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TECHNICAL REPORT

THERMAL STABILITY OF ALIPHATIC DIESTERS

By

R. LeMar

ASTIA

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*R. LeMar*

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Approved by:

*A. C. Hanson*

**A. C. HANSON**  
**Laboratory Director**

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## **ABSTRACT**

The thermal stability of the ethyl and n-butyl diesters of adipic and sebacic acid was evaluated at 475°F under nitrogen in the presence of four metals (in and above the fluid) for several time periods. Di-2-ethylhexyl sebacate was tested for comparison purposes. Changes in several physical and chemical diester properties and metal specimen weights were determined after exposure.

The adipates showed greater stability as regards changes in viscosity, neutralization number and weight of immersed steel specimen than did the sebacates. The reverse was true as regards changes in color, precipitate volume and degree of carbonization. The longer-chain sebacates sublimed large amounts of acidic material onto cooler regions of the test cell. None of the diesters were corrosive to specimens in the gas phase, although staining did occur. None of the diesters were corrosive to immersed copper, aluminum or monel metal during exposure. All were corrosive to immersed steel.

Comparison of these results with results from similar tests on two diesters with steel omitted, show that steel and the diesters have a mutually deleterious effect. Steel caused greater color change, freezing point change, precipitate volume and carbonization. It also appears that adipic acid is more rapidly decomposed than sebacic acid in the presence of dissolved iron salts. Corrosivity tests on these diesters (after thermal exposure) in the presence of air indicated some of them to be corrosive to steel. It was found that these diesters could undergo considerable chemical decomposition with only moderate changes in most of their physical properties in the presence of copper, aluminum and monel metal.

## **RECOMMENDATIONS**

The pure, unstabilized aliphatic adipate or sebacate diester fluids should not be used in high-temperature power transmission systems containing steel.

Common steel (not corrosion resistant) is best avoided for use as a structural material in high temperature power transmission systems where it may come into contact with diester fluid or vapor.

Further evaluation is recommended on other diesters and fluid types. The response of these fluids to stabilizing additives at high temperatures should be evaluated.

# THERMAL STABILITY OF ALIPHATIC DIESTERS

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## THERMAL STABILITY OF ALIPHATIC DIESTERS

### OBJECT

To evaluate a series of straight-chain diesters for their resistance to thermal degradation of a type affecting their use as power transmission fluids.

To evaluate a series of straight-chain diesters for relationships between thermal degradation effects and molecular structure.

### INTRODUCTION

Diester type fluids have proven useful as base materials for formulation of lubricating and power transmission fluids. Military Specifications on such fluids have included physical requirements difficult to meet without use of synthetic compounds (e.g. diesters) for the base fluid. Examples of such specifications are MIL-L-6387A, "Lubricating Oil, Synthetic Base", and MIL-L-25336, "Lubricating Oil, Aircraft Turbine Engine, High Film Strength, Synthetic Base". These specifications require viscosities of 3.0 to 4.5 centistokes minimum at 210°F and 7,500 to 13,000 centistokes maximum at -65°F. Pour points of -75°F maximum and flash points of 350-400°F minimum are also listed.

The versatility of the diester type fluid is shown in the following qualitative description of their characteristics: (1) Good thermal stability, (2) low pour points, (3) good viscosity-temperature slope, (4) low volatility, (5) good lubricity, (6) good response to stabilizing additives, and (7) reasonable cost. The diesters most exploited and evaluated are those made from branched-chain alcohols, e.g., di-2-ethylhexyl sebacate. These are useful because such branching reduces the pour points of these compounds below that of straight chain diesters of similar carbon chain length, thus permitting their use at temperatures as low as -75°F.

Not as much interest or investigation has been found as regards the straight-chain diesters probably because of their higher pour points.

Since diester-type fluids are a versatile and useful base stock especially at low temperatures, it was of interest to explore the relationships between their high temperature stability and their molecular nature. With regard to experimental work on diesters, high temperature tests have generally come to employ the apparatus described by Method 5308.4

of Federal Test Method Standard No. 791 (Corrosiveness and Oxidation Stability of Light Oil, Metal Strips). This method is modified to use an inert gas instead of air. Pressurized bombs have also been used as test containers by some investigators to indicate pressure rise inside the system during high temperature exposure.

In discussion of the pyrolytic breakdown of diesters, Adams and Rice<sup>(1)</sup> have summarized some effects of molecular structure on this process. When the alcohol portion contains B-carbon hydrogens, pyrolysis yields the free acid plus 1-alkenes derived from the alcohol portion. If the alcohol portion contains no B-carbon hydrogens, decomposition proceeds via a free radical process which usually requires a temperature about 100°F higher than that required for the alkene formation. The free dibasic acid from the above decomposition undergoes further breakdown to form a mono-carboxylic acid plus carbon dioxide.

Korshak and Rogozhin<sup>(2)</sup> noted the temperatures at which pure dicarboxylic acids began to liberate large quantities of carbon dioxide and found these values for adipic and sebacic acids to be 580°F and 680°F, respectively. These dibasic acids heat stability increased with length of the carbon chain, however those with an odd number of carbon atoms had somewhat lower decomposition points than the adjacent lower even-numbered homolog. Adams<sup>(3)</sup> evaluated several types of diesters and monoesters. With regard to di-2-ethylhexyl sebacate, it was found in 6 and 20 hour tests at 600°F, that decomposition proceeds at a constant rate. In the presence of metal catalysts, the rate of breakdown increases with test time. Analysis of the gaseous product indicated most of the gas from the noncatalyzed test to be an olefin with a 2-ethylhexyl skeleton. When metal catalysts are present, hydrogen, carbon dioxide, carbon monoxide and hydrocarbon gases are present in addition to the olefin. It is postulated that metals, especially iron, react with the free acid formed by pyrolysis of the ester to form a salt which then undergoes decarboxylation to give carbon dioxide. Thus, tests had indicated that iron present in the system must be first corroded to form diester-soluble salts which then appear to catalyze further diester breakdown. Other tests on isooctyl diesters of adipic and sebacic acid substantially confirmed this hypothesis, although differences were noted in amount and proportions of gases evolved.

In addition, tests were carried out with methyl laurate which confirmed the stabilizing effect to be expected when no B-carbon hydrogen is present in the alcohol portion of the compound. Thus this ester is as stable in the presence of metals at 700°F as the common diesters are at 600°F.

In view of the previously described versatility and value of diester type compounds as base stocks for hydraulic fluids, it was decided to proceed with tests designed to permit analysis of structural effects on thermal stability and to more fully explore a number of factors related to performance of these fluids in hydraulic systems.

## PROCEDURE

### Synopsis

A series of straight-chain diesters and one branched-chain alcohol type diester were exposed to an elevated temperature under nitrogen for two time periods. Metal specimens were located in and above the liquid phase. Tests were carried out in a glass system at atmospheric pressure. Stability of the fluids was evaluated by measuring thermally induced changes in several physical and chemical fluid properties. In addition, the condensate formed on the inner surface of the upper portion of the test cell was examined. After test completion, the thermally degraded diesters were examined for their corrosiveness to several metals.

### Materials Tested

The diesters tested are described in Table I.

TABLE I

### DESCRIPTION OF DIESTERS TESTED

| <u>NAME</u>        | <u>MOLECULAR WEIGHT</u> | <u>SPECIFIC GRAVITY 20/20°C</u> | <u>MOLECULAR STRUCTURE</u>                                                                                                                                                                                                                     |
|--------------------|-------------------------|---------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Diethyl adipate    | 202.24                  | 1.007                           | $  \begin{array}{c}  \text{O} \\  \parallel \\  \text{---} \text{COC}_2\text{H}_5 \\  \diagup \quad \diagdown \\  (\text{CH}_2)_4 \\  \diagdown \quad \diagup \\  \text{---} \text{COC}_2\text{H}_5 \\  \parallel \\  \text{O}  \end{array}  $ |
| Di-n-butyl adipate | 258.35                  | 0.965                           | $  \begin{array}{c}  \text{O} \\  \parallel \\  \text{---} \text{COC}_4\text{H}_9 \\  \diagup \quad \diagdown \\  (\text{CH}_2)_4 \\  \diagdown \quad \diagup \\  \text{---} \text{COC}_4\text{H}_9 \\  \parallel \\  \text{O}  \end{array}  $ |

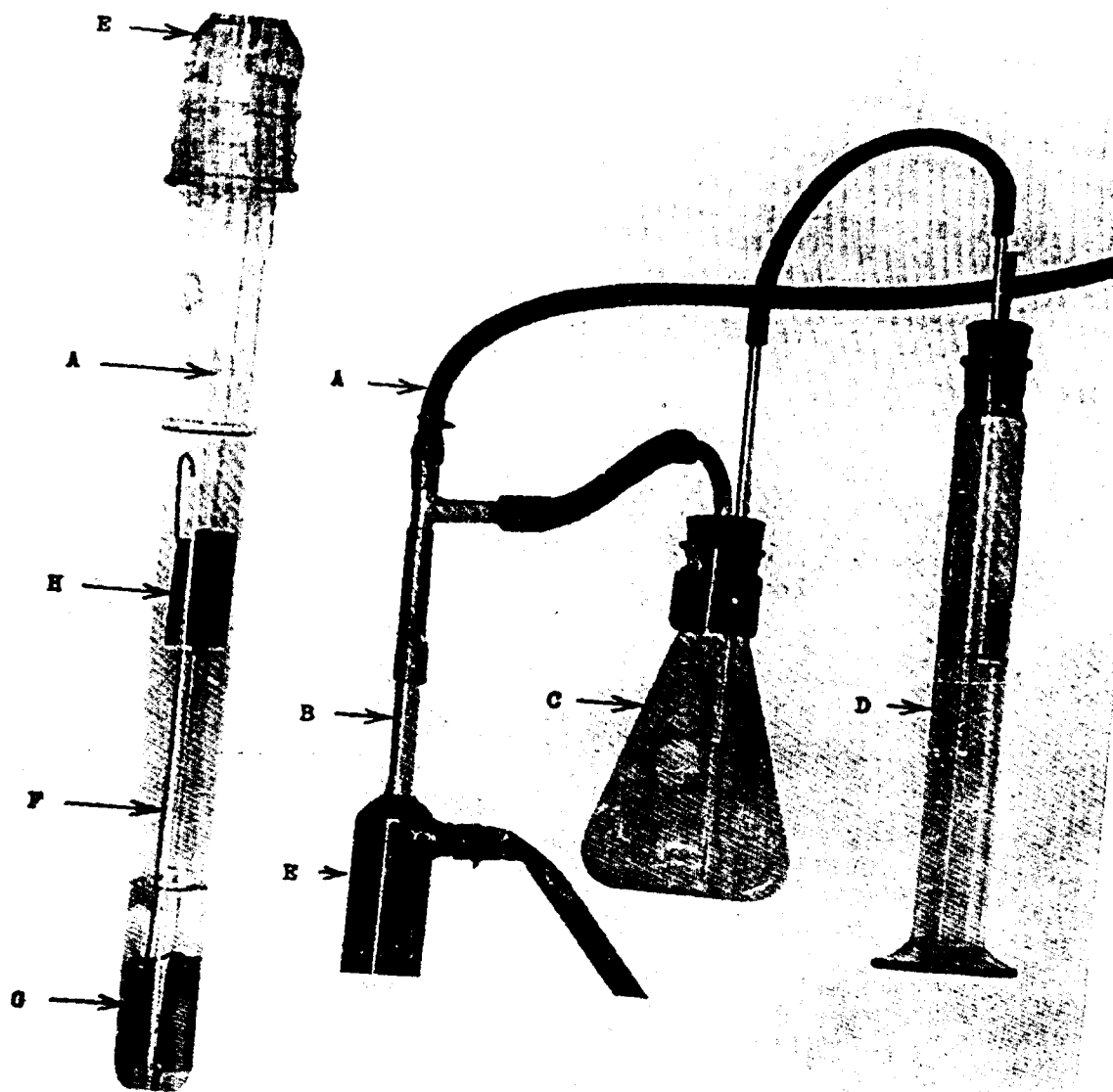
TABLE I (Cont.)

| <u>NAME</u>              | <u>MOLECULAR WEIGHT</u> | <u>SPECIFIC GRAVITY 20/20°C</u> | <u>MOLECULAR STRUCTURE</u> |
|--------------------------|-------------------------|---------------------------------|----------------------------|
| Diethyl sebacate         | 258.35                  | 0.965                           |                            |
| Di-n-butyl sebacate      | 314.45                  | 0.936                           |                            |
| Di-2-ethylhexyl sebacate | 426.66                  | 0.916                           |                            |

#### Apparatus Used

The high temperature bath and test cell apparatus used was basically that described in Federal Test Method Standard No. 791, Method 5308.4, entitled, "Corrosiveness and Oxidation Stability of Light Oils (Metal Strips)". Modifications made in this apparatus are illustrated in Figure 1 and described as follows:

1. Temperature:  $475 \pm 2^\circ\text{F}$ .
2. Nitrogen tube (A): This was used to introduce nitrogen of 99.9% purity into the system. It extended to the bottom of the test tube. A T-connection was attached to the



TEST SYSTEM ASSEMBLY

FIGURE 1

condenser outlet (B). This outlet was sealed around the nitrogen tube thereby causing all of the nitrogen or gaseous decomposition products to pass through the T-connection through a trap (C) to a glass tube (D) immersed in a non-volatile, transparent liquid. The nitrogen inlet pressure could be adjusted so that the internal cell pressure was sufficient to force the column of liquid inside the inlet tube (D) several inches below the liquid level. When nitrogen was being passed through the system for flushing or when the concentration of gaseous diester decomposition products produced excess pressure inside the test cell system, such gases bubbled from the inlet tube tip, up through the column of liquid and into the atmosphere so that unit (D) also served as a pressure relief valve. The use of this device permitted conducting the fluid exposure under a small, positive pressure thus allowing build-up of gaseous decomposition products about the gas phase-metal specimens and assured that air could not accidentally enter the system during exposure.

3. Condenser (E): Cooling water was passed through the condenser at a temperature of 50-60°F.

4. Metal test specimens: The metal specimens, their Federal Specification identifications and dimensions are listed as follows:

Low-carbon steel, F.S. QQ-S-636, (2" x 3/4" x 1/16").

Copper, F.S. QQ-C-501, (2" x 1/2" x 1/16").

Aluminum alloy, F.S. QQ-A-355 (2" x 1/2" x 1/16").

A 1/8" diameter hole was drilled near the 2" edge of each specimen for support on the monel wire rack. The monel metal wire (16" x 1/16") was fashioned so as to form a support (F) for the metal specimens listed above. One set of these three specimens (G) was placed on the monel wire framework so that their top edge was 1/2" below the fluid surface. A second set of the three specimens (H) was placed so that their bottom edge was 4" above the fluid surface.

In some of the 48 hour tests on two diesters the steel specimen was omitted from the test system.

#### Method Used

1. Preparation of metal specimens: The metal specimens and monel metal wire specimen rack were polished with 240 grit silicon carbide paper. Then the specimens were wiped with sterile gauze, placed in boiling VM & P naphtha for 2-3

minutes, allowed to flash dry and immersed in boiling, anhydrous methanol for 5-10 seconds, after which they were stored in a desiccator for 1-2 hours prior to use.

2. Assembly of test apparatus: Each metal specimen and the monel metal wire holder were weighed to within  $\pm 0.1$  mgm. The specimens were suspended on the wire holder and placed in the test tube as specified previously. The test fluid (50.0 ml) was pipetted into the bottom of the test tube which was then fitted with its water condenser, modified as previously shown. The test system was flushed with nitrogen for 5-10 minutes and then placed in a constant temperature block at  $475 \pm 2^\circ\text{F}$  with no nitrogen flowing through the system. After the test fluid had reached test temperature, the test system was again flushed with nitrogen for one minute, and the nitrogen pressure was adjusted to maintain a small, positive pressure within the test system for the duration of the test, i.e., either 24 or 48 hours.

3. Determination of thermal effects: At test end, the test tube and condenser were removed from the high temperature block and the fluid was cooled to room temperature under nitrogen. Thereafter the exposed fluid, residues and metal specimens were evaluated as follows:

A. Exposed fluid: The fluid was removed by pipette from the test tube and centrifuged at a relative centrifugal force of 600 G's for 15 minutes. The clear fluid was decanted from the precipitate and tested as follows:

1. Color, freezing point, viscosity and neutralization number values were determined. These values were compared with corresponding data for the unexposed fluids, which are listed in Table II. The test methods used are also included in Table II.

2. Fluid weight loss was approximated indirectly by comparing the original fluid weight with the total weight of fluid recovered after test, i.e., fluid pipetted from the test cell plus fluid recovered from a methanol rinse of the bottom of the test tube plus fluid removed from the metal specimens in cleaning them.

3. Corrosivity of exposed fluid: Fluids which had been exposed for 48 hours at  $475^\circ\text{F}$  were stored at room temperature under air for 1-2 weeks. They were then tested for their corrosiveness by immersing polished steel, copper and aluminum specimens in the fluid inside a sealed container. The specimens were rated visually after 24 hours of exposure at  $220^\circ\text{F}$ .

TABLE II

UNEXPOSED DIESTER PROPERTIES AND TEST METHOD IDENTIFICATION

| PROPERTY                                     | ASTM<br>METHOD<br>NUMBER | PROPERTIES OF UNEXPOSED DIESTERS |        |           |        |               |
|----------------------------------------------|--------------------------|----------------------------------|--------|-----------|--------|---------------|
|                                              |                          | ADIPATES                         |        | SEBACATES |        |               |
|                                              |                          | ETHYL-                           | BUTYL- | ETHYL-    | BUTYL- | 2-ETHYLHEXYL- |
| Color                                        | D156-53T                 | <1                               | <1     | <1        | 0      | 0             |
| Freezing Pt.,<br>OF                          | *D97-57                  | -15                              | -25    | +30       | +12    | <-90          |
| Viscosity, cs.<br>@100°F                     | D445-60                  | 2.40                             | 3.75   | 4.08      | 6.14   | 12.66         |
|                                              | D445-60                  | 1.01                             | 1.42   | 1.51      | 2.07   | 3.35          |
| Neut. No.<br>(Acid No.),<br>mg KOH<br>per gm | D664-58                  | 0                                | 0.1    | 0.05      | 0      | 0             |
| Precipitate<br>ml/50 ml                      | ** -                     | 0                                | 0      | 0         | 0      | 0             |

\*See Results Section on Freezing Pt. data for further explanation on how Freezing Pt. values were obtained.

\*\*See method in Procedure Section, Part 3a.

## B. Residues and test cell condensates.

1. Precipitates: The amount of precipitate obtained from centrifuging the fluid was observed.

2. Carbonization: Several of the diesters produced black films and deposits on the test tube interior and/or gas phase metal specimens. Their extent was observed and rated.

3. Condensate formed in test cell: After the fluid residue had been removed from the test cell, 25 ml. of methanol was placed in the test tube-condenser assembly. The methanol was refluxed in the system for thirty minutes to dissolve and collect condensed films from the upper part of the test tube and the condenser. The methanol-condensate mixture was removed and the methanol evaporated by heating at 130°F for six hours in a forced draft oven. The weight of this nonvolatile condensate was determined.

4. Acidity of condensate: The acidity of the above condensate was determined by ASTM Method No. D664-58.

C. Metal specimen weight change: The metal specimens and monel metal wire specimen holder were removed and cleaned by consecutive immersion in two beakers of boiling, anhydrous methanol. After cooling, the metals were weighed and their weight changes in terms of mg./cm.<sup>2</sup> of specimen surface area were calculated.

## RESULTS

Table III includes data showing thermally induced changes for the following properties; color, freezing point, viscosity, neutralization number, fluid weight and corrosivity. Comments on each of these items follow:

1. Color: All the materials eventually darkened to a similar level. The adipates, however reacted more rapidly, darkening in 24 hours. The steel specimen catalyzed this phenomena since without it, very little increase in color was noted.

2. Freezing Point: The straight-chain diesters did not show a true pour point in that crystallization (after supercooling) occurred. The frozen mass was removed from the pour point bath and allowed to warm slowly. After melting had started, the thermometer was removed, the melting crystals were stirred to form a liquid-crystal "slurry". The thermometer was reinserted and the lowest temperature reached was recorded as the freezing point.

TABLE III

## THERMALLY-INDUCED EFFECTS ON FLUID PROPERTIES

| PROPERTY                                                           | EXPOSURE<br>TIME<br>(HOURS) | ADIPATE DIESTERS |                |                        |  | SEBACATE DIESTERS |                |                    |                        |
|--------------------------------------------------------------------|-----------------------------|------------------|----------------|------------------------|--|-------------------|----------------|--------------------|------------------------|
|                                                                    |                             | ETHYL-           | BUTYL-         | BUTYL-<br>W/O<br>STEEL |  | ETHYL-            | BUTYL-         | 2-ETHYL-<br>HEXYL- | ETHYL-<br>W/O<br>STEEL |
| Color change                                                       | 24<br>48                    | +8<br>>+8        | +8<br>>+8      | -<br>2                 |  | +5<br>>+8         | +4.5<br>+8     | -<br>+7            | -<br>2                 |
| Freezing Pt.<br>change (°F)                                        | 24<br>48                    | +5<br>+5         | +9<br>+10      | -<br>0                 |  | +2<br>+4          | +1<br>+1       | -<br>none detected | -<br>0                 |
| Viscosity<br>change (%)<br>@100°F                                  | 24<br>48                    | -0.4<br>-0.8     | -1.6<br>-3.2   | -<br>+2.4              |  | +2.5<br>+7.6      | +0.2<br>+5.7   | -<br>-0.6          | -<br>+1.0              |
| Viscosity<br>change (%)<br>@210°F                                  | 24<br>48                    | -0.5<br>-2.0     | -0.7<br>-2.8   | -<br>+2.1              |  | +3.3<br>+6.6      | +1.9<br>+4.8   | -<br>-2.1          | -<br>+4.1              |
| Neut. No.<br>change                                                | 24<br>48                    | +0.39<br>+0.95   | +0.24<br>+0.54 | -<br>+5.48             |  | +2.46<br>+4.70    | +3.30<br>+5.14 | -<br>+3.75         | -<br>4.16              |
| Fluid wt.<br>loss (%)                                              | 24<br>48                    | 4<br>4           | 4<br>5         | -<br>3                 |  | 4<br>4            | 2<br>2         | -<br>3             | -<br>3                 |
| Corrosivity;<br>number of cor-<br>rosion dots<br>on steel<br>panel | 48                          | 24               | 0              | 0                      |  | 10                | 0              | 6                  | 5                      |

The adipates were more affected than the sebacates. No change occurred in the absence of steel.

3. Viscosity: The two straight-chain sebacates consistently showed viscosity increases, whereas the adipates decreased in viscosity. The magnitude of the sebacate change was larger in most cases. The branched-chain alcohol sebacate showed a small viscosity decrease. Both diesters tested without steel displayed viscosity increases.

4. Neutralization Number Change: The sebacates showed larger increases in acidity than did the adipates. However, dibutyl adipate without steel, showed an acid increase similar to that produced in all the 48 hour sebacate tests.

5. Fluid Weight Loss: Estimated weight losses from exposure varied from 2-5%. There is little or no variation between the 24 and 48 hour results. Without steel, weight losses were slightly less.

6. Corrosivity: None of the 48 hour exposed diesters showed any effect on copper and aluminum specimens so this data was not tabulated. Both ethyl diesters caused the formation of very small pits on the steel specimen surface, the number of which is tabulated. The di-2-ethylhexyl sebacate also produced some pitting on the steel specimen. None of the unexposed fluids produced such attack.

Table IV provides information on residues and condensates observed and/or measured at the end of the 24 and 48 hour exposure periods. Comments on each of these items follows:

1. Precipitate: This was the amount of residue observed after centrifuging the exposed fluid sample. The adipates produced larger amounts of such residue than did the sebacates. With steel included, the butyl diesters formed more precipitate than did the corresponding ethyl diesters. It was unexpected that the same amount of precipitate would be found in both the 24 and 48 hour tests for the adipates. Without steel no precipitate was formed.

2. Carbonization: A number of these tests produced black films on the interior of the test cell and on the gas phase specimens. The deposit on the specimens was powdery and easily removable with rubbing, but not by solvent. The film on the glass was not removable with solvent or hydrochloric acid. A hot, concentrated, oxidizing mixture of sulfuric and nitric acid slowly attacked this film indicating it to probably be a combination of carbon and a degraded resin-like product. The amount of such product produced was judged visually by the scale shown at the top of page 13.

TABLE IV

RESIDUES AND TEST CELL CONDENSATES FORMED  
DURING THERMAL EXPOSURE TESTS AT 475°F

| PARAMETER                                             | EX-<br>POSURE<br>TIME<br>(HRS.) | ADIPATE DIESTERS |          |                        |  | SEBACATE DIESTERS |          |                        |                        |
|-------------------------------------------------------|---------------------------------|------------------|----------|------------------------|--|-------------------|----------|------------------------|------------------------|
|                                                       |                                 | ETHYL-           | BUTYL-   | BUTYL-<br>W/O<br>STEEL |  | ETHYL-            | BUTYL-   | 2-<br>ETHYL-<br>HEXYL- | ETHYL-<br>W/O<br>STEEL |
| Precipitate<br>(ml/50 ml)                             | 24                              | 0.15             | 0.25     | -                      |  | trace             | 0.02     | -                      | -                      |
|                                                       | 48                              | 0.15             | 0.25     | 0                      |  | 0.01              | 0.07     | 0.05                   | 0                      |
| Carboni-<br>zation<br>(degree of)                     | 24                              | moderate         | none     | -                      |  | none              | none     | -                      | -                      |
|                                                       | 48                              | severe           | moderate | none                   |  | moderate          | moderate | none                   | none                   |
| Condensate<br>formed in<br>test cell<br>(gm)          | 24                              | 0.1039           | 0.0978   | -                      |  | 0.4598            | 0.2473   | -                      | -                      |
|                                                       | 48                              | 0.1337           | 0.1194   | 0.2437                 |  | 0.5586            | 0.2580   | 0.3628                 | 0.5752                 |
| Acidity of<br>condensate<br>(mg KOH/gm<br>condensate) | 24                              | 2.4              | 3.6      | -                      |  | 0.9               | 26.3     | -                      | -                      |
|                                                       | 48                              | 3.1              | 4.5      | 4.5                    |  | 1.4               | 31.1     | 155.                   | 1.8                    |

Severe - Test cell surface and metal specimens above the fluid level were coated with a black film.

Moderate - Some film formation on the test cell at the fluid-nitrogen interface.

None - No film formation.

Diethyl adipate was the most active in producing such decomposition products. In the tests without steel, no such films were found.

3. Condensate Formation: The values indicate the weight of the condensate formed on the test cell surfaces above the liquid level during exposure. With steel included, the sebacates deposited more such residue than did the corresponding adipates. The dibutyl adipate residue was increased by the absence of steel.

4. Acidity of Condensate: The values indicate the amount of potassium hydroxide neutralized per gram of the condensates in (3) above. With steel included, the butyl diesters' condensates are more acid than those of the corresponding ethyl diesters. The longer chain sebacates showed high levels of acidity. Two sebacates (butyl and 2-ethylhexyl) caused formation of large, white crystals near the bottom of the condenser during test. It is likely that these were crystals of sebacic acid which had sublimed from the hot fluid surface. The steel specimens did not greatly influence the condensate acidity.

Table V lists the metal specimen weight changes. With regard to the specimens in the gas phase, the maximum weight change was 0.07 mg./cm<sup>2</sup>. With both adipates (especially the 48 hour test), carbon formation was observed on the steel panel. This carbon was easily removable by wiping the specimen (as was done before weighing). Both adipates and sebacates generally gave a blue coloration to these specimens. The copper and aluminum specimens showed no discoloration.

With regard to the specimens in the liquid phase, the copper and aluminum specimens showed no weight changes greater than 0.06 mg./cm<sup>2</sup>, although occasional light staining was observed on the copper specimen. However, the immersed steel specimens showed large weight losses in all cases. The 48 hour test series definitely indicated the sebacates as being more corrosive to steel than the adipates.

TABLE V

METAL SPECIMEN WEIGHT CHANGES AFTER 24 AND 48 HOURS  
AS MILLIGRAMS PER SQUARE CENTIMETER

| METAL<br>AND<br>LOCATION      | EX-<br>POSURE<br>TIME<br>(HRS.) | ADIPATE DIESTERS |        |                        | SEBACATE DIESTERS |        |                        |                        |
|-------------------------------|---------------------------------|------------------|--------|------------------------|-------------------|--------|------------------------|------------------------|
|                               |                                 | ETHYL-           | BUTYL- | BUTYL-<br>W/O<br>STEEL | ETHYL-            | BUTYL- | 2-<br>ETHYL-<br>HEXYL- | ETHYL-<br>W/O<br>STEEL |
| Steel<br>(gas<br>phase)       | 24                              | +0.03            | -0.01  | -                      | +0.03             | -0.01  | -                      | -                      |
|                               | 48                              | -0.06            | -0.01  | -                      | -0.07             | -0.03  | +0.01                  | -                      |
| Steel<br>(liquid<br>phase)    | 24                              | -0.15            | -0.23  | -                      | -0.33             | -0.31  | -                      | -                      |
|                               | 48                              | -0.46            | -0.41  | -                      | -1.49             | -1.83  | -1.03                  | -                      |
| Copper<br>(gas<br>phase)      | 24                              | +0.01            | +0.01  | -                      | 0                 | -0.05  | -                      | -                      |
|                               | 48                              | 0                | -0.02  | 0                      | 0                 | +0.01  | 0                      | +0.01                  |
| Copper<br>(liquid<br>phase)   | 24                              | 0                | -0.01  | -                      | 0                 | 0      | -                      | -                      |
|                               | 48                              | +0.04            | -0.06  | -0.02                  | 0                 | +0.03  | +0.04                  | -0.01                  |
| Aluminum<br>(gas<br>phase)    | 24                              | +0.01            | 0      | -                      | -0.01             | -0.01  | -                      | -                      |
|                               | 48                              | 0                | -0.02  | -0.01                  | +0.01             | 0      | 0                      | 0                      |
| Aluminum<br>(liquid<br>phase) | 24                              | +0.02            | 0      | -                      | -0.02             | -0.01  | -                      | -                      |
|                               | 48                              | +0.02            | -0.01  | -0.01                  | 0                 | +0.04  | +0.04                  | +0.01                  |

Tests without steel show extremely small weight changes, never greater than 0.02 mg./cm<sup>2</sup> for the copper and aluminum specimens.

The monel metal wire specimen weight changes are not listed as they never exceeded 0.02 mg./cm<sup>2</sup>. The monel wire specimen generally showed a yellowish stain above the liquid level and a small black area when the metal specimens were in contact with it.

## DISCUSSION

In terms of fluid effects, the two ethyl diesters can be compared to the two butyl diesters in the presence of steel, copper and aluminum specimens plus the monel wire specimen rack. Several correlations can be drawn where the two ethyl diesters show a consistent difference from the two butyl diesters as regards the property changes measured. One such correlation is the condensate acidity as both butyl diesters produced condensates having greater acidity than did the corresponding ethyl compounds. Both ethyl diesters were more corrosive to steel in the gas phase than the butyl diesters. In the corrosivity tests, the ethyl compounds were more corrosive to steel than the butyl compounds.

Comparison can also be made between di-2-ethylhexyl sebacate and the two straight-chain alcohol sebacates. The branched-chain alcohol diester showed greater stability than did the straight-chain sebacates, in terms of changes in color, freezing point, viscosity, neutralization number and weight of immersed steel specimens. Both dibutyl and di-2-ethylhexyl sebacate produced white crystal deposits on the upper portion of the test cell. No analysis of these crystals was performed but in view of their degree of acidity and their white, crystalline form, it is likely that sebacic acid (from the decomposing diester) sublimed onto cooler portions of the test cell. Though this appears probable from the composition of the test fluid, it is interesting to note that Trop<sup>(4)</sup> found similar deposits formed in a similar type of test at 700°F except that the test fluids were of silicone and hydrogenated, mineral oil type.

When the two straight-chain sebacates are compared with the corresponding adipates in the tests where all the metals were present, a number of consistent differences in degree of change in physical properties are noted. Thus, the sebacates gave less color, precipitate and carbon formation. Conversely the adipates showed less change in viscosity, neutralization number and steel corrosion (liquid phase).

The subject of diester stability is further considered topic-wise as follows:

1. Molecular structure effects on fluid stability: As regards the straight-chain diesters, the acid portion of the compound appeared to be more significant than the alcohol portion in terms of the number of property effects measured in that six, consistent correlations could be made between the two acid types, whereas only three such comparisons could be made between the two alcohol types. The branched-chain sebacate showed smaller changes in fluid properties (and metal corrosion), but showed instability in the amount and acidity of sublimed, acidic material deposited at the bottom of the condenser.

2. Effects of metals on fluid stability: The two tests on diesters in the absence of steel specimens, when compared to tests where steel was included, indicate that common steel has deleterious effects on these diesters. Among fluid properties affected by steel, were color, freezing point, precipitate volume, carbonization and viscosity. As regards neutralization number change when steel was absent, dibutyl adipate contained a much larger amount of acid than it did after exposure with steel included. Since the latter test showed both low acid content and steel weight loss (compared with the sebacates) and greater carbonization tendencies, it is likely that adipic acid is eliminated from the system, in the presence of steel, by decarboxylation. The carbon dioxide formed can then react with the gas phase steel specimen to form carbon. Diethyl sebacate tested without steel, gave a neutralization number value which is close to that obtained from tests with steel included. The mechanism involved in this phenomena can be clarified by a discussion of Adam's<sup>(3)</sup> work. He found that iron sebacate dissolved in sebacate diesters, produces breakdown similar in nature and extent as is observed in the presence of steel. He postulates that the metal reacts with the free acid from thermal breakdown of the diester into olefin and free acid, to form the metal salt. This is said to be followed by decarboxylation of the salt. However, Adams<sup>(3)</sup> also found in tests on isooctyl sebacate and adipate that the adipate showed much lower neutralization number values than the sebacate after exposure (6 hours at 550°F). These results which are in essential agreement with results from this Laboratory can be interpreted to indicate that the iron salt either decomposes or catalyzes the breakdown of free acid that is present and that adipic acid (or iron salt) is more susceptible to this action than is sebacic acid (or iron salt). As a result, the concentration of free adipic acid is kept at a relatively low value thereby reducing the amount of attack on iron or common steel, as when compared with the sebacates wherein both acid concentration and steel

attack are greater. This explanation also indicates why carbon formation was much greater for the adipates where steel specimens are placed in the gas phase. Since more of the adipic acid is decarboxylated, more carbon dioxide is formed which in turn is broken down by the gas phase steel specimen to form carbon. Adam's observation that neutralization number change is not a reliable indication of thermal decomposition when metals are present, is confirmed by these tests. However, when neutralization number results are interpreted in conjunction with other tests, they give insight into the nature of thermal degradation reactions in the presence of metals.

3. Effect of exposure time on stability: Comparison of results from the 24 and 48 hour tests on the four straight-chain diesters, indicates that it is difficult to make any overall, consistent correlations. As regards color, freezing point and precipitate formation, the sebacates showed a greater rate-of-change between 24 and 48 hours, than did the adipates. With regard to viscosity change, neutralization number and immersed steel and copper specimen weight losses, both adipates and sebacates show more than a two-fold increase in several instances. The cell condensate weights show only a small increase in this time interval but their acidity increases.

4. Conclusions on thermal effects on diesters usefulness as high temperature fluids: When all the test metals were present, both adipates and sebacates show undesirable reactions. The adipates showed a greater tendency to form insoluble residue and produce more carbonization than the sebacates. These tendencies toward carbonization and precipitate formation make the pure adipates undesirable for use as hydraulic fluids in steel-containing systems.

The sebacates on the other hand, show greater viscosity change, more steel corrosion and greater build-up of free acid in solution. Results also indicated that with longer chain sebacates, free sebacic acid might sublime from the hot diester onto cooler portions of the hydraulic system producing a considerable crystal deposit thereon as was especially noted with the branched-chain alcohol sebacate. Presumably these deposits should readily redissolve in the fluid, although under some circumstances they might act to temporarily block small orifices in the system which could be objectionable. These tendencies toward free acid build-up, steel corrosion, viscosity increase and sublimed crystal formation make the pure sebacates undesirable for use as hydraulic fluids in steel-containing systems, except for short time periods of less than 24 hours.

In addition to the objectionable properties listed on the preceding page, corrosivity tests indicated that some of these compounds, after exposure to high temperatures, could produce pitting-type corrosion on immersed steel after air had entered the system.

The tests carried out in the absence of steel indicate that diester physical properties undergo impressively small changes, even though the neutralization number, weight loss and condensed residue values indicate considerable chemical breakdown has occurred. The diesters evaluated in this report do not, however, appear promising for use as long-term, high-temperature fluids unless the thermally-induced dissociation to form the free acid that occurs even in the absence of steel, can be prevented by stabilizing additives.

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The thermal stability of the ethyl and n-butyl diesters of adipic and sebacic acid was evaluated at 4750F under nitrogen in the presence of four metals (in and above the fluid) for several time periods. Di-2-ethylhexyl sebacate was tested for comparison purposes. Changes in several physical and chemical diester properties and metal specimen weights were determined after exposure.

The adipates showed greater stability as regards changes in viscosity, neutralization number and weight of immersed steel specimen than did the sebacates. The reverse was true as regards changes in color, precipitate volume

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Comparison of these results with results from similar tests on two diesters with steel omitted, show that steel and the diesters have a mutually deleterious effect. Steel caused greater color change, freezing point change, precipitate volume and carbonization. It also appears that adipic acid is more rapidly decomposed than sebacic acid in the presence of dissolved iron salts. Corrosivity tests on these diesters (after thermal exposure) in the presence of air indicated some of them to be corrosive to steel. It was found that these diesters could undergo considerable chemical decomposition with only moderate changes in most of their physical properties in the presence of copper, aluminum and monel metal.

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