AEROSPACE RECOMMENDED PRACTICE

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Superseding ARP5088

Test Method for the Determination of Total Acidity in Polyol Ester and Diester Gas Turbine Lubricants by Automatic Potentiometric Titration

RATIONALE

This document has been reaffirmed to comply with the SAE 5-year Review policy.

1. SCOPE:

The test method describes the procedure for determination of the total acid number of new and degraded polyol ester and diester based gas turbine lubricants by potentiometric titration technique. The method was validated to cover an acidity range 0.05 to 6.0 mg KOH g^{-1}. The method may also be suitable for the determination of acidities outside of this range and for other classes of lubricant.

1.1 Purpose:

The total acid number can be used to assist in the assessment of a lubricant during condition monitoring and for quality assurance/specification verification.

WARNING: This document may involve hazardous materials, operations, and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. APPLICABLE DOCUMENTS:

The following publications form a part of this document to the extent specified herein. The latest issue of SAE publications shall apply. The applicable issue of other publications shall be the issue in effect on the date of the purchase order. In the event of conflict between the text of this document and references cited herein, the text of this document takes precedence. Nothing in this document, however, supersedes applicable laws and regulations unless a specific exemption has been obtained.

2.1 ISO Publications:

Available from ANSI, 11 West 42nd Street, New York, NY 10036-8002.

ISO 3696 Water Purity

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3. DEFINITIONS:

3.1 TOTAL ACID NUMBER (TAN):

The quantity of base, expressed in milligrams of potassium hydroxide per gram of sample required to titrate the sample potentiometrically to an aqueous pH 11 end point.

3.2 CLEAN OIL/LUBRICANT:

A sample of oil with a total acid number greater than 0.05 mg KOH/g and less than 1.5 mg KOH/g. Most new oils and lightly stressed used oils will fall into this category. A sample size of 20 g shall be used for samples falling into this total acid number range.

3.3 DEGRADED OIL/LUBRICANT:

A sample of oil with a total acid number of 1.5 mg KOH/g or greater. Most highly stressed oils will fall into this category, particularly samples from laboratory oxidation tests and static engine tests. A sample size of 2.5 g shall be used for samples falling into this total acid number range.

4. TEST REQUIREMENTS:

4.1 Outline of Method:

The test portion is dissolved in a mixture of toluene and propan-2-ol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a silver/silver chloride reference electrode. The cell voltage corresponding to aqueous pH 11 buffer is taken as the end point.

4.2 Apparatus:

4.2.1 Potentiometric Titration Apparatus: An automatic titrimeter capable of titrating to a fixed end point using either variable or fixed titrant increments.

The burette shall have a maximum size of 10 mL and a dispensing accuracy of ±0.01 mL.

4.2.2 Glass Indicating Electrode: Pencil type; a glass electrode specifically designed for non-aqueous titrations is recommended.

4.2.3 Reference Electrode: Pencil type; silver/silver chloride electrode filled with the lithium chloride electrolyte (4.3.4). Other electrodes, which can be shown to give equivalent performance on the samples to be tested, may be used provided they are filled with the lithium chloride electrolyte (4.3.4).

The electrode shall be made of glass and shall be provided with a movable joint in the form of a sleeve or plug to facilitate easy washing of the reference electrolyte cell. A double junction design is preferable with the electrolyte cells filled with the lithium chloride electrolyte (4.3.4).

4.2.3 (Continued):

Combined electrodes are not recommended for this method as ideal storage conditions for each part of the electrode cannot be provided by a single solution when alcoholic reference electrolytes are in use.

4.2.4 Titration Vessel: The vessel shall have a capacity of 150 to 250 mL and be inert to the reagents.

4.2.5 Stirrer: A stirrer with variable speeds and fitted with a propeller or paddle of chemically inert material. The stirrer must be electrically grounded (earthed).

NOTE: Some types of apparatus may be sensitive to interference by static electricity when the apparatus is approached by the operator. In these cases the titration vessel should be surrounded with a close-fitting cylinder of copper gauze which is electrically grounded (earthed). Refer to the equipment manufacturer if in doubt.

4.3 Reagents/Materials:

Use only reagents of recognized analytical grade (where available) and water conforming to ISO 3696 Grade 3 or equivalent purity.

4.3.1 Aqueous pH 4, pH 7 and pH 11 buffer solutions.

NOTE: These solutions must be replaced at regular intervals consistent with their stability or when contamination is suspected. Information relating to their stability should be obtained from the manufacturer.

4.3.2 Ethanol: [98% min v/v] (C_2H_5OH).

4.3.3 Lithium chloride (LiCl).

4.3.4 Lithium Chloride Reference Electrolyte: Prepare a 1 M or 2 M solution of the lithium chloride (4.3.3) in the ethanol (4.3.2). Commercially available solutions may be used where available.

NOTE: Potassium chloride electrolyte must not be used to fill single junction reference electrodes or to fill the outer cell of a double junction reference electrode. Use of other electrodes could affect the precision. It is desirable to reserve the electrode for non-aqueous titrations.

4.3.5 Potassium hydrogen phthalate ($KHC_8H_4O_4$).

4.3.6 Potassium hydroxide (KOH).

4.3.7 Potassium Hydroxide: Standard volumetric alcoholic solution, c(KOH) = 0.1 M.

Add 6 to 7 g of the potassium hydroxide (KOH) (4.3.6) to 1000 mL ± 10 mL of the propan-2-ol (4.3.8) in a 2 L flask. Boil gently under reflux for 10 min and then shake to ensure it dissolves completely. Cool and stopper the flask.

Allow the solution to stand in the dark for two days and then filter the supernatant liquid through a 5 µm PTFE membrane filter. Store in a suitable amber glass bottle.

During dispensing the solution must be protected from atmospheric carbon dioxide (CO_2) by means of a guard tube containing soda lime or soda non-fibrous silicate absorbent. The solution must not come in contact with cork, rubber, or saponifiable stopcock grease.

Standardize frequently enough to detect concentration changes of 0.001 M by potentiometric titration against 0.1 to 0.15 g of the potassium hydrogen phthalate (4.3.5). The latter should be dried for 2 h at 105 °C, weighed to an accuracy of 0.0002 g and dissolved in approximately 100 mL of carbon-dioxide free water.

NOTE: Commercial methanolic, ethanolic, or propanolic based potassium hydroxide solution may also be used.

4.3.8 Propan-2-ol (C_3H_7OH).

4.3.9 Titration Solvent: Add 500 mL ± 5 mL of the toluene (4.3.10) and 5 mL ± 0.2 mL of the water to 495 mL ± 5 mL of the propan-2-ol (4.3.8). The titration solvent should be made up in large quantities and its blank value determined daily by titration prior to use.

4.3.10 Toluene ($C_6H_5CH_3$).

4.3.11 Ammonium peroxodisulphate ($(NH_4)_2S_2O_8$).

4.3.12 Sulphuric acid (H_2SO_4), 95 to 98%.

4.3.13 Ammonium Peroxodisulphate Cleaning Solution: Weigh 8 g of the ammonium peroxodisulphate (4.3.11) into a glass beaker. Carefully add 100 mL of the concentrated sulphuric acid (4.3.12) and gently stir. Before use the solution should be left overnight for the solid to dissolve completely.

5. PREPARATION AND MAINTENANCE OF THE ELECTRODE SYSTEM:

Although the electrodes are not particularly fragile they should be handled carefully at all times. The following procedures are very important because pH measurements will only be as good as the condition of the electrodes.

5.1 Preparation of Electrodes for Calibration:

5.1.1 Glass Electrode: The glass electrode (4.2.2) should be wiped dry with a clean soft absorbent tissue before use.

5.1.2 Reference Electrode: Remove the reference electrode (4.2.3) from the storage solution. Wipe the electrode with clean soft absorbent tissue taking care not to disturb the lower sleeve/plug. Uncover the filling aperture(s) to allow the electrolyte (4.3.4) to diffuse freely during use. Gently release the lower sleeve or plug and drain a few drops of electrolyte to flush the glass joint. Check the electrolyte level(s) and refill as necessary. Immerse the electrode in water for 5 min to remove any surplus electrolyte adhering to the outside of the electrode and allow water to drain off.

5.2 Testing of Electrodes:

5.2.1 Prepare the electrodes as detailed in 5.1.

5.2.2 Immerse the electrodes in the aqueous pH 4, pH 7, and pH 11 buffer solutions (4.3.1) consecutively to establish electrode response, washing all the electrodes with the water after each buffer. This should be performed daily and recorded permanently.

5.2.3 The meter/electrode combination is suitable for use when the mV reading for the pH 7 buffer (4.3.1) and the relative slope for the pH buffers (4.3.1) are within the electrode manufacturer's tolerances.

5.3 Calibration Requirements:

5.3.1 Determine the cell potential of the pH 11 buffer solution (4.3.1) daily. The reading obtained is taken as the end-point for the titrations and must be entered into the instrumental program where this is not done automatically.

NOTE: The use of temperature correction is recommended. Due to the significant effect of temperature on the pH of the pH 11 buffer (4.3.1) it is desirable to keep this as close to the buffer manufacturer's calibration temperature as possible.

5.3.2 Conditioning of the Electrodes for Non-aqueous Titrations: Immerse the electrode assembly in the titration solvent (4.3.9) for a period of 10 min. Rehydrate the glass electrode (4.2.2) by immersing the bulb in water for 2 min and then allow excess to drain off.

5.4 Storage of Electrodes:

When the electrodes are not in use, immerse the lower half of the glass electrode (4.2.2) in water and the lower half of the reference electrode (4.2.3) in reference electrolyte (4.3.4). Cover the filling aperture(s) of the reference electrode during storage.

Do not allow either electrode to dry out, especially the glass electrode.

5.5 Cleaning of Electrodes:

5.5.1 Glass Electrode: When in regular use, clean the glass electrode (4.2.3) weekly by immersing the tip in 0.1 M hydrochloric acid for a minimum period of 12 h. If more aggressive cleaning is required, immerse the electrode tip in the ammonium peroxodisulphate cleaning solution (4.3.13) for 5 min followed by a thorough wash with water. The ammonium peroxodisulphate treatment should be carried out routinely at monthly intervals when the electrode is in regular use.

5.5.2 Reference Electrode: Clean the reference electrode (4.2.3) as necessary by flushing with the propan-2-ol (4.3.8) followed by the reference electrolyte (4.3.4).

6. PROCEDURE:

6.1 Test the electrodes and calibrate the automatic titrimeter (4.2.1) as detailed in 5.1, 5.2, and 5.3.

6.2 Prepare the electrodes for non-aqueous titration as detailed in 5.3.2.

6.3 Set up the apparatus in accordance with the manufacturer's instructions ensuring that the overall titration rate is not greater than 0.2 mL min^{-1}. If the titration unit is only capable of performing fixed rate titrations, set the titration rate to 0.1 mL min^{-1}.

Examples of suitable titrimeter methods are given in Appendix A.

6.4 The burette should be filled with the 0.1 M alcoholic potassium hydroxide solution (4.3.7) and the tip immersed approximately 25 mm in the titration solvent (4.3.9).

6.5 Perform a "blank" determination in duplicate on 125 mL ± 2 mL of the titration solvent (4.3.9) daily or immediately after changing to a fresh batch of the titration solvent (4.3.9). Take the mean of the two determinations as the "blank" titration.

If the blank is very low and insufficient data points are obtained when using 125 mL of the titration solvent (4.3.9) a larger volume of the solvent should be used and the blank equivalent to 125 mL calculated.

6.6 Ensure that the test portion is representative. Weigh (to the nearest 0.001 g) into the titration vessel, either 20 g ± 1 g of clean lubricant or 2.5 g ± 0.1 g of degraded lubricant and add 125 mL ± 2 mL of the titration solvent (4.3.9).

6.7 Perform the titration using the procedure prescribed for the equipment taking care to limit the speed of stirring to avoid spattering or stirring air into the solution.

6.8 On completion of the titration rinse the electrodes and burette tip with the titration solvent (4.3.9). Rehydrate the glass electrode (4.2.2) by immersing the bulb in water for 2 min and then allow excess to drain. If either of the electrodes require further cleaning proceed with the appropriate cleaning procedure detailed in 5.5.

Store the electrodes for short periods (less than 0.75 h) in the titration solvent (4.3.9) and for longer periods as detailed in 5.4.

NOTE: Do not allow the electrodes to remain immersed in the titration solvent (4.3.9) for longer than is necessary between titrations. This will keep the dehydration of the glass electrode (4.2.2) to a minimum.

6.9 If the resulting total acid number falls outside the range for the sample size used (see 3.2 and 3.3) repeat the determination using the correct sample size.

7. EXPRESSION OF RESULTS:

Most modern automatic titrimeters have integral calculation methods or can be programmed for a specific application. In either case, check that the calculation used is as detailed in 7.1.

7.1 Calculate the total acid number, expressed in milligrams of KOH per gram of sample, using Equation 1:

$$\text{Total acid number} = \frac{(V_1 - V_0) \times c \times 56.1}{m} \quad \text{(Eq.1)}$$

where:

V_1 = Volume, in milliliters, of the alcoholic KOH solution (4.3.7) used to titrate the test portion to the end-point.
V_0 = Volume, in milliliters, of the alcoholic KOH solution (4.3.7) used for the blank titration.
c = Actual concentration, in moles per liter, of the alcoholic KOH solution (4.3.7).
m = Mass, in grams, of the test portion.

8. PRECISION:

8.1 Clean Oils (20 g sample size):

Repeatability - The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test, exceed the following value only in one case in twenty.

$$0.028(x)^{0.3} \tag{Eq.2}$$

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical materials would, in the long run, exceed the following value only in one case in twenty.

$$0.115(x)^{0.3} \tag{Eq.3}$$

where:

x = Result obtained.

8.2 Degraded Oils (2.5 g sample size):

Repeatability - The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test, exceed the following value only in one case in twenty.

$$0.061(x+0.362) \tag{Eq.4}$$

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical materials would, in the long run, exceed the following value only in one case in twenty.

$$0.166(x+0.362) \tag{Eq.5}$$

where:

x = Result obtained.

NOTE: The precision of this method has been calculated from data obtained from a round robin conducted in 1995. This involved the analysis of six clean and six laboratory degraded synthetic ester based lubricating oils by eight laboratories. A 20 g sample size was used for the clean oils and a 2.5 g sample size was used for the degraded oils.