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GB/T 12581-2006

Replacing GB/T 12581-1990

Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils

加抑制剂矿物油氧化特性测定法

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Issued by: General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China;

Standardization Administration of the People's Republic of China.

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Foreword

This Standard modifies and adopts ASTM D943-04a "Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils".

This Standard is redrafted in accordance with ASTM D943-04a. In order to suit the China's national conditions, this Standard is revised when adopting ASTM D943-04a.

The main differences between this Standard and ASTM D943-04a are as follows:

— Because there is no supply of Nochromix or Micro in China, the cleaning agent is replaced with chromic acid cleaning solution.

— The normative reference ASTM D5770 in the original standard has no corresponding China standard, and this Standard only applies to the determination for acid number of lubricating oil during oxidation test, thus it is taken as Appendix A in standard revision.

— Partial normative references of this Standard adopt the national current effective standards corresponding to the standards referenced in ASTM D943-04a.

— Expression of repeatability and reproducibility is modified to traditional expression type of China.

— There is no keyword content in the national standard, therefore the chapter of keywords in ASTM D943-04a is deleted.

This Standard replaces GB/T 12581-1990 "Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils".

The main revision content of this Standard over GB/T 12581-1990 is as follows:

— As the oxidation lifetime of newly developed oils is extended largely, in order to reduce the sample consumption due to sampling or as it is difficult to determine the titration end point with indicator due to sample darkening, two methods such as Appendix A and GB/T 7304 are added for the determination method of acid number of this Standard based on the reservation of SH/T 0163, for the selection of acid number determination.

— Partial normative references adopt the corresponding national standards and professional standards.

— Add the requirements for protecting sample against illumination.

— Refine the requirements for sampling time interval and specify the treatment method when the oxidation lifetime exceeds 10000h.

— Add the selective method using oil level indicator strip to indicate the oil level.

— Delete "oxidation stability test device diagram" and add "oil level indicator strip" diagram.

— Add the content of precision requirements for two sets of repeated test results in two laboratories.

— Propose another selection for metal bath as a liquid heating bath, and allow electronic temperature measuring equipment to replace thermometer.

— Illustrate the procedure to set and measure bath temperature in more detail.

— Add Appendix A "Semiquantitative Microdetermination of Acid Number of Lubricating Oils during Oxidation Testing" and Appendix B "Procedure for Packaging Catalyst Coils".

Appendix A in this Standard is normative and Appendix B is informative.

This Standard was proposed by China Petrochemical Corporation.

This Standard shall be under the jurisdiction of Sinopec Research Institute of Petroleum Processing.

Drafting organization of this Standard: PetroChina Company Limited Lubricating Oil Research and Development Center.

Chief drafting staffs of this Standard: Yu Bing, Su Jiang and Li Jianxin.

The previous edition replaced by this Standard is as follows:

— GB/T 12581-1990.

Standard Test Method for Oxidation Characteristics of Inhibited Mineral Oils

1 Scope

1.1 This Standard specifies the evaluation of the oxidation stability of inhibited steam turbine oils in the presence of oxygen, water, and copper and iron metals at an elevated temperature. This test method is limited to a maximum testing time of 10000h. This test method is also used for testing other oils, such as hydraulic oils and circulating oils having a specific gravity less than that of water and containing rust and oxidation inhibitors.

1.2 This Standard adopts SI units.

1.3 This Standard is involved in some materials, operations and equipment with hazard, but does not purport to address all of the safety concerns. Therefore, it is the responsibility of the user of this Standard to establish appropriate safety and protective measures and determine the applicability of management system prior to use.

2 Normative References

The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. For dated reference, subsequent amendments (excluding corrigendum) or revisions of these publications do not apply. However, all parties who enter into an agreement according to this Standard are encouraged to study whether the latest edition of these documents is applicable. For undated references, the latest edition of the normative document is applicable to this Standard.

GB/T 514 "Liquid in Glass Thermometers for Petroleum Products-Specification"

GB/T 699 "Quality Carbon Structural Steels"

GB/T 4756 "Petroleum Liquids-Manual Sampling" (GB/T 4756-1998, eqv ISO)3170:1988)

GB/T 4945-2002 "Standard Test Method for Acid and Base Number of Petroleum Products and Lubricants by-Colour-indicator Titration"

GB/T 5231 "Wrought Copper and Copper Alloys Chemical Composition Limits and Forms of Wrought Products"

GB/T 6682 "Water for Analytical Laboratory Use-Specification and Test Methods" (GB/T 6682-1992, neq ISO 3696:1987)

GB/T 7304 "Petroleum Products and Lubricants-Determination of Neutralization Number-Potentiometric Titration Method"

GB/T 17039 "Standard Practice for Utilization of Test Data to Determine Conformance with Specifications"

SH/T 0163 "Standard Test Method for Acid Number of Petroleum Products by Semi-micro Color Indicator Titration"

SH/T 0565 "Standard Test Method for Determination of the Sludging Tendencies of Inhibited Mineral Oils"

3 Summary of Test Method

The sample is contacted with oxygen in the presence of water and an iron-copper catalyst at 95°C. The test continues until the measured acid number of the sample is 2.0mgKOH/g or above. The number of test hours required for the sample to reach 2.0mgKOH/g is the "oxidation lifetime".

4 Significance and Use

This test method is widely used for specification purposes and is considered of value in estimating the oxidation stability of lubricants, especially those that are prone to water contamination. It should be recognized, however, that correlation between results of this method and the oxidation stability of a lubricant in field service may vary markedly with field service conditions and with various lubricants. The precision statement for this method was determined on steam turbine oils.

Note: In the course of testing a lubricant by this method, other signs of deterioration, such as sludge formation or catalyst coil corrosion, may appear that are not reflected in the calculated oxidation lifetime. The application of alternative criteria for evaluation of lubricants using this test apparatus is under study. Test Method SH/T 0565 is now available for sludge tendency measurement.

5 Apparatus

5.1 Oxidation Cell, of borosilicate glass, as shown in Figure 1, consisting of a test tube, condenser, and oxygen delivery tube. The test tube has a calibration line at 300mL (maximum error 1mL) at 20°C.

heating liquid itself to a depth of 355±10mm.

Note: Metal heating baths meeting the test method requirements may also be used. It is not known what types of heating baths were used in developing the precision statement.

5.2.1 Studies have suggested that direct sunlight or artificial light may adversely influence the results of this test. To minimize effects of light exposure on the sample, light shall be excluded from the sample by one or more of the following ways:

5.2.1.1 Use of heating baths that are constructed of metal, or combinations of metals and other opaque materials, that prevent light from entering the test tube from the sides is preferred. If a viewing window is included in the design, this viewing window shall be fitted with an opaque cover and be kept closed when no observation is being made.

5.2.1.2 If glass heating baths are used, the bath shall be wrapped with aluminum foil or other opaque material.

5.2.1.3 Bright light entering the test tube from directly overhead can be eliminated by use of an opaque shield.

5.3 Flowmeter, with a capacity of at least 3L/h, and an accuracy of 0.1L/h.

5.4 Heating Bath Thermometer-oxidation characteristic No. 2 thermometer having a range from 72 to 126°C, and conforming to the requirements for thermometer GB-58 as prescribed in GB/T 514. Alternatively, temperature measuring devices of equal or better accuracy may be used.

5.5 Oxidation Cell Thermometer, oxidation characteristic No. 1 thermometer having a range from 80 to 100°C, graduated in 0.1°C, total length-250mm, stem diameter-6.0 to 7.0mm, calibrated for 76-mm immersion, and conforming to the requirements for thermometer GB-57 as prescribed in GB/T 514. Alternatively, temperature measuring devices of equal or better accuracy may be used.

5.6 Thermometer Bracket, for holding the oxidation cell thermometer, of 1Cr18Ni9Ti stainless steel, having the dimensions shown in Figure 2. The thermometer is held in the bracket by two fluoroelastomer O-rings of approximately 5mm inside diameter. Alternatively, thin stainless steel wire may be used.

length and 15.9 to 16.5mm inside diameter. The turns of wire are evenly spaced, and two consecutive turns of the same wire are 3.96 to 4.22mm apart, center to center. The mandrel shown in Figure 3 is designed to produce such a coil. Using this mandrel, the iron wire is wound on a thread of 14.98-mm diameter, while the copper wire is wound on a thread of 15.9-mm diameter. The smaller diameter is to allow for springback of the iron wire after winding, so as to give 15.9-mm consistent inside diameter. Use of a very soft annealed steel wire may allow use of identical thread diameters for the two wires. Any arrangement that leads to the coil configuration described above is satisfactory.

8.3 Catalyst storage

The catalyst coil may be stored in a dry, inert atmosphere prior to use. A suitable procedure for catalyst storage is given in Appendix B. Before use it should be inspected to ensure that no corrosion products or contaminating materials are present. For overnight storage (less than 24h) the coil may be stored in n-Heptane.

N-Heptane used for catalyst storage must be free of traces of water and corrosive materials. Redistilled n-Heptane conforming to 6.6 and stored in a tightly sealed bottle is suitable.

8.4 Cleaning new glassware

Wash new oxygen delivery tubes, condensers, and test tubes with a hot detergent solution and rinse thoroughly with tap water. Clean the interiors of the test tubes, exteriors of the condensers, and both interiors and exteriors of the oxygen delivery tubes with cleaning reagent. Rinse thoroughly with tap water until all cleaning solution is removed. Rinse all parts with distilled water and allow drying at room temperature or in an oven. The final distilled water rinse may be followed by an isopropyl alcohol rinse, or acetone rinse, optionally followed by dry air blowing, to hasten drying at room temperature.

8.5 Cleaning used glassware

Immediately following termination of a test, drain the oil completely from the test tube. Rinse all the glassware with n-Heptane to remove traces of oil, wash with a hot detergent solution using a long-handled brush, and rinse thoroughly with tap water. If deposits still adhere to the glassware, a method that has been found useful is to fill the test tubes with detergent solution, insert the oxygen delivery tubes and condensers, and place the tubes in the heating bath at test temperature. Several hours soaking in this manner often serves to dissolve all adhering deposits except iron oxide. Subsequent rinsing with hot (50°C) hydrochloric acid will serve to remove iron oxide. After all deposits are removed, rinse all glassware with a cleaning reagent. Rinse thoroughly with tap water until all acid is removed. Rinse all parts with distilled water and allow drying at room temperature or in an oven. The final distilled water rinse may be followed by an isopropyl alcohol rinse, or acetone rinse, optionally followed by dry air blowing, to hasten drying at room temperature. Store glassware in a dry dust-free

condition until ready to use.

8.6 Cleaning used sampling tube

Immediately following termination of a test, drain the oil completely from the sampling tube. Rinse the tube with n-Heptane to remove traces of oil and any tenacious organic residues. Repeat the rinsing procedure with n-Heptane and blow dry with air or nitrogen.

9 Procedure

9.1 Adjust the heating bath temperature to approximately 95°C before proceeding. The final bath temperature adjustment is described in detail in 9.5.

9.2 Fill the empty oxidation cell with 300mL of the oil sample to the graduation mark. Slide the catalyst coil over the inlet of the oxygen delivery tube. If the wires are uneven at one end of the coil, position the coil so that this end is down. Place the oxygen delivery tube with the catalyst coil into the test tube. Place the condenser over the oxygen delivery tube and test tube. Place the sampling tube holder over the oxygen delivery tube. Insert the syringe sampling tube through the syringe sampling tube spacer, and into the sampling tube holder, as shown in Figure 5. Position the bottom end of the sampling tube inside the catalyst coil. Insert a stopper in the connector of the sampling tube. Immerse the test tube in the heating bath. Adjust the heating bath liquid level so that the tube is immersed in the liquid to a depth of 355±10mm. Connect the condenser to the cooling water. The temperature of the outlet water should not exceed 32°C at any time during the test.

Note: As an alternative to using the sampling tube holder and sampling tube spacer, the sampling tube may be secured to the oxygen delivery tube using a suitable adhesive tape or clamp. The sampling tube is taped or clamped to the oxygen delivery tube at a distance of approximately 25mm above the top of the condenser. The bottom of the sampling tube is positioned at 152±6mm from the bottom curved end of the oxygen delivery tube.

9.3 Connect the oxygen delivery tube to the oxygen supply through the flowmeter using new polyvinyl chloride flexible tubing no more than 600mm in length. Before using, the interior of the new polyvinyl chloride flexible tubing should be rinsed with n-Heptane and blown dry with air. Adjust the rate of flow to 3±0.1L and continue flow for 30min.

9.4 Raise the condenser unit from the oxidation cell and add 60mL of distilled water into the test tube, and record the oxidation time.

9.5 To set the bath temperature use only a new, undepleted, oil sample with water and oxygen flowing as described in 9.2 or a dummy cell used specifically for temperature measurement. The dummy cell shall contain undepleted oil sample with

A — the number of test hours when acid number was last measured below 2.0mgKOH/g, in h;

B — the number of test hours when acid number was measured above 2.0mgKOH/g, in h;

C — the acid number at A hours, in mgKOH/g;

D — the acid number at B hours, in mgKOH/g.

11 Report

11.1 Report the calculated hours to 2.0mgKOH/g acid number (oxidation lifetime), in h.

11.2 If the acid number is still less than 2.0mgKOH/g after 10000h, the test shall be terminated. Since the maximum oil oxidation lifetime is limited to 10000h, report the test life and acid number as >10000h (AN=*x.xx*).

12 Precision

The following criteria should be used for judging the acceptability of results (95% confidence) in the data range from 700 to 3900h:

12.1 Repeatability r

The difference between concurrent test results obtained by the same operator with the same apparatus according to the same test method on identical test materials, would not exceed the value of Formula (2):

$$r=0.192X \quad (2)$$

Where,

$\overline{X}$ — the arithmetic mean of duplicate determination results.

12.2 Reproducibility R

The difference between two single and independent results, obtained by different operators working in different laboratories with different apparatuses and with the same method on identical test material, would not exceed the value of Formula (3):

$$R=0.33\,\overline{X} \quad (3)$$

Where,

$\overline{X}$ — the arithmetic mean of two determination results.

Note: Reproducibility with duplicate tests, R'.

If two successive tests are performed by each operator in 12.2, the difference between the averages of the two sets of results from the tests would not exceed the value of Formula (4):

$$R' = 0.302\,\overline{X} \tag{4}$$

Where,

$\overline{X}$ — the mean value of the averaged results from the two laboratories.

If more than two results are obtained by one or both of the laboratories, the reproducibility of the mean value can be calculated according to GB/T 17039.

Appendix A

(Normative)

Semiquantitative Microdetermination of Acid Number of Lubricating Oils during Oxidation Testing

A.1 Scope

A.1.1 This test method belongs to semiquantitative microdetermination method, applies to monitor the variation of acidic component of lubricating oil sample during the oxidation test within the acid number of 0.02mgKOH/g~1.0mgKOH/g, and is applicable to steam turbine oils, hydraulic oils and other circulating oils.

Note: This method is the microdetermination edition of GB/T 4945, and the results obtained from two methods are similar.

A.1.2 This test method is design for the condition of limited sample quantity. This method should not replace the method with higher accuracy, e.g. GB/T 4945 or GB/T 7304, and this method is not applicable to the monitoring of in-use oils.

A.2 Term

For the purposes of this Standard, the following term applies.

Acid number

Alkali quantity required for the sample dissolved through titration in designated solvent reaching the designated end point, which is expressed with milligram of potassium hydroxide/gram of sample.

Note: In this test method, when sample is dropped into volumetric solution to change the solution color from blue green to orange yellow, the acid number may be calculated through comparing the drops of added sample with the drops of added reference sample for using reference sample to make the volumetric solution have the same color change, because this is a direct comparison method, the obtained acid number may be reported as milligram of potassium hydroxide/gram of sample.

A.3 Summary of test method

A.3.1 Use a dropper to drop the sample into a portion of 2.0mL volumetric solution, and record the sample drops required for volumetric solution changing into stable orange yellow from green blue.

Dissolve potassium hydroxide into isopropyl alcohol to prepare into about 0.1M solution. Calibrate this solution with pure potassium hydrogen phthalate dissolved into 100mL of water, and detect the end point by using phenolphthalein as an indicator. (commercially available reagents may be used)

Warning — Corrosive, toxic if inhaled, alkalic, stimulating to dermatitis.

A.6.4 Dodecenyl succinic anhydride

Warning — Stimulating to skin and eye.

A.6.5 P-naphtholbenzein indicator solution

P-naphtholbenzein must meet the specification requirements in Appendix A of GB/T 4945-2002. Prepare solution containing 10g/L of p-naphtholbenzein in mixed 50:50 methylbenzene and isopropyl alcohol solvent.

Warning — Flammable, vapor harmful.

Note: Fisher and other companies may provide p-naphtholbenzein indicator solution.

A.6.6 Isopropyl alcohol

Warning — Flammable, report indication; if no inhibition, generate peroxide and form explosive mixture when the container for storing isopropyl alcohol or reagent preparation bottle is empty and near to dryness.

A.6.7 Volumetric solution

Mix 350mL of methylbenzene, 350mL of isopropyl alcohol and 7mL of p-naphtholbenzein solution in a 1L plastic bottle, add 15mL of 0.1M potassium hydroxide isopropyl alcohol solution, and mix uniformly. (Warning — Flammable, vapor harmful, corrosive)

Note: The concentration of volumetric solution will drop with time, thus the volumetric solution needs to be replaced periodically, and one replacement every month may meet the requirements.

A.6.8 Methylbenzene

Warning — Flammable, vapor harmful.

A.7 Procedure

A.7.1 Sampling

Extract a minimum of test oil from oxidation cell according to the procedure specified in the oxidation test method.

The difference between two continuous test results, obtained by the same operator with the same apparatus and with the same test method on identical sample, would not exceed the value of Formula (A.3):

$$r_a=0.2\times \overline{A}_n \qquad (A.3)$$

Where,

$\overline{A}_n$ — the arithmetic mean of two determination results.

A.9.1.2 Reproducibility R.

The difference between two single and independent results, obtained by different operators working in different laboratories with different apparatuses and with the same method on identical sample, would not exceed the value of Formula (A.4):

$$R_a=0.7\times \overline{A}_n \qquad (A.4)$$

Where,

$\overline{A}_n$ — the arithmetic mean of two determination results.

A.9.2 Bias

This test method has no bias as the acid number is only determined according to the test method.

Appendix B

(Informative)

Procedure for Packaging Catalyst Coils

B.1 Materials

B.1.1 Test tubes, borosilicate glass, 250-mm length, 25-mm outside diameter, approximately 22-mm inside diameter.

B.1.2 Caps, for test tubes, polyethylene cylindrical shape designed to closely grip outside surface of test tube.

B.1.3 Desiccant bags, of silica gel granules.

B.1.4 Flushing tube, stainless steel or glass, approximately 5mm outside diameter, 305mm long, to deliver nitrogen to bottom of test tube.

B.1.5 Nitrogen gas, 99.7% minimum purity.

Warning — Compressed gas under high pressure. Gas reduces oxygen available for breathing.

B.2 Procedure

Flush a new test tube with nitrogen gas, using the flushing tube, to blow out any loose particles. The tube must be visibly clean and dry. Hold the tube on an angle and gently slide the catalyst coil into the tube. Add a desiccant bag that has been folded lengthwise to fit in the tube. Insert the nitrogen flushing tube down the middle of the test tube, to the bottom, and blow nitrogen through the tube for several seconds. Immediately after withdrawing the flushing tube, seal the test tube with a polyethylene cap.

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