SAE The Engineering Society
For Advancing Mobility
Land Sea Air and Space®
INTERNATIONAL
400 Commonwealth Drive, Warrendale, PA 15096-0001

AEROSPACE INFORMATION REPORT

SAE AIR4713

Issued 1992-08
Reaffirmed 2002-05

Aerospace - Chlorinated Solvent Contamination of MIL-H-5606/MIL-H-83282 Vehicle Hydraulic Systems

TABLE OF CONTENTS

TO PLACE A DOCUMENT ORDER:
Tel: 877-606-7323 (inside USA and Canada)
Tel: 724-776-4970 (outside USA)
Fax: 724-776-0790
Email: custsvc@sae.org
SAE WEB ADDRESS: http://www.sae.org

FOREWORD

In June 1982 a study entitled "Investigation of Air Force MIL-H-5606 Hydraulic System Malfunctions Induced by Chlorine Solvent Contamination" (AFWAL-TR-82-4027) was issued by the Air Force Wright Aeronautical Laboratories (AFWAL/MLB) and the University of Dayton Research Institute (Bibliography 1). Information in that study reported that in 1975 a large number of C-141 mishaps occurred involving stuck selector valves in landing gear and door systems throughout the Military Airlift Command (MAC). Analysis of hydraulic fluid from a problem aircraft hydraulic system revealed the presence of the chlorinated solvent 1,1,2- trichlorotrifluoroethane and water. Auger spectroscopy surface analysis of the stuck valve and spool assembly involved revealed the presence of elements chlorine, oxygen, iron, and carbon. With this proof of chlorinated solvents being the cause of stuck valves in a C-141 mishap, a fleet wide survey of aircraft hydraulic systems was performed to determine the level of chlorinated solvents and water in hydraulic systems. Simultaneously, maintenance overhaul procedures were modified to eliminate the use of chlorinated solvents as much as possible. A maximum limit was tentatively established for chlorine contamination in C-141 hydraulic systems at 200 parts per million (ppm) chlorine, based on the Navy's success with a 200 ppm limit with the P-3 aircraft. Upon establishing this limit, C-141 aircraft were drained and flushed if their systems exceeded this limit. The use of chlorinated solvents was banned from use in the C-141 hydraulic systems and component overhauls. As a result of that study, a level of 200 ppm maximum allowable chlorine limit was established.

a. Summary: Chlorine contamination of aircraft hydraulic fluids has been known to cause considerable amounts of damage to hydraulic flight control systems and their corresponding component parts. In an effort to statistically reveal the origins of, and the damages caused by chlorine contamination, a survey was presented to randomly selected aerospace corporations and government organizations by the Fluids Panel of Committee A-6. Based on the preliminary data, a problem exists with chlorine contamination in hydraulic systems. Data contained in a follow-up survey identified chlorofluorocarbon based cleaning fluids as the common chlorine containing fluid in use.

   The source of the chlorine containing contaminants is primarily solvents used in cleaning/degreasing of aircraft parts. Care must be exercised when such solvents are specified to minimize all opportunities for their being introduced into the hydraulic fluid. Such solvents are normally miscible with the hydraulic fluid and their presence can only be determined by laboratory analytical techniques such as those outlined in this document.

b. Types and Percentages Measured: During 1975 and 1976 hydraulic fluid samples were taken from Air Force aircraft at various bases. Aircraft sampled included C-141, B-52, F-105, F-111, F-4, T-38, C-5A, KC-135, F-106 aircraft, and crash accident samples. Also sampled were test stands, servicing carts, and new hydraulic fluids in order to study when and how the chlorinated solvents were introduced into operational hydraulic systems. When these initial samples were taken, chlorine content was measured at the various ALC laboratories by x-ray fluorescence techniques which were later recognized to contain possible serious analytical errors. While any particular data point could be in question, the overall trends of chlorine contamination in hydraulic fluids are considered to be valid.

c. Analysis Results: Of the 250 aircraft fluid samples analyzed, results are given in parts per million chlorine, number of samples analyzed with that value, and the percentage of the total samples.

(1) 300 ppm and above: 1 sample, < 1%
(2) 200 - 300 ppm: 5 samples, 2%
(3) 100 - 199 ppm: 38 samples, 15%
(4) 0 - 100 ppm: 205 samples, 82%

Of the ground equipment fluid samples (703 total), 52% contained over 200 ppm chlorine. Of the new fluid samples analyzed (25 total), 8% were over 200 ppm chlorine.

It can be seen from this data that ground support equipment and new fluid can be a source of contamination. These data further document that the then current levels of chlorine in hydraulic fluid systems were at a serious level, Air Force wide, as these chlorinated solvent levels were in the ranges which had caused corrosion in Navy aircraft.

1. SCOPE:

Although there is controversy regarding the chemical form of chlorine and its relation to harmful effects in the hydraulic fluid (i.e., chloride ions versus organic chloro-compounds versus total chlorine in all forms), it is generally agreed that total chlorine content should be measured and controlled. In the near future, the ban on the manufacture of chlorinated solvents, out of concern for depletion of the ozone layer, may in itself diminish or eliminate chlorine contamination related aircraft malfunctions. It is generally accepted that hydraulic fluid contamination should be held to a minimum under all conditions. The benefits of low contamination levels are improved performance, lower maintenance due to lower wear, corrosion and erosion, longer fluid life, longer component life, etc.

Contaminants can be classified into two general types: those that are insoluble and those that are soluble in the hydraulic fluid. The insoluble solid type is most common and is usually referred to as particulate matter. Its measurement and removal have been the subject of much investigation and standardization which is well documented in technical literature. The insoluble liquid type contaminant is much less common. The resulting two phase system is often observed as hazy or cloudy fluid appearance and the recommended action is to remove the contaminated hydraulic fluid from the system.

Soluble type contaminants are more difficult to detect and to determine quantitatively. They can easily escape notice, particularly when present in small amounts. Gross contamination usually results in significant changes in fluid physical properties and can be determined by such changes. Smaller amounts are difficult to detect and measure and usually require sophisticated analytical techniques - such as infrared and other spectral techniques, gas chromatography (both head space and electron capture), microcoulometry, x-ray fluorescence, etc.

Generally, the presence of undesirable soluble contaminants is unknown until they have been shown to cause performance problems. Hydraulic fluid formulations contain soluble additives in base stocks giving beneficial effects on performance. The range of possible undesirable soluble contaminants can encompass innumerable materials - solids, liquids or gases.

1.1 Purpose:

Of all the potential soluble contaminants, this SAE Aerospace Information Report (AIR) covers only chlorine containing materials, their detection, their effects, and suggests ways to prevent their contaminating aircraft hydraulic fluids. This document will limit itself to "chlorine containing compounds” in MIL-H-5606 and MIL-H-83282 fluids. The presence and effects of other types of materials will not be discussed in this document.

2. APPLICABLE DOCUMENTS:

2.1 SAE Publications:

Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001.

AIR810	Degradation Limits of Hydrocarbon-Based Hydraulic F1uids, MIL-H-5606, MIL-H-83282, and MIL-H-46170 used in Hydraulic Test Stands

2.2 Military Publications:

Available from Standardization Documents Order Desk, Building 4D, 700 Robbins Avenue, Philadelphia, PA 19111-5094.

MIL-H-5440	Hydraulic System, Aircraft, Type I and II, Design, Installation, and Data Requirements for
MIL-H-5606	Hydraulic Fluid, Petroleum Base; Aircraft, Missile and Ordnance
MIL-H-83282	Hydraulic Fluid, Fire Resistant, Synthetic Hydrocarbon Base, Aircraft

3. FLUID SAMPLE ANALYSIS TECHNIQUES:

3.1 Fluid Sample Analysis Techniques:

Since experience has shown that low levels (under 200 ppm) of chlorine are of interest, the standard analyses for chlorine in organic compounds involving destructive decomposition followed by chloride ion determination are not applicable. Therefore, other techniques have been developed. For gross contamination, standard methods for chlorine analysis can be used.

Summaries of analytical methods applicable for small amounts of chlorine are given in the following paragraphs. Care must be taken in discussing contamination reported or measured to distinguish between the level of chlorine contamination as compared to the level of a specific solvent contamination.

3.2 Specific Analysis Techniques:

3.2.1 Gas Chromatography: Volatile contaminants can be determined by gas chromatography using thermal conductivity or electron capture as the means of detection. The sample is chromatographed on a column containing silicon oil or other suitable materials as a liquid phase to separate the components of interest. A dual column, dual detector system is required since the oven temperature is programmed during the analysis. The chromatogram generated from the sample is compared directly with a reference chromatogram for an equal amount of hydraulic fluid. The concentration of contaminant is determined by comparing the peak area ratio of the contaminant versus a standard hydraulic fluid component with the same ratio for a reference sample containing a known concentration of the contaminant. Thus, a component of the fluid is used essentially as an internal standard rather than directly comparing contaminant peak areas in the sample and reference mixture since the ability to reproducibly inject a sample is limited for the small amount injected (see A.3).

3.2.1 (Continued):

The method is reported to detect as little as 0.02% of chlorinated solvents such as trichloroethylene, perchlorethylene, or trichloroethane with a precision of ±2% at 3% contaminant level and a ±10% at a 1% contaminant level.

Analyses consisting of a combination of gas chromatography and mass spectroscopy give both positive identification and quantification of contaminants.

3.2.2 Microcoulometric Procedure: Coulometric procedures for chlorine analysis are accepted for many materials. The technique is claimed to have the relative advantage of small sample size, sensitivity, and low cost (Appendix A.3).

Using a standard microcoulometric technique, liquid samples are injected into a flowing stream of gas containing about 80% oxygen and 20% argon (by volume). The gas and sample flow through a combustion tube maintained at approximately 800 °C. The chlorine is converted to chloride and oxychloride which then flow into a titration cell where they react with silver ions present. The silver ions thus consumed are coulometrically replaced. The current required to replace the silver ions is a measure of the chlorine content of the injected sample.

The microcoulometer can be utilized precisely in ranges of 0 to 500 ppm total chlorine. It is expedient to dilute higher chlorine level samples with standard new fluid prior to analysis.

The microcoulometric technique has also been used as a method to differentiate between volatile and relatively nonvolatile (residual) sources of chlorine. The method utilizes the injection of a small sample by microliter syringe into a quartz boat which is inserted into the combustion tube and in this manner consistent, quantitative determinations of the chlorine present in these compounds are obtained. After evaluation of the volatile compounds, the sample is moved into the combustion tube for ignition which releases the chlorine present in high boiling and nonvolatile (residual) portions of the sample. Correct sample size allows for an accurate determination of chlorine levels in the 10 to 500 ppm range.

3.2.3 X-ray Fluorescence Spectroscopy Method: Proposed method for chlorine content in MIL-H-5606/ MIL-H-83282 hydraulic fluid. This method covers the determination of chlorine in a petroleum base hydraulic fluid in the range of 0 to 500 ppm chlorine.

3.2.3.1 Summary of Method: A sample is placed in the x-ray beam and the intensity of the chlorine Kα line at 4.79 A is measured. This value is converted to ppm chlorine content using a previously prepared calibration graph.

3.2.3.2 Apparatus: X-ray fluorescence spectrometer using either helium or a vacuum in the optical path. Vacuum is not recommended because it is less reliable in that the chlorinated solvents may be vaporized from the sample.

a. The instrument should be equipped as follows:

(1) Pulse-height analyzer, with nominal settings of 2 and 5
(2) Detector capable of measuring chlorine Kα x-rays
(3) Analyzing crystal , suggest germanium
(4) X-ray tube, suggest chromium target

3.2.3.3 Reagents:

a. p-Dichlorobenzene-Fisher Reagent grade, or equivalent
b. MIL-H-5606 or MIL-H-83282 hydraulic fluid that is free of any chlorine containing materials

3.2.3.4 Calibration:

a. Prepare calibration standards

(1) Place approximately 10 g of hydraulic fluid in a beaker (100 ml)
(2) To the hydraulic fluid, add 3.1750 ± 0.0001 g of dichlorobenzene
(3) Transfer this mixture into a container capable of holding at least 1000 g of hydraulic fluid
(4) Rinse out the small beaker with hydraulic fluid three times and transfer the rinsings to the large container
(5) To the large container add sufficient hydraulic fluid to make the total solution weigh 1000.0 ± 0.1 g. This solution represents a 1000 ppm chlorine content.
(6) Using the stock solution, prepare by dilution a series of standards containing 100, 250, 500, and 750 ppm chlorine.

b. Select a series of x-ray cells to be used for the analysis and label them. Adjust the X-ray parameters under chlorine conditions using a piece of sodium chloride crystal to achieve the maximum output.

NOTE 1: Background intensity values for the x-ray cells are negligible and normalized by preparing a calibration curve for each cell.

c. Prepare a calibration curve for each cell with the coordinates, intensity value versus concentration (ppm). The graphs will be used to determine the chlorine content of the samples.

3.2.3.4 (Continued):

NOTE 2: Instrument sensitivity can change, affecting the validity of the calibration curves. Prior to analyzing a sample, a standard should be measured and a correction "C" made on the calibration curve if warranted.

d. Place a sample in a clean x-ray cell and using the appropriate parameters for chlorine Kα measure the x-ray intensity. Two 60 s exposures should yield a count sufficient for the analysis.

NOTE 3: The exposure time can vary depending on instrument parameters and settings.

NOTE 4: Since the chlorine is present as a volatile halogenated solvent, the sample should be refrigerated prior to the analysis.

NOTE 5: A short exposure time should be used for the vacuum instruments to minimize errors due to the volatile nature of the solvent.

e. Average the two readings and refer to the specific cell calibration curve to obtain the chlorine sample.

NOTE 7: Excessive particulate (cloudy appearance) in the sample can affect the accuracy of the analysis.

f. After the sample is analyzed, clean the x-ray cell by washing the cell components twice with petroleum ether and allowing the cell to air dry.

3.2.3.5 Calculations: Calculate the correction "C" for instrument sensitivity change in Figure 1:

$$\boxed{C = \frac{I}{D}}$$

FIGURE 1

where:

I = counting rate at the time the calibration curve was prepared.
D = counting rate for the daily calibration test to ascertain a change in the instrument.

a. Apply correction factor "C" to each calibration curve as required.

3.2.3.5 (Continued):

NOTE 6: Calibration data may be stored on computer tape and updated with the proper program. This will permit the analyst to create a new graph quickly.

3.2.3.6 Precision: The following criteria should be used for determining the reliability of the results:

a. Repeatability: Duplicate results by the same operator should be suspect if the values of the results differ by greater than 20 ppm in the range of 0 to 500 ppm.

b. Reproducability: The results submitted by two laboratories should be suspected if the two results differ by greater than 50 ppm in the range of 0 to 500 ppm.

4. SOLUBLE CHLORINE CONTAINING CONTAMINANTS:

4.1 Potential Contaminant Sources:

Chlorine containing materials may be introduced into the hydraulic fluid from a number of sources. The most likely are as follows:

Cleaning with chlorinated hydrocarbon solvents by immersion or by vapor degreasing prior to original installation or during repair of system components has been common practice. Sufficient time may not be allowed for evaporation of the solvent if baking or compressed air drying are not used. Even if drying procedures are used, blind passages may not be effectively cleared of cleaning solvent residue unless adequate circulation is provided.

Used fluid containing chlorinated solvents sent for reclamation can be processed without the chlorine content of the fluid being decreased.

Transfer of fluid from supplier containers to an aircraft system may be accomplished using transfer equipment that has been flushed with chlorinated solvent between uses. Flushing with hydraulic fluid only is recommended.

Test benches in component overhaul shops or in airframe overhaul and maintenance facilities may be contaminated with chlorinated solvents which in turn contaminate the components and the aircraft systems. Hydraulic fluid servicing carts require periodic cleaning and maintenance. If chlorinated solvents are used for this work, they can later be introduced into aircraft systems.

Salts can enter aircraft engines and other assemblies from sea level operation from coastal bases or from washing of aircraft with detergents.

Tube bending lubricants in some cases are heavily chlorinated. If chlorinated lubricants are used for hydraulic tubing formation, extreme care should be taken to assure removal of the lubricant.