



International Standard

4326

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Non-ionic surface active agents — Polyethoxylated derivatives — Determination of hydroxyl value — Acetic anhydride method

Agents de surface non ioniques — Dérivés polyéthoxylés — Détermination de l'indice d'hydroxyle — Méthode à l'anhydride acétique

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 4326 was developed by Technical Committee ISO/TC 91, *Surface active agents*, and was circulated to the member bodies in June 1976.

It has been approved by the member bodies of the following countries :

Australia	Ireland	Romania
Austria	Japan	South Africa, Rep. of
Belgium	Korea, Rep. of	Switzerland
Brazil	Mexico	Turkey
Chile	Netherlands	United Kingdom
France	New Zealand	USA
Germany, F.R.	Philippines	USSR
India	Poland	

The member body of the following country expressed disapproval of the document on technical grounds :

Spain

Non-ionic surface active agents — Polyethoxylated derivatives — Determination of hydroxyl value — Acetic anhydride method

0 INTRODUCTION

The classical method for the determination of the hydroxyl value described in this International Standard requires, because of the toxic effects of pyridine and acetic anhydride, that all handling and the titration be conducted under a well ventilated fume hood. However, for information, it is pointed out that annex C of ISO 4327 provides a procedure using a special apparatus which reduces the danger due to pyridine and acetic anhydride.

1 SCOPE

This International Standard specifies a method for the determination of the hydroxyl value of polyethoxylated condensates by esterification of the hydroxyl groups with acetic anhydride.

2 FIELD OF APPLICATION

This method is applicable to the determination of the hydroxyl groups of polyethoxylated condensates of aliphatic and alicyclic compounds (in particular, of ethylene oxide adducts of primary fatty alcohols, of alkylphenols and of fatty acids) and can be used for the determination of hydroxyl values from 10 to 1 000.

However, certain substances present in these materials may react with the acetic anhydride or with the standard volumetric sodium hydroxide solution used and consequently falsify the results.

The possible interferences are detailed below :

- Primary and secondary amines, amides, tertiary alcohols, thiols and epoxides undergo side reactions which affect the accuracy of the method.
- Long-chain fatty acids and esters may interfere by forming anhydrides which are more stable than acetic anhydride and are not completely decomposed at the end of the method.
- Other free acids interfere by reacting with the standard volumetric sodium hydroxide solution; bases,

including some tertiary amines, interfere by reacting with the acetic acid produced. In these cases a correction may be made for the acidity or alkalinity (see ISO 4314).

Epoxides are known to interfere, but the method can still be used if it is possible to eliminate them, by cold vacuum distillation, without affecting the hydroxyl value. By this means, free ethylene oxide, which interferes at levels above 0,5 % (*m/m*), can be eliminated.

The presence of water in the sample is revealed by reaction with the acetic anhydride, but the method may nevertheless be used without risk if the precautions described in the procedure are followed.

This method is not applicable to propoxylated products.

3 REFERENCES

ISO 607, *Surface active agents and detergents — Methods of sample division.*

ISO 2211, *Liquid chemical products — Measurement of colour in Hazen units (platinum-cobalt scale).*

ISO 4314, *Surface active agents — Determination of free alkalinity or free acidity — Titrimetric method.*

ISO 4317, *Surface active agents — Determination of water content — Karl Fischer method.*

ISO 4327, *Non-ionic surface active agents — Polyalkoxylated derivatives — Determination of hydroxyl value — Phthalic anhydride method.*

4 DEFINITION

hydroxyl value $I(\text{OH})$: The number of milligrams of potassium hydroxide needed to neutralize the acetic acid required to acetylate the hydroxyl groups in 1 g of the material, or the number of milligrams of potassium hydroxide corresponding to the hydroxyl groups in 1 g of the material.

NOTE — The number of moles of potassium hydroxide corresponding to the hydroxyl value is equal to the number of hydroxyl groups present in 1 kg of the material.

5 PRINCIPLE

Esterification of the hydroxyl group by acetic anhydride in pyridine solution.

Hydrolysis of the excess of acetic anhydride with water.

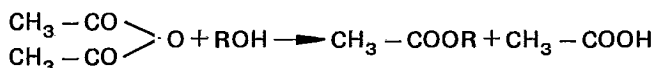
Neutralization of the acidity which appears during the esterification, and of the acetic acid formed during the hydrolysis, by sodium hydroxide solution in the presence of phenolphthalein as indicator.

Calculation of the hydroxyl value from the difference between the volumes of sodium hydroxide solution used for the titration of the blank and of the test solution.

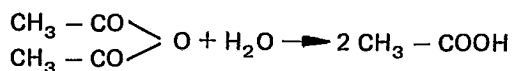
6 REACTIONS

The reactions occurring are as follows :

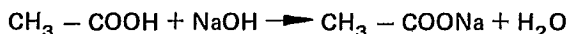
a) Esterification



b) Hydrolysis of the excess acetic anhydride



c) Neutralization of the acetic acid formed



7 REAGENTS

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

7.1 Pyridine, boiling temperature between 114,5 and 115,5 °C.

7.2 Acetic anhydride solution in pyridine (acetylation reagent).

Mix carefully 1 volume of acetic anhydride, of minimum purity 97 %, and 10 volumes of the pyridine (7.1), avoiding overheating.

Store in a dark glass bottle fitted with a ground glass stopper. Do not use this solution if its colour exceeds 200 Hazen units on the platinum-cobalt scale (determined by ISO 2211).

7.3 Sodium hydroxide, 0,5 N standard volumetric solution.

7.4 Phenolphthalein, 10 g/l solution in pyridine.

Dissolve 1 g of phenolphthalein [3,3-bis(4-hydroxyphenyl) phthalide] in 100 ml of the pyridine (7.1).

8 APPARATUS

Ordinary laboratory apparatus and :

8.1 Burette, capacity 50 ml, complying with the requirements of class A of ISO/R 385.

8.2 Flat-bottomed flasks, capacity 250 ml, with conical ground glass sockets.

8.3 Air condensers, of effective length 800 mm, with conical ground glass joints.

8.4 One-mark pipettes, capacities 15 and 25 ml, complying with the requirements of ISO 648.

9 SAMPLING

Laboratory samples of polyethoxylated surface active agents shall be prepared and stored according to the instructions given in ISO 607.

10 PROCEDURE

All the necessary apparatus shall be absolutely clean and dry.

10.1 Test portion

It is essential that the approximate water content of the test portion be known; if necessary, determine the water content of the sample by the method specified in ISO 4317.

Weigh, to the nearest 0,001 g, into a dry and previously tared flask (8.2), a mass of the laboratory sample as specified in the table below :

Hydroxyl value $I(\text{OH})$	Mass of test portion, m_0 g
Lower than 40	8 to 10
40 to 200	$\frac{380}{I(\text{OH})} \pm 0,5$
Over 200	$\frac{380 \pm 100}{I(\text{OH})}$

NOTE — For water contents between 0,25 and 1 % (m/m), the mass (m_0), in grams, of the test portion shall not exceed :

$$\frac{9,3 (V_0 + 25)}{I(\text{OH}) + 32 [\text{H}_2\text{O}]}$$

where

V_0 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (7.3) used for the blank test (see clause 11);

$I(\text{OH})$ is the estimated hydroxyl value, in milligrams of potassium hydroxide per gram;

$[\text{H}_2\text{O}]$ is the percentage, by mass, of water in the test sample.

WARNING — All the operations specified below shall be conducted under a well ventilated fume hood.

10.2 Determination

10.2.1 Acetylation

Using a pipette, add, as carefully as possible, exactly 15 ml of the acetylation reagent (7.2) to the flask. Moisten the condenser joint with the pyridine (7.1) and attach the condenser (8.3) to the flask. Swirl to mix the contents. Heat the flask for 1 h in a boiling water bath, the contents of the flask being below the level of the water. Swirl to mix after about 10 min in the bath.

10.2.2 Hydrolysis and titration of excess reagent

Add 2 ml of water, through the condenser, to the flask and swirl. Heat the flask in the boiling water bath for 5 min. Cool the flask and contents to below 30 °C. Add 70 ml of water through the condenser. Remove the condenser and rinse the ground glass joint with water.

Using a pipette (8.4), add 25 ml of the standard volumetric sodium hydroxide solution (7.3).

Add 0,2 ml of the phenolphthalein indicator solution (7.4) and titrate with the standard volumetric sodium hydroxide solution (7.3) with vigorous stirring, until the solution remains pink for 15 s.

10.3 Blank test

Carry out a blank test at the same time as the determination, using the same reagents, but replacing the test portion with 2 or 3 drops of water.

11 EXPRESSION OF RESULTS

11.1 Method of calculation

The hydroxyl value, $I(\text{OH})$, corresponding to the test portion, is given by the formula

$$\frac{(V_0 - V_1) \times T \times 56,10}{m_0} + C$$

where

V_0 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (7.3) used for the blank test;

V_1 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (7.3) used for the determination;

T is the exact normality of the standard volumetric sodium hydroxide solution (7.3);

m_0 is the mass, in grams, of the test portion;

C is the positive acid value, or the negative alkali value, of the material (see ISO 4314); this value shall be ignored if it is 0,3 or less.

11.2 Precision

For compounds having hydroxyl values of 40 or more, comparative analyses have given the following statistical results :

11.2.1 Repeatability

The difference found between the results of two determinations carried out on the same sample simultaneously or in rapid succession by the same analyst using the same apparatus should not exceed 1,1 % of the mean value.

11.2.2 Reproducibility

The difference between the results obtained on the same sample in two different laboratories should not exceed 2,8 % of the mean value.

12 TEST REPORT

The test report shall include the following particulars :

- all information necessary for the complete identification of the sample;
- the reference of the method used (reference to this International Standard);
- the results and the method of expression used;
- the test conditions;
- any operational details not specified in this International Standard, or regarded as optional, as well as any incidents likely to have affected the results.