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PHTHALIC ANHYDRIDE FOR INDUSTRIAL USE

METHODS OF TEST

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BRIEF HISTORY

The ISO Recommendation R 1389, *Phthalic anhydride for industrial use – Methods of test*, was drawn up by Technical Committee ISO/TC 47, *Chemistry*, the Secretariat of which is held by the Ente Nazionale Italiano di Unificazione (UNI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1389, which was circulated to all the ISO Member Bodies for enquiry in February 1968. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Austria	Iran	Spain
Belgium	Ireland	Sweden
Brazil	Italy	Switzerland
Cuba	Korea, Rep. of	Thailand
Czechoslovakia	Netherlands	Turkey
France	New Zealand	U.A.R.
Germany	Portugal	United Kingdom
Hungary	Romania	
India	South Africa, Rep. of	

No Member Body opposed the approval of the Draft.

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided to accept it as an ISO RECOMMENDATION.

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PHTHALIC ANHYDRIDE FOR INDUSTRIAL USE

METHODS OF TEST

1. SCOPE

This ISO Recommendation describes methods of test for phthalic anhydride for industrial use.

2. SAMPLE*

The laboratory sample should have a mass of not less than 500 g. It should be preserved in a clean, dry and airtight glass-stoppered bottle of such a size that it is nearly filled by the sample. If it has been necessary to seal the container, care should be taken to avoid contaminating the contents in any way. Before carrying out the tests described, the sample should be ground to a fine powder and thoroughly mixed. Avoid undue exposure to moist air which might lead to the formation of phthalic acid.

3. MEASUREMENT OF COLOUR OF THE MOLTEN MATERIAL

3.1 Principle

Comparison of the colour of the molten sample with that of colour standards, and expression in terms of Hazen colour units.

NOTE. – The Hazen colour unit is defined as the colour of a solution containing one part per million of platinum in the form of chloroplatinic acid and in the presence of two parts per million of cobalt (II) chloride hexahydrate.

3.2 Reagents

Distilled water or water of equivalent purity should be used in the test.

3.2.1 *Cobalt (II) chloride,* hexahydrate ($CoCl_2.6H_2O$).

3.2.2 *Hydrochloric acid,* ρ 1.19 (g/ml) solution, approximately 38 % (m/m).

3.2.3 *Chloroplatinic acid.*

Dissolve 1.000 g of platinum in a small quantity of aqua regia contained in a glass or porcelain basin by heating on a boiling-water bath. When the metal has dissolved, evaporate the solution to dryness. Add 4 ml of the hydrochloric acid (3.2.2) and again evaporate to dryness. Repeat this operation twice more.

or

3.2.4 *Potassium chloroplatinate.*

3.3 Apparatus

Ordinary laboratory apparatus and

3.3.1 *Two matched flat-based colorimetric tubes,* of approximately 20 mm external diameter and having a graduation mark 100 mm above the base and with glass stirrers.

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* Sampling of chemical products will form the subject of a further ISO Recommendation.

3.3.2 *Electrically heated aluminium block,* maintained at 170 ± 3 °C with holes 22 mm in diameter and at least 120 mm in depth but such that the tops of the flat-based tubes project above the surface of the block.

3.4 Preparation of colour standards

3.4.1 Dissolve 2.0 g of cobalt (II) chloride (3.2.1) and either the chloroplatinic acid (3.2.3) or 2.490 g of potassium chloroplatinate (3.2.4) in 200 ml of hydrochloric acid (3.2.2). Warm, if necessary, to obtain a clear solution, and after cooling transfer to a 2000 ml one-mark volumetric flask. Dilute to the mark and mix thoroughly.

This solution has a colour of 500 Hazen units.

3.4.2 From this solution prepare a series of colour standards ranging from 0 Hazen colour units upwards, at intervals of 10 units. For each 10 units pipette 5.0 ml of the solution (3.4.1) into a 250 ml one-mark volumetric flask and dilute to the mark. Transfer each standard solution to a storage bottle and keep in the dark. Check these standards at intervals of 1 month against freshly prepared standards.

3.5 Procedure

3.5.1 Introduce into one of the colorimetric tubes (3.3.1) a quantity of the laboratory sample sufficient to reach the graduation mark after melting. Pour the colour standard selected into the other tube to the mark.

3.5.2 Place the tube containing the sample in the electrically heated block (3.3.2) and as soon as it has melted, compare the colour with that of the standard by looking down the tubes against a white background, taking care to avoid side illumination. If the sample has partly sublimed during the test, dislodge and stir in the particles of sublimed material. Repeat with other colour standards if necessary until the closest match is obtained.

3.6 Expression of result

Report the result to the nearest 10 Hazen colour units. If the colour of the sample does not match that of any of the colour standards, report if possible an approximate value for the colour with an appropriate note. Where matching proves impossible, give a description of the colour of the sample. Record also the presence of any black particles, visible impurities, etc.

4. DETERMINATION OF CRYSTALLIZING POINT

4.1 Principle

Slow cooling of the melted sample and observation of the temperature of crystallization.

4.2 Apparatus

Ordinary laboratory apparatus and

4.2.1 *Oil bath* regulated at 150 °C.

4.2.2 *Thick-walled test tube,* nominal size 100 mm × 25 mm, inside a 150 mm × 50 mm test tube acting as air-jacket.

4.2.3 *Thermometer,* of the mercury-in-glass type, for use at 100 mm immersion and covering a convenient range, (for example 100 to 150 °C*) graduated at intervals of 0.1 °C and having a maximum error of 0.2 °C.

The thermometer is placed in the inner test tube (4.2.2) and supported by a cork, so that the thermometer immersion mark is level with the top of the cork.

If the thermometer has a contraction chamber the distance from the bottom of the bulb to the top of the contraction chamber should not be more than 35 mm.

* The crystallizing point of pure phthalic anhydride is 131.5 °C.

4.2.4 *Glass stirrer* fitted through a slit in the side of the cork so that a loop in the stirrer surrounds the thermometer (4.2.3).

4.3 Procedure

4.3.1 Introduce about 20 g of the laboratory sample into the inner test tube (4.2.2). Heat the test tube and contents in the oil bath (4.2.1) at a temperature of 150 °C until the sample is molten. Insert the thermometer (4.2.3) into the liquid and allow the test tube to cool. The test tube must be surrounded by the outer air-jacket during the cooling period.

4.3.2 When the temperature has reached 135 °C, stir the material in the tube vigorously to induce crystallization. As crystallization occurs, the temperature will remain constant or will rise slightly. Observe the temperature throughout this period, and record the highest temperature reached as the crystallizing point.

5. DETERMINATION OF FREE ACIDITY

5.1 Principle

Potentiometric titration of the free acidity present with a standard solution of triethylamine in anhydrous ethyl methyl ketone.

5.2 Reagents

5.2.1 *Acetone.*

5.2.2 *Triethylamine* free from primary and secondary amines, 0.1 N solution in ethyl methyl ketone previously standardized with pure phthalic acid using the procedure described below (see clause 5.4).

NOTE. – Ethyl methyl ketone of satisfactory dryness may be obtained by treatment with calcium chloride, decantation and distillation.

5.2.3 *Phthalic acid.*

5.3 Apparatus

Ordinary laboratory apparatus and

5.3.1 *Microburette* 10 ml, graduated in 0.02 ml or smaller divisions.

5.3.2 *pH meter* with glass-calomel electrode system.

The saturated aqueous solution of potassium chloride in the calomel electrode is replaced by a saturated solution of potassium chloride in methanol. The calomel electrode should preferably be of the sleeve type provided with a ground glass joint.

5.3.3 *Magnetic stirrer.*

5.4 Procedure

5.4.1 Weigh, to the nearest 0.01 g, a quantity of the laboratory sample not exceeding 10 g and containing not more than 150 mg of phthalic acid. Transfer this test portion to a dry 150 ml beaker and dissolve in 75 ml of acetone (5.2.1).

5.4.2 Place the glass and calomel electrodes in the solution, stir by means of the magnetic stirrer (5.3.3), close the beaker to reduce evaporation and titrate potentiometrically with the triethylamine solution (5.2.2) from the microburette (5.3.1). On nearing the equivalence point, add the triethylamine solution in portions of 0.02 ml, reading the corresponding potential each time.

5.4.3 If the test portion contains less than 8 mg of phthalic acid, the potential increments Δ_1, Δ_0 and Δ_2 will coincide with the large changes in potential at the start of the titration. Accordingly, if the volume of triethylamine solution used is less than 0.5 ml, add at least 10 mg of phthalic acid (5.2.3) and repeat the determination.

5.5 Expression of results

5.5.1 Calculate the potential increments corresponding to the addition of the triethylamine solution in amounts of 0.02 ml. Let the three largest increments be Δ_1, Δ_0 and Δ_2, Δ_0 being the largest increment, Δ_1 preceding Δ_0, and Δ_2 following Δ_0.

Calculate the volume (V_1) of the triethylamine solution using the following formula :

$$V_1 = V + \frac{0.02 \times (\Delta_0 - \Delta_1)}{2\Delta_0 - (\Delta_1 + \Delta_2)}$$

where V is the volume, in millilitres, of the triethylamine solution (5.2.2) added to reach the potential between Δ_0 and Δ_1.

NOTE. – The suggested calculation of the volume of triethylamine solution is not exact. The differences between the theoretical values and the values obtained in this way are negligible, however, as only very small amounts of titrant are added when the equivalence point is approached. For the sake of simplicity, the suggested method is preferred.

5.5.2 Free acidity (A), expressed as phthalic acid ($1,2\text{-}(COOH)_2.C_6H_4$), is given, as a percentage by mass, by the following formula :

$$A = \frac{(16.6 \times V_1) - m}{m_1 \times 10}$$

where

m is the mass, in milligrammes, of phthalic acid added (see clause 5.4.3);

m_1 is the mass, in grammes, of the test portion;

V_1 is defined as in clause 5.5.1.

6. DETERMINATION OF PHTHALIC ANHYDRIDE CONTENT

6.1 Principle

Solution of a test portion in an excess of standard sodium hydroxide solution and back-titration of the excess with standard hydrochloric acid using phenolphthalein as indicator.

6.2 Reagents

Distilled water or water of equivalent purity should be used in the test.

6.2.1 *Sodium hydroxide,* N standard volumetric solution.

6.2.2 *Hydrochloric acid,* N standard volumetric solution.

6.2.3 *Phenolphthalein,* 5 g/l ethanolic solution.

Dissolve 0.5 g of phenolphthalein in 100 ml of ethanol 95 % (V/V) and make faintly pink by the addition of dilute sodium hydroxide solution.

6.3 Apparatus

Ordinary laboratory apparatus and

6.3.1 *Conical flask,* of borosilicate glass, capacity 250 ml.

6.4 Procedure

6.4.1 Place 2 g of the laboratory sample, weighed to the nearest 0.005 g, in the conical flask (6.3.1), add 50 ml of sodium hydroxide solution (6.2.1), and heat on a boiling-water bath until completely dissolved. Allow the mixture to cool.

6.4.2 Add 0.5 ml of the phenolphthalein solution (6.2.3), and titrate immediately with the hydrochloric acid (6.2.2) until the pink colour has disappeared.

6.5 Expression of results

Phthalic anhydride content $[C_6H_4(CO)_2O]$ is given, as a percentage by mass, by the following formula :

$$\frac{(50 - V_2) \times 7.406}{m_2} - 0.89\,A - 1.51\,B$$

where

V_2 is the volume, in millilitres, of the hydrochloric acid solution (6.2.2) used;

m_2 is the mass, in grammes, of the test portion;

A is the free acidity expressed as a percentage by mass of phthalic acid (see clause 5.5);

B is the maleic anhydride content expressed as a percentage by mass (see clause 7.6).

7. DETERMINATION OF MALEIC ANHYDRIDE CONTENT

7.1 Principle

Preparation of a cathodic polarogram and reference to a calibration curve.

7.2 Reagents

Distilled water or water of equivalent purity should be used in the test.

7.2.1 *Acetone.*

7.2.2 *Benzene.*

7.2.3 *Nitrogen,* free from oxygen.

7.2.4 *Hydrochloric acid,* approximately 0.2 N solution.

7.2.5 *Maleic anhydride,* standard solution in acetone containing 0.200 mg/ml.

7.3 Apparatus

Ordinary laboratory apparatus and

7.3.1 *Polarograph.*

7.3.2 *Separating funnel,* capacity 300 ml.

7.4 Procedure

7.4.1 Weigh, to the nearest milligramme, about 0.5 g of the laboratory sample, into a 200 ml conical flask and dissolve in 20 ml of acetone (7.2.1). Add 50 ml of hydrochloric acid (7.2.4) and evaporate to about 25 ml on a boiling-water bath.

After cooling, filter through a filter paper, wash with about 20 ml of water, then transfer the filtrate and washings to the separating funnel (7.3.2) and extract twice with 25 ml portions of benzene (7.2.2) to remove 1,4-naphthaquinone. Place the aqueous solution in a 100 ml volumetric flask and dilute to the mark.

7.4.2 Transfer to a polarographic cell and subject to a slow stream of the pure nitrogen (7.2.3) for 10 to 15 minutes to remove all oxygen. Record the polarogram of this solution at potentials from – 0.4 to – 0.8 V. Read the value of the average diffusion current. By referring to the calibration curve prepared as described in clause 7.5, determine the amount of maleic anhydride present in the sample solution.

NOTE. – The temperature and rate of fall of the mercury drops should be the same as in preparing the calibration curve.

7.5 Preparation of the calibration curve

7.5.1 Into a series of seven 100 ml beakers, introduce 3, 5, 7, 10, 12, 15 and 20 ml portions of the standard maleic anhydride solution (7.2.5). Dilute 10 ml of the standard maleic anhydride solution (7.2.5) to 100 ml with acetone (7.2.1) in a one-mark volumetric flask. Into a second series of five 100 ml beakers, introduce 1, 2, 5, 10 and 20 ml portions of the diluted standard solution.

7.5.2 Dilute each of the solutions in the beakers to about 20 ml with acetone (7.2.1), add 50 ml of hydrochloric acid (7.2.4) to each and proceed in the same way and under the same conditions as described in clause 7.4 omitting the extraction with benzene.

7.5.3 From the results obtained, draw a calibration chart by plotting the average diffusion current against the maleic anhydride content, expressed in grammes per 100 ml of solution.

7.6 Expression of results

Maleic anhydride (OCOCH : CHCO) content is given, as a percentage by mass, by the following formula :

$$B = \frac{100\,a}{m_3}$$

where

a is the maleic anhydride content, in grammes per 100 ml, of the sample solution (read from the calibration curve);

m_3 is the mass, in grammes, of the test portion.

8. DETERMINATION OF ASH

8.1 Apparatus

Ordinary laboratory apparatus.

8.2 Procedure

Slowly burn approximately 50 g, weighed to the nearest gramme, of the laboratory sample in several portions, in a platinum or silica basin previously weighed to the nearest 0.1 mg and ignite finally in a furnace at 600 ± 30 °C until all carbonaceous matter has disappeared. Cool in a desiccator and weigh to the nearest 0.1 mg. Repeat this series of operations of ignition, cooling, and weighing until the mass recorded is constant.

Retain the residue for the determination of iron, if required, as described in section 13.

8.3 Expression of results

Ash is given, as a percentage by mass, by the following formula :

$$\frac{100\,m_4}{m_5}$$

where

m_4 is the mass, in grammes, of the residue;

m_5 is the mass, in grammes, of the test portion.

9. DETERMINATION OF IMPURITIES OXIDIZABLE IN THE COLD BY POTASSIUM PERMANGANATE

NOTE. – This method is not specific for maleic anhydride, for which the method given in section 7 should be used.

9.1 Principle

Oxidation of unsaturated organic acids and anhydrides with excess of cold potassium permanganate solution in the presence of sulphuric acid, followed by iodometric determination of the permanganate remaining.

9.2 Reagents

Distilled water or water of equivalent purity should be used in the test.

9.2.1 *Sulphuric acid,* ρ 1.84 (g/ml), solution approximately 96 % (m/m).

9.2.2 *Potassium iodide.*

9.2.3 *Potassium permanganate,* 0.1 N standard volumetric solution.

9.2.4 *Sodium thiosulphate,* 0.1 N standard volumetric solution.

9.3 Apparatus

Ordinary laboratory apparatus and

9.3.1 *50 ml burette,* graduated in 0.05 ml or smaller divisions.

9.4 Procedure

9.4.1 Weigh, to the nearest 0.005 g, about 5 g of the laboratory sample, add 100 ml of water and heat gently until the sample is dissolved. Cool rapidly to room temperature. (Phthalic anhydride is completely soluble under these conditions when hot; a precipitate forms on cooling but this in no way interferes with the rest of the determination.)

9.4.2 After cooling, add 3 ml of the sulphuric acid solution (9.2.1) cool again to 20 ± 1 °C and add 25.0 ml of the potassium permanganate solution (9.2.3) by means of a pipette. Mix thoroughly and leave to stand at 20 ± 1 °C for 5 minutes. At the end of this time, add 1 g of potassium iodide (9.2.2) and titrate the liberated iodine with the sodium thiosulphate solution (9.2.4) from the burette (9.3.1) (the colour change is very sensitive and does not require the addition of starch as indicator, except with coloured solutions).

9.4.3 Carry out a blank test omitting the test portion.

9.5 Expression of results

The content of oxidizable matter, expressed as maleic anhydride (OCOCH : CHCO), is given, as a percentage by mass, by the following formula :

$$\frac{0.098 \times (V_4 - V_3)}{m_6}$$

where

V_3 is the volume, in millilitres, of the sodium thiosulphate solution (9.2.4) used in the test;

V_4 is the volume, in millilitres, of the sodium thiosulphate solution (9.2.4) used in the blank;

m_6 is the mass, in grammes, of the test portion.

10. MEASUREMENT OF COLOUR STABILITY

10.1 Principle

Measurement of colour of the sample after a specified heat treatment.

10.2 Apparatus

Ordinary laboratory apparatus and

10.2.1 *Two matched flat-based colorimetric tubes,* of approximately 20 mm external diameter and having a graduation mark 100 mm above the base.

10.2.2 *Electrically heated aluminium block,* maintained at 250 ± 3 °C, with holes 22 mm in diameter and of depth at least 120 mm but such that the tops of the flat-based tubes project above the surface of the block.

10.2.3 *Thermometer* of the mercury-in-glass type covering a convenient range and graduated at intervals of 1 °C.

10.3 Procedure

10.3.1 Introduce into one of the colorimetric tubes (10.2.1) a quantity of the laboratory sample sufficient to reach the graduation mark after melting. Close it with a vented cork covered with aluminium foil and carrying the thermometer. Adjust the thermometer so that the top of the bulb is 40 mm below the graduation mark on the tube.

10.3.2 Place the tube containing the sample in the electrically heated block (10.2.2). At the end of 90 minutes from the time of reaching 250 °C withdraw the tube and allow it to cool to 150 °C. Measure the colour of the heat-treated sample as described in clause 3.5.

11. MEASUREMENT OF COLOUR AFTER TREATMENT WITH SULPHURIC ACID

11.1 Principle

Measurement of colour of the sample after a specified treatment with hot sulphuric acid.

11.2 Reagent

11.2.1 *Sulphuric acid,* ρ 1.84 (g/ml), solution approximately 96 % (m/m).

NOTE. – The reagent should be tested by heating as described in clause 11.4 and rejected if any colour develops.

11.3 Apparatus

Ordinary laboratory apparatus and

11.3.1 *Two matched flat-based colorimetric tubes,* of approximately 20 mm external diameter and having a graduation mark 100 mm above the base.

11.3.2 *Conical flask,* of borosilicate glass, capacity 100 ml and fitted with a ground glass stopper.

11.4 Procedure

11.4.1 Place 5.0 g of the laboratory sample in the 100 ml flask (11.3.2) and add 50 ml of sulphuric acid (11.2.1). Immerse the loosely stoppered flask in a boiling-water bath for 3 hours, swirling from time to time.

11.4.2 Allow to cool and transfer the liquid to one of the colorimetric tubes (11.3.1) and measure the colour as described in clause 3.5.

12. DETERMINATION OF 1,4-NAPHTHAQUINONE CONTENT

12.1 Principle

Development of a pink colour when phthalic anhydride containing 1,4-naphthaquinone is heated with tin (II) chloride and comparison of the colour produced with a series of prepared reference colours.

12.2 Reagents

Distilled water or water of equivalent purity should be used in the test.