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INTERNATIONAL STANDARD

NORME INTERNATIONALE

Insulating liquids – Test method for detection of potentially corrosive sulphur in used and unused insulating oil

Liquides isolants – Méthode d'essai pour la détection du soufre potentiellement corrosif dans les huiles usagées et neuves

IEC 62535:2008

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

INSULATING LIQUIDS – TEST METHOD FOR DETECTION OF POTENTIALLY CORROSIVE SULPHUR IN USED AND UNUSED INSULATING OIL

FOREWORD

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International Standard IEC 62535 has been prepared by IEC technical committee 10: Fluids for electrotechnical applications.

The text of this standard is based on the following documents:

FDIS	Report on voting
10/746/FDIS	10/749/RVD

Full information on the voting for the approval of this standard can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

The committee has decided that the contents of this publication will remain unchanged until the maintenance result date indicated on the IEC web site under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed;
- withdrawn;
- replaced by a revised edition; or
- amended.

INTRODUCTION

In recent years, several failures of transformers and reactors due to copper sulphide formation in/on the cellulose insulation have been reported worldwide. The tendency of transformer oils to form copper sulphide in the presence of copper is seen as one of the major contributing factors.

The most common reason for such failures is arcing between adjacent disks or conductors of a winding, due to the formation of deposits of copper sulphide on the cellulosic insulating paper.

It has been demonstrated that existing test methods for corrosive sulphur, ASTM D1275 method A and DIN 51353, are unable to detect oils having potentially corrosive behaviour.

For this reason, IEC technical committee 10 has prepared this International Standard for the detection of potentially corrosive sulphur in mineral insulating oils. The wrapped conductor test method is suitable for used and unused mineral oils.

This test method is based on a study performed by Conseil International des Grands Réseaux Electriques (CIGRE) working group A2.32 [1][1].

Health and safety

This International Standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of the standard to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

The mineral oils which are the subject of this standard should be handled with due regard to personal hygiene. Direct contact with eyes may cause slight irritation. In the case of eye contact, irrigation with copious quantities of clean running water should be carried out and medical advice sought.

Some of the tests specified in this standard involve the use of processes that could lead to a hazardous situation. Attention is drawn to the relevant standard for guidance.

Environment

This standard involves mineral oils, chemicals and used sample containers. The disposal of these items should be carried out in accordance with current national legislation with regard to the impact on the environment. Every precaution should be taken to prevent the release into the environment of mineral oil.

[1] Figures in square brackets refer to the bibliography.

INSULATING LIQUIDS – TEST METHOD FOR DETECTION OF POTENTIALLY CORROSIVE SULPHUR IN USED AND UNUSED INSULATING OIL

1 Scope

This International Standard specifies a test method for detection of potentially corrosive sulphur in used and unused mineral insulating oil.

Most recent failures due to corrosive sulphur are related to the formation of copper sulphide deposits in and on the surface of winding cellulosic paper.

The test method uses a copper conductor, wrapped with one layer of paper, immersed in the oil and heated to evaluate the capability of the oil to yield copper sulphide and transfer it to paper layers.

The growth of copper sulphide on bare copper may cause the presence of conductive particulates in the oil, which can act as nuclei for electrical discharge and may lead to a fault. Other test methods exist using a bare copper strip immersed in oil and heated to detect the corrosive behaviour of oil against copper. ASTM D1275 Method B is also used for this test and a modified procedure using low oil volumes is included in Annex A.

Tests with and without paper are considered as complementary and may lead to different results.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC 60475, *Method of sampling liquid dielectrics*

IEC 60554-3-1, *Specification for cellulosic papers for electrical purposes – Part 3: Specifications for individual materials – Sheet 1: General purpose electrical paper*

ASTM D1275, *Methods A and B: Standard test method for corrosive sulfur in electrical insulating oils*

ASTM D130, *Standard test method for corrosiveness to copper from petroleum products by copper strip test*

DIN 51353, *Testing of insulating oils; detection of corrosive sulfur; silver strip test*

EN 13601, *Copper and copper alloys. Copper rod, bar and wire for general electrical purposes*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
potentially corrosive sulphur
organo-sulphur compounds present in transformer oils that may cause copper sulphide formation.

NOTE Some of these compounds may be initially corrosive, or become corrosive under certain operating conditions

4 Sampling

Samples shall be taken, following the procedure given in IEC 60475. Ensure that the test portion is representative by thoroughly mixing.

5 Procedure

5.1 Principle

A piece of copper conductor wrapped with Kraft paper is immersed in the oil and subjected to heating for 72 h at 150 °C in a sealed glass headspace vial.

The copper is examined for indications of discolouration and the paper is examined for the presence of copper sulphide deposits.

5.2 Apparatus and materials

The following apparatus and materials shall be used:

- Glass headspace vial as used for chromatography, capacity approximately 20 ml, with a nominal diameter of 22,5 mm to 23 mm.

NOTE 1 Vials are commonly available from suppliers of chromatography consumables and from instrument manufacturers.

- PTFE-faced silicone septum and aluminium cap for sealing the vial.
- Crimping tool.
- Heating chamber or oven capable of being maintained at 150 °C ± 2 °C.
- Flat, unvarnished, paper-wrapped copper conductor obtained from a transformer manufacturer or winding supplier. Dimension of the flat copper: approximately 7,5 mm x 1,5 mm (or with a surface area corresponding to these dimensions). Wrapping paper width 10 mm to 14 mm. The most suitable have proven to be flat conductors having four layers of wrapped paper. The paper adjacent to copper should be wound gap to gap (the gap should be in the tolerance $^{+1,00}_{-0,2}$ mm, the negative value means overlapping). This is the layer used with the copper conductor for the test itself. The rest of the paper layers have only a mechanical and protective function during transport and storage.

NOTE 2 Possible sources of supply are :

- Asta Elektrodraht GmbH & Co. (Austria)
- Essex Nexans L+K GmbH, (Germany)
- Siemens AG, Trafowerk Nuremberg (Germany).[2]

- Kraft paper according to IEC 60554-3-1:
  - Density: 0,70 to 0,85 g/cm^3
  - Thickness: 0,060 mm to 0,100 mm

2 This information is given for the convenience of the users of this International Standard and does not constitute an endorsement by the IEC.

  - Air permeability M or H
  - Conductivity: < 4 mS/m
  - Free nitrogen content: 0 %
- Cu-ETP according to EN 13601, (old material code: E-Cu58):
  - Material code: CW 004A
  - Oxygen content: < 0,04 % (w/w)
  - Cu: 99,90 %
- Solvent for rinsing:
  - Cyclohexane or heptane, analytical grade.

5.3 Method

Pour 50 ml of oil into a beaker of 100 ml and leave in the open air for 60 min (protected from sunlight).

Transfer 15 ml of this oil into the headspace vial. The precision given by a measuring cylinder is adequate, as is use of a headspace vial pre-marked at 15 ml.

Cut the conductor in 30 mm ± 3 mm lengths. Unwrap the outer layers of the copper conductor and leave only one layer in contact with the copper. Do not touch paper or copper with fingers during this and subsequent operations and ensure that all tools are pre-cleaned with solvent.

Place the wrapped flat conductor inside the headspace vial and close it with the septum (PTFE face towards the oil) and close the cap using a crimping tool. The crimped cap should be sufficiently tight such that hand rotating of the cap on the vial is not possible.

NOTE It is essential that, if a butyl rubber septum is used, the PTFE face seals correctly to the glass vial. The hot oil must have no access to the butyl rubber, which contains sulphur.

Place in a heating chamber for 72 h ± 30 min at 150 °C ± 2 °C.

After the vial has cooled, remove the cap and take out the wrapped conductor. Tweezers should always used to handle the conductor and the paper.

Unwrap the paper for evaluation of the copper surface.

Rinse the copper conductor with cyclohexane or heptane, and allow to dry for 2 min in air.

Prior to evaluation, degrease the paper by immersion in 50 ml of solvent in a beaker for 1 min. Repeat the degreasing twice in fresh solvent and allow the paper to dry for at least 5 min until all solvent is evaporated.

Carry out the test in duplicate.

Carry out a blank test, in order to ensure that all materials used are sulphur free. The blank test should be carried out with a white oil or other oil containing less than 5 mg/kg sulphur. Such a test will also assist in detecting changes to the copper.

6 Inspection and interpretation

6.1 General

All inspections should be carried out under very good light conditions. Bright daylight or strong fluorescent lighting has been proven to be satisfactory. It is important to view objects with light from different angles.

Both the copper and the paper shall be inspected for signs of sulphide formation. The results from the duplicate tests must show the same discolouration.

6.2 Copper

Examine all surfaces of the copper for discolouration and note the appearance and colour. The result is positive if the copper strip has one of the following colours: graphite grey, dark brown or black. All other colours are considered a negative result.

6.3 Paper

Examine both the inside and outside surfaces of the paper strip. A magnifying glass (approx. 5 × magnification) can be helpful.

Copper sulphide deposition on the paper appears metallic, from clearly shiny to almost lustreless, often with a lead- or tin-like appearance. It can also have the appearance of silver, brass or bronze. The metal-like surface of sulphide can have an overlay of blue and/or purple due to interference phenomena. Other discolourations (i.e. by-products of paper ageing and oil deterioration) shall not to be taken as copper sulphide formation.

Copper sulphide may be formed both on the outside as well as the inside of the paper. Even though sulphide may be formed anywhere, particular attention should be paid to edges and inside bends. Note that deposits localized at some edges may come from copper mechanically transferred to the paper while cutting the conductor. Sometimes the paper surface is smoothed at the edges by the cutting tool. If any shiny appearance of the paper is limited to such edges, it shall not be considered a positive result unless confirmed to be sulphide.

Although copper sulphide formation is often clearly evident even when the paper is discoloured, it may possibly be obscured by strong discoloration. SEM-EDX, or alternative methods to determine total copper and sulphur content of the paper may be used to assist the interpretation. An example of a method using SEM-EDX to evaluate the presence of copper sulphide deposits on paper is described in Annex B.

In case of doubt concerning the composition of the precipitate, the result cannot be considered as corrosive unless the precipitate is positively identified as copper sulphide.

X-ray diffraction or determination of copper and sulphur content of the paper may also give guidance. It is also highly recommended in those cases to analyse for both copper and sulphur on paper from an unused test specimen.

6.4 Result

If, for both of the duplicate samples, a positive result is found for copper, or paper, or both, the oil shall be reported as potentially corrosive. If, for both samples, a negative result is obtained for both copper and paper, the oil shall be reported as non-corrosive.

If the results for the duplicate sample are different, the test shall be repeated.

NOTE If there are any doubts in the interpretation of the results of inspection of paper, the composition of precipitate should be analysed by other methods (for example by SEM-EDX). If the precipitate is identified as copper sulphide, the oil must be reported as potentially corrosive.

7 Repeatability and reproducibility

Repeatability: according to inter-laboratory tests carried out by CIGRE WG A2.32, duplicate results had 100 % agreement.

Reproducibility: according to inter-laboratory tests carried out by CIGRE WG A2.32, 2 laboratories out of 16 had different results. In these cases the oils differed from the original delivered batches.

8 Report

The test report shall contain at least the following information:

- testing laboratory;
- the type and identification of the product tested;
- a reference to this International Standard;
- the result of the test (see 6.4);
- any deviation, by agreement or otherwise, from the procedure specified;
- the date of the test.