitor additives at 0.5% concentration in Skydrol 500 Base.

None of the materials examined appear to be as effective as the presently used additives. Copper attack and acidity development were greater in all cases, copper attack actually being increased by the additives in some cases.

A series of inhibitors and metal deactivators were studied previously in Skydrol 500 type formulations in the Oxidation and Corrosion Test. In an effort to shorten and simplify such screening, a heat test was run on the same samples. Samples were held at 150°C. for 48 hours and examined for weight loss, acidity development, and color development. Results are as follows:

Sample	Weight Loss, %	Acidity		Color, Gardner	
		Initial	Final	Initial	Final
A1 Skydrol 500	29.7	0.04	15.8	2	5
A2 N-4713	29.5	0.10	37.1	2	Black
A3 N-125	24.7	0.08	25.0	2	6
A4 M-2	31.1	0.06	24.3	2	Black
A5 N-5520	24.9	0.09	41.1	2	Black

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						25.
B1	Dibutyl phenyl phosphate	37.4	0.02	22.7	2	13
B2	Skydrol 500	24.3	0.04	12.8	2	5
B3	J-1363	29.2	0.09	18.9	2	14
B4	J-1362	25.9	0.09	23.9	2	8
B5	N-3337	21.4	0.07	23.0	2	12

The identity of samples is as follows: Skydrol 500 is regular material, M-2 is Skydrol 500 Base with 0.5% benzo(c)cinnoline 5 oxide, and all other samples contained Skydrol Base with 1.0% phenyl glycidyl ether and 0.5% inhibitor. These are as follows: N-4713 is di-o-ethylphenylthiourea, N-125 is bis[2-(2-benzothiazolyl-mercapto)ethyl]ether, N-5520 is diphenylthiourea, N-3337 is β , β' -thiodipropionitrile, J-1363 is 1,2-di-(t-octylmercapto)ethylene and J-1362 is 1,2-di(t-butylmercapto)ethylene. None of the materials appeared successful in suppressing acidity development. It was concluded that a simple heat test was insufficient for selecting inhibitors and copper deactivators for Skydrol 500.

In an effort to improve the heat stability of Skydrol 500, samples of dibutyl phenyl phosphate (FH-87) containing various materials were heated in an oven at 150°C. for 24 hours. Results are as follows:

Sample	Weight Loss
A. FH-87	1.7%
B. FH-87 + 0.5% Phenyl -naphthylamine (PAN)	1.5%
C. FH-87 + 12% Acryloid R3876X	1.8%
D. FH-87 + 12% Acryloid R3876X + 0.5% PAN	1.9%
E. FH-87 + 12% Acryloid R3876X + 0.5% Oronite 250	2.6%
F. Skydrol 500	1.9%

These data indicate that neither phenyl α -naphthylamine nor Oronite 250 (a dialkyl selenide) are effective in reducing weight loss at 150°C. due to decomposition in either Skydrol 500 or its components.

6. Thin Film Corrosion Tests

The Naval Air Experiment Station had been testing Skydrol 500 and reported considerable corrosion in the thin film corrosion test at 225°F. To help correlate our data with theirs and since we had never run this particular test, a series of tests were carried out. Metal specimens were supplied by the Navy. A description of the test and the results obtained follows.

A "thin film corrosion test" as outlined in military specification, MIL-E-7083A (Aer) Fluid Hydraulic

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Noninflammable Hydrolube, Aircraft was carried out using Skydrol 500. Two sets of samples were run at 225°F., and one set at 200°F. The specification calls for a temperature of 200°F.

The procedure used can be summarized as follows: metal panels (provided for this test by the Navy and polished by them) were cleaned by boiling one minute in isopropyl alcohol, one minute in C.P. benzene, wiped with filter paper, and then boiled one minute in C.P. benzene. Each panel was weighed and the following pairs were placed in six ounce screw cap bottles containing 150 ml. of Skydrol 500: steel and copper, steel and 24ST aluminum, and steel and 61S aluminum. The metal panels were completely immersed in the fluid and allowed to soak for five minutes. The thoroughly wetted surfaces were then put together so that the steel was uppermost in the couple. The bottle was sealed with the cap, an aluminum liner being used to prevent contact between the vapors and the regular plastic cap liner. The jars were then placed in an oven held at the desired temperature for 14 days. The samples were identified as follows:

1. Steel and Copper at 225°F.
2. Steel and Aluminum 24ST at 225°F.
3. Steel and Aluminum 61S at 225°F.
4. Steel and Copper at 225°F.
5. Steel and Aluminum 24ST at 225°F.
6. Steel and Aluminum 61S at 225°F.
7. Control, Skydrol 500 only, at 225°F.
8. Steel and Copper at 200°F.
9. Steel and Aluminum 24ST at 200°F.
10. Steel and Aluminum 61S at 200°F.
11. Control, Skydrol 500 only, at 200°F.

The following observations were made during the test: At no time were the bottles removed from the oven or the metal specimens disturbed in any way. At the end of seven days, all bottles containing copper specimens had some precipitate. Bottle 1, at 225°F., had some solids but the fluid was clear while the fluid in bottle 4, also at 225°F., was cloudy. The precipitate was white to blue in both cases. The fluid in bottle 8 at 200°F. was also clear and there was some precipitate present. All other bottles were free of precipitate and cloudiness. After ten, twelve, and fourteen days, the same results were observed except that the amount of precipitate in the bottles containing the copper increased slightly.

At the end of exactly fourteen days, the bottles were removed from the oven. The following observations were

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then made. The series run at 225°F. will be described first. The fluid in bottles 1 and 4 (copper) was darker than the control (bottle 7), that in bottle 1 being clear and that in bottle 4 being cloudy. There was some precipitate in both bottles 1 and 4. The fluid in bottles 2, 3, 5, 6, and 7 was perfectly clear and of the same color. The metal specimens were removed from the fluid. The small amount of solids on the copper drained with the fluid from the specimen. In all cases the metals slid apart easily, there being no tendency to stick. The metal specimens were cleaned in the same manner as before the test. The copper specimens were changed in color and appeared to be lightly etched with the contact surfaces being stained. A very few small pits were observed in the contacting surface of the copper from bottle 4. The steel appeared unchanged from bottles 1 and 4. The aluminum-steel specimens appeared unchanged. However, on cleaning, a small amount of white solids was noted on the contacting surfaces. No precipitate was present in bottles 2, 3, 5, and 6 and none formed on standing for several days or on cooling to about 8°C.

The following observations were made on the 200°F. series: There was less precipitate in the bottle containing the copper (bottle 8) than in those run at 225°F. and the precipitate was more gelatinous and less dense. Again, the fluid from bottle 8 was darker than the control but not as dark as the 225°F. fluid. Bottles 9, 10, and 11 were all the same color and no precipitate was present. The metal specimens slid apart easily. The copper had changed color and was stained on the contacting surface. Only a minute amount of precipitate was found between the steel-aluminum 24ST couple and none between the steel-aluminum 61S couple. No precipitate formed in bottles 9 and 10 on standing for several days.

The weight changes for the various specimens are tabulated on page 29.

A series of photographs were taken of the various specimens and fluid after the test. These are listed as follows:

- A. Test Results at 225°F. - Bottles 1, 2, 3, 4, 5, 6, and 7.
- B. Test Results at 200°F. - Bottles 8, 9, 10 and 11.
- C. Fluids after Copper-Steel Couple Removed. Bottle 8 at 200°F. Bottles 1 and 4 at 225°F.
- D. Copper-Steel Couples Immediately after Removal from Fluid.

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- E. Aluminum 24ST - Steel Couples Immediately after Removal from Fluid.
- F. Aluminum 61S - Steel Couples Immediately after Removal from Fluid.
- G. Copper and Steel Specimens after Cleaning - Contact Surfaces.
- H. Copper and Steel Specimens after Cleaning - Non-contact Surfaces.
- I. Various Fluids after Test. (From left to right)
 - Copper-steel test at 225°F. - clear
 - Copper-steel test at 225°F. - cloudy
 - Copper-steel test at 200°F.
 - Aluminum 61S-steel test cooled to 8.5°C. with specimens present.
 - Aluminum 61S-steel test cooled to 8.5°C.
 - Control at 225°F.

Our results differed from those of the Navy in showing much less corrosion on copper and less precipitate and in showing no changes with aluminum. After discussion with Naval personnel, it was decided to repeat these tests at both laboratories.

An important point to be noted in this test was the decreased attack on copper at 200°F. as compared to 225°F. This emphasizes that Skydrol 500 is satisfactory for the temperatures for which it was designed but will attack metals and decompose at higher temperatures.

A second test was carried out to help correlate the results with the Naval Air Experiment Station. A detailed report of the procedure and the results obtained follows:

A "thin film corrosion test" as outlined in military specification, MIL-F-7083A (Aer), Fluid; Hydraulic, Noninflammable, Hydrolube, Aircraft was carried out using Skydrol 500, Skydrol, and Hydrolube H-2. The purpose of the test was to confirm results obtained in the previous test and to obtain comparative data. Skydrol 500 and Skydrol were run at test temperatures of 225°F. and 200°F.; Skydrol 500, Skydrol, and Hydrolube H-2 were run at 160°F. The specification calls for a test temperature of 200°F.

The procedure used can be summarized as follows: Metal panels (provided for this test by the Navy and polished

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<u>Bottle No.</u>	<u>Metal</u>	<u>Temp. °F.</u>	<u>Original weight, g.</u>	<u>Total change in wt., mg.</u>	<u>Change in wt., mg. per sq. cm.</u>
1	Copper Steel	225 225	53.5281 23.5494	-81.9 - 1.3	-2.05 -0.03
2	Aluminum 24ST Steel	225 225	16.1841 23.7427	+ 0.1 - 0.7	0 -0.02
3	Aluminum 61S Steel	225 225	15.9475 23.7635	- 0.7 - 1.1	-0.02 -0.03
4	Copper Steel	225 225	53.3652 23.4633	-78.8 - 1.5	-1.97 -0.04
5	Aluminum 24ST Steel	225 225	16.4648 22.9787	- 0.4 - 1.9	-0.01 -0.05
6	Aluminum 61S Steel	225 225	15.3948 23.7424	- 0.7 - 1.8	-0.02 -0.05
8	Copper Steel	200 200	53.2497 22.8201	-15.5 - 2.0	-0.39 -0.05
9	Aluminum 24ST Steel	200 200	16.1068 23.0226	- 0.6 - 0.7	-0.02 -0.02
10	Aluminum 61S Steel	200 200	16.2795 23.7570	- 0.6 - 1.5	-0.02 -0.04

Area not measured for each panel; however, panels are rather uniform and area calculated to be approximately 40 sq. cm.

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by them) were cleaned by boiling one minute in isopropyl alcohol, one minute in C.P. benzene, wiped with filter paper, and then boiled one minute in C.P. benzene. Each panel was weighed and the following pairs were placed in six ounce screw cap bottles containing 150 ml. of test fluid: steel and copper, steel and 24ST aluminum, and steel and 61ST aluminum. The metal panels were completely immersed in the fluid and allowed to soak for five minutes. The thoroughly wetted surfaces were then put together so that the steel was uppermost in the couple. The bottle was sealed with the cap, an aluminum liner being used to prevent contact between the vapors and the regular plastic cap liner. The jars were then placed in an oven held at the desired temperature for 14 days. The jars were examined daily for visual changes. At no time were the jars removed from the oven or the metal specimens disturbed in any way.

The samples are identified in Table 1. The numbers are used to identify the samples throughout the test and in the photographs taken at the end of the test.

The observations made during and after the test will be reported by grouping the samples according to test temperature. The results of the 225°F. test will be reported first. During the first four days darkening of the copper was observed. On the fifth day a small amount of fuzz was noted on the steel in the copper-steel couples in Skydrol 500 and the fluid was hazy. The steel in the copper-steel couple in Skydrol (jar 7) appeared to have rust spots although the fluid was clear. On the sixth day the fluid in jar 1 was clear and that in jar 4 was hazy and the amount of fuzz on the steel had increased (Skydrol 500). Sediment was forming in the bottom of both jars. These phenomena became more marked on the seventh and eighth days and on the eighth day the fluid (Skydrol) in jar 7 became hazy. By the tenth day the fluid in jar 4 was clear and considerable brown sediment was noted in both 1 and 4. On the eleventh day a haze was noted in jar 9 for the first time (Skydrol with aluminum 61ST-steel couple). Little change was noted from the eleventh day to the end of the test. At no time was any sediment or noticeable change observed in jars 2, 3, 5, and 6 which contained aluminum-steel couples and Skydrol 500 or in jar 8 which contained aluminum 24ST-steel and Skydrol.

At the end of the test the jars were removed from the oven and these observations were made: The fluid (Skydrol 500) in jars 1 and 4 was darker in color than the control (jar 10) and a dark brown precipitate was present. The fluid in jars 2, 3, 5, 6, and 10 was

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31. perfectly clear and of the same color. No precipitate formed in these even after several days at room temperature. The fluid (Skydrol) in bottles 7, 8, and 9 was cloudy and considerable fluffy solid was present in all jars. None was observed in the control (jar 11). On standing several days at room temperature no sediment was noted in jar 11 while some material settled in jars 7, 8, and 9.

The metal specimens were removed from the fluid. In all cases the specimens slid apart easily, there being no tendency to stick. The metal specimens were cleaned in the same manner as before the test. The copper specimens were changed in color and non-contact surfaces appeared to be lightly etched with the contact surfaces being stained. The steel from the copper-steel couples appeared to be lightly stained. On cleaning the aluminum-steel samples, a small amount of white solids was noted on the contacting surfaces. Removal of these solids by cleaning left some small stains. The steel from the aluminum-steel couples in Skydrol appear to be etched and was discolored. The weight changes of the metal specimens are given in Table 2. Photograph 1 shows the fluids in the jars after the test had been completed. Photographs 2 and 3 show the metal surfaces after cleaning, contact and non-contact surfaces, respectively.

The weight loss data for a previous thin film corrosion test on Skydrol 500 at 225°F. and at 200°F. are given in Table 3 for comparative purposes. All weight losses are calculated on a total surface area of 40 sq. cm. since the specimens are fairly uniform.

The observations made on the test at 200°F. are as follows: During the first five days no changes were noted except for a slight darkening of the copper. The fluid in jars 13 and 16 (copper-steel in Skydrol 500) appeared to be slightly hazy on the sixth and seventh days but no deposit was noted on the metal specimens until the eighth day. The amount of deposit increased slightly from day to day until the end of the test in jars 13 and 16 and a small amount settled to the bottom of the jar. The solid material was bluish-white and fluffy as compared to the dark brown heavier material obtained with copper-steel couples in Skydrol 500 at 225°F. At no time during the test was any sediment or noticeable change observed in jars 14, 15, 17, and 18 which contained aluminum-steel couples in Skydrol 500 or in jars 19, 20, 21 which contained the metal specimens in Skydrol.

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32.
At the end of the fourteen-day period, the jars were removed from the oven. The fluid (Skydrol 500) in jars 13 and 16 was darker than in jar 22, the control, and a fluffy bluish-white sediment was present. The fluid (Skydrol 500) in bottles 14, 15, 17, 18, and 22 was perfectly clear and of the same color. The fluid (Skydrol) in jars 19, 20, 21, and 23 was perfectly clear and of varying shades of green. No precipitate formed in any of the jars from this test (except 13 and 16 where it was already present) on cooling to room temperature and allowing to stand for several days.

The metal specimens were removed from the fluid. In all cases the specimens slid apart easily, there being no tendency to stick. The copper specimens were changed in color and the steel specimens from the copper-steel couples were covered with a small amount of solid which was readily removed by the cleaning procedure. All other metal specimens appeared to be essentially unchanged. The weight changes of the metal specimens are given in Table 4. The fluids in the jars are shown in Photograph 4 and the metal specimens are shown in Photographs 5 and 6, contact and non-contact surfaces, respectively. The weight loss data from a previous thin film corrosion test on Skydrol 500 at 200°F. are given in Table 3 for comparative purposes.

During the 160°F. test the following observations were made: There were no changes observable in any of the jars during the entire test except for a slight darkening of the copper specimens. At the end of the fourteen-day period, the jars were removed from the oven. No change was noted. However, on cooling the fluid (Hydrolube H-2) in jars 24, 25, and 26 to room temperature after removal of the specimens, a slight cloudiness was noted and a black sediment settled to the bottom. The fluid (Skydrol 500 and Skydrol) in all other jars was clear after several days at room temperature. Colors were quite similar to those of the control samples.

On removing the metal specimens from the jars, it was found that they slid apart easily, there being no tendency to stick. The metals from the Hydrolube H-2 test will be described first. The copper was bright and shiny with stains on the contact surface and the steel from the copper-steel couple was also stained (jar 24).

The contact surfaces of the aluminum-steel couples (jars 25 and 26) were discolored, the aluminum being yellow and the steel black. Deposits were removed in

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the cleaning leaving stains. The copper specimens from the Skydrol 500 (jar 27) and the Skydrol (jar 30) were darkened and stained slightly on the contact surfaces. None of the other metal specimens from jars containing these two fluids were changed in any way. The weight changes of the metal specimens are given in Table 5. Photograph 7 shows the fluids after the test. Photographs 8 and 9 show the metal specimens after cleaning, contact and non-contact surfaces, respectively.

The test data given in this report point up the variations that can occur in such a test method as the thin film oxidation test. Skydrol and Skydrol 500 exhibit some corrosion to copper at any temperature studied but are entirely satisfactory toward aluminum and steel. It is of interest to note that Skydrol 500 at 200°F. exhibits similar copper attack to that of Hydrolube H-2 at 160°F. with lesser steel attack.

The results of the tests may be summarized as follows: Results from test to test and even among samples in the same test do not appear to be reproducible depending greatly upon the surface condition of the metal specimens and other factors. This has also been observed by the NAES testing. Skydrol 500 and Skydrol exhibit some corrosion to copper at any temperature studied, the amount of corrosion increasing with increasing temperature. These results have also been observed in the oxidation and corrosion tests as normally run. Skydrol 500 and Skydrol are entirely satisfactory toward aluminum and steel. It is of interest to note that Skydrol 500 at 200°F. exhibits similar copper attack to that of Hydrolube H-2 at 160°F. with lesser steel attack.

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TABLE I

IDENTITY OF SAMPLES

Jar Number	Metal Couple Present			Fluid	Temperature
	Copper- Steel	Aluminum 24ST-Steel	Aluminum 61ST-Steel		
1	X			Skydrol 500	225°F.
2		X		" "	" "
3			X	" "	" "
4	X			" "	" "
5		X		" "	" "
6			X	" "	" "
7	X			Skydrol	" "
8		X		" "	" "
9			X	" "	" "
10	--	--	--	Skydrol 500	" "
11	--	--	--	Skydrol	" "
13	X			Skydrol 500	200°F.
14		X		" "	" "
15			X	" "	" "
16	X			" "	" "
17		X		" "	" "
18			X	" "	" "
19	X			Skydrol	" "
20		X		" "	" "
21			X	" "	" "
22	--	--	--	Skydrol 500	" "
23	--	--	--	Skydrol	" "
24	X			Hydrolube H-2	160°F.
25		X		" "	" "
26			X	" "	" "
27	X			Skydrol 500	" "
28		X		" "	" "
29			X	" "	" "
30	X			Skydrol	" "
31		X		" "	" "
32			X	" "	" "
33	--	--	--	Hydrolube H-2	" "
34	--	--	--	Skydrol 500	" "
35	--	--	--	Skydrol	" "

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TABLE 2

METAL SPECIMEN WEIGHT CHANGES -- 225°F. TEST

Jar No.	Metal	Fluid	Original Weight, g.	Total change in weight, mg.	Change in weight, mg. per sq. cm.
1	Copper Steel	Skydrol 500	53.4356 23.5722	-57.5 + 2.2	-1.44 +0.06
2	Aluminum 24ST Steel	" "	16.6033 23.6590	+ 0.2 - 0.8	+0.01 -0.02
3	Aluminum 61ST Steel	" "	15.7954 23.1940	- 0.8 - 1.2	-0.02 -0.03
4	Copper Steel	" "	53.1519 15.6234	-40.4 + 5.9	-1.01 +0.15
5	Aluminum 24ST Steel	" "	16.7029 23.0874	- 0.4 - 0.8	-0.01 -0.02
6	Aluminum 61ST Steel	" "	15.5560 20.0069	+ 1.2 + 0.1	+0.03 0
7	Copper Steel	Skydrol	53.3210 21.2964	- 5.6 -12.2	-0.17 -0.31
8	Aluminum 24ST Steel	" "	17.0472 18.9982	+ 1.4 -18.8	+0.04 -0.47
9	Aluminum 61ST Steel	" "	15.4622 23.3686	+ 2.2 -20.1	+0.06 -0.50

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TABLE 3

METAL SPECIMEN WEIGHT CHANGES -- SKYDROL 500

<u>Metal</u>	<u>Temperature</u>	<u>Original Weight, g.</u>	<u>Total change in weight, mg.</u>	<u>Change in weight, mg. per sq. cm.</u>
Copper	225°F.	53.5281	-81.9	-2.05
Steel	"	23.5494	- 1.3	-0.03
Aluminum 24ST	"	16.1841	+ 0.1	0
Steel	"	23.7427	- 0.7	-0.02
Aluminum 61ST	"	15.9475	- 0.7	-0.02
Steel	"	23.7635	- 1.1	-0.03
Copper	"	53.3652	-78.8	-1.97
Steel	"	23.4633	- 1.5	-0.04
Aluminum 24ST	"	16.4648	- 0.4	-0.01
Steel	"	22.9787	- 1.9	-0.05
Aluminum 61ST	"	15.3948	- 0.7	-0.02
Steel	"	23.7424	- 1.8	-0.05
Copper	200°F.	53.2497	-15.5	-0.39
Steel	"	22.8201	- 2.0	-0.05
Aluminum 24ST	"	16.1068	- 0.6	-0.02
Steel	"	23.0226	- 0.7	-0.02
Aluminum 61ST	"	16.2795	- 0.6	-0.02
Steel	"	23.7570	- 1.5	-0.04

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TABLE 4

METAL SPECIMEN WEIGHT CHANGES -- 200°F. TEST

Jar No.	Metal	Fluid	Original Weight, g.	Total change in weight, mg.	Change in weight, mg. per sq.cm.
13	Copper Steel	Skydrol 500	53.0064	-13.4	-0.34
		" "	21.5960	- 1.6	-0.04
14	Aluminum 24ST Steel	" "	17.0990	- 1.7	-0.04
		" "	19.0333	- 0.8	-0.02
15	Aluminum 61ST Steel	" "	15.8269	- 2.0	-0.05
		" "	23.4393	- 1.6	-0.04
16	Copper Steel	" "	52.4116	-25.6	-0.64
		" "	23.0129	+ 0.1	0
17	Aluminum 24ST Steel	" "	16.7492	- 1.2	-0.03
		" "	23.7303	- 1.2	-0.03
18	Aluminum 61ST Steel	" "	15.7112	- 0.2	-0.01
		" "	21.5281	- 1.3	-0.03
19	Copper Steel	Skydrol	53.8931	-65.1	-1.63
		"	23.9586	- 1.1	-0.03
20	Aluminum 24ST Steel	" "	17.3663	- 0.3	-0.01
		" "	22.7990	- 1.0	-0.03
21	Aluminum 61ST Steel	" "	16.1604	- 0.5	-0.01
		" "	21.5514	- 0.9	-0.02

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TABLE 5

METAL SPECIMEN WEIGHT CHANGES -- 160°F. TEST

Jar No.	Metal	Fluid	Original Weight, g.	Total change in weight, g.	Change in weight, mg. per sq. cm.
24	Copper Steel	Hydrolube H-2	52.3658	-18.1	-0.45
		"	22.1810	- 2.0	-0.05
25	Aluminum 24ST Steel	" "	16.8112	- 0.7	-0.02
		" "	21.7205	- 3.8	-0.10
26	Aluminum 61ST Steel	" "	16.2667	- 1.5	-0.04
		" "	23.9669	- 5.2	-0.13
27	Copper Steel	Skydrol 500	54.6217	- 6.1	-0.15
		" "	24.3267	- 1.7	-0.04
28	Aluminum 24ST Steel	" "	16.9318	- 1.5	-0.04
		" "	24.4910	- 1.7	-0.04
29	Aluminum 61ST Steel	" "	16.1940	- 2.0	-0.05
		" "	22.9145	- 0.9	-0.02
30	Copper Steel	Skydrol	54.2995	-20.5	-0.51
		"	23.9581	- 1.9	-0.05
31	Aluminum 24ST Steel	" "	16.8345	- 2.1	-0.05
		" "	19.4128	- 1.2	-0.03
32	Aluminum 61ST Steel	" "	15.9833	- 1.0	-0.03
		" "	23.6478	- 1.1	-0.03

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A list of the captions for photographs 1 through 9 are as follows:

Photograph 1 - Fluids From 225°F. Test

Copper-steel	Aluminum 24ST-steel	Aluminum 61ST-steel	Controls
1,4-Skydrol 500	2,5-Skydrol 500	3,6-Skydrol 500	10-Skydrol 500
7 - Skydrol	8 - Skydrol	9 - Skydrol	11-Skydrol

Photograph 2 - Metals From 225°F. Test - Contact Surfaces

Copper-steel	Aluminum 24ST-steel	Aluminum 61ST-steel
1,4-Skydrol 500	2,5-Skydrol 500	3,6-Skydrol 500
7 - Skydrol	8 - Skydrol	9 - Skydrol

Photograph 3 - Metals From 225°F. Test - Non-Contact Surfaces

Copper-steel	Aluminum 24ST-steel	Aluminum 61ST-steel
1,4-Skydrol 500	2,5-Skydrol 500	3,6-Skydrol 500
7 - Skydrol	8 - Skydrol	9 - Skydrol

Photograph 4 - Fluids From 200°F. Test

Copper-steel	Aluminum 24ST-steel	Aluminum 61ST-steel	Controls
13,16-Skydrol 500	14,17-Skydrol 500	15,18-Skydrol 500	22-Skydrol 500
19 - Skydrol	20 - Skydrol	21 - Skydrol	23-Skydrol

Photograph 5 - Metals From 200°F. Test - Contact Surfaces

Copper-steel	Aluminum 24ST-steel	Aluminum 61ST-steel
13,16-Skydrol 500	14,17-Skydrol 500	15,18-Skydrol 500
19 - Skydrol	20 - Skydrol	21 - Skydrol

Photograph 6 - Metals From 200°F. Test - Non-Contact Surfaces

Copper-steel	Aluminum 24ST-steel	Aluminum 61ST-steel
13,16-Skydrol 500	14,17-Skydrol 500	15,18-Skydrol 500
19 - Skydrol	20 - Skydrol	21 - Skydrol

Photograph 7 - Fluids From 160°F. Test

Copper-steel	Aluminum 24ST-steel	Aluminum 61ST-steel	Controls
24-Hydrolube H-2	25-Hydrolube H-2	26-Hydrolube H-2	33-Hydrolube H-2
27-Skydrol 500	28-Skydrol 500	29-Skydrol 500	34-Skydrol 500
30-Skydrol	31-Skydrol	32-Skydrol	35-Skydrol

Photograph 8 - Metals From 160°F. Test - Contact Surfaces

Copper-steel	Aluminum 24ST-steel	Aluminum 61ST-steel
24-Hydrolube H-2	25-Hydrolube H-2	26-Hydrolube H-2
27-Skydrol 500	28-Skydrol 500	29-Skydrol 500
30-Skydrol	31-Skydrol	32-Skydrol

Photograph 9 - Metals From 160°F. Test - Non-Contact Surfaces

(Same as Photograph 8)

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7. Hydrolytic Stability

Considerable concern had been expressed by potential users of Skydrol 500 concerning its hydrolytic stability. Tests were, therefore, started to study Skydrol 500 in the hydrolytic stability test, to compare Skydrol 500 and regular Skydrol (7000) in the test and to examine the test procedure. Data for the first two runs are given in Table 6.

The data were obtained by a modified Hydrolytic Stability Test from military specification MIL-F-7100, the so-called "coke bottle" test. The general procedure calls for sealing 75 grams of test oil, 25 grams of water, and a copper test strip in a "coke bottle" and rotating end over end in an oven maintained at 93°C. (200°F.). After 48 hours the bottles are removed and the contents examined.

Certain modifications in the test procedure were made. These modifications may be described as follows:

The time, temperature, rate of rotation, apparatus, and charges are the same as for MIL-F-7100. The copper specimen is cleaned by the technics used for Oxidation and Corrosion Tests -- including both benzene and acetone washes and not scrubbing with a stiff brush as recommended in the specification method. After the test has been completed, the procedure calls for centrifugation to remove the sludge and weighing of the centrifuge tube after drying to obtain sludge weight. This procedure may be satisfactory for fluids with low specific gravity but is not too feasible for our fluids. We do not centrifuge but obtain sludge by filtration through tared fritted glass filter crucibles, washing the sludge with water. Drying and reweighing gives the sludge weight.

In the tests described, we did not wash the fluids until the wash water was neutral to litmus as called for in the specification. The fluid was given one water wash and then dried. We then determined total acidity by titration of both the water and the oil layers. Our total acidity results would probably have been the same if we had removed the water soluble acidity from the fluid. Such a procedure is long, involving many washes and considerable care to make necessary analytical separations. It is felt that the important data are total acidities.

The limits set by the specification are as follows: The change in weight of the copper strip shall be less than 0.5 mg. per sq. cm. The acid number increase of the

DSW 620665

fluid shall not be greater than 0.5 NN and the acid content of the water layer and washes shall not exceed 10 mg. of KOH. By our calculation method this means that the increase in acidity shall not be greater than 0.63 NN. Our acidity values are calculated as neutralization number for the oil layer as it stands. Acidity values for the water layer are calculated on the basis of 75 grams of fluid charged, the entire water layer and wash being titrated. The viscosity change shall not be more than -5 to +15 per cent from the original viscosity at 130°F. The amount of material (sludge) shall not be greater than 0.5 per cent, or 0.375 grams.

Our data indicate that Skydrol 500 fails on acidity development and copper attack. Skydrol 7000 fails on the same properties but is closer to specification limits. As is expected with copper losses of greater than 2 mg. per sq. cm., such losses are not too reproducible from test to test, and we have variations of from 2.96 to 5.01 in our tests on Skydrol 500. Test 8, bottles 2 and 4, were run without copper. It appears that acidity development is greater without copper. The test seems fairly reproducible except for high copper attack fluids.

We have previously run this test on the base stock used for Skydrol 500. Copper weight changes of -3.8 to -5.2 mg. per sq. cm. and total acidities of 2.06 to 2.15 NN were found. These data are in line with those obtained on the finished fluid.

The significance of the test described here in regard to service of the fluid is not known. Obviously Skydrol 7000 does not pass the test and yet has shown remarkable service life. Skydrol 500 is poorer on hydrolytic stability, both by this test and others.

Further test work was undertaken on Skydrols 7000 and 500 using the "coke bottle" hydrolytic stability test. The results are summarized in Table 6. The method used is the same as described except that drying of the oil in runs 10, 12, and 13 was accomplished by evacuation.

Results from test 10 test using the same procedure for work-up seem fairly reproducible. We cannot explain the loss of viscosity in tests 8 and 9 and the gain of viscosity in tests 10, 12, and 13 except by the change in work-up procedure, possibly removing some low viscosity material by evacuation. However, all the viscosity results are within the specification limits of ± 15 to the percent change.

DSW 620666

STANDARD

HYDROLYTIC

STABILITY

H₂O

R.W. NO. 1

BOTTLE NO.

FLUID SKYDRA NO.

WATER % BY WT.

ACIDITY, NN

INITIAL

WATER LAYER

OIL LAYER

TOTAL

VISCOSITY, CS, 130°F

INITIAL

FINAL

LOSS, %

EFFECT ON COPPER

WT. CHANGE, MG./CM.²

SLUDGE

APPEARANCE

WT. %

L.B.A.

L.B.A.

L.B.A.

L.B.A.

L.B.A.

L.B.A.

L.B.A.

L.B.A.

L.B.A.

8

9

9

9

9

9

9

9

9

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

10

1

2

3

4

1

2

3

4

1

2

3

4

1

2

3

4

1

2

3

4

1

2

3

4

1

500

500

500

500

7000

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7000

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7000

500

7000

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7000

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7000

500

7000

500

7000

25

25

25

25

25

25

25

25

2

2

2

2

1

1

2

2

2

2

5

10

25

25

25

25

25

0.03

0.03

0.03

0.03

0.13

0.03

0.13

0.03

0.13

0.03

0.13

0.03

0.13

0.03

0.13

0.03

0.03

0.03

0.03

0.03

0.03

0.03

0.03

0.03

0.03

1.72

1.61

1.73

1.76

0.64

1.73

0.62

1.67

0.68

0.57

0.65

0.42

0.26

0.14

0.58

0.43

0.36

0.90

1.15

1.66

1.24

1.24

1.24

1.24

1.24

1.18

1.94

1.15

2.21

0.82

1.11

0.39

1.10

0.41

1.48

0.60

1.16

0.62

0.19

0.66

0.87

0.93

2.15

1.82

1.24

1.24

1.24

1.24

1.24

1.24

2.90

3.55

2.88

3.97

0.66

2.84

0.91

2.97

1.09

2.05

1.25

1.57

0.84

0.33

1.24

1.30

1.29

3.05

3.07

2.90

2.90

2.90

2.90

2.90

2.90

7.53

7.53

7.53

7.53

8.71

7.53

8.71

7.63

8.71

7.53

8.71

7.53

8.71

7.53

8.71

7.53

8.71

7.53

8.71

7.53

8.71

7.53

8.71

7.53

8.71

7.18

2.14

2.42

2.35

8.34

7.23

8.40

7.22

9.36

7.91

9.39

7.93

9.51

7.80

9.47

8.13

8.30

8.46

8.44

8.45

8.45

8.45

8.45

8.45

8.45

-4.7

-5.2

-1.5

-2.4

-4.3

-4.0

-2.6

-4.1

-7.5

+5.0

+2.8

+5.3

+2.1

+3.6

+8.9

+6.7

+10.2

+12.3

+12.1

+12.1

+12.1

+12.1

+12.1

+12.1

+12.1

-2.96

-3.38

-

-

-1.56

-5.01

-1.61

-4.45

-2.94

-0.14

-3.21

-0.10

-1.88

-0.51

-2.74

-0.15

-0.10

-3.41

-4.55

-4.74

-4.74

-4.74

-4.74

-4.74

-4.74

L.B.A.

L.B.A.

L.B.A.

L.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

Lr.B.A.

Dx.B.A.

0.01

0.00

0.01

0.00

0.06

0.02

0.05

0.02

0.09

0.01

0.07

0.04

0.04

0.03

0.05

0.02

0.01

0.05

0.05

0.02

0.02

0.02

0.02

0.02

0.02

The data of test 8 show that copper seems to affect the test using Skydrol 500 only in that less acidity is found when copper has been used. Attention is called to the better performance of Skydrol 7000 as compared to Skydrol 500 (test 9) and the fact that neither are within the MIL-P-7100 specification limits.

Since 25% water seemed too great from practical standpoints and since various discussions indicated that 2% water might be a better figure, tests were run using various concentrations of water. Test 10 results indicated lessened copper attack and acidity development for Skydrol 500 and increased for Skydrol 7000 using 2% water. With both fluids, excess water was present at the end of the test. However, during the tests all the water was in solution in the Skydrol 500 samples but not in the Skydrol 7000 samples. Test 12 was run since it was thought that undissolved water might be necessary to get copper attack. Both 1% and 2% water were used. It appears from the results that our assumption was incorrect since with Skydrol 7000, similar results were obtained at 1% and 25% water. Furthermore, using less water with Skydrol 500 (1% compared to 2%) gave increased copper attack and decreased acidity. A series was also run (test 13) increasing the water content. The best results were obtained with 2%. It should be noted that results are comparable from test to test at the same water concentration.

Based on these data, it appears that Skydrol 500 is within specification limits only in test 12, bottle 2, in which 1% water was used. Copper attack is just at the upper limit. It is interesting to compare the performance of Skydrols 7000 and 500 at low water concentrations, 2% or less, where copper attack is less for Skydrol 500 and acidity development is about the same. Based on service life of Skydrol 7000, these phenomena might be interpreted to mean that Skydrol 500 would be satisfactory from a hydrolytic stability standpoint.

Hydrolytic stability tests using the "coke bottle" technic had shown that the results with Skydrol type fluids depend upon the concentration of water. It was desired to determine if this were true with other type ester base fluids. A series of tests were conducted using Turbo Oil #15, a commercially available synthetic lubricant based on di-2-ethyl hexyl sebacate. Results are as tabulated on page 43.

These data indicate that water concentration has little effect upon the results using a diester base fluid. Such phenomena appear to be characteristic of phosphate ester base fluids.

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Test Number	18-1	18-2	18-3	18-4
Fluid charged, g.	98	95	90	75
Water charged, g.	2	5	10	25
Acidity, NN				
Initial	0.13	0.13	0.13	0.13
Oil layer	0.01	0.02	0.02	0.02
Water layer	0.28	0.23	0.25	0.24
Total	0.29	0.25	0.27	0.26
Viscosity, cs., 130°F.				
Initial	8.78	8.78	8.78	8.78
Final	8.71	8.75	8.74	8.76
Effect on copper, wt. change, mg./cm. ²	0.00	0.00	0.00	0.00
Sludge weight, g.	0.023	0.056	0.019	0.012

8. Solubility of Water in Skydrol 500

The procedures given in the section on Pydraul F9 were used to determine the solubility of water in Skydrol 500. The results were as follows:

Solubility of water at 75°F. 2.17%, 2.29%
 Solubility of water at 210°F. 4.22%, 3.99%, 4.19%,
 3.99%
 Average: 4.1%

The acidity of the Skydrol 500 was measured before and after exposure to conditions similar to the water solubility determination at 210°F. for an extended period. The initial acidity was 0.05 NN; after about 4-5 hours, 0.24 NN; and after 10 hours, 0.38 NN.

9. Skydrol 500 from WADC Packing Test

A sample of Skydrol 500 from a packing test at Wright Field was examined. The fluid was quite dark but was easily clarified by filtration through Attapulugus earth. This reduced the acid number from 0.21 NN to 0.12 NN. Spectrographic analysis showed the presence of silicon. It is apparent that the fluid had become contaminated during the test.

10. Physical Measurements

Data concerning specific heat, variation of density with temperature, electrical properties, and thermal conductivity for Skydrol 500 are given in Section M of this report.

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44.

D. Fluids OS-45 and OS-45-1

Fluids OS-45 and OS-45-1 are derived from a tetraalkyl silicate base stock. These fluids have found considerable use as dielectric coolants and high temperature hydraulic fluids. Most of the work concerned with these fluids is reported in final reports on job numbers 117-2380 and 117-2507. However, certain of their characteristics were studied under this job number following routines established in the study of other fluids. The data are given in this report under section M in order that both method and results may be in one place.

E. Fluid OS-41

1. Inhibitor Studies

Fluid OS-41 was developed as a high specific gravity synthetic torque converter fluid. It consists of Aroclor 1248, Santicizer 141, Acryloid HF-855 and a defoamer. The fluid was of interest to several potential users and several five-gallon lots were prepared.

It was reported that Fluid OS 41 attacks steel at high temperatures in the presence of asbestos clutch plates. A regular oxidation and corrosion test was run at 250°F. for 168 hours using Fluid OS-41 and OS-41 with inhibitors. The data are as follows:

Sample	1	2	3	4	5	6
Viscosity, cs., 130°F.						
Initial	13.81	15.22	14.05	14.19	13.99	13.92
Final	14.26	15.86	14.08	14.91	15.44	14.51
Acidity, NN						
Initial	0.04	1.86	0.03	0.05	0.06	0.19
Final	0.31	2.36	0.30	0.10	0.31	2.05
Fluid evap., %	1.2	1.1	0.9	1.2	1.7	1.5
Effect on metals, wt. change, mg./cm. ²						
Copper	-1.49	-0.04	-0.12	-0.43	-0.85	-0.25
Steel	-0.02	+0.01	0.00	0.00	-0.01	0.00
Aluminum	0.00	0.00	0.00	0.00	0.00	0.01
Magnesium	-0.27	-0.01	-0.01	0.00	-0.31	-0.02
Cadmium	-0.09	-0.02	-0.01	-0.02	-0.20	0.00
plated steel						

The identity of samples is as follows: Sample No. 1 is Fluid OS-41 alone while sample No. 2 through No. 6

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contain various additives. These are sample 2, 1.0% Emery's dimer acid; sample No. 3, 1.0% phenyl glycidyl ether; sample No. 4, 0.9% phenyl glycidyl ether and 0.1% Shell's WDS; sample No. 5, 1.0% phenyl alpha-naphthylamine; and sample No. 6, 1.0% Santolube 394C. The data show that under the conditions of this test, steel was not attacked. However, copper, magnesium, and cadmium plated steel were corroded. All additives except phenyl alpha-naphthylamine suppressed magnesium and cadmium plated steel attack and decreased copper attack, dimer acid and phenyl glycidyl ether being most effective.

2. Hydrolytic Stability

A regular "coke bottle" hydrolytic stability test was run on Fluid OS-41 and several other fluids for comparative purposes. Results are as follows:

Fluid	Pydraul F9	OS-41	OS-54
Acidity, NN			
Initial	0.08	0.17	0.16
Water layer	0.03	0.16	0.19
Oil layer	0.03	0.12	0.11
Total	0.11	0.28	0.30
Viscosity, cs., 130°F.			
Initial	20.91	13.94	22.05
Final	20.13	13.75	21.93
% Change	-3.7	-1.4	-0.5
Effect on copper, wt. change, mg./cm. ²	-0.05	-0.22	-0.20
Sludge, weight, g.	0.002	0.014	0.021

These results indicate that all three fluids would pass MIL-F-7100 requirements, the military specification from which the test was taken.

3. Physical Measurements

Data concerning specific heat and thermal conductivity for Fluid OS-41 are given in Section M of this report.

Fluid L-3A (Fluid OS-22)

Fluid L-3A consists of 55 volume (60.4 weight) per cent triphenyl phosphate and 45 volume (39.6 weight) per cent monolene-50E. A total of forty gallons of this fluid were prepared. The analytical data for the finished fluid are as follows:

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46.

Viscosity, 210°F.	3.19 cs.
100°F.	15.53 cs.
Viscosity Index	63
Acidity	0.21 NN
Specific Gravity, 25/25°C.	1.065
Flash Point	340°F.
Fire Point	425°F.
Pour Point	-55°F.
Color	115 APHA

The 25 gallons of fluid was sent to Axelson as requested for evaluation.

All Fluid L-3A was normally prepared using Ucon DLB-50B. The supplier stated that this material was being replaced with a similar product called Ucon DLB-50E. A sample of this latter material was examined and blended into Fluid L-3A. Physical properties are given below:

	Fluid L-3A from:			
	Ucon DLB-50E	Ucon DLB-50B	Ucon DLB-50E	Ucon DLB-50B
Viscosity, cs., 210°F.	3.25	3.19	2.44	2.45
100°F.	15.68	15.53	7.63	8.03
Viscosity Index	72	63	157	143
Acidity, NN	0.20	0.21	0.34	0.38
Sp. Gr., 25/25°C.	1.0644	1.0649		
Flash Point, °F.	385	340		
Fire Point, °F.	445	425		
Pour Point, °F.	-45	-55		

The final formulations seem quite similar except for somewhat higher flash, fire, and pour points when Ucon DLB-50E is used. A sample of the Ucon DLB-50E was submitted to Douglas and was approved by them for use in Fluid L-3A.

Data concerning specific heat and thermal conductivity are given in Section M of this report.

G. Fluid OS-54

1. Formulation Data

A series of fires resulting from leakage in hydraulic power steering systems in automobiles aroused considerable interest in a non-flammable type fluid for this use. The desired properties of such a fluid were supplied by the Saginaw Steering Gear Division of General Motors and were those of their presently used fluid, Texamatic Type A. After an examination of these properties and a review of previous fluid data,

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it was felt that a fluid based on equal proportions of Santicizer 141 and Aroclor 1248 with a viscosity index improver might be satisfactory. A series of samples were made up from a base stock (equal weights of Santicizer 141 and Aroclor 1248) and various amounts of Acryloid HF855. The data for these samples as well as the properties desired are as follows:

	Viscosity at:		Vis. Index	Specific Gravity	Pour Point
	210°F.	100°F.		25/25°C	
Base stock	2.65	14.8	-52	--	--
Base stock + 5% Acryloid HF855	5.53	29.5	135	--	--
Base stock + 6% Acryloid HF855	6.20	33.2	140	--	--
Base stock + 7% Acryloid HF855	6.95	37.3	144	--	--
Base stock + 8% Acryloid HF855	7.72	41.7	145	--	--
Base stock + 9% Acryloid HF855	8.50	46.2	146	--	--
Desired properties	7.44	41.6	140	--	-35°F.
Fluid OS-54	7.64	41.2	145	1.209	-30°F.

From these data it seemed that the fluid containing 8% Acryloid HF855 was most suitable. A larger batch was prepared using this formula and sent to Saginaw Steering Gear for evaluation as Fluid OS-54.

2. Preparation of Larger Amounts

Since preliminary tests on Fluid OS-54, proposed as a non-flammable type power steering fluid were promising, the prospective customer asked for more material. A twelve-gallon batch was prepared in the laboratory consisting of 46% Santicizer 141, 46% Aroclor 1248, and 8% Acryloid HF855. This lot of OS-54 had a viscosity of 7.41 cs. at 210°F., 40.3 cs. at 100°F., and a specific gravity of 1.210 at 25/25°C. These properties are quite similar to those of previous samples. The material was sent to the prospective customers for evaluation.

In order to assist the development program on Fluid OS-54, a 4000-lb. batch was prepared in the interim production facilities.

The following table is given the analysis of this material in comparison with typical properties derived from previous work.

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Fluid OS-54

<u>W Building</u>	<u>Typical Properties</u>
<u>Prep.</u>	

Lot V-1277

Acidity, NN	0.10	.04 - .10
Moisture	0.19%	
Sp. Gr., 25/25°C.	1.211	1.209 - 1.210
Viscosity, cs., +210°F.	7.34	7.26 - 7.72
+100°F.	39.46	39.20 - 41.72
Viscosity Index	+144	+145
Pour Point	-35°F.	-30°F.

Fluid OS-54 became of interest to the Navy for ship-board use and 200 gallons were ordered. It was felt that a defoamer would be necessary for this use, therefore four drums of the OS-54 batch were individually defoamed in the Pilot Plant facilities by the addition of 50 ppm of DC Fluid 200, 350 cs. at 25° grade.

The analysis of a composite samples from these four drums, identified as Lot W-250, is as follows:

Appearance	Pale yellow, slightly opalescent viscous liquid
Moisture	0.10%
Acidity, NN	0.11
Sp. Gr., 25/25°C.	1.2109
Viscosity, cs., +210°F.	7.24
+100°F.	39.46
Viscosity Index	+142.7
Pour Point	- 40°F.

Twenty gallons of defoamed OS-54 were furnished to Douglas Aircraft Company for testing purposes. Four five-gallon cans of OS-54 were individually defoamed in the Pilot Plant. This material was sent under the same analyses as the preceeding.

3. Hydrolytic Stability

The hydrolytic stability of Fluid OS-54 was determined by the regular "coke bottle" technic. The data are given in Section E of this report. Fluid OS-54 passes the test.

4. Fluid OS-54-1

A sample of Fluid OS-54 was prepared using an oil-free Acryloid viscosity index improver obtained from the Douglas Aircraft Company. A quart of this formulation, identified as Fluid OS-54-1, was furnished to the Navy for testing purposes.

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The analysis of this formulation is as follows:

Viscosity, 100°F.	44.37 cs.
210°F.	7.34 cs.
Specific Gravity, 25/25°C.	1.2323
Acidity	0.27 NN
Moisture	0.12%
Pour Point	-25°F.

This sample was prepared with the oil-free Acryloid because it is believed that the oil in the Acryloid usually used in formulating this Fluid is the cause of high values obtained in Navy's oxygen demand test and Diesel ignition test.

H. Steam Turbine Lubricants

Considerable interest was expressed in a non-flammable type steam turbine lubricant. It was suggested that fluids based on tricresyl phosphate and Aroclor 1242 be studied. A base stock consisting of 25% tricresyl phosphate and 75% Aroclor 1242 was prepared (called ST Base) and mixtures containing 3 weight per cent (called ST-3) and 4 weight per cent (called ST-4) of Acryloid 794 were also prepared. Data for these mixtures as well as specifications for a steam turbine lubricant are as follows:

	Specifi- cations	ST Base	ST-3	ST-4
Viscosity, cs, 210°F.		2.81	1.3044	6.42
SUS 40 - 50		35.7	43.8	47.2
Viscosity, cs, 100°F.		21.50	37.74	44.30
SUS 140 - 170		104	176	206
Viscosity Index		-212	+74	+103
Pour Point, °F.	+20 max.	- 5	- 5	- 5
Sp. Gr., 25/25°C.			1.3044	
Acidity, NN			0.02	
Flash Point, °F.			355	
Pire Point, °F.			665	

The sample labeled ST-3 appeared to be satisfactory from a viscosity and pour point standpoint. Two gallons of fluid were prepared and submitted to the Engine Test Laboratory for demulsification and rust tests. One gallon was filtered through filter paper only. The other gallon was stirred with 0.5% Attapulugus earth and filtered (called Fluid ST-3a). This was done to determine if emulsification agents, if present, could be removed. Both samples were treated with 50 parts per million silicone defoamer (DQ200 - 350 cs. at 25°C.). A regular code of 2% hydrolytic stability test was carried out using Fluid ST-3. The data are as follows:

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Sample	Pydraul F9	Fluid ST-3
Acidity, NN		
Initial	0.08	0.03
Oil layer	0.03	0.02
Water layer	0.08	0.05
Total	0.11	0.07
Viscosity, cs., 130°F.		
Initial	20.91	17.43
Final	20.13	17.31
% Change	-3.7	-0.7
Effect on copper, wt change,		
mg./sq. cm.	-0.05	-0.06
Sludge weight, grams	0.002	0.009

Comparative data are given for Pydraul F9. Both fluids are quite satisfactory in this test and give similar results.

The two samples were examined by Mr. D. W. Dinsmore and Mr. E. P. Cunningham in the Engine Test Laboratory. Results are as follows quoting from memos dated 6-22-54 and 7-8-54.

"The following physical data have been obtained on two samples of proposed turbine oils:

	<u>Sample ST-3</u>	<u>Sample ST-3a</u>
Viscosity at 100°F., SUS	174.5	
Viscosity at 210°F., SUS	43.6	
Viscosity Index	74.1	
Demulsibility		
Characteristics, 3	1	2
Minutes to break	2	3
ASTM D-665*	1.5	3.5
Turbine Oil Rust	2.5	3.5

*10 = perfect

Based on these data, it is concluded that either lubricant is quite satisfactory with regard to demulsibility characteristics, however, the rusting characteristics are very poor."

"Continued evaluation of these materials has been confined to the clay filtered sample identified as ST-3a with the following data being obtained.

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Blend	ASTM D-665 Rust*	
	With Water Wash	Without Water Wash
ST-3a	3.5, 3.5	
ST-3a + 0.2% (w) Santolube 70 50 ppm Santolene C	5.0, 5.0	
ST-3a + 0.2% (w) Armeen 16D 50 ppm Santolene C	5.0, 5.0	
ST-3a + 50 ppm Santolene C	3.0, 2.0	
ST-3a + 500 ppm Santolene C	2.5, 2.5	
Pydraul F-9, W-62		3.0, 2.0
TCP, V-594		3.5, 3.0
Aroclor 1248, A-614		3.5, 2.5
Aroclor 1242, #194		4.0

*18 hours using salt water.

Pydraul F9 has been reported to have borderline rust inhibiting properties, however, our results do not confirm this. The use of distilled water in place of salt water might be the answer. A definite improvement over Pydraul F9 is shown by the addition of Santolube 70 or Armeen 16D to the ST-3a base fluid."

Reasoning from these data it was concluded that samples containing rust inhibitors should be submitted to interested groups for evaluation.

About five gallons of Fluid ST-3a, called Fluid OS-58 for sampling purposes, was prepared. This material consists of 3% Acryloid 794, 24.25% tricresyl phosphate, 72.75% Aroclor 1242 and 50 parts per million silicone defoamer (DC200 -- 350 cs.). Part of the fluid was converted to Fluid OS-58-1 by the addition of 50 parts per million Santolene C and 0.1% Santolube 70. The rest was converted to Fluid OS-58-2 by the addition of 50 parts per million Santolene C and 0.2% Santolube 70. The rust inhibitors and defoamer were added after Attapulugus earth filtration. The properties of the two samples were as given on page 52.

Samples of these products were sent to Duquesne Light Co., General Electric, and Westinghouse for evaluation.

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Fluid	OS-58-1	OS-58-2
Viscosity, cs., 210°F.	5.28	5.32
100°F.	36.39	36.64
Viscosity Index	+84	+79
Pour Point, °F.	- 5	- 5
Acidity, NN	0.07	0.09
Sp. Gr., 25/25°C.	1.301	1.301

I. Low Temperature Industrial Fluids (Fluid OS-57)

There are many applications for non-flammable type industrial hydraulic fluids that cannot be filled by Pydruol F9 because of its low temperature properties. It was suggested that other fluids of the phosphate ester-Aroclor type, in addition to those already studied, be examined. It was felt that the mixture of 30% 2-ethylhexyl diphenyl phosphate (FH41) and 70% Aroclor offered promise as a base stock. Fluids were examined starting with those containing Aroclors 1248 and 1242 in equal mixture and finally ending with those containing only Aroclor 1242 as the Aroclor portion of the base stock.

The following system of naming was used: LT-1 Base consisted of 30% FH41, 35% Aroclor 1248, and 35% Aroclor 1242. The amount of Acryloid 794 added as viscosity index improver was indicated by the use of a second number. For example, LT-1-5 means 5% Acryloid 794 in LT-1 Base. LT-2 Base consisted of 30% FH41, 57.5% Aroclor 1242, and 17.5% Aroclor 1248. LT-3 Base consisted of 30% FH41 and 70% Aroclor 1242. The data for these series of fluids are as follows:

Fluid	Viscosity, cs.			Viscosity Index	Pour Point, °F.
	210°F.	100°F.	0°F.		
LT-1 Base	2.60	16.13		-117	-25
LT-1-5	7.32	42.11		+137	-25
LT-1-8	11.74	67.03		+144	-20
LT-2 Base	2.50	14.63		- 99	-25
LT-2-5	7.06	38.63		+142	-25
LT-2-8	11.43	61.50		+149	-25
LT-3 Base	2.42	13.40	2810	- 81	-25
LT-3-3	4.71	25.01		+120	-25
LT-3-4	5.69	30.05		+138	-25
LT-3-5	6.80	35.42	6570	+147	-25
LT-3-8	6.06	31.88	63.0	+142	-25

Specifications for a low temperature fluid of this type include viscosity of 150 SUS (32 cs.) at 100°F. with a maximum of 4000 SUS (875 cs.) at 0°F. It can be seen

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that Fluid LT-3-4.4 meets the 100°F. requirement but is too viscous at 0°F. The specific gravity at 25/25°C. of this fluid was 1.257 with a flash point of 360°F. and a fire point of 495°F.

Because of the high 0°F. viscosity of the LT-3 fluids, the ratio of FH41 to Aroclor 1242 was changed to 70:30 for the LT-4 Base. This base did not appear to give the necessary viscosity properties and hence LT-5 Base was prepared consisting of 25% Aroclor 1242 and 75% FH41. A satisfactory fluid based on viscosity characteristics was prepared in LT-5-7.5. The series was also extended to include LT-6 Base which consisted of 20% Aroclor 1242 and 80% FH41. The physical properties of these fluids are as follows:

Fluid	Viscosity, cs.			Viscosity Index	Sp.Gr. 25/25°C.	Pour Point, °F.
	210°F.	100°F.	0°F.			
LT-4 Base	2.44	10.98	560	+ 23	1.165	-60
LT-4-4.7	5.45	22.53	850	+174	1.148	-55
LT-4-6	6.57	26.78	930	+174	1.143	-55
LT-5 Base	2.44	10.77	490	+ 31	1.152	-55
LT-5-6	6.41	25.28	630	+176	1.131	-55
LT-5-7.5	7.90	30.87	650	+172	1.126	-55
LT-5-9	9.47	36.66	640	+169	1.121	-55
LT-6 Base	2.43	10.59	420	+ 36	1.138	-60
LT-6-6	6.22	23.75	490	+180	1.119	-55
LT-6-8	8.28	30.97	510	+174	1.116	-55

The flash point of LT-5-7.5 was found to be 380°F. and the fire point, 470°F. The fluid was called Fluid OS-57. Two batches were prepared in the Interim Production facilities for testing in an Askania Regulator by U.S. Steel Co. This material had the following properties:

Batch	1	2
Viscosity, cs., 210°F.	7.76	7.73
100°F.	30.56	30.45
0°F.	635	650
Acidity, NN	0.18	0.08
Sp. Gr., 25/25°C.	1.125	1.124
Moisture, %	0.14	0.22

The thermal stability of Fluid OS-57 was studied in the following manner: One hundred grams of the fluid were placed in a 150 mm. beaker and the beaker was placed uncovered in a Fisher isotherm oven. The oven was thermostatically controlled at the desired temperature. After a given period of time the beaker was removed from the

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oven and weight loss, acidity, appearance, and in some cases viscosity were determined.

The data for a test run at 175°C. (347°F.) are as follows:

<u>Time in Hours</u>	<u>Wt. Loss, %</u>	<u>Acidity, NN</u>	<u>Appearance</u>
0	0.0	0.08	Light yellow
6	0.8	5.1	Deep yellow
12	18.1	---	Black, 2 layers
18	20.3	---	Black, 2 layers
24	21.0	133	Black, 2 layers

A similar test was carried out at 150°C. (302°F.). The data are as follows:

<u>Time in Hours</u>	<u>Wt. Loss, %</u>	<u>Acidity, NN</u>	<u>Appearance</u>
0	0.0	0.08	Light yellow
25	1.0	1.51	Medium yellow
49	2.9	12.4	Orange
72	19.2	--	Black, 2 layers
96	21.7	--	Black, 2 layers
168	23.0	--	Black, 2 layers
312	28.3	--	Black, 2 layers

The data for the thermal stability test at 125°C. (257°F.) are as follows:

<u>Time</u>		<u>Wt. loss, %</u>		<u>Acidity, NN</u>		<u>Viscosity, cs.</u>		<u>Viscosity</u>	<u>Appearance</u>
<u>Hours</u>	<u>Days</u>	<u>%</u>				<u>210°F.</u>	<u>100°F.</u>	<u>Index</u>	
0	0	0.0		0.08		7.73	30.45	172	Light yellow
24	1	0.4		0.33		7.48	29.47	172	Yellow
48	2	0.6		0.57		7.47	29.33	172	Yellow
72	3	1.6		0.82		7.44	29.44	172	Medium yellow
120	5	1.6		1.42		7.43	29.45	172	Deep yellow
168	7	1.6		1.85		7.43	29.54	172	Light orange
240	10	3.3		6.12		7.53	30.00	171	Deep orange
312	13	4.6		15.6		7.79	30.92	171	Brown
360	15	8.0		---		----	---	---	Black, 2 layers

The thermal stability of Fluid OS-57 is compared to that of Pydraul F9 and Skydrol 7000 in the graph on the following page. It would appear that Fluid OS-57 is similar in thermal stability to Skydrol and will be suitable for use at similar temperatures. Fluid OS-57 will not be satisfactory for use at 175°C. nor at 150°C.

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OVER TESTS

175°C.

150°C.

125°C.

A. C. IV

in

15. 2/4.

SKTORU

SYDNEY F-7

SKYDOL

FILED 00-57

Fluid
05-5

DSW 620681

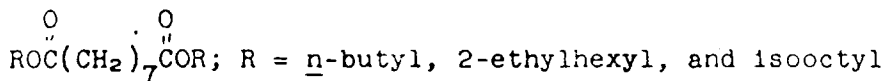
J. Preparation of Esters (Prepared by L. W. Bannister)

1. Azelate Esters

Raw Materials Used:

1. Azelaic acid	Emery Industries, Inc.
2. 2-Ethylhexanol	#597
3. Iso-octanol	Enjay Co., Inc.
4. n-Butanol	#540
5. Sulfuric acid	#213
6. Sodium carbonate	#512
7. Potassium permanganate	#518
8. Sodium metabisulfite	#522
9. Attapulugus earth	#608

a. Dialkyl Azelates (symmetrical)



Azelaic acid has recently become commercially available from Emery Industries, Inc. and it was of interest to prepare some of its esters for evaluation as functional fluids (specifically for utility in jet turbine lubricants) and as plasticizers.

The esters indicated above were all prepared by the same standard procedure: 1 mole of the acid or acid anhydride was stirred and heated with 2.2-2.3 moles of the alcohol at 100-110° in the presence of a catalytic amount of sulfuric acid. The water formed during the reaction was distilled out under reduced pressure, azeotroping with some of the excess of alcohol used. When esterification was complete (2-6 hours) the solution was cooled to 60-80° and washed first with sodium carbonate solution and then with water. Steam-distillation was used to remove the excess of alcohol, following which another carbonate wash was applied, excess carbonate being washed out with water.

Permanganation was carried out at 70-80° for four hours. Decolorization with sodium metabisulfite was followed by washing with: (1) water, (2) carbonate solution, (3) more water. Dehydration at 90-100° (20 mm.) and filtration through Attapulugus earth afforded the ester.

In the case of dibutyl azelate a separator was used during the esterification to separate the water from the distillate and return the butanol to the reaction flask. Yields and properties of these esters are shown below.

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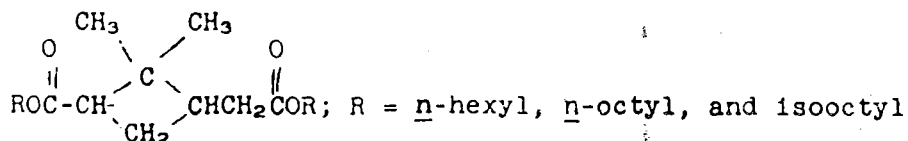
	Di-(2-Ethyl- hexyl)- Azelate	Di-(iso- octyl)- Azelate	Dibutyl Azelate
Molecular Weight	412.63	412.63	300.42
Yield, %	96	90	94
Viscosity, cs., 210°F.	3.30	3.40	1.87
130°F.	7.07	8.03	3.73
100°F.	11.13	12.55	5.29
-40°F.	1270	1390	Solid
-65°F.	6300	7870	Solid
Acidity, NN	0.08	0.10	0.08
Sp. gr., 25/25°C.	0.9168	0.9169	0.9419
n_D^{25}	1.4476	1.4476	1.4377
Pour Point	----	----	-15°F.
Viscosity Index	+145	+166	----

2. Pinate Esters

Raw Materials Used:

- | | |
|---------------------------|--|
| 1. Pinic acid (95) | Southern Regional Research
Laboratories |
| 2. n-Octanol | duPont Co. |
| 3. Iso-octanol | Enjay Co., Inc. |
| 4. n-Hexanol | Carbide and Carbon |
| 5. Sulfuric acid | #213 |
| 6. Sodium carbonate | #512 |
| 7. Potassium permanganate | #518 |
| 8. Sodium metabisulfite | #522 |
| 9. Attapulugus earth | #608 |
| 10. Norit | #663 |

a. Dialkyl Pinates (symmetrical)



Although pinic acid from pinene is still high priced, work being conducted at the Southern Regional Research Laboratories on the oxidation of pinene may lead to an attractively priced pinic acid. Esters of this acid have already been shown by the law to have good properties for functional fluid and plasticizer uses.

Therefore, the three pinate esters indicated above were given preliminary screening as functional fluids and as plasticizers (Darby's group). Each of these pinates was prepared by heating pinic acid at 100-110° with an excess (45% excess of n-hexanol, 15%

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excesses of the other two alcohols) of the alcohol in the presence of catalytic amounts of sulfuric acid. During the esterification the pressure of the system was gradually reduced in order to remove water of esterification, pressure being maintained at 30 mm. during the last hour of the 3-hour esterification period.

After being washed with carbonate solution and with water the crude esters were steamed free of unreacted alcohol, re-washed with carbonate solution and water, permanganated at 70-80°, re-washed (water, carbonate solution, water) and dehydrated. The esters were then stirred with 2% each of Norit and Attapulugus earth before filtering through Attapulugus earth. Yields and properties are summarized below:

	<u>n-Hexyl Pinate</u>	<u>n-Octyl Pinate</u>	<u>Isooctyl Pinate</u>
	Very slightly yellow	Very slightly yellow	Medium yellow
Color	yellow	yellow	
Molecular Weight	354.51	410.62	410.62
Yield, %	--	91	97
Viscosity, cs., 210°F.	2.76	3.63	4.07
130°F.	6.73	8.90	11.13
100°F.	10.54	15.06	19.44
-40°F.	1420	2220	11150
-65°F.	9190	13100	---
Viscosity Index	+116	+145	+126
Acidity, NN	0.12	0.07	0.36
Sp. Gr., 25/25°C.	0.9483	0.9322	0.9379
n_D^{25}	1.4498	1.4524	1.4540
Pour Point	---	Below -85°F.	-55°F.

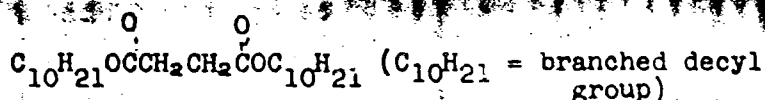
3. Succinate Esters

Raw Materials Used:

1. Succinic anhydride	Monsanto
2. Maleic anhydride	# 49
3. Diethyl succinate	F. B. Zienty
4. Isodecanol	Enjay Co., Inc.
5. Tridecanol	Enjay Co., Inc.
6. Stercx AH	Monsanto (Anniston)
7. Sulfuric acid	#217
8. Sodium methoxide	W-Bldg.
9. Sodium carbonate	#512
10. Potassium permanganate	#518
11. Sodium metabisulfite	#522
12. Attapulugus earth	#608
13. Carbon dioxide	
14. p-Toluenesulfonic acid	Fisher Scientific
15. Nickel formate catalyst	Monsanto

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a. Di-isodecyl Succinate (MW = 398.62)



The "isodecyl" alcohol used in this preparation is made by Enjay via the oxo process on C_9 olefins.

1. From Succinic Anhydride

A mixture of 200.1 g. (2.00 moles) of succinic anhydride, 697 g. (4.41 moles) of Enjay's isodecyl (i.e., branched chain) alcohol, and 3 ml. of 98% sulfuric acid was stirred and heated at 100-110° as the pressure on the system was gradually reduced to 20 mm. When no more water distilled through the straight take-over still head attached to the reactor, the reaction was stopped (6 hours). The crude ester was washed with carbonate solution and water at 50-60° and was then steamed at 110° until 5 liters of distillate had been collected. After a re-washing with carbonate solution and water the ester was dehydrated at 95° (20 mm.) for an hour and filtered through Attapulugus earth. There was thus obtained 749 g. (94%) of light yellow di-isodecyl succinate, n_D^{25} 1.4477, sp. gr. 25/25° 0.9201, N.N. 0.03. Other properties of this material are listed in tabular form at the end of this section.

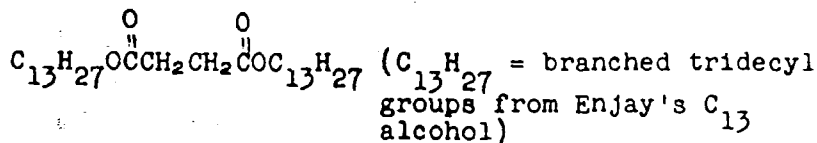
2. From Di-isodecyl Maleate

Di-isodecyl maleate, prepared from Enjay's isodecyl (i.e., branched chain) alcohol and maleic anhydride as described in the final report on Job No. 117-2221, was hydrogenated over nickel formate catalyst at 80° and 700 psi by D. B. Merrifield. Interestingly, the up-take of hydrogen was 127% of theory. The quantitative yield of crude di-isodecyl succinate, after filtration through Attapulugus earth, was medium-yellow and opalescent, n_D^{25} 1.4477, sp. gr. 25/25° 0.9197, N.N. 0.064. It was permanganated for 4 hours at 75-85°, taking up a considerable quantity of permanganate. After decolorization with sodium metabisulfite the ester was washed in the usual manner and dehydrated at 100° (12 mm.). Since it was about the same medium-yellow color as it had been prior to permanganation it was treated with 1% of Norit before

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filtering through Attapulugus earth. The product was then light-yellow, n_D^{25} 1.4481, sp.gr. 25/25° 0.9225, N.N. 0.42.

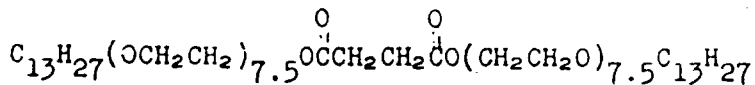
b. Di-tridecyl Succinate (MW = 482.75)



Enjay's tridecyl alcohol used in this preparation is made from propylene tetramer via the oxo process.

The procedure for the preparation of this ester was the same as that given in (1) above for the conversion of succinic anhydride to di-isodecyl succinate except that 827.1 g. (4.13 moles) of Enjay's tridecyl alcohol was substituted for the isodecyl alcohol. Time of esterification was only 1.75 hours, however, and the work-up included permanganation at 70-80°. The dehydrated ester, 909 g. (94.2%), was filtered through Attapulugus earth as a medium-yellow oil. The properties are listed in the table at the end of this section.

c. Di-(Sterox AH) Succinate (MW = 1143.5)



Sterox AH is one of a series of compounds prepared at Anniston by alkylation of n-tridecanol with ethylene oxide, Sterox AH having an average molecular formula of $C_{13}H_{27}(OCH_2CH_2)_{7.5}OH$. It was of interest to prepare the succinate of this compound for screening as a functional fluid.

This succinate was prepared by alcoholysis of ethyl succinate by either basic or acidic catalysis. When Sterox AH and an equivalent amount of ethyl succinate were heated at 100-110° under reduced pressure without a catalyst no alcoholysis took place. When 0.6% of sodium methoxide was added and heating resumed under reduced pressure alcohol was evolved; the reaction mixture was maintained at 100-110° (15 mm.) overnight, its total loss in weight being equivalent to a 95% evaluation of ethanol. Carbon dioxide was then bubbled into the reaction mixture at room temperature for 2 hours. Volatiles were removed by heating for 3 hours at

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100-110° (15 mm.), and the product (quantitative yield) was filtered through a Buchner funnel. Properties of this Sterox AH succinate are given in the table at the end of this section.

When 3% of p-toluenesulfonic acid was used as the catalyst an 87% of the theoretical alcohol was evolved at 100-110° (40 mm.) over a period of 36 hours. The crude ester was washed at 50-60° with an equal volume of a solution of sodium carbonate and salt. Four layers were obtained, of which the lower two apparently aqueous layers were discarded. The organic layers were stirred with another volume of more dilute salt solution at 50-60° and the slight middle layer was discarded with the aqueous layer. The organic layer was washed once again with salt solution, dehydrated at 100° (10 mm.) and filtered. A 61.1% yield of Sterox AH succinate was thus obtained; its properties are listed below.

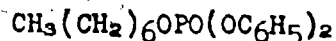
	Di-isodecyl succinate	Di-tridecyl succinate	Di-(Sterox AH) Succinate (by NaOMe catalysis)	Succinate (by TsOH catalysis)
Viscosity, cs., 210°F.	3.21	5.17	15.13	13.07
130°F.	8.09	15.99	---	---
100°F.	13.46	30.18	98.79	78.78
-40°F.	5650	>20000	---	---
-65°F.	---	---	---	---
Viscosity Index	+117	+112	+138	+143
Acidity, NN	0.03	0.18	0.13	0.50
Sp. gr., 25/25°C.	0.9201	0.9123	1.0224	1.0152
n _D ²⁵	1.4477	1.4545	---	---
Pour Point	-60°F.	-45°F.	+55°F.	+15°F.
Color	lt. yellow	lt. yellow	dark red	dark red

4. Phosphate Esters

Raw Materials Used:

1. Phosphorus oxychloride	#244
2. n-Heptanol	Eastman Kodak
3. "Alphanol 79"	Shell Chem. Co. Ltd.
4. Phenol	USP Monsanto
5. Plant lye	#229
6. Potassium permanganate	#518
7. Sodium metabisulfite	#522
8. Sulfuric acid	#213
9. Norit	#663
10. Attapulugus earth	#608

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a. n-Heptyl Diphenyl Phosphate (MW = 348.41)

This compound was made by the Santicizer 141 Tentative Process to extend Monsanto's series of alkyl diphenyl phosphates. The yield of unpurified, slightly yellow n-heptyl diphenyl phosphate was 87.4%. Its properties are listed in the table at the end of this section.

b. "Alphanol 79" Diphenyl Phosphate (MW = 359.2)

Late in 1952 there became available from Shell Chemical Co. Ltd., a supply of mixed C₇, C₈ and C₉ primary alcohols designated by the trade name "Alphanol 79". Interest in this alcohol prompted preliminary process studies and sample preparations. Among the esters prepared and tested as plasticizers and functional fluids was "Alphanol 79" diphenyl phosphate.

This compound was prepared according to the Santicizer 141 Tentative Process in 84% yield. The properties of this light yellow fluid are tabulated below.

	n-Heptyl Diphenyl Phosphate	"Alphanol 79" Diphenyl Phosphate
Viscosity, cs., 210°F.	2.32	2.52
130°F.	----	6.09
100°F.	8.72	9.73
-40°F.	2120.	3710.
-65°F.	----	----
Viscosity Index	+ 84	+ 93
Acidity, NN	0.06	0.16
Sp.gr., 25/25°C.	1.0978	1.0936
n _D ²⁵	1.5086	1.5082
Pour Point	----	- 70°F.

5. Adipate Esters

Raw Materials Used:

1. Adipic acid	duPont
2. Ethoxy dethoxy propanol	Carbide and Carbon
3. p-Toluenesulfonic acid	
4. Sodium carbonate	#512
5. Norit	#563
6. Attapulgus earth	#508

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a. Di-(ethoxyethoxypropyl) Adipate (MW = 430)



Ethoxy ethoxy propanol, presumably prepared by interaction of Ethyl Cellosolve and propylene oxide has recently come on the market. The average molecular weight (160) of the commercial product indicates some higher molecular weight impurities, probably mainly ethoxy ethoxy propoxy propanol. It was of interest to examine derivatives of this relatively cheap new alcohol with regard to their utility as plasticizers and/or functional fluids. To this end the adipate ester was prepared and screened to these uses.

Adipic acid (1 mole) and ethoxyethoxypropanol (Carbide and Carbon) (2.25 mole, calculated on the basis of an average molecular weight of 160 for this alcohol) were stirred and heated at 100-120° under vacuum in the presence of a catalytic amount of p-toluenesulfonic acid. After twenty hours, titration of an aliquot of the reaction mixture indicated that esterification had taken place with only 90% of the original carboxylic acid groups; therefore, another 0.25 mole of ethoxyethoxypropanol was added to the reaction mixture and the reaction was continued for another eighteen hours at 110-120°. At this point titration of an aliquot indicated that 97% of the original carboxylic groups had been esterified. The mixture was then washed with sodium carbonate solution and twice with water, all at 50-60°, and was then steamed at 105-110° until five volumes of distillate had been collected. After another wash with carbonate solution and two washes with water, the batch was dehydrated at 100-110° (10 mm.), stirred with 1% each of Norit and Attapulugus earth, and filtered through Attapulugus earth. The yield and properties of this di(ethoxyethoxypropyl) adipate are as follows:

Yield	97%
Color	yellow
n_D^{25}	1.4420
Specific Gravity, 25/25°	1.0238
Acidity, NN	0.04
Viscosity (cP), 210°F.	3.25
100°F.	12.56
40°F.	4059
Viscosity Index	145
Pour Point	70°F.

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Preliminary Screening

Viscosity Index Improvers

A sample of Acrylate VI Improver (A) was received from Dr. Palmer and was part of his Pilot Plant preparation. This material was examined in various functional fluid base stocks. Results are as follows:

Sample	Viscosity in cs.			Viscosity Index
	210°F.	100°F.	-40°F.	
Pydraul Base	3.85	39.80	--	-252
+ 1% A	3.97	44.10	--	-285
+ 3% A	5.45	54.56	--	- 19
+ 5% A	6.81	63.47	--	+ 53
+10% A	11.07	101.3	--	+102
2-Ethylhexyl diphenyl phosphate	2.45	9.68	5804	+ 78
+ 5% A	4.10	16.46	25000	+174
Dibutyl phenyl phosphate	1.44	4.17	194	--
+ 5% A	2.47	6.95	Sepr.	+190
+10% A	3.96	11.37	Sepr.	+244
Tetraoctyl silicate	2.28	6.75	235	+164
+ 5% A	3.36	9.80	373	+222

These data indicate that the Acrylate VI Improver functions satisfactorily in Pydraul Base (a 50:50 mixture of Aroclor 1248 and tricresyl phosphate) and in tetraoctyl silicate resulting in the expected increase in viscosity and in viscosity index. In the only example of alkyl diaryl phosphate studied, the viscosity index is improved but an unusually high viscosity was found at -40°F. With the example of dialkyl aryl phosphate studied, actual separation of polymer occurred at -40°F. It appears that this VI improver may have value as a replacement for Santodex in Pydraul F9 and further work is planned.

Work at Central Research by Dr. Joseph Fields has resulted in three variations of 2-ethylhexyl acrylate/ethyl acrylate copolymers for use as viscosity index improvers in dibutyl phenyl phosphate to prepare Skydrol 500 type fluids. Samples of the polymer solutions, which were labeled J-1072, J-1073, and J-1074 and a sample of Acryloid R3876X, the regularly used VI improver for Skydrol 500, were dissolved in dibutyl phenyl phosphate so that the viscosity of the solution was about four centistokes at 210°F. The viscosity data are as follows:

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Sample	Viscosity, in cs.				V.I.
	210°F.	100°F.	-40°F.	-65°F.	
Dibutyl phenyl phosphate					
+ Acryloid R3876X	4.03	11.85	501	2640	241
+ J-1072	4.01	11.88	507	1870	239
+ J-1073	4.03	11.67	470	1800	243
+ J-1074	4.06	11.53	426	1720	265

All three samples from Dr. Fields were soluble at -65°F. and gave good viscosity index improvement. Shear stability is a very important characteristic of this type material and was determined. These samples and the base stock, dibutyl phenyl phosphate, were put through the G.M.-71 Diesel Injector Shear Test by Dr. Palmer's group and samples taken after five and ten passes were returned to us for analysis. The data are as follows:

Sample	No. of passes	Viscosity, cs.				VI	% loss of VI
		210°F.	100°F.	-40°F.	-65°F.		
Dibutyl phenyl phosphate (FH87)	0	1.45	4.18	---	---	89	----
	5	1.46	4.18	---	---	---	----
	10	1.46	4.18	---	---	---	----
FH87 + Acryloid R3876X	0	4.03	11.85	501	2640	241	----
	5	3.44	10.18	---	----	221	13.2
	10	3.31	9.79	500	2220	217	15.8
FH87 + J-1072	0	4.01	11.88	507	1870	239	----
	5	3.33	9.88	---	----	217	14.7
	10	3.17	9.44	495	1810	209	20.0
FH87 + J-1073	0	4.03	11.67	470	1800	243	----
	5	3.07	8.98	---	----	209	22.1
	10	2.89	8.52	426	1540	200	27.9
FH87 + J-1074	0	4.06	11.53	426	1720	265	----
	5	2.88	8.38	---	----	202	35.8
	10	2.72	7.97	379	1390	192	41.5

The % loss in VI was calculated as the decrease in viscosity index improvement caused by shear. It appears that the copolymer designated J-1072 is somewhat similar in shear characteristics to the Acryloid R3876X showing slightly more shear after both 5 and 10 passes. Both J-1073 and J-1074 are much less shear stable. The viscosity of the J-1072 blend at -65°F. is considerably lower than that of the R3876X blend.

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2. Base Stocks

During the period covered by this report, a number of liquids were submitted by other groups for screening as functional fluid base stocks. The results of the preliminary screening given these materials are summarized in the following paragraphs.

A sample of butyl 9 (10) carbobutoxystearate was submitted by Central Research for evaluation as a functional fluid. The data obtained are as follows:

Viscosity, 210°F.	3.72 cs.
130°F.	9.42 cs.
100°F.	15.14 cs.
Viscosity Index	+155
Specific Gravity, 25°/25°C.	0.9093
Flash Point	520°F.
Fire Point	520°F.
Pour Point	+35°F.

This material has low volatility and satisfactorily high flash and fire points. The viscosity index is excellent but the product is deficient in low temperature properties for most uses.

A sample of "hydrogenated toluene pyrolysate" was examined for the Phosphate Division. The viscosities were 1.47 cs. at 210°F., 2.92 cs. at 130°F., 4.14 cs. at 100°F., 348 cs. at -40°F., and 3730 cs. at -65°F. The flash point was 240°F. and the fire point was 250°F. These data indicated that the product would be of value merely as a base for petroleum type fluids and offers no advantages in either flammability or viscosity.

Several samples of derivatives of unsaturated fatty acids (UFA) which had been prepared at Dayton were examined for pour point properties. Results are as follows:

<u>Compound</u>	<u>Lot No.</u>	<u>Pour Point</u>
N,N-Dibutyl UFA amide	J-609	-50°F.
N,N-Dimethyl epoxy UFA amide	J-456	+55°F.
2-Ethylhexyl epoxy UFA	J-455	-10°F.
Butyl ester of UFA + approx. 1 mole butyl fumarate	J-510	-45°F.
Butyl ester of UFA + approx. 1 mole butyl fumarate	J-511	-40°F.

These relatively high pour points indicate that these products would have little use as functional fluids for low temperature applications.

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Five esters from Dayton were preliminarily screened for functional fluids use. The data are as follows:

Sample No.	J-843	J-844	J-863	J-1436	J-1256
Viscosity, cs,					
210°F.	8.99	21.23	3.52	2.58	1.13
100°F.	17.45	150.4	16.46	8.44	2.85
-40°F.	Solid	Solid	9140	Solid	72
-65°F.	--	--	--	--	270
Viscosity index	200	136	101	153	99
Sp.gr., 25/25°C.	1.034	0.919	0.893	0.886	0.886
Flash point, °F.	395	395	320	395	285
Fire point, °F.	455	450	355	465	300

These samples may be identified as follows: J-843 is di(2-ethylhexyl)- α,α -diphenylglutarate, J-844 is tri-decyl tridecyloxypropionate (crude), J-863 is tridecyl tridecyloxypropionate (distilled), J-1436 is n-decyl β -n-decyloxypropionate, and J-1256 is 2-ethylhexyl β -trimethylsilylpropionate. The first four materials are deficient in low temperature properties. However, because of their high viscosity indexes, work will be done to determine high temperature stability. Further testing is also planned for the silylpropionate.

A number of samples received from Central Research and the Phosphate Division were examined. The data are as tabulated in the table on the following page.

In general, these products, except for the trimethyl-adipate ester and the nonyl β -nonyloxypropionate, do not exhibit properties that make them of interest as functional fluids, particularly because of low temperature characteristics. The two compounds mentioned will be further examined. The unusually high flash and fire points of the silicon fluoride derivative are of interest.

Five samples were preliminary screened as functional fluids. The data are as follows:

Sample No.	N-26	N-27	N-28	N-38	J-1706
Viscosity, cs., 210°F.	2.41	2.13	1.48	1.05	9.56
100°F.	9.71	8.08	4.48	2.38	107.6
-40°F.	1500	1160	320	Solid	Solid
-65°F.	8800	8350	1710	Solid	Solid
Viscosity Index	+66	+60	+37	+133	+64
Sp. Gr., 25/25°C.	0.908	1.151	1.029	1.020	0.867
Flash Point, °F.	390	385	325	265	400
Fire Point, °F.	490	490	435	320	515
Boiling Point, °F.	410	410	350	310	425

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Material	Lot. No.	Viscosity, cs.		VI	Sp. Gr. 25/25°C.	Pour Pt. °P.	Flash Pt. °P.	Fire Pt. °P.
		210°F. 100 P.	ca. -40°F.					
2-Ethylhexyl trimethyladipate	J-1274	2.82	11.71	3500	92	-70		
Nonyl-β-nonyloxypropionate	J-1055	2.38	7.80	820	179	-80	340	585
Pentaerythritol-tetra-2-carbutoxyethyl-ether	H-1206	9.04	0.9	Too thick	127	-50	385	415
Di(2-ethylhexyl)β-carbo-(2-ethylhexoxy)ethanephosphorate	J-767	10.00	71.1	Too thick	125	-55	315	445
Trl(dodecyl-tridecyl)triethylfluoride	J-834	5.21	22.0	Solid	107	38	525	585
Bisphenyl benzylphosphonate	J-791	1.78	0.42	Solid	37	0		
Tricetyl thionophosphate	52-12-6	0.04	1.23				250	290
Hexamethyl phosphoramide	53-13-53	1.10	2.74				295	380

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Samples N-26, N-27, N-28, and N-38 were submitted from Anniston and sample J-1706 from Central Research. The identity of these materials is as follows:

N-26 bis(2-ethylhexyl)2-ethylhexanephosphonate
 N-27 tetraethyl ethane-1,2-diphosphonate
 N-28 dibutyl α -acetoxvethanephosphonate
 N-38 bis(dimethylamido)methanephosphonate
 J-1706 di(tridecyl)tridecanote, the high boiler from the Guerbet reaction on tridecyl alcohol.

Samples N-26, N-27, and N-28 have sufficiently interesting properties to warrant stability testing. This will be done. Sample N-38 is deficient in low temperature properties and no further studies are planned. Sample J-1706 is deficient in low temperature properties. However, such a viscous fluid may be of value for high temperature work. Stability studies will be carried on when further quantities of sample are obtained.

Preliminary screening data were completed for a number of samples submitted by Central Research personnel. The data are given in the following table (see next page):

The identity of the samples are as follows:

K-141 n-Butyl β -n-butoxypropionate
 K-142 Tridecyl β -tridecyloxypropionate
 K-149 2-Butyl-2-ethylpropanediol-1,3-dilaurate
 K-150 2-Butyl-2-ethylpropanediol-1,3-dipelargonate
 K-151 Ester Mixture (esterification of 2-butyl-2-ethylpropanediol-1,3 with lauric and pelargonic acids).
 K-152 2,2-Dimethylpropanediol-1,3-pelargonate laurate.
 K-153 Ester Mixture (esterification of 2,2-dimethylpropanediol-1,3 with pelargonic and lauric acids).
 K-384 Nonyl β -tridecyloxypropionate
 K-385 Decyl β -decyloxypropionate
 K-386 2-Ethylhexyl β -tridecylpropionate
 K-387 Decyl β -nonyloxypropionate
 J-1711 1,4-Bis(2-ethylhexoxy)-2,3,5,6-tetrachlorobenzene
 J-1713 1,2,4-Tri(2-ethylhexoxy)-3,5,6-trichlorobenzene
 J-1712 Mixture of compounds in J-1711 and J-1713
 J-1714 1,4-Bis(2-ethylhexoxy)octachlorobiphenyl
 J-1715 1,4-Bis(2-ethylhexoxy)X,X,X,X-tetrachlorobiphenyl

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Test	Viscosity, ss. 210°F. 100°F. -40°F.	Viscosity -65°F.	Viscosity Index	Specific Gravity 25/25	Flash Point °F.	Fire Point °F.	Pour Point °F.
1-1711	0.89	1.94	25.1	72	220	245	---
1-1712	1.04	19.41	11700	---	430	500	-70°
1-1713	4.75	22.66	Solid	Solid	460	535	-5° (crystals -10)
1-1714	3.34	14.42	2400	18000	430	490	---
1-1715	4.14	18.91	Solid	Solid	455	515	-20° (crystals -25)
1-1716	3.34	12.76	Solid	Solid	440	505	+5° (crystals +0)
1-1717	3.33	12.58	Solid	Solid	535	480	+5° (crystals +0)
1-1718	3.20	13.05	4200	too high to run	---	---	---
1-1719	2.43	8.58	1400	9300	---	---	---
1-1720	2.48	9.18	1600	13300	---	---	---
1-1721	2.43	8.30	1190	10500	---	---	---
1-1722	5.02	47.87	---	---	355	505	-35
1-1723	7.70	80.9	---	---	480	545	-40
1-1724	9.75	110.6	---	---	475	555	-45
1-1725	108.9	19200	---	---	560	630	---
1-1726	27.36	1420	---	---	510	625	+30

70.

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The general class of alkoxypropionates have been previously examined. (Samples K-141, K-142, and K-384 through K-387). The n-butyl β -n-butoxypropionate is too volatile for most fluid uses. All these alkoxypropionates are somewhat deficient in low temperature properties (K-384 through K-387). However, the mixed esters are better in this characteristic than the symmetrical esters previously examined. The most important consideration is the thermal stability of these esters. This will be determined at a future date.

The series of diol esters (K-149 through K-153) are deficient in low temperature properties. However, it is expected that these esters may have unusual thermal stability. This will be studied at a future date.

The chlorine containing aromatic ethers (J-1711 through J-1715) are interesting having fair viscosity properties (especially J-1711, J-1712, and J-1713) and lower pour points as compared to the Aroclors. Such products may be of value in certain industrial applications. However, stability to heat and corrosive action must be determined. Preliminary tests have shown little breakdown of J-1712 or J-1715 at 350°F. for 75 hours. Further tests will be conducted.

Data on viscosity and cloud points on a series of organic phosphorus compounds were requested by Dr. Chadwick. The results are as follows:

Compound	Viscosity, cs.		Viscosity Index	Cloud Point, °F.
	210°F.	100°F.		
$\text{CH}_3\text{PO}/\text{N}(\text{CH}_3)_2/2$	1.05	2.38	133	--
$(\text{CH}_3\text{O})_2\text{POH}$	0.53	0.92	163	Below -70
$\text{CH}_3\text{PO}(\text{OCH}_3)_2$	0.66	1.40	90	Below -70
$\text{CH}_3\text{PO}/\text{OCH}(\text{CH}_3)_2/2$	0.70	1.48	102	Below -70
$\text{C}_4\text{H}_9\text{PO}(\text{OC}_4\text{H}_9)_2$	1.10	2.87	78	Below -70
$\text{CH}_2=\text{CHPO}(\text{OCH}_2\text{CH}_2\text{Cl})_2$	2.20	8.26	72	Below -70

Viscosity data were requested by an operating department on 2-ethylhexanol. The data determined are as follows: 1.15 cs. at 210°F., 5.56 cs. at 100°F. and 960 cs. at -40°F.

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L. Miscellaneous Investigations

1. Tricresyl Phosphate

In connection with an inquiry from the Development Department, it was found that 0.05% (by volume) tricresyl phosphate (TCP) will not dissolve in a 1:1, methanol:water solution at 25°C.

Attempts to prepare the requested solution by dissolving the TCP first in methanol and then adding the required amount of water, under otherwise identical conditions, proved unsuccessful.

The solubility of triphenyl phosphate (TPP) in tricresyl phosphate (TCP) was examined in an attempt to elucidate the composition of cresyl diphenyl phosphate (Santicizer 140). Samples containing 10, 20, 30, 40, and 50 weight percent TTP in TCP were prepared. Seeded samples at room temperature indicated that about 30% is saturation concentration at about 25°C. At 5°C. considerable material separated from the 30% solution while none separated from the 20% solution of TTP in TCP. Santicizer 140 separates into a solid and a liquid phase on cooling, the solid phase having been identified by the Analytical Laboratory as triphenyl phosphate. Our data merely indicate that TTP is quite soluble in TCP and do not indicate the amount present in Santicizer 140 since the solubility of TTP in all triaryl phosphates possible in Santicizer 140 is not known.

The heat stability of tricresyl phosphate (A-11) was studied. Previous work had shown that in 24 hours, A-11 developed acidity equivalent to 7 ml. N/2 NaOH at 150°C. and 26 ml. N/2 NaOH at 175°C. per mole of ester charged. The present work indicated that the acidity developed at 200°C. in 24 hours was equivalent to 38 ml. N/2 NaOH per mole of ester. It was also found that 316 stainless steel was discolored but was not corroded by tricresyl phosphate at 200°C. (after 24 hours exposure). The A-11 darkened appreciably in the absence and presence of stainless steel.

2. Phosphate Ester-Diester Blends

The Patent Department requested that viscosity data be obtained on certain mixtures in order to present arguments with regard to certain functional fluid patent applications. These data are as follows:

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<u>Sample</u>	<u>Viscosity</u>
1. 50% tricresyl phosphate 50% di(2-ethylhexyl)adipate	12,300 cs. at -40°F.
2. 50% tricresyl phosphate 50% di(2-ethylhexyl)sebacate	17,400 cs. at -40°F.
3. 50% tricresyl phosphate 50% diamyl adipate	3,400 cs. at -40°F.
4. 50% tricresyl phosphate 50% di(n-butyl)adipate	125 cs. at 0°F.
5. 90% tricresyl phosphate 10% diamyl adipate	Solid at -40°F.
6. 95% di(2-ethylhexyl) phenyl phosphate 5% Acryloid HF855	2,880 cs. at -40°F.

M. Physical Measurements Section (Prepared by W. E. Koerner
and O. B. Cecil)

1. Specific Heat

a. Apparatus and Methods

a 1/2 pint narrow-mouth Dewar flask was used as the calorimeter. The energy added to the calorimeter was calculated from observations of the voltage drop across the resistance heater in the calorimeter and the current flowing in the heating circuit for a measured time interval. A six volt storage battery was used as the source of power. The voltage drop across the heater was about five volts, and the current was about one ampere.

A five to seven minute heating period was used. This quantity of heat resulted in a 2.5°C. temperature rise when the calorimeter contained water and a 4 to 5°C. temperature rise when the calorimeter contained a sample of functional fluid. A mercury-in-glass thermometer with 0.2°C. or 0.1°C. divisions was used to measure the temperature. The true temperature rise was determined graphically or by using the average of the rates of temperature change before and after the heating period to apply a correction to the observed temperature rise.

Two experiments at 25°C. using water in the calorimeter were made to determine the heat capacity of the calorimeter. The average of the two experiments, 1.7 calories per °C., was used in subsequent

calculations. The best literature value for the increase in the specific heat of glass with increasing temperature was 0.036% increase per °C. This value was used in calculating the calorimeter heat capacity at temperatures above 25°C. An error of 7% in the heat capacity of the calorimeter will result in an error of only 1% in the specific heat since only about 15% of the total heat input is used to heat the calorimeter itself.

b. Results

A summary of our experimental data is shown in Table 7 below. Each value is the mean of at least two determinations.

TABLE 7

Sample Description	Temperature(°C)	Specific Heat*
OS-40 (composite)	24	0.38
dated 12/3/52	63	0.41
(same as Skydrol 500)	101	0.44
OS-41	24	0.32
dated 10/1/52	61	0.35
	99	0.36
OS-45 (Batch L)	25	0.45
dated 10/1/52	60	0.48
	100	0.54
L-3A	24	0.38
dated 10/6/52	60	0.41
	100	0.42
Pydraul F-9	23	0.31
dated 8/11/53	59	0.33
	107	0.36

*These values are the same as heat capacities measured as cal./g./°C. or Btu/lb./°F.

The experimentally determined specific heats for each fluid were plotted as a function of temperature and the best straight line was drawn through each set of points. The equation for each of these straight lines is shown below:

OS-40: $\text{Specific Heat} = 0.376 + 8.00 \times 10^{-4} t$

OS-41: $\text{Specific Heat} = 0.300 + 8.39 \times 10^{-4} t$

OS-45:

$$\text{Specific Heat} = 0.418 + 1.17 \times 10^{-3} t$$

L-3A:

$$\text{Specific Heat} = 0.382 + 5.05 \times 10^{-4} t$$

Pydraul F-9:

$$\text{Specific Heat} = 0.296 + 6.28 \times 10^{-4} t$$

where t is in $^{\circ}\text{C}$. These equations provide a means for calculating approximate specific heat values outside the range of experimental measurements.

2. Density Variation with Temperature

a. Apparatus and Methods

A Vycor pycnometer was used for the density measurements. Appropriate corrections for the variation in volume of the pycnometer with temperature were made. The temperatures were measured with calibrated thermometers.

b. Results

A summary of the experimental data are shown in Table 8.

TABLE 8

Temperature($^{\circ}\text{C}$.) Density(g./ml.) Volume (ml./g.)

Pydraul F-9 (Lot S-1010) dated 1/29/53

25.0	1.2576	0.7952
60.0	1.2277	0.8146
95.6	1.1972	0.8353
130.8	1.1671	0.8568
164.6	1.1375	0.8791
198.4	1.1074	0.9030

Skydrol 500 (5/20/53) dated 6/11/53

-35.0	1.1104	0.9006
-10.0	1.0805	0.9255
25.0	1.0592	0.9441
50.0	1.0183	0.9821
75.0	0.9777	1.0228

OS-45 (Batch L) dated 6/11/53

-35.0	0.9558	1.0689
-10.0	0.9103	1.0986
25.0	0.8921	1.1210
50.0	0.8566	1.1673

126.3	0.8199	1.2197
177.2	0.7825	1.2780
225.3	0.7474	1.3380

Oronite 250 (dilauryl selenide) 6/22/53

25.0	0.9201	1.0868
120.6	0.8514	1.1745

A straight line resulted when the density of each functional fluid was plotted as a function of temperature. The equations for these straight lines are shown below:

Pydraul F-9:

$$d_t = 1.2796 - 8.64 \times 10^{-4} t$$

Skydrol 500:

$$d_t = 1.0806 - 8.49 \times 10^{-4} t$$

OS-45:

$$d_t = 0.9106 - 7.22 \times 10^{-4} t$$

Oronite 250:

$$d_t = 0.9381 - 7.18 \times 10^{-4} t$$

where d_t is the density in g./ml. at $t^\circ\text{C}$.

Considering OS-45-1 to consist of 99.5% OS-45 and 0.5% Oronite 250 and assuming that the density of the mixture is directly proportional to the percentages of the components, the following equation for OS-45-1 can be calculated:

$$d_t = 0.9107 - 7.22 \times 10^{-4} t$$

3. Electrical Properties

a. Apparatus and Methods

A General Radio megohm bridge was used for the resistivity measurements. The dissipation factor and dielectric constant measurements were made on a General Radio capacitance bridge. The DC resistivity reading was made 60 seconds after the initial application of the measuring voltage to the cell.

b. Results

The results which we obtained are listed below:

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Pydraul F-9 (Lot S-1010) dated 1/29/53

60~ Dissipation Factor 32.9%
 1000~ Dissipation Factor 2.2%
 Specific Resistivity 0.15×10^5 megohm-cm.
 Dielectric Constant(1000~) 6.25

OS-45-1 (dated 6/9/53)

60~ Dissipation Factor 71.8%
 1000~ Dissipation Factor 5.2%
 Specific resistivity 0.20×10^5 megohm-cm.
 Dielectric Constant(1000~) 2.84

Skydrol 500

Specific Resistivity of sample dated 5-20-53
 36 megohm-cm.
 Specific Resistivity of sample dated 7-22-53
 46 megohm-cm.

The very low resistivity of Skydrol 500 prompted us to measure the electrical properties of the base stock for this functional fluid and several other alkyl-aryl phosphates. Our results are summarized in Table 9 below.

TABLE 9

<u>Sample Description</u>	<u>Specific Resistivity (megohm-cm.)</u>
Dibutyl phenyl phosphate (Skydrol 500 base)	25
Dibutyl phenyl phosphate (from PCl_3 NBP A-41472)	152
Tri-2-ethylhexyl phosphate (Flexol TOF)	1520
Di-2-ethylhexyl phenyl phosphate	92
2-Ethylhexyl n-butyl phenyl phosphate	911
Tricresyl phosphate	1000 to 10000

The values for TCP are those of Will and Hewitt determined in 1951. The data above suggest that very low resistivities are not an inherent characteristic of alkyl-aryl phosphates.

DSW 620702

4. Thermal Conductivity

a. Apparatus and Methods

Thermal conductivity measurements were made utilizing a method and an adaptation of a cell described by Hutchinson in the 1945 Transactions of the Faraday Society (p. 87). The cell used in making the earlier measurements consisted essentially of a Pyrex tube with a coiled tungsten filament located at the axis of the tube. The experimental technique consisted of filling the cell with the liquid in question and passing a measured current through the filament while the entire cell was immersed in a thermostat. The filament was also utilized as one arm in a Wheatstone bridge in which the filament heating current also served as the bridge current. This measurement of the resistance combined with the current measurement enabled one to calculate the heat dissipation in the filament, and from previous calibration of the resistance value could be used to calculate the temperature of the filament. A knowledge of the thermostat temperature permitted a value for ΔT to be obtained. These values are all related to the thermal conductivity of the liquid in the cell by the following equation:

$$\frac{\Delta T}{Q} = \frac{A}{K} + B$$

where:

ΔT = $T_{\text{filament}} - T_{\text{thermostat}}$ in $^{\circ}\text{C}$.
 Q = heat dissipated in the filament in calories/sec.
 K = thermal conductivity of the liquid in the cell measured in cal./cm. $^{\circ}\text{C}$. sec.

A and B = constants depending on the geometry of the apparatus and the thermal conductivity of Pyrex glass.

Because of the geometry of the cell, it was not feasible to attempt to calculate the constants A and B , but rather to "calibrate" the cell by measuring two liquids whose thermal conductivity was known. The results of these determinations resulted in two simultaneous equations which permitted the evaluation of the constants. Water and carbon tetrachloride were utilized as the two liquids.

However, closer examination of the literature existing on the thermal conductivities of liquids revealed a rather large spread in the values for some liquids and even a major discrepancy in one of the liquids used as one of our calibration liquids. This led us to design and use a new type cell. Whereas the former cell used a coiled tungsten filament, the new cell used a straight wire platinum filament. Another added feature was a four-lead type of arrangement designed to eliminate end effects. These improvements enabled the direct calculation of the cell constants A and B. Using these calculated constants, several liquids whose thermal conductivities have been reported in the literature were measured. Table 10 shows the agreement between our values and the literature values.

TABLE 10

Material	K X 10 ⁵ (cal/°C. cm. sec.)			
	Observed (25°C.)	Literature		
		Value	t (°C.)	Source
H ₂ O	148	143	20	Riedel
CH ₃ OH	50.5	50.3	30	Bridgman
CHCl ₃	32.0	33.0	12	ICT (Weber)
C ₂ H ₅ Br	23.6	28.6	30	Bridgman
CCl ₄	25.2	24.6	20	Riedel
		26.3	0	ICT (Goldschmidt)
		38.0	20	Bates

The dimensions of the cell and the calculation of the constants A and B are given below: The complete equation relating the measured values and the thermal conductivity is:

$$\frac{\Delta T}{Q} = \frac{1}{2\pi l K_1} \ln \frac{r_2}{r_1} + \frac{1}{2\pi l K_2} \ln \frac{r_3}{r_2}$$

where:

K_1 = thermal conductivity of liquid in the cell measured in cal./cm. °C. sec.

K_2 = thermal conductivity of glass = 0.002 cal./cm. °C. sec.

l = filament length = 8.45 cm.

r_1 = filament diameter = 0.008 cm.

r_2 = inside tube diameter = 1.07 cm.

r_3 = outside tube diameter = 1.2 cm.

ΔT = $T_{\text{filament}} - T_{\text{thermostat}}$

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$$\text{constant } A = \frac{1}{2\pi l} \ln \frac{r_2}{r_1} = \frac{2.303}{(2)(3.1416)(8.48)} \frac{\log 1.07}{0.0058}$$

$$A = 0.0978 \text{ cm}^{-1}$$

$$\text{constant } B = \frac{1}{2\pi l} \ln \frac{r_2}{r_1} = \frac{2.303}{(2)(3.1416)(8.48)(0.002)}$$

$$\frac{\log 1.26}{1.07}$$

$$B = 1.53 \text{ cm}^{-1}$$

The experimental procedure was the same as that discussed earlier except that the straight wire filament had a much smaller resistance and necessitated the use of a Mueller bridge for the resistance measurements. The thermostatted bath was maintained within $\pm 0.01^\circ\text{C}$. Currents up to 75 milliamperes were used with resulting maximum temperature differentials of approximately 0.5°C . Resistance values of the straight wire filament were determined at various power inputs. The temperatures were determined from a previous calibration of the resistance value of the filament. The slope of the straight line obtained from a plot of temperature of the filament (ordinate) vs. power input (abscissa) gave $\frac{\Delta T}{Q}$ which was used directly to calculate the $\frac{\Delta T}{Q}$ thermal conductivity of the liquid in the cell.

b. Results

Thermal conductivities for six functional fluids and sixteen component materials were measured at two temperatures, 28 and 81°C . The results are given in Table 11, page 81.

The mean deviation from the mean of duplicate runs made on the same sample in the cell was $\pm 0.4\%$ at 28°C . and $\pm 0.7\%$ at 81°C . Greater difficulty in controlling the thermostat temperature at the higher temperature accounted for this difference.

Analysis of the data showed that thermal conductivities of functional fluids could be calculated from the thermal conductivities of their component materials by means of a simple linear relationship as given below:

$$K_f = \frac{V_1}{V} K_1 + \frac{V_2}{V} K_2 + \frac{V_3}{V} K_3 + \dots + \frac{V_n}{V} K_n$$

where: K_f = thermal conductivity of functional fluid

where: K_A = thermal conductivity of component A
 K_B = thermal conductivity of component B

% A = % component A present in F

% B = % component B present in F

Calculated and observed values agree within 3% (see Table 12).

TABLE 11

Substance	$K \times 10^5$ (cal./cm. °C. sec.)*	
	28°C.	81°C.
Skydrol 7000	29.9	29.6
OS-40 (Skydrol 500)	32.1	32.2
OS-41	27.5	27.3
OS-45	33.1	32.9
L-3A	31.6	31.6
Pydraul F-9	27.5	26.6
Aroclor 1248	24.0	23.5
Dioctyl phthalate	32.4	30.1
Dibutyl phthalate	32.5	30.9
2-Ethyl hexyl diphenyl phosphate	31.3	29.9
Isooctyl diphenyl phosphate	30.0	30.7
Tri (2-ethyl hexyl) phosphate	31.2	28.5
Tricresyl phosphate	31.7	31.1
Silester 12	32.9	32.4
Tetraethyl silicate	30.3	34.4
Tetra (2-ethyl hexyl) silicate	31.9	30.7
D1 (2-ethyl hexyl) azelate	35.6	33.6
D1 (2-ethyl hexyl) sebacate	36.0	35.1
Ucon DLB-50	33.0	30.9
Paraplex AF-52	37.2	36.7
Santodex	30.5	30.2
Acryloid HF355	33.6	33.7

TABLE 12

Functional Fluid	$K \times 10^5$ (cal./cm. °C. sec.)					
	28°C.			81°C.		
	obs.	calc.	% error	obs.	calc.	% error
Skydrol	29.9	30.8	+3.0	29.6	30.4	+2.7
OS-41	27.5	27.8	+1.1	27.3	26.8	-1.8
OS-45	33.1	33.4	+0.9	32.9	32.9	0.0
L-3A	31.6	31.2	-1.3	31.6	31.1	-1.6
Pydraul F9	27.5	28.0	+1.8	26.6	27.4	+3.0

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A difficulty in the method appears if one realizes that whenever a new silicate or phosphate ester is employed in preparing a new fluid, the thermal conductivity of that ester must be measured. This difficulty could be alleviated with only a slight decrease in accuracy by assigning values to classes of compounds such as silicate esters, phosphate esters, etc. Using this method results could be calculated to agree within 4% of the observed results (see Table 13).

TABLE 13

Functional Fluid	$K \times 10^5$ (cal./cm. °C. sec.)					
	28°C.			81°C.		
	obs.	calc.	% error	obs.	calc.	% error
Skydrol	29.9	31.1	+4.0	29.6	30.2	+2.0
OS-41	27.5	27.6	+0.4	27.3	27.0	-1.1
OS-45	33.1	32.4	+2.1	32.9	33.0	+0.3
L-3A	31.6	31.8	+0.6	31.6	33.4	+3.8
Pydraul F9	27.5	27.6	+0.4	26.6	26.9	+1.1

Listed below in Table 14 are the values assigned to the different classes studied. Assigned values were average values of all measurements made on various members of a given class. Since little variation between members of a class was observed, it appeared to be desirable to use the data in this form. Exceptions to the above were the viscosity index improvers. A relatively large variation between these compounds was observed and it would appear advisable to use the reported value for each compound. An asterisk denotes classes of which only one compound was measured, but the values are probably representative of the class.

TABLE 14

Substance	$K \times 10^5$ (cal./cm. °C. sec.)	
	28°C.	81°C.
*Aroclors	24.0	23.5
*Azelates	35.6	33.5
Phthalates	32.5	30.5
Phosphates	31.0	30.1
*Sebacates	36.0	35.1
Silicates	31.7	32.5
+Ucon DLB-50	33.0	30.9
+Paraplex AP-52	37.2	36.7
+Santodex	30.5	30.2
+Acrylics H855	33.6	33.7

*Only one compound of class measured, but value probably representative of the class.
 +Should use individual values for additives.

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V. CONCLUSIONS

1. Pydraul F9

Pydraul F9 has found considerable utility as a non-flammable type industrial hydraulic fluid. Principal areas of use have been in the die-casting industry. The field of industrial fire resistant fluids is highly competitive and much of the work was done with the aim of reducing costs and providing data for further uses of the fluid.

In an effort to reduce costs, the effects of increasing the Aroclor to tricresyl phosphate ratio were investigated. Such a change resulted in somewhat higher pour point. Samples were submitted to Douglas for approval and a formulation change was adopted for manufacture which resulted in about one-half cent per pound savings.

The tricresyl phosphate used in Pydraul F9 was always made from coal tar cresols. Increased use of this ester made it desirable to use material made from petroleum cresols or from purchased tricresyl phosphate. No significant differences in physical properties were found in Pydraul F9 made from each of the three types of tricresyl phosphate. Douglas examined these samples for lubricity in the 4-Ball Wear Test and found them to be approximately equivalent. Hence, used alone, each type was approved for Pydraul F9 manufacture.

Two competitive fluids to Pydraul F9 were given a preliminary screening. Lindol HF has properties similar to regular tricresyl phosphate. Houghto Safe 271 is a water based fluid and this is reflected in its properties which in preliminary screening are inferior to those of Pydraul F9. Relative evaporation of Pydraul F9 and Houghto-Safe 271 at room temperature was found to be essentially zero and about 40%, respectively, in 65 days.

A great many properties of Pydraul F9 were determined at the request of various groups. These may be summarized as follows: Skydrol 7000 and Pydraul F9 are compatible to 0°C. or lower. The solubility of water was shown to be small in Pydraul F9 ranging from 0.18% at 75°F. to 0.55% at 210°F. Pydraul F9 is quite hydrolytically stable as demonstrated by the regular "coke bottle" test. Specific heat, variation of density with temperature, electrical properties, and thermal conductivity were determined for Pydraul F9.

The flammability characteristics of Pydraul F9 were studied. Its behavior on spraying into open flames in an incinerator was determined in comparison to mineral oil.

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and a water based fluid. There was no flash back during the test; however, the Pydraul F9 burned in the flames. Pydraul F9 was decidedly better than mineral oil. Pydraul F9's flammability in contact with molten nitrates was examined in iron, porcelain, and nickel crucibles. Using the iron and porcelain crucibles, dropping or spraying Pydraul F9 onto the surface of the molten nitrates did not cause ignition. In the nickel crucible no ignition occurred at low volatilization rates, but at high rates, intermittent combustion occurred.

Several new types of triaryl phosphates were examined as base stocks for Pydraul F9 but none offered any advantage. Several defoamers were screened but were found to be less effective than the presently used silicone.

A number of used Pydraul F9 samples were examined as a sales service to various customers. Evaluations were made based on physical properties as to the usability and condition of the fluid. Also several hydraulic system components were examined for resistance to Pydraul F9.

2. Skydrol 7000

Skydrol 7000 is used as a non-flammable type aircraft hydraulic fluid and is receiving continually widening acceptance. Various properties were determined to aid the sales effort and to learn more about the fluid. Complete compatibility of 25% Skydrol 7000 in aviation gasoline, 10% Skydrol 7000 in Skydrol 500 and 15% MIL-O-5606 mineral oil hydraulic fluid in Skydrol 7000 was found under the conditions studied. Water solubility in Skydrol 7000 was shown to be about 0.5% at 75°F. and 1.75% at 210°F.

The hydrolytic stability of Skydrol 7000 was studied in detail in conjunction with Skydrol 500. In general, the fluid will not pass the military specifications for hydrolytic stability. However, no evidence of hydrolytic instability has ever been reported in actual use.

Several used samples of Skydrol 7000 were examined as a customer service and recommendations made. Thermal conductivity was determined.

3. Skydrol 500

Skydrol 500 was developed in cooperation with the Douglas Aircraft Co. to meet military specification MIL-R-7100 for a non-flammable type aircraft hydraulic fluid. This fluid consists essentially of the base stock, dibutyl phenyl phosphate, and various additives including a

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viscosity index improver and a copper deactivator-inhibitor pair. Considerable effort was expended in testing the various materials for suitability for pilot plant and larger scale production of fluid.

The effectiveness and utility of the copper deactivator-inhibitor pair can only be demonstrated by Oxidation and Corrosion Tests. At first, results obtained by our laboratory and by the Douglas laboratory did not agree. After many runs it was demonstrated that most of the differences were caused by the use of insufficiently dry air. The first copper deactivator proposed by Douglas was unsatisfactory because of insolubility and efforts were made by both groups to find better materials. Our search resulted in no better compounds than the second one proposed by Douglas. This material, ethylene bis tolyl sulfide, is used in the formulation as it now stands. Specifications were proposed for the fluid and large amounts were formulated in the Interim Production facilities and Pilot Plant.

In order that the two Skydrols may be readily identifiable, a search was made for a purple dye for Skydrol 500 (Skydrol 7000 is green). A relatively heat stable purple dye (Alizarine Irisol N) was found and has been adopted for use in Skydrol 500.

The results reported by the Naval Air Experiment Station on a thin film corrosion test at 225°F. using Skydrol 500 indicated rather severe corrosion and a series of tests were run in our laboratory to attempt to check their results. The data from the first series did not show the same results as reported by the Navy, corrosion being less severe. After discussion with Navy personnel, cooperative testing on Skydrol 500 in the thin film corrosion test was continued. Results for a second series of tests indicated that the test is not reproducible, results depending greatly upon the surface condition of the metal test specimens. Comparative tests were run using Skydrol 500, Skydrol 7000, and Hydrolube H-2 at three temperatures. Our results were similar to those obtained by the Navy who also found erratic, non-reproducible test data.

The hydrolytic stability of Skydrol 500 was studied by the "coke bottle" technic since some concern about this property was expressed by potential users. Skydrol 500 does not pass the test (as defined by military specification MIL-F-7100) and is somewhat poorer than Skydrol 7000 which also does not pass the specification. Some questions were raised as to the test method. Studies showed that the amount of water greatly affected the results with regard to copper corrosion, acidity development, and sludge formation. The test appeared to be

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reproducible with a given fluid at a definite water concentration. Overall, the test does not appear to correlate with actual use experience.

The solubility of water in Skydrol 500 was shown to be appreciable, being about 2.2% at 75°F. and 4.1% at 210°F. The specific heat, variation of density with temperature, electrical properties, and thermal conductivity of Skydrol 500 were determined.

4. Fluid OS-41

Fluid OS-41 was previously developed as a high specific gravity fluid for use in torque converters. Since some corrosive action toward iron was reported, an oxidation and corrosion test was run using various additives. In no case was iron corroded. However, the additives reduced attack on copper, magnesium, and cadmium-plated steel. The fluid was hydrolytically stable in the "coke bottle" test. Specific heat and thermal conductivity were determined for Fluid OS-41.

5. Fluid OS-54

A series of fires resulting from leakage in hydraulic power steering systems in automobiles aroused considerable interest in a non-flammable type fluid for this use. Fluid OS-54 was formulated to meet the physical requirements and samples submitted for testing. Such tests for utility in power steering units are continuing.

Fluid OS-54 has properties that appear to make it potentially useable in catapult systems. Fluid in a four-drum quantity was supplied to the Navy for tests after a catapult fire and explosion. These tests are still underway. Since the fluid contains a small amount of oil which is used as a carrier for the viscosity index improver and since performance in the oxygen demand test is borderline, a sample called OS-54-1 of oil-free material was prepared for the Navy.

6. Steam Turbine Lubricants

A definite need exists for a fire resistant steam turbine lubricant. A fluid meeting the physical property specifications was made up from Aroclor 1242 and tricresyl phosphate with various additives (Fluid OS-58). Tests by the Engine Test Laboratory indicated that the fluid passed demulsification tests and with the addition of certain rust inhibitors would pass the rust test specifications. Samples were then prepared and were sent to various interested groups for testing. These tests are not yet complete.

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7. Fluid OS-57

Formulation for a low temperature industrial non-flammable type hydraulic fluid was devised (Fluid OS-57). It is felt that such a fluid is needed to fit into certain applications where the pour point of Hydraul F9 makes the latter inoperable. Two batches were prepared in the Interim Production facilities and the fluid is under test by prospective customers. Thermal stability tests indicated that Fluid OS-57 is similar to Skydrol 7000 in this characteristic and much poorer than Pydraul F9.

8. Miscellaneous Fluids

Physical measurements of specific heat, electrical properties, variation of density with temperature, and thermal conductivity were made on the silicate ester base high temperature fluids (OS-45 and OS-45-1).

Alternate raw materials were examined for use in formulating Fluid L-3A and larger samples prepared for test work by prospective customers.

9. Preliminary Screening

Preliminary screening on many liquids was carried out. These materials were either synthesized in our laboratories or submitted by other groups. Azelates, pinates, succinates, adipates, and phosphates were prepared by our group. Certain of these esters as well as some of the materials submitted by other groups will be given further evaluation.

10. Physical Measurements

The physical properties of specific heat, variation of density with temperature, electrical characteristics, and thermal conductivity were determined for many of the fluids discussed in this report. A method of calculating thermal conductivity of a fluid from the thermal conductivity of the various components was developed and shown to be sufficiently accurate for most work.

VI. APPENDIX

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

117-2507	Tetraalkyl Silicates
117-2509	Functional Fluids - Minor Plant Investigations
1952-53	
117-2510	Functional Fluids - Exploratory Investigations
1952-53	

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117-2633 Sales Service Work -- Functional Fluids
 117-2689 Pilot Plant Investigations and Consultations,
 1954
 117-2690 Exploratory Research for 1954.
 117-2716 Synthetic Lubricants
 117-2720 Adipate and Azelate Esters, Pilot Plant Prepara-
 tion.

The work covered by this report is recorded on the following notebook pages:

A30502, 4, 5, 9, 11-13, 15-23, 25, 26, 29-34, 38, 42-45, (REH)
 47-50
 A-30464, 65, 75, 80-82, 84, 85-89 (REH)
 A32101-06, 08, 18, 19, 21, 23, 25, 31, 37, 38 (LWB)
 A36062 (LWB)
 A48863, 76, 900 (RSM)
 A51001, 32 (RSM)
 A45645, 46, 49, 50 (RSM)
 A37252, 54, 56, 59, 60, 62-3, 66, 69-79, 81-2, 84-90 (REH)
 93-4, 96-300
 A52203-5, 07-12, 14-18, 21-29 (REH)

Specific Heats (WEK, OBC)

A-32670-6
 A-34055-64; 34065-67; 34070-79
 A-41320-28

Densities (WEK, OBC)

A-41251-3
 A-41255
 A-36753-4

Electrical Properties (WEK, OBC)

A-36751
 A-41269-70

Thermal Conductivity (WEK, OBC)

A-32677-82
 A-34094-95, 34097-99
 A-35101, 03-07, 09-19, 21-30, 35-41, 43-46
 A-36866-900
 A-39801-48
 A-41391-06

R. E. Hatton

W. E. Koerner

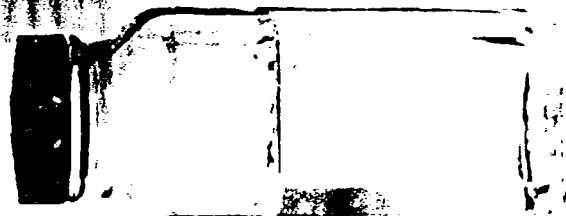
L. J. Eammett

G. B. Lee

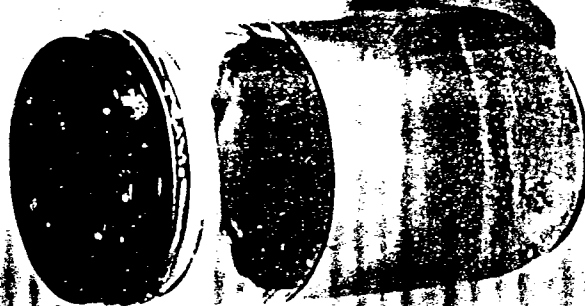
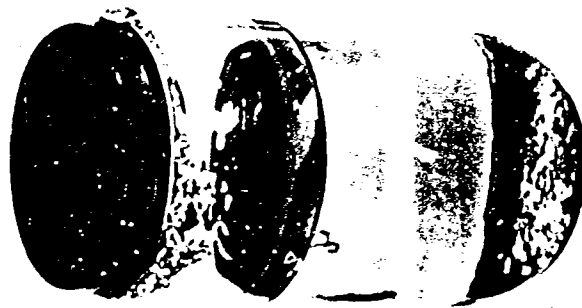
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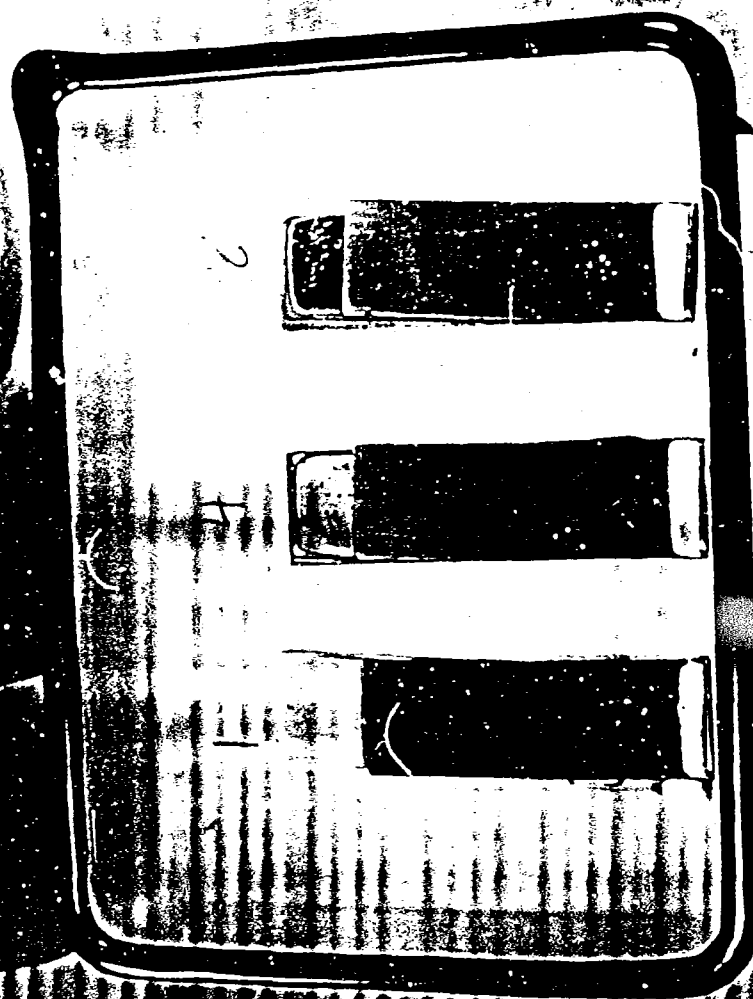
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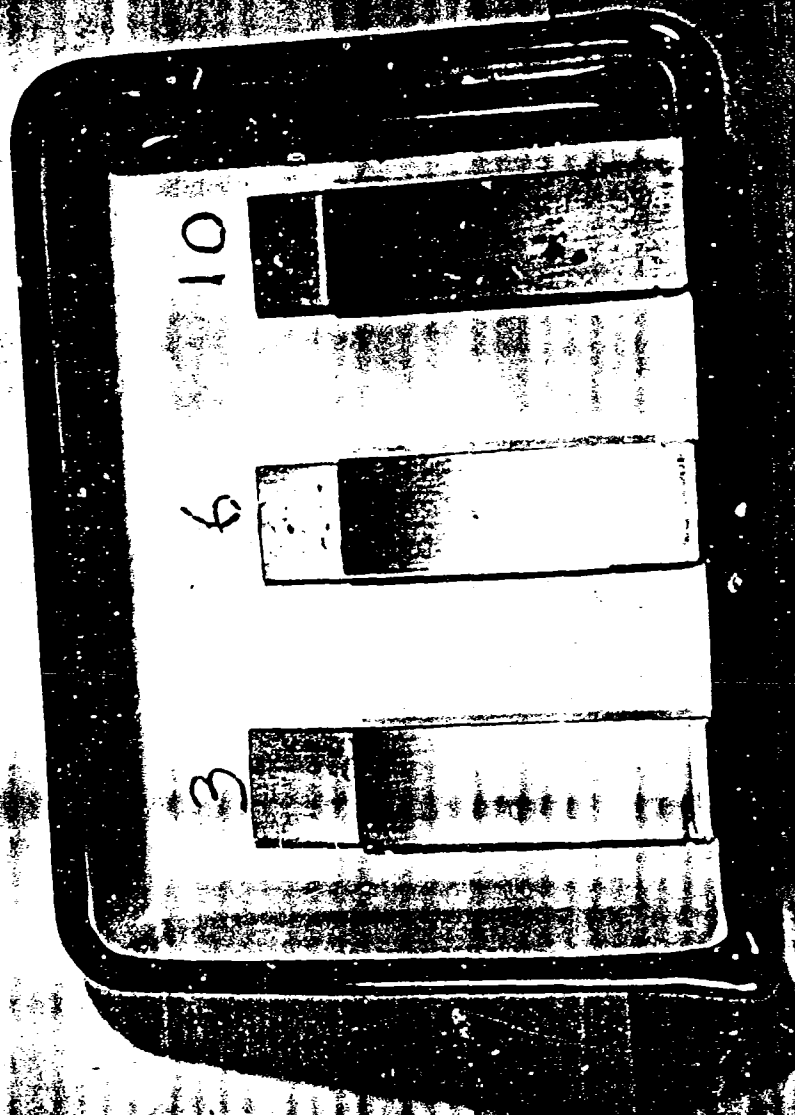
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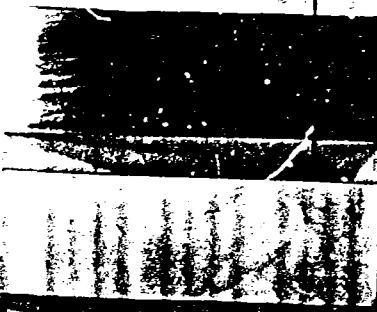
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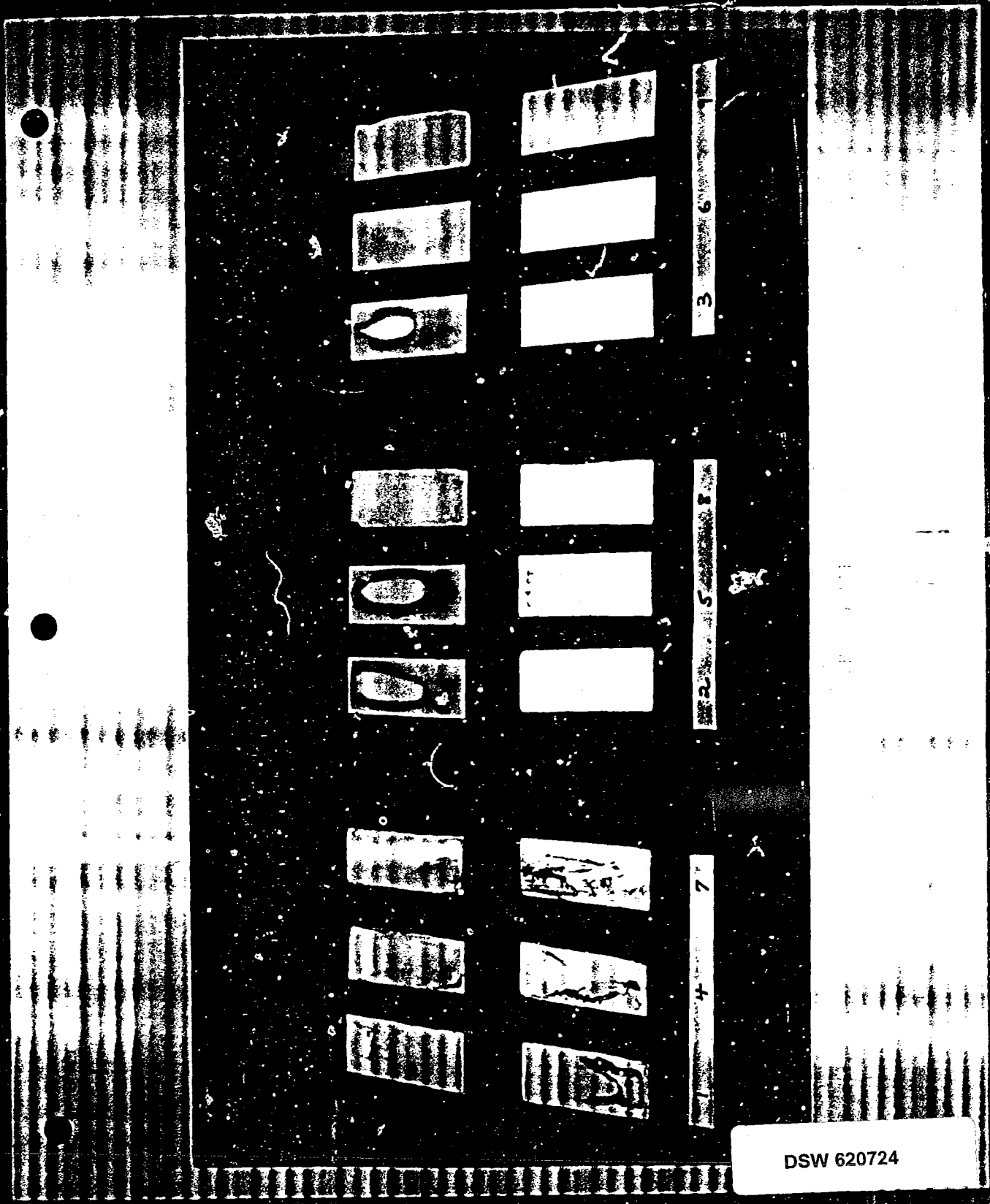


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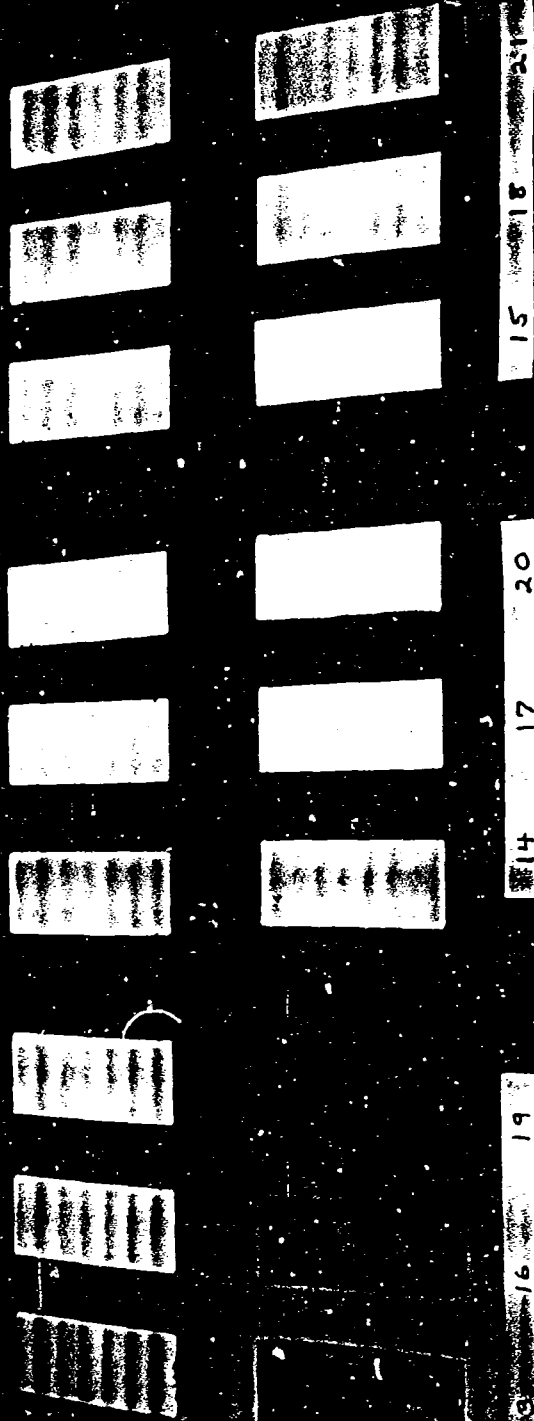
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PHOTOGRAPH 5

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FIRST GRAPH 7

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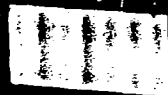
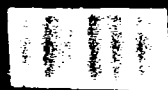
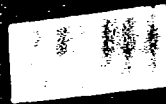


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