Indian Standard

METHODS OF TEST FOR NATURAL RUBBER

PART 4 DETERMINATION OF TOTAL COPPER

[NR : 4]

(Second Revision)

UDC 678·4 : 543 [546·56]

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0. FOREWORD

0.1 This Indian Standard (Second Revision) was adopted by the Bureau of Indian Standards on 14 April 1988, after the draft finalized by the Rubber Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

0.2 Methods of test for natural rubber had been originally covered in the following four parts of IS : 3660:

IS : 3660 (Part 1)-1972 Determination of dirt, volatile matter, ash, total copper, manganese, rubber hydrocarbon, viscosity (shearing disk viscometer), and mixing and vulcanizing of rubber in a standard compound (*first revision*)

IS : 3660 (Part 2)-1968 Determination of solvent extract and nitrogen content

IS : 3660 (Part 3)-1971 Plasticity and plasticity retention index

IS : 3660 (Part 4)-1979 Determination of colour, accelerated storage-hardening test and vulcanization characteristics (MOD test)

0.2.1 While reviewing various test methods for natural rubber, the Committee decided to align them with the corresponding International standards. No unification of test methods for natural and synthetic rubber has been considered necessary. However, in revising test methods for natural rubber, the Committee had decided to revise and split the standard into further parts and publish individual test methods under natural rubber (NR) series. For proper referencing of the existing test methods and the new methods under revision, a table showing correspondence of the various methods of test covered in the earlier 4 parts of IS : 3660 with the presently split parts retaining the original NR number have been given in Appendix A.

0.2.2 In order to facilitate cross-reference, it has been decided to retain the original discrete NR series numbers assigned to various test methods in original IS : 3660.

0.3 The test method given in this standard will supersede the test method as given under NR : 4 of IS : 3660 (Part 1)-1972. All the four parts of the original IS : 3660 shall be withdrawn when it is completely revised.

0.4 The method of test for determination of copper was originally published as NR : 4 of IS : 3660 (Part 1)-1966 wherein only photoelectric absorptiometer method was prescribed. Since at that time most of the laboratories were not equipped with photoelectric absorptiometer. This standard was subsequently revised in 1972 and in the first revision, Nessler method for determination of copper was included as routine method along with photoelectric absorptiometer method.

0.4.1 The committee has now observed that most of the laboratories are equipped with photoelectric absorptiometer. Therefore, in view of the desirability of accuracy of test results and also to align it with the corresponding ISO standard, only the photoelectric absorptiometer method is being retained in this revision.

0.5 In the preparation of this standard, assistance has been derived from ISO 8053-1986 'Rubber and rubber latex — Determination of copper content — Photometric method' issued by the International Organization for Standardization (ISO).

0.6 Copper in certain forms is known to catalyse the oxidative breakdown of natural rubber although the mechanism by which degradation is brought about is not fully understood. It is recognized also that other forms of copper may be present without degradation taking place, but no generally accepted method is available for distinguishing between the active and inactive forms. At present, therefore, there is no alternative to determining the total amount of copper in rubber.

0.7 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960*.

*Rules for rounding off numerical values (*revised*).

1. SCOPE

1.1 This standard (Part 4) prescribes a method for the quantitative determination of total copper content in raw natural rubber.

2. QUALITY OF REAGENTS

2.1 Unless specified otherwise, pure chemicals and distilled water (*see* IS : 1070-1977*) shall be employed in tests.

NOTE — 'Pure chemical' sshall mean chemicals that do not contain impurities which affect the result of analysis.

3. OUTLINE OF THE METHOD

3.1 Five grams of the raw natural rubber is ashed in a silica crucible. The ash is extracted with a hydrochloric acid-nitric acid mixture and the solution made alkaline with ammonium hydroxide. Any iron present is complexed with ammonium citrate. The aqueous solution is then shaken with solution in chloroform of zinc diethyldithiocarbamate to form and extract the yellow copper complex. The optical density of this solution is measured photometrically and is proportional to the concentration of copper.

4. APPARATUS

4.1 Electrophotometer, Absorptiometer or Spectrophotometer — capable of measuring optical density at approximately 435 nm.

4.2 Matched Absorption Cells —10 to 50 mm in path length.

4.3 Silica Crucibles — nominal capacity 50 or 80 ml.

4.4 Muffle Furnace — capable of maintaining a temperature of 550 ± 25°C.

5. REAGENTS

5.1 Light Magnesium Oxide

5.2 Sodium Sulphate, Anhydrous

5.3 Hydrochloric Acid-Nitric Acid Mixture — The following are mixed together:

a) 2 volumes of hydrochloric acid (*see* IS : 265-1976†),

b) 1 volume of nitric acid (*see* IS : 264-1976‡), and

c) 3 volumes of water.

5.4 Citric Acid Solution — Dissolve 50 g of citric acid (solid) in 100 ml of water.

5.5 Ammonia Solution — density 0·890 g/ml.

5.6 Litmus Paper

5.7 Zinc Diethyldithiocarbamate Reagent — Dissolve 1 g of solid zinc diethyldithiocarbamate in 1 litre of chloroform. If zinc diethyldithiocarbamate is not available, the reagent may be prepared as follows:

Dissolve 1 g of sodium diethyldithiocarbamate in water and add 2 g of zinc sulphate. Extract the resulting zinc diethyldithiocarbamate by shaking with 100 ml of chloroform and separate the chloroform solution. Dilute to 1 litre. Store in an amber coloured bottle; this reagent is stable for at least six months.

NOTE — 1, 1, 1—Trichloroethane may be used in place of chloroform.

5.8 Standard Copper Solution — Weigh 0·393 g of copper sulphate pentahydrate ($CuSo_4.5H_2O$) into a small beaker aud dissolve in water. Add 3 ml of concentrated sulphuric acid. Transfer the solution to a 1 000-ml one-mark volumetric flask and dilute to the mark with water to form the stock solution. Pipette 10 ml of this stock solution into a 100-ml one-mark volumetric flask and dilute to the mark with water. This solution contains the equivalent of 0·01 mg of copper per millilitre and should be freshly prepared from the stock solution when required.

6. PROCEDURE

6.1 Preparation of Sample — For the determination of copper in natural rubber, cut the homogenized test portion prepared according to **3.1.1** of IS : 3660 (Part 1)-1972.

NOTE — At all stages of sample preparation, care should be taken to avoid contamination.

6.2 Preparation of Calibration Curve — If the magnesium oxide method of ashing is to be used, prepare a series of standard solutions, each containing 0·1 g of magnesium oxide dissolved in 10 ml of the dilute hydrochloric acid-nitric acid mixture. If the rubber is to be ashed by wrapping in filter paper and then placing directly in the muffle furnace, omit the magnesium oxide. To these solutions, add portions of the standard copper solution ranging from 0 to 10 ml followed in each case by 5 ml of citric acid solution. Add ammonia solution drop by drop until the solutions are just alkaline to litmus paper. Cool the solutions, transfer individually to a separating funnel and add further 2 ml of ammonia solution to each. Pipette 25 ml of zinc diethyldithiocarbamate reagent into each solution and shake for 2 minutes. Immediately after separation, draw the chloroform layer into a stoppered flask containing about 0·1 g of anhydrous sodium sulphate. If turbidity persists after standing for

*Specification for water for general laboratory use (*second revision*).

†Specification for hydrochloric acid (*second revision*).

‡Specification for nitric acid (*second revision*).

about 30 minutes, make further small additions of anhydrous sodium sulphate until the solution becomes clear.

6.2.1 Decant each chloroform solution through a plug of glass wool or a small filter paper into the cell of the electrophotometer, absorptiometer or spectrophotometer, and measure the optical density at the absorption maximum (about 435 mm). Correct the reading by subtracting the optical density of the solution containing no added copper. If the optical density is measured on a double beam or null point instrument, the cell containing the blank solution should be placed in the reference beam and the optical density of each standard solution measured against that of the solution containing no added copper. Plot the reading thus obtained for each solution against the appropriate concentration of copper to give the calibration curve, which should be checked periodically according to local conditions and the type of instrument used.

6.3 Ashing — Weigh, to the nearest 5 mg, a 5 g test portion of the raw rubber and place in a silica crucible containing 0·1 g magnesium oxide distributed over the base and partly up the side of the crucible. Support the crucible in a hole cut in an asbestos board so that about two-thirds of the crucible projects below the asbestos. Commence a blank determination using a similar crucible and the same amount of magnesium oxide, and give identical treatment throughout the test and blank determinations. Heat the crucible and contents with a small gas flame until a dry carbonaceous residue remains, and then transfer the crucible to a muffle furnace at a temperature of 550 ± 25°C and heat until all carbon has been oxidized. Remove the crucible and allow to cool.

6.3.1 As an alternative to the above method of ashing, wrap the 5 g test portion, weighed to the nearest 5 mg, in a piece of ashless filter paper about 150 mm in diameter and place in a transparent silica crucible having clean unetched walls. Place the crucible and contents in furnace at 550 ± 25°C and close the door. Because of the risk of igniting flammable gases, the furnace door should not be opened during the first hour. Also commence a blank determination using a similar filter paper and crucible, and give identical treatment throughout the test blank determinations. When all the carbon has been oxidized, remove the crucible and allow it to cool.

6.4 Moisten the contents of the crucible with 0·5 to 1 ml water, then add 10 ml of the dilute hydrochloric acid-nitric acid mixture and heat the crucible, covered with a clockglass, on a steam bath for 30 to 60 minutes. Wash the contents of the crucible into a small beaker or flask, add 5 ml of citric acid solution and then add ammonia solution drop by drop until the solution is just alkaline to litmus paper. Cool the solution by immersion in running water, transfer to a separating funnel, add further 2 ml of ammonia solution and then dilute to about 40 ml with water. Pipette 25 ml of zinc diethyldithiocarbamate reagent into the solution and shake the funnel 2 minutes. After separation, immediately transfer the chloroform layer into a stoppered flask containing about 0·1 g of anhydrous sodium sulphate. If turbidity persists after standing for about 30 minutes, make further small additions of anhydrous sodium sulphate until the solution becomes clear.

6.5 Photometric Measurement of Colour — Decant the chloroform solution through a plug of glass wool or a small filter paper into the cell of the electrophotometer, absorptiometer or spectrophotometer, and measure the optical density at the wavelength used in preparing the calibration curve (about 435 mm). Correct the reading by subtracting the optical density of the blanks solution. If the optical density is measured on a double beam or null point instrument, the cell containing the blank solution should be placed in the reference beam and the optical density of the test solution measured against that of the blank. The reading thus obtained, used in conjunction with the calibration curve, gives the concentration of copper in the test solution and hence in the rubber.

NOTE — All precautions and safeguards required for carrying out of trace metal analysis shall be observed.

7. EXPRESSION OF RESULT

7.1 The result should be expressed as parts per million (ppm) of copper calculated by mass.

APPENDIX A

(*Clause* 0.2.1)

TABLE SHOWING CORRESPONDENCE OF VARIOUS METHODS OF TEST COVERED IN THE EXISTING IS : 3660 (PART 1)-1972, IS : 3660 (PART 2)-1968, IS : 3660 (PART 3)-1971, AND IS : 3660 (PART 4)-1979 WITH THE REVISION/PROPOSED REVISION OF ALL THE FOUR PARTS OF IS : 3660

Existing Test Methods			Proposed Revision		Remarks
Test Methods	IS : No.	Part (Series)	IS : No.	(Series)	
(1)	(2)	(3)	(4)	(5)	(6)
NR Series					
Determination of dirt	IS : 3660-1972	Part 1 (NR : 1)	IS : 3660 (Part 1)-1985	(NR : 1)	
Determination of volatile matter	IS : 3660-1972	Part 1 (NR : 2)	IS : 3660 (Part 2)-1985	(NR : 2)	
Determination of ash	IS : 3660-1972	Part 1 (NR : 3)	IS : 3660 (Part 3)-1988	(NR : 3)	
Determination of total copper	IS : 3660-1972	Part 1 (NR : 4)	IS : 3660 (Part 4)-1988	(NR : 4)	Under revision
Determination of manganese	IS : 3660-1972	Part 1 (NR : 5)	IS : 3660 (Part 5)	(NR : 5)	Under revision
Determination of iron	IS : 3660-1972	Part 1 (NR : 6)	Deleted since this test is no longer being done		
Determination of rubber hydrocarbon	IS : 3660-1972	Part 1 (NR : 7)	IS : 3660 (Part 6)	(NR : 7)	
Determination of viscosity by shearing disk viscometer	IS : 3660-1972	Part 1 (NR : 8)	IS : 3660 (Part 7)	(NR : 8)	
Mixing and vulcanizing in a standard compound	IS : 3660-1972	Part 1 (NR : 9)	IS : 3660 (Part 8)	(NR : 9)	Under revision
Determination of solvent extract	IS : 3660-1968	Part 2 (NR : 10)	IS : 3660 (Part 9)	(NR : 10)	
Determination of nitrogen content	IS : 3660-1968	Part 2 (NR : 11)	IS : 3660 (Part 10)	(NR : 11)	
Determination of plasticity	IS : 3660-1971	Part 3 (NR : 12)	IS : 3660 (Part 11)	(NR : 12)	
Determination of plasticity retention index (PRI)	IS : 3660-1971	Part 3 (NR : 13)	IS : 3660 (Part 12)	(NR : 13)	
Determination of colour	IS : 3660-1979	Part 4 (NR : 14)	IS : 3660 (Part 13)	(NR : 14)	
Determination of storage-hardening test	IS : 3660-1979	Part 4 (NR : 15)	IS : 3660 (Part 14)	(NR : 15)	
Determination of vulcanization characteristics (MOD test)	IS : 3660-1979	Part 4 (NR : 16)	IS : 3660 (Part 15)	(NR : 16)	
Method for preparation of test samples	IS : 3660-1972	Part 1 (Clause 3)	IS : 3660 (Part 16)	(NR : 17)	