



AEROSPACE INFORMATION REPORT

Society of Automotive Engineers, Inc.
400 COMMONWEALTH DRIVE, WARRENDALE, PA. 15096

AIR 1416

Issued January 1977
Revised

PHOSPHATE ESTER AIRCRAFT HYDRAULIC FLUID CONTAMINATION WITH CHLORINE CONTAINING COMPOUNDS

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1. SUMMARY	2
2. BACKGROUND	2
3. TECHNICAL DISCUSSION	3
3.1 Fluid Sampling	3
3.2 Fluid Sample Analysis Techniques	3
3.2.1 X-Ray Fluorescence Spectroscopy Method	3
3.2.2 Microcoulometric Procedure	3
3.2.3 Infrared Procedure	4
3.2.4 Gas Chromatography	4
3.2.5 Chloride Ion Determination	4
3.3 Soluble Chlorine Containing Contaminants - Types and Percentages Measured	5
3.4 Potential Contaminant Sources	5
3.5 Contamination Effects - Laboratory Results	6
3.6 Contamination Effects - Airplane In-Service Results	7
4. RECOMMENDATIONS	8
4.1 Contaminant Removal Methods	8
4.2 Contaminant Allowable Limits	8
4.3 Recommended Maintenance Practices	9
5. REFERENCES	10

PREPARED BY
SUBCOMMITTEE A-6A, FLUID POWER SYSTEMS, OF
SAE COMMITTEE A-6, AEROSPACE FLUID POWER & CONTROL TECHNOLOGIES

SAE Technical Board rules provide that: "All technical reports, including standards, approved practices recommended, are advisory only. Their use by anyone engaged in industry or trade is entirely voluntary. There is no agreement to adhere to any SAE standard, recommended practice, and no commitment to conform to or be guided by any technical report. In formulating and approving technical reports, the Board and its committees will not investigate or consider patents which may apply to the subject matter. Prospective users of the report are responsible for protecting themselves against liability for infringement of patents."



Documents

Document Sharing Hub

AIR 1416: Phosphate Ester Aircraft Hydraulic Fluid Contamination with Chlorine Containing Compounds

1. SUMMARY

Laboratory and in-service data have shown that chlorine containing compound contamination of aircraft fire resistant phosphate ester base hydraulic fluids under some conditions accelerates wear of the metering edges of valves. The mechanism for the phenomena is not clearly defined. However, the preponderance of evidence indicates that total chlorine levels in such aircraft hydraulic fluids should be kept at low levels. Some of the background data are summarized in this Aerospace Information Report (AIR).

The source of the chlorine containing contaminants is primarily solvents used in cleaning, repairing and servicing the aircraft hydraulic system and components. 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 AIR.

Of all the potential soluble contaminants, this AIR covers only chlorine containing materials, their detection, their effects, and suggests ways to prevent their contaminating aircraft hydraulic fluids. Care should be taken to eliminate all contaminants and further studies are recommended to determine their effects on hydraulic system and fluid performance.

2. BACKGROUND

It is generally accepted that hydraulic fluid contamination should be held to a minimum under all conditions. The benefits of low contamination levels are cited to be 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 the technical literature. Filters are normally used to remove this type contaminant. 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 much more difficult to detect and measure and usually require the more sophisticated analytical techniques - such as infrared and other spectral techniques, gas chromatography, gel permeation chromatography, atomic adsorption, etc.

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

This AIR will limit itself to "chlorine containing compounds" in phosphate ester aircraft hydraulic fluids. Other types of materials may be just as, or even more, undesirable; their presence and effects will not be discussed in this document.

There are published accounts of hydraulic valve corrosion/erosion attributed to the presence of chlorine-containing contaminants in the hydraulic fluid. These chlorine-containing contaminants included chloro-organic compounds (such as solvents, by-products of formation, etc.) and inorganic chloride ions. A survey of the members of the Commercial Jet Transport Aircraft Hydraulic Systems Panel, SAE Committee A-6A, showed that the majority have experienced such contamination and the consensus appeared to be that such contamination had led to reduced system performance.

3. TECHNICAL DISCUSSION

3.1 Fluid Sampling: The goal in taking a sample from the hydraulic system is to provide a small but representative amount of hydraulic fluid for examination. Recommended sampling techniques have been developed by those working in the contamination field and are well documented.

3.1.1 In terms of the subject matter of this AIR, the sample for analysis must be as representative of all the fluid in the system as possible and should not be contaminated during the sampling or by the sample container. Detailed procedures are available from the aircraft hydraulic system designers, component suppliers, fluid suppliers and various technical committees.

3.2 Fluid Sample Analysis Techniques: 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 the total chlorine content should be measured.

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. Detailed analytical procedures are available from hydraulic fluid suppliers, airframe manufacturers and analytical instrument producers.

3.2.1 X-Ray Fluorescence Spectroscopy Method: This procedure was specifically developed to measure low levels of chlorine in phosphate ester base hydraulic fluids. The method is applicable over the concentration range 3-300 ppm total chlorine and requires only 5 ml of sample. The lower limit of detection has been reported to be 3 ppm chlorine (Reference 1).

The method relies upon the establishment of a linear standard calibration curve. A series of chlorine standards is made by dilution of a 1000 ppm stock chlorine containing solution. This initial standard solution is prepared from a known chloro-organic compound and a stock sample of phosphate ester fluid which is known to contain less than 50 ppm chlorine. The intensity is measured on the chlorine K line for each standard. An absolute background intensity is measured and subtracted from the measured intensities for both standards and unknowns. A calibration curve of peak intensity versus concentration of chlorine added is then plotted. The intercept on the negative concentration axis (abscissa) represents the concentration of chlorine in the stock phosphate ester fluid, while the intercept on the intensity axis (ordinate) represents the intensity due to this determined chlorine concentration. The chlorine content of an unknown is then easily found from the intensity by simple proportion.

3.2.1.1 Based on linear regression analysis, the standard error of estimate for the calibration curve is ± 2 ppm chlorine over the concentration range 10 - 300 ppm added chlorine (Reference 2).

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

Using standard microcoulometric technique, liquid samples are injected into a flowing stream of gas containing about 80 vol. percent oxygen and 20 percent argon. The gas and sample flow through a combustion tube maintained at approximately 800° C. The chlorine is converted to chloride and oxy-chloride 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 parts total chlorine per million. It is expedient to dilute higher chlorine level samples with standard new fluid prior to analysis.

- 3.2.2.1 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 - 500 ppm range.
- 3.2.3 Infrared Procedure: For volatile contaminants a procedure has been developed utilizing infrared analysis in the vapor phase. Infrared analysis of chlorinated-solvent contaminants in the liquid phase has been reported to have a detectable limit of 1 percent. The vapor phase procedure is reported to have a threshold limit for identification of approximately 10 ppm and is quantitative from a minimum of 25 ppm (this varies with the volatility and infrared activity of the compound). (Reference 3.)
- 3.2.3.1 The basic principle underlying this infrared method involves the volatilization of a relatively low boiling point contaminant from a relatively non-volatile fluid and the analysis of the vapor phase. The method provides a quantitative measure of liquid phase concentration due to the application of Henry's Law. The procedure utilized is as follows: A measured sample of fluid (25 ml) is transferred to a 160 ml Pyrex container which is fitted with a two-way stopcock. The container is placed in a boiling water bath for 5 minutes, attached to an evacuated 110 ml IR gas cell and the cell and fluid container brought to equilibrium. This results in a vapor sample at lower than ambient pressure. An IR spectrum is then run to compare peak locations for qualitative identification and/or to measure peak height for quantification. A calibration curve is made up using measured amounts of standard contaminants in the base fluid. The method is dependent on Henry's Law and can be applied to single or mixed contaminants. If care is taken to utilize the same parameters for analyzing an unknown as for the standards, it becomes unnecessary to accurately measure container volumes or pressure, comparison alone under controlled conditions being a sufficient criterion. Normal precautions in working with glass systems under pressure/vacuum conditions should, of course, be observed.
- 3.2.4 Gas Chromatography: Volatile contaminants can be determined by gas chromatography using thermal conductivity or electron capture as the means of detection.
- 3.2.4.1 The sample is chromatographed on a column containing silicone oil or other suitable material 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 standard 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. (Reference 3.)
- 3.2.4.2 This method is reported to detect as little as 0.2% of chlorinated solvents such as trichloroethylene, perchlorethylene or trichloroethane with a precision of $\pm 2\%$ at a 3% contaminant level and a $\pm 10\%$ at a 1% contaminant level.
- 3.2.4.3 For more sophisticated analyses a combination of gas chromatography and mass spectroscopy will give positive identification and quantification.
- 3.2.5 Chloride Ion Determination: The amount of chloride ion present may be determined on an aqueous extraction of the hydraulic fluid using silver nitrate turbidimetry which is reported sensitive to approximately 0.1 ppm.