BRITISH STANDARD

BS EN 62021-2:2007

Insulating liquids — Determination of acidity —

Part 2: Colourimetric titration

The European Standard EN 62021-2:2007 has the status of a British Standard

ICS 29.040.10

British Standards

National foreword

This British Standard is the UK implementation of EN 62021-2:2007. It is identical to IEC 62021-2:2007.

The UK participation in its preparation was entrusted to Technical Committee GEL/10, Fluids for electrotechnical applications.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Insulating liquids - Determination of acidity - Part 2: Colourimetric titration

(IEC 62021-2:2007)

Liquides isolants -
Détermination de l’acidité -
Partie 2: Titrage colorimétrique
(CEI 62021-2:2007)

Isolierflüssigkeiten -
Bestimmung des Säuregehaltes -
Teil 2: Kolorimetrische Titration
(IEC 62021-2:2007)

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CENELEC

European Committee for Electrotechnical Standardization
Comité Européen de Normalisation Electrotechnique
Europäisches Komitee für Elektrotechnische Normung

Central Secretariat: rue de Stassart 35, B - 1050 Brussels

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Foreword

The text of document 10/692/FDIS, future edition 1 of IEC 62021-2, prepared by IEC TC 10, Fluids for electrotechnical applications, was submitted to the IEC-CENELEC parallel vote and was approved by CENELEC as EN 62021-2 on 2007-07-01.

The following dates were fixed:

– latest date by which the EN has to be implemented at national level by publication of an identical national standard or by endorsement	(dop)	2008-04-01
– latest date by which the national standards conflicting with the EN have to be withdrawn	(dow)	2010-07-01

Annex ZA has been added by CENELEC.

Endorsement notice

The text of the International Standard IEC 62021-2:2007 was approved by CENELEC as a European Standard without any modification.

CONTENTS

INTRODUCTION

The standardized method given in IEC 62021-1 is a method for measurement of acidity in used and unused mineral oil and is a potentiometric titration requiring special instrumentation for measurement of acidity. Historically, acidity of insulating oil was measured by colourimetric titration as described in IEC 60296, 1982 edition. With the revision of IEC 60296, the colourimetric titration was deleted as that method used high volumes of sample and solvent, generating undesirable volumes of waste.

However, there is still a market requirement for having colourimetric titration as many labs use this method.

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.

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.

INSULATING LIQUIDS – DETERMINATION OF ACIDITY –

Part 2: Colourimetric titration

1 Scope

This part of IEC 62021 describes a procedure for determination of the acidity of unused and used electrical mineral insulating oils.

NOTE 1 In unused and used mineral insulating oils, the constituents that may be considered to have acidic characteristics include organic acids, phenolic compounds, some oxidation products, resins, organometallic salts and additives.

The method may be used to indicate relative changes that occur in a mineral insulating oil during use under oxidizing conditions that may or may not be shown by other properties of the resulting mineral oil.

The acidity can be used in the quality control of unused mineral oil.

As a variety of oxidation products present in used mineral oil contribute to acidity and these products vary widely in their corrosion properties, the test cannot be used to predict corrosiveness of a mineral oil under service conditions.

NOTE 2 The acidity results obtained by this test method may or may not be numerically the same as those obtained by potentiometric methods, but they are generally of the same magnitude. The potentiometric method uses an endpoint at pH 11,3 to ensure titration of all species, whereas the colourimetric methods uses an indicator changing colour at approximately pH 9,5. This may lead to slightly higher results for oils with acidities above 0,3 mg KOH/g oil when using the potentiometric method.

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 60567: *Oil-filled electrical equipment – Sampling of gases and of oil for analysis of free and dissolved gases – Guidance*

ISO 5725: *Accuracy (trueness and precision) of measurement methods and results*

ISO 6619: *Petroleum products and lubricants – Neutralization number – Potentiometric titration method*

3 Terms and definitions

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

3.1
acidity

quantity of base, expressed in milligrams of potassium hydroxide per gram of sample, required to titrate colourimetrically a test portion in a specified solvent to the neutralization point of Alkali Blue 6B

3.2
unused oil

mineral insulating oil that has not been used in, or been in contact with electrical equipment

4 Principle

The test portion is dissolved in a specified solvent and titrated colourimetrically with alcoholic potassium hydroxide to a specified colour using Alkali Blue 6B indicator.

5 Reagents

Only reagents of recognized analytical grade and de-ionized water or water of equivalent purity shall be used.

5.1 Titration reagent

Standard alcoholic solution 0,05 mol/l potassium hydroxide.

Add 3,0 g of potassium hydroxide to 1 000 ml ± 10 ml of 2-propanol. Boil gently for 10 min to effect solution. Cool and stopper the flask.

Allow the solution to stand in the dark for 2 days and then filter the supernatant liquid through a 5 µm membrane filter. Store in a suitable amber glass bottle.

The concentration of this solution is approximately 0,05 mol/l and shall be standardized as described in 8.1. For periodic tests on equipment in service, faster titration may be achieved by the use of 0,1 mol/l potassium hydroxide by agreement between the laboratory and the equipment owner, although this may result in poorer precision and detection limit.

Commercial alcoholic potassium hydroxide solution may be used, if necessary diluting to 0,05 mol/l with 2-propanol. This shall be standardized as described in 8.1.

Store and use in such a manner that the solution is protected from atmospheric carbon dioxide and in such a way that it does not come into contact with cork, rubber or saponifiable stopcock grease. The solution may be protected by inert gas or by means of a guard tube containing soda-lime absorbent.

5.2 Titration solvent

2-propanol (isopropanol; IPA), pure.

5.3 Potassium hydrogen phthalate, primary standard

This should be dried before use for 2 h at 105 °C.

5.4 Standard hydrochloric acid solution

A 0,1 mol/l solution of hydrochloric acid in de-ionized water, prepared as in ISO 6619, may be used. Other acids may be used, provided they are certified against a primary standard.

5.5 Alkali blue 6B indicator solution

Dissolve 2 g ± 0.1 g of alkali blue 6B in 100 ml of 2-propanol or azeotropic ethanol containing 1 ml of the hydrochloric acid solution. After 24 h, carry out a titration to check whether the indicator has been sufficiently sensitized. The indicator is satisfactory if the colour changes distinctly from blue to red comparable to that of a 10 % solution of cobalt nitrate. If sensitization is insufficient, repeat the addition of the hydrochloric acid solution and check again after 24 h. Continue until sensitization is satisfactory. Filter and store in a brown bottle in the dark.

Commercial alkali blue 6B solution may be used as an alternative if the concentration is within the range 0,05 % to 5 %. If the concentration is not 2 %, the amount added to the solvent in 8.2 and 8.3 should be adjusted to maintain the same ultimate concentration.

5.6 Cobalt nitrate solution

$Co(NO_3)_2.6H_2O$ solution, 10 % in water.

6 Apparatus

6.1 Titration vessel

This should be as small as possible, sufficient to contain the solvent, sample and stirrer and be inert to the reagents. Glass conical vessels are preferred.

6.2 Stirrer

Stirring may be manual by swirling the solution on the titration vessel, or mechanically using a variable speed stirrer fitted with a propeller, paddle or magnetic bar of chemically inert surface material.

6.3 Burette

A burette or syringe capable of adding aliquots of 0,001 ml shall be used.

7 Sampling

Samples shall be taken following the procedure given in IEC 60475 and/or IEC 60567.

Ensure that the test portion is representative by thoroughly mixing, as any sediment present may be acidic or have adsorbed acidic material from the liquid phase.

8 Procedure

Rinse and fill the burette with 0,05 mol/l alcoholic potassium hydroxide solution (5.1).

Standardize the alcoholic potassium hydroxide solution at least every two weeks against potassium hydrogen phthalate (5.3) or certified standard 0,1 mol/l acid.

Carry out a blank titration on the solvent (5.2) each day and after changing to a fresh batch of solvent.

8.1 Standardization of alcoholic potassium hydroxide solution

Standardize the alcoholic potassium hydroxide solution, using a suitable indicator, against 0,1 g to 0,16 g of potassium hydrogen phthalate, weighed to an accuracy of 0,000 2 g and dissolved in approximately 100 ml of carbon dioxide free water.

Alternatively the standardization can be performed by potentiometric titration.

Calculate the molarity M to the nearest 0,000 5 using Equation (1):

$$\text{Molarity} = \frac{1\,000 \times m \times p}{204{,}23 \times V} \qquad (1)$$

where

m is the mass of potassium hydrogen phthalate, in grams;

p is the percent purity of the potassium hydrogen phthalate;

V is the volume of potassium hydroxide solution, in millilitres.

Alternatively, certified standard 0,1 mol/l acid may be used to standardize the alcoholic potassium hydroxide solution.

Calculate the molarity M to the nearest 0,000 5 using Equation (2):

$$\text{Molarity} = \frac{V_1 \times M_A}{V_0} \qquad (2)$$

where

V_1 is the volume of 0,1 mol/l standard acid used to titrate the solution, in millilitres;

M_A is the molarity of the standard hydrochloric acid;

V_0 is the volume of potassium hydroxide solution, in millilitres.

8.2 Blank titration

Perform a blank titration at a temperature not above 25 °C on 10 ml ± 0,1 ml aliquots of the solvent containing 0,5 % of alkali blue 6B indicator solution (5.5) using the standardized alcoholic potassium hydroxide solution. The endpoint shall be as soon as a colour change from blue to a red colour comparable to that of the cobalt nitrate solution (5.6) is obtained and persists for at least 15 s.

Carry out triplicate titrations and calculate the mean result, in millilitres to the nearest 0,001 ml, as the blank value V_0.

Protect the solvent from atmospheric carbon dioxide and use within 8 h.

8.3 Sample titration

Weigh 5 g of sample to the nearest 0,01 g into the titration vessel. Add 10 ml ± 0,1 ml of the solvent solution containing 0,5 % of alkali blue 6B indicator solution (5.5). Swirl to dissolve the oil and immediately titrate at a temperature not above 25 °C with the standardized potassium hydroxide solution. A typical end point is as described in 8.2. However, since the colour change may vary for different oils, pre-titration may be necessary to establish this. In such cases, the endpoint shall be reached as soon as a stable colour change, which persists for at least 15 s, is obtained.

NOTE Before titrating, the colour may vary from blue to green and at the endpoint from red to light orange to dark yellow-brown, depending on the original colour of the oil.

Carry out determinations for each oil sample and note the result, in millilitres, to the nearest 0,001 ml, as the titration value V_1.

9 Calculation of results

Calculate, for each determination, the acidity to the nearest 0,005, expressed as mg KOH/g of oil, using Equation (3):

$$\text{Acidity} = \frac{(V_1 - V_0) \times M \times 56{,}1}{m} \tag{3}$$

where

V_1 is the volume of alcoholic KOH solution used to titrate the test sample, in millilitres;

V_0 is the mean volume of alcoholic KOH solution used for the blank titration, in millilitres;

M is the molarity of alcoholic KOH solution;

m is the mass of the test portion used, in grams.

10 Precision

The repeatability and reproducibility limits were established in accordance with ISO 5725.

10.1 Repeatability

The difference between successive 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 method, exceed the values shown below only in one case in 20:

– unused oils	–15 %;
– used oils	–10 %.

NOTE The repeatability values for unused oils only apply where the result is significantly above the quantification limit, which has been established as 0,01 mg KOH/g oil.

10.2 Reproducibility

The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values shown below only in one case in 20:

- unused oils – 35 %;
- used oils – 20 %.

NOTE The reproducibility values for unused oils only apply where the result is significantly above the quantification limit, which has been established as 0,01 mg KOH/g oil.

11 Report

The test report shall contain at least the following information.

- The type and identification of the product tested.
- A reference to this International Standard.
- The result of the test (see Clause 9) expressed to the nearest 0,01 mg KOH/g of oil.
- Any deviation, by agreement or otherwise, from the procedure specified.
- The date of the test.

Annex A
(informative)

Determination of acidity in electrical insulating oils by photometric titration

A.1 Principle

A sample of new or used oil is dissolved in a mixture of toluene and 2-propanol containing a small amount of water. The solution is titrated at ambient temperature with alcoholic potassium hydroxide. The neutralization of acid components in oil is detected by the colour change of the added para-naphtolbenzein indicator, using a photometric sensor at 660 nm.

A.2 Reagents and solvents

- Para-naphtolbenzein indicator (1 % in alcoholic solution)
- Potassium hydroxide solution in 2-propanol (1 mol/l)
- Potassium hydrogen phthalate
- 2-Propanol, anhydrous, HPLC grade
- Toluene, HPLC grade
- Demineralized water, conductivity < 0,1 µS/cm
- Methanol, HPLC grade
- CO_2 absorbing agent, 8-20 mesh
- Water absorbing agent, 10-20 mesh

NOTE It is recommended to filter all solvents, solutions and oil samples prior to use.

A.2.1 Preparation of titration solutions and solvents

A.2.1.1 Potassium hydroxide alcoholic solution (0,05 mol/l)

Introduce 50 ml of the potassium hydroxide solution in 2-propanol (1 mol/l) into a volumetric vessel of 1 l. Make up to 1,0 l with 2-propanol.

A.2.1.2 Potassium hydrogen phthalate solution (0,05 mol/l)

Crush 10 g of potassium hydrogen phthalate in a mortar and dry at 120 °C for 1 h, then cool in a desiccator containing a water-absorbing agent. Weigh about 5 g of dried potassium hydrogen phthalate precisely in a scoop and introduce it in a volumetric vessel of 500 ml. Wash the scoop several times with small amounts of water into the volumetric vessel. Make up to 500,0 ml with demineralised water.

Calculate the molarity to the nearest 0,000 5 using following Equation (A.1):

$$\text{Molarity } (M_{\text{KPH}}) = \frac{m}{204{,}23 \times 0{,}5} \qquad \text{(A.1)}$$

where m is the mass of potassium hydrogen phthalate, in gram.

A.2.1.3 Titration solvent

The composition of the titration solvent in % volume/volume is: 50 % toluene, 49,5 % 2-propanol, 0,5 % demineralized water. 500 µl of para-naphtolbenzein indicator solution is added per 100 ml of titration solvent.

A.3 Apparatus

A.3.1 Volumetric titrator

The apparatus shall be equipped with an automatic burette of 5 ml capacity with a dispensing accuracy of ±0,01ml. A guard tube containing the water and carbon dioxide absorbing agents is necessary for the reservoir for the alcoholic potassium hydroxide solution.

A.3.2 Titration vessel

The titration vessel shall have a 100 ml capacity and be inert to the reagents.

NOTE The vessel volume should be such that the photometer probe is covered by liquid during the titration.

A.3.3 Titration stand

A suitable stand shall be provided to support the titration vessel, stirrer, automatic burette and photometric sensor.

A.3.4 Stirrer

The stirrer shall be mechanical or electrical, having variable speed.

A.3.5 Recorder/printer

A device shall be required to record/print out the data coming from the titrator and photometric sensor.

NOTE 1 Installing the titration apparatus in a fume hood will eliminate solvent vapours from the laboratory environment.

NOTE 2 An automatic sampler may be used to increase the productivity of analyses.

A.3.6 Photometric sensor

A suitable sensor is equipped with a glass-fibre light guide probe measuring the transmission of light in the visible region, equipped with a filter allowing measurements to be made in a bandwidth of less than 10 nm at any visible wavelength.

The molecular structures of para-naphtolbenzein indicator in acidic and basic media are indicated in Figure A.1. The UV transmission rate is maximum at 660 nm in acidic media, giving the solution an orange colour (Figure A.2). It is minimum at 660 nm in basic media, changing the solution to green colour. The wavelength of the photometric sensor therefore is set at 660 nm.

NOTE Phenolphthalein indicator may also be used at 550 nm.

A.4 Procedure

A.4.1 Preparation and maintenance of the titration system

It is necessary to clean the titration vessel, stirrer and photometric sensor with methanol and to air-dry them before each use.

NOTE If the photometer and its controller cannot be set to achieve the manufacturer's recommended parameters, this may be an indication that the photometer is dirty and should be cleaned more thoroughly.

A.4.2 Determination of acidity of the titration solvent

Install the photometric sensor on the titration stand and connect it to the titrator. Flush the automatic burette 3 times into a beaker using the KOH solution. The tubes carrying the KOH solution should not contain bubbles after these operations. Fix a cleaned titration vessel to the titration stand.

Introduce 50 ml ± 0,1 ml of titration solvent into the titration vessel. Start the stirrer. Place the tip of the automatic burette in the centre of the solution, at about 2,5 cm from the stirrer. The optical path of the photometric sensor should be void of any bubbles. If there are bubbles, adjust stirring speed to eliminate them. Set the voltage on the photometric sensor at 1 000 mV.

Start titrating with the potassium hydroxide alcoholic solution (0,05 mol/l) and the automatic burette. The printer will print the titration curve (in mV vs. ml), the first derivative of the titration curve (in mV/ml vs. ml) and the volume of KOH solution used (in ml). Note volume of KOH used for neutralization of titration solvent as V_0.

NOTE The above procedure should be carried out daily.

A.4.3 Determination of molarity of the potassium hydroxide alcoholic solution (0,05 mol/l)

Proceed as follows:

a) fix a cleaned titration vessel to the titration stand;

b) introduce 1 ml ± 0,01 of potassium hydrogen phthalate water solution (0,05 mol/l) into the titration vessel. Add 50 ml of titration solvent;

c) titrate as in A.4.2.

Calculate the molarity of the KOH solution to the nearest 0,000 5 using the following Equation (A:2):

$$\text{Molarity} = \frac{1 \times M_{\text{KHP}}}{V} \qquad \text{(A.2)}$$

where

M_{KHP} is molarity of potassium hydrogen phthalate;

V is volume of potassium hydroxide solution, in millilitres.

Calculate the final value of molarity as the average of 3 determinations.

NOTE Procedure A.4.3 need only be carried out each month. The potassium hydroxide alcoholic solution has been found quite stable with time when suitably stored; see 5.1.

A.4.4 Titration of soluble acidity in the oil sample

Proceed as follows:

a) fix a cleaned titration vessel to the titration stand;

b) for new oils or only slightly used oils, introduce 20 g ± 0,01 g of oil in the titration vessel. For highly used oils, introduce 5 g ± 0,01 g of oil;

c) add 50 ml ± 0,1 ml of titration solvent and titrate as in A.4.2.

Calculate the acidity of the oil sample KOH to the nearest 0,000 5, using the following Equation (A.3):

$$\text{Acidity} = \frac{(V_1 - V_0) \times M \times 56{,}1}{m} \tag{A.3}$$

where

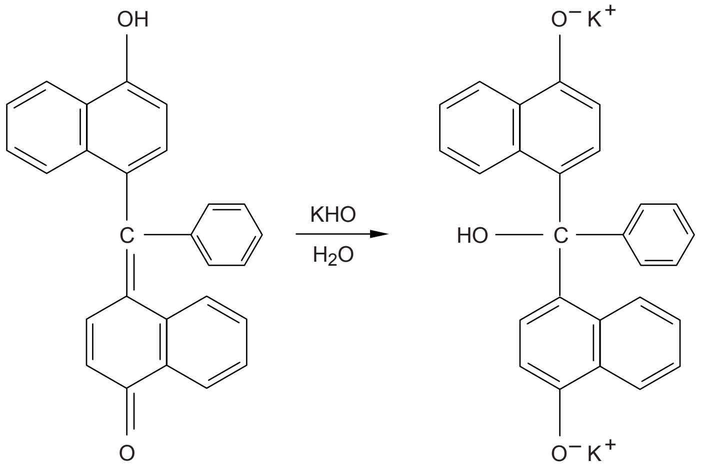
V_1 is the volume of alcoholic KOH solution used to titrate the test sample, in millilitres;

V_0 is the mean volume of alcoholic KOH solution used for the blank titration (titration solvent), in millilitres;

M is the molarity of alcoholic KOH solution;

m is the mass of the test portion used, in grams.

NOTE On modern equipment, data measured in A.4.2, A.4.3 and A.4.4 may be stored in the memory of the equipment to automate calculations.



IEC 681/07

Figure A.1 – Molecular structure of para-naphtolbenzein indicator in (I) acidic media and (II) basic media

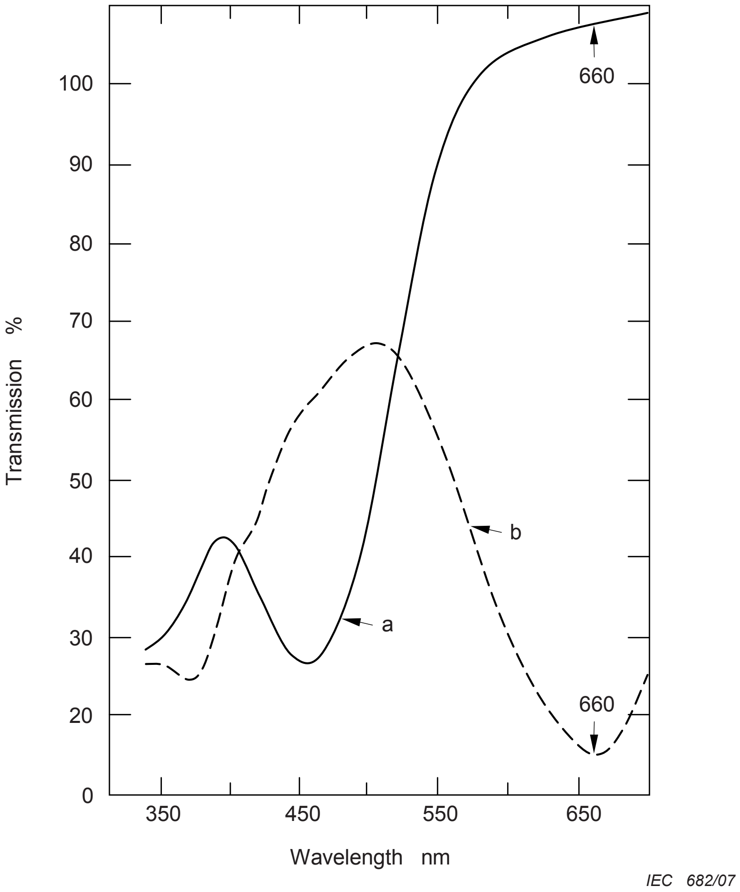


Figure A.2 – UV spectra of para-naphthol-benzein indicator in toluene/2-propanol/water solution in (a) acidic media, (b) basic media

Annex ZA
(normative)

Normative references to international publications with their corresponding European publications

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.

NOTE When an international publication has been modified by common modifications, indicated by (mod), the relevant EN/HD applies.

Publication	Year	Title	EN/HD	Year
IEC 60475	- [1]	Method of sampling liquid dielectrics	-	-
IEC 60567	- [1]	Oil-filled electrical equipment - Sampling of gases and of oil for analysis of free and dissolved gases - Guidance	EN 60567	2005 [2]
ISO 5725	Series	Accuracy (trueness and precision) of measurement methods and results	-	-
ISO 6619	- [1]	Petroleum products and lubricants - Neutralization number - Potentiometric titration method	-	-

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[1] Undated reference.

[2] Valid edition at date of issue.

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