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Technical specification of polyisobutylene-based polymers for pharmaceutical rubber closures

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CHINA NATIONAL PHARMACEUTICAL PACKAGING ASSOCIATION
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Preface

This document is drafted in accordance with the provisions of GB/T 1.1-2020 "Guidelines for Standardization Work Part 1: Rules for Structure and Drafting Standardization Documents".

This document replaces YBX 2004-2014 "polyisobutylene-based polymers for Pharmaceutical Rubber Closures". Compared with YBX 2004-2014, except for structural adjustments and editorial changes, the main technical changes are as follows:

a) Added terms and definitions (see Chapter 3);
b) Added requirements for the application of new antioxidants in polyisobutylene-based polymers for pharmaceutical use rubber closures (see 4.1);
c) Changed the project standard of bromine content in brominated butyl rubber (see 4.2);
d) Changed the project standard of unsaturation in butyl rubber (see 4.2);
e) Added description of the impact of some technical requirements on the production and application of pharmaceutical use rubber closures (see 4.2);
f) Changed the testing method for rubber identification (infrared spectroscopy) (see 5.2);
g) Updated the ignition temperature in the ash content testing method (see 5.5);
h) Removed the rigid requirement for inspection rules (see Chapter 6);
i) Added the reference method for determination of epoxidized soybean oil (ESBO) content potentiometric titration method (see Appendix C);
j) Added the reference method for the determination of calcium stearate in butyl rubber titration method (see Appendix F).

Please note that some content in this document may involve patents. The publishing institution of this document does not assume responsibility for identifying patents.

This document is proposed and managed by the China Pharmaceutical Packaging Association.

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The previous versions of this document and the files be replaced are as follows:

——- First released standard in 2014 as YBX 2004-2014;
——This is the first revision.

Introduction

Pharmaceutical use rubber closures are an important variety of pharmaceutical packaging materials. polyisobutylene-based polymers, due to its excellent airtightness and chemical stability, has become the most important rubber raw material for pharmaceutical rubber closures. The stability of the quality of polyisobutylene-based polymers determines the stability of the production process and product quality of pharmaceutical rubber closures. At present, there is not national standard for the synthesis of polyisobutene rubber in China. In order to stabilize the quality of polyisobutylene-based polymers used for pharmaceutical use rubber closures, it is necessary to develop this document based on the requirements for pharmaceutical packaging.

The formulation of this document can effectively strengthen the quality control of polyisobutylene-based polymers used for pharmaceutical use rubber closures, standardize the production and inspection of polyisobutylene-based polymers used for pharmaceutical use rubber closures. polyisobutylene-based polymers used for pharmaceutical rubber closures includes butyl rubber (IIR), chlorinated butyl rubber (CIIR), brominated butyl rubber (BIIR), and brominated Isobutene-p-methylstyrene copolymer rubber (BIMSM).

The main inspection items in this document include appearance, mooney viscosity, volatile matter, ash content, unsaturation, halogen content, and physical and mechanical properties. It mainly refers to ASTM D3188-2006, ASTM D3958-2006, and the product indicators of major butyl rubber manufacturers. With the control of these indicators, pharmaceutical use rubber closures manufacturers can have stable production formulas and processes when organizing the production.

The setting and inspection methods for other items in the technical specifications for polyisobutylene-based polymers for pharmaceutical use rubber closures, such as rubber identification of metal elements (including tin, lead, copper, chromium, cadmium, barium), oligomer content, antioxidants, epoxidized soybean oil (ESBO), and calcium stearate, are based on the items and inspection methods in the draf of national drug packaging container (material) standard"polyisobutylene-based polymers for pharmaceutical use rubber closures" drafted by the Shanghai Institute for Food and Drug Control. The technical indicators integrate the indicators of the draft standard of Shanghai Institute for Food and Drug Control and the product indicators of major butyl rubber manufacturers at home and abroad. These projects provide guarantees for the compatibility and safety of rubber closures with drugs, making it more convenient for manufacturers of pharmaceutical rubber closures to design formulations for different drugs, allowing them to choose different rubber varieties and specifications.

Technical specification of polyisobutylene-based polymers for pharmaceutical rubber closures

1 Scope

This document specifies the technical requirements, test methods, inspection rules, labeling, packaging, transportation, and storage of polyisobutylene-based polymers for pharmaceutical use rubber closures (hereinafter referred to as "rubber closures").

This document is applicable to polyisobutylene-based polymers used for rubber closures.

2 Normative References

The contents of the following documents constitute essential clauses of this document through normative references in the text. Among them, for referenced documents with dates, only the version corresponding to that date is applicable to this document; The latest version (including all modifications) of the referenced document without a date is applicable to this document.

GB/T 528 Determination of tensile stress-strain properties of vulcanized rubber and thermoplastic rubber

GB/T 1232.1 Determination of unvulcanized rubber using a disc shear viscometer Part 1: Determination of Mooney viscosity

GB/T 4498.1 Rubber - Determination of ash content - Part 1: Muffle furnace method

GB/T 6038 Rubber test compound formulation, mixing and vulcanization equipment and operating procedures

GB/T 6682 Specification and test methods of water for laboratory

GB/T 7764 Rubber identification Infrared spectroscopy

GB/T 24131.1 Determination of volatile matter content in raw rubber Part 1: Hot roller method and oven method

3 Terms and Definitions

The following terms and definitions apply to this document.

3.1

Mooney Viscosity

The measurement of the viscosity of raw rubber or rubber compound by a Mooney shear disc viscometer.

3.2

Volatiles

The mass lost of a material during thermal baking at a specified temperature.

3.3

Ash

The residue of material incineration under specified conditions.

3.4

Metal

Elements with metallic properties.

3.5

Oligomers

Polymers composed of fewer repeating units.

3.6

Antioxidant

Compound used to delay oxidative deterioration.

3.7

Degree of Unsaturation

A quantitative indicator of the degree of unsaturation of organic molecules.

3.8

Tensile Strength

Maximum tensile stress applied during the process of breaking a specimen.

3.9

Elongation at Break

Percentage elongation at break of the specimen

4 Technical Requirements

4.1 Product Classification and Technical Requirements

4.1.1 General Provisions

Polyisobutylene-based polymers used for rubber closures typically contains antioxidant 1010, antioxidant 1076, or antioxidant BHT. When polyisobutylene-based polymers containing other types of antioxidants, it should be evaluated according to the requirements of the relevant review and approval, Compatibility studies should be conducted if necessary.

4.1.2 Product Classification

According to the structure of the product, it can be divided into four types, namely:

a) Butyl rubber or IIR in English, a copolymer of isobutene and isoprene formed by polymerization.

b) Chlorinated butyl rubber or CIIR, Chlorinated isobutylene isoprene copolymer prepared by chlorination process using isobutylene isoprene copolymer as raw material;

c) Brominated butyl rubber or BIIR, Brominated isobutylene isoprene copolymer prepared by bromination process using isobutylene isoprene copolymer as raw material;

d) Brominated Isobutene-p-methylstyrene copolymer rubber or BIMSM in English, synthesized by polymerization and bromination of isobutylene and p-methylstyrene as raw material.

4.1.3 Technical Requirements

The technical requirements for products with different structures are shown in Tables 1 to 4, Table 1 specifies the requirements for butyl rubber, Table 2 specifies the requirements for chlorinated butyl rubber, Table 3 specifies the requirements for brominated butyl rubber, and Table 4 specifies the requirements for brominated Isobutene-p-methylstyrene copolymer rubber.

Table 1 Requirements for Butyl Rubber

Inspection item		Item indicators	Test method
Appearance		White to light yellow rubber block, uniform color, no obvious color spot or stain	Visual
Identification (infrared spectroscopy)		The infrared spectra of the samples shall be basically consistent with those of typical samples	GB/T 7764
Mooney viscosity of raw rubber,mL(1+4)100°C (or mL(1+8)125°C)		Nominal value ±5	GB/T 1232.1
Volatiles/%		≤0.3	GB/T 24131.1
Ash/%		≤0.3	GB/T 4498.1
Metal	Tin/%	≤0.0003	Appendix A
	Lead/%	≤0.0003	
	Copper/%	≤0.0003	
	Cadmium/%	≤0.0003	
	Chromium/%	≤0.0003	
	Barium/%(reference index)	≤0.0003	
Oligomer content (reference index)		The ratio of the total area of oligomers to the area of internal standard should not exceed 2	Appendix B
Antioxidant content/%		≤0.10	Appendix D
Degree of Unsaturation /mol%		Nominal value ±0.2	Appendix E
Calcium stearate content/%		≤1.0	Appendix F
Physical and mechanical properties (150°C,40 min)	Tensile strength/MPa	≥10.0	GB/T 528
	Elongation at break/%	≥400	

Table 2 Requirements for Chlorinated Butyl Rubber

Inspection item		Item indicators	Test method
Appearance		White to light yellow rubber block, uniform color, no obvious color spot or stain	Visual
Identification (infrared spectroscopy)		The infrared spectra of the samples shall be basically consistent with those of typical samples	GB/T 7764
Mooney viscosity of raw rubber,mL(1+8)125℃		Nominal value±5	GB/T 1232.1
Volatiles/%		≤0.5	GB/T 24131.1
Ash/%		≤0.5	GB/T 4498.1
Metal	Tin/%	≤0.0003	Appendix A
	Lead/%	≤0.0003	
	Copper/%	≤0.0003	
	Cadmium/%	≤0.0003	
	Chromium/%	≤0.0003	
	Barium/%(reference index)	≤0.0003	
Oligomer content (reference index)		The ratio of the total area of oligomers to the area of internal standard should not exceed 2	Appendix B
Antioxidant content/%		≤0.12	Appendix D
Calcium stearate content/%		≤2.0	Appendix F
Chlorine content (mass fraction,%)		1.25±0.10	Appendix G
Physical and mechanical properties (150℃,40 min)	Tensile strength/MPa	≥10.0	GB/T 528
	Elongation at break/%	≥400	

Table 3 Requirements for Brominated Butyl Rubber

Inspection item		Item indicators	Test method
Appearance		White to light yellow rubber block, uniform color, no obvious color spot or stain	Visual
Identification (infrared spectroscopy)		The infrared spectra of the samples shall be basically consistent with those of typical samples	GB/T 7764
Mooney viscosity of raw rubber,mL(1+8)125℃		Nominal value ±5	GB/T 1232.1
Volatiles/%		≤0.5	GB/T 24131.1
Ash/%		≤0.5	GB/T 4498.1
Metal	Tin/%	≤0.0003	Appendix A
	Lead/%	≤0.0003	
	Copper/%	≤0.0003	
	Cadmium/%	≤0.0003	
	Chromium/%	≤0.0003	
	Barium/%(reference index)	≤0.0003	
Oligomer content (reference index)		The ratio of the total area of oligomers to the area of internal standard should not exceed 2	Appendix B
Epoxy Soybean Oil (ESBO) Content/%		≤1.6	Appendix C
Antioxidant content/%		≤0.12	Appendix D
Calcium stearate content/%		≤2.5	Appendix F
Bromine content (%)		Nominal value±0.2	Appendix G
Physical and mechanical properties (150℃,40 min)	Tensile strength/MPa	≥10.0	GB/T 528
	Elongation at break/%	≥400	

Table 4 Requirements for Brominated Isobutene-p-methylstyrene Copolymer Rubber

Inspection item		Item indicators			Test method
Appearance		White to pale yellow plastic block, uniform color, no obvious spots or stains			Visual
Identification (infrared spectroscopy)		The infrared spectra of the samples are basically consistent with those of typical samples			GB/T 7764
Mooney viscosity of raw rubber,mL(1+8)125°C		Nominal value±5			GB/T 1232.1
Bromine content/mol%		0.75±0.07 （3 433）	0.47±0.10 （3 035）	1.20±0.10 （3 745）	Appendix G
Volatiles/%		≤0.5			GB/T 24131.1
Ash/%		≤0.3			GB/T 4498.1
Metal	Tin/%	≤0.0003			Appendix A
	Lead/%	≤0.0003			
	Copper/%	≤0.0003			
	Cadmium/%	≤0.0003			
	Chromium/%	≤0.0003			
	Barium/%(reference index)	≤0.0003			
Calcium stearate content/%		≤1.5			Appendix F
Physical and mechanical properties (150°C,40 min)	Tensile strength/MPa	≥7.0			GB/T 528
	Elongation at break/%	≥400			

4.2 Influence of some technical requirements on production and application of rubber closures

4.2.1 Mooney viscosity

Mooney viscosity of raw rubber has an influence on mixing process, vulcanization process and hardness of rubber closures.

4.2.2 Volatiles

Volatiles in raw rubber, including moisture and low molecular weight organic compounds, may affect the compatibility of rubber closures with packaged drugs.

4.2.3 Ash

The ash content of raw rubber has an effect on the ash content of rubber closures.

4.2.4 Metal

Metal elements in raw rubber, especially heavy metal elements, may have an impact on the safety and quality of drugs packaged by rubber closures.

4.2.5 Oligomer

Oligomers in raw rubber may have an impact on the compatibility of rubber closures with packaged drugs.

4.2.6 Antioxidants

Antioxidants in raw rubber may have an impact on the compatibility of rubber closures with packaged drugs.

4.2.7 Degree of unsaturation

The raw rubber degree of unsaturation has an influence on the sulfur chemical process of rubber closures and the hardness of products.

5 Test methods

The polyisobutylene-based polymers for rubber closures follow up technical requirements and limits, using appropriate test methods.

Unless otherwise specified, all reagents used in this document are analytically pure reagents, and the testing water used is purified water or Grade III water conforming to GB/T6682.

5.1 Appearance

Take a proper amount of this product, remove the sample package, and visually inspect it in a bright place of natural light.

5.2 Identification (infrared spectroscopy)

Infrared spectrum identification of rubber shall be carried out according to reflection analysis (attenuated total reflection ATR) or transmission analysis (thin film) in GB/T 7764.

5.3 Mooney viscosity

Mooney viscosity of raw rubber shall be tested according to GB/T1232.1.

5.4 Volatiles

The volatile components of raw rubber shall be tested according to oven method B in GB/T24131.1.

5.5 Ash

Raw rubber ash shall be tested according to GB/T4498.1 method A (burning temperature 800°C ± 25°C).

5.6 Metal

Conduct the test according to the method specified in Annex A.

5.7 Oligomer

Conduct the test according to the method specified in Annex B.

5.8 Epoxidized soybean oil (ESBO) content

Conduct the test according to the method specified in Annex C.

5.9 Antioxidant

Conduct the test according to the method specified in Annex D.

5.10 Degree of unsaturation

Conduct the test according to the method specified in Annex E.

5.11 Calcium stearate content

Conduct the test according to the method specified in Annex F.

5.12 Halogen content

Conduct the test according to the method specified in Annex G.

5.13 Physical and mechanical properties

5.13.1 The physical and mechanical properties of polyisobutylene-based polymers for rubber closures need to be compounded, mixed and vulcanized according to the inspection formula of the rubber, and standard test pieces are made and cut and measured according to GB/T 528.

5.13.2 Rubber standard inspection formula is as follows.

a) Butyl rubber standard inspection formula

Butyl rubber 100.00 g, high abrasion carbon black 50.00 g, zinc oxide 3.00 g, stearic acid 1.00 g, accelerator TMTD 1.00 g, sulfur 1.75 g, total 156.75 g.

b) Chlorinated rubber standard inspection formula

Chlorinated rubber 100.00 g, general carbon black 40.00 g, zinc oxide 5.00 g, stearic acid 1.00 g, total 146.00 g.

c) Brominated rubber standard inspection formula

Brominated rubber100.00 g, general carbon black 40.00 g, zinc oxide 5.00 g, stearic acid 1.00 g, total 146.00 g.

d) Brominated isobutylene-p-methylstyrene copolymer rubber standard inspection formula

Brominated isobutylene-p-methylstyrene copolymer rubber 100.00 g , general carbon black 50.00g, zinc oxide 1.00 g , stearic acid 1.00 g , accelerator DM 1.00g, sulfur 0.50g, total 153.50 g.

5.13.3 Operate the compounding, mixing and vulcanization processes of rubber according to GB/T 6038.

5.13.4 Determination of physical and mechanical properties of rubber according to GB/T528.

6 Inspection rules

Polyisobutylene-based polymers for rubber closures manufacturers and users should be clear release and acceptance criteria, and clear inspection rules.

7 Label, packaging, transportation and storage

7.1 Label

Packaged products should be clearly labeled with product name, specifications, batch number, manufacture date, trademark, net weight, implementation standards and the name and address of the manufacturer.

7.2 Packaging

The product should be packed by more than two layers of suitable packaging materials. The inner package should be easy to peel, or use soluble materials that will not pollute the product; The outer package should be solid and durable for the protection of the product during storage, transportation and handling.

7.3 Transportation

Transport should be dry, clean carriage loading, covered with tarpaulin, to prevent the sun or rain wet lead to rubber deterioration.

7.4 Storage

It should be stored in a room temperature, ventilated, clean and dry warehouse, stacked neatly, and maintained a certain distance. Outdoor stacking and direct sunlight are strictly prohibited. Avoid pollution.

8 Validity period

2 years from the manufacture date.

Appendix A

(Normative)

Determination of Metal Elements (Inductively Coupled Plasma Atomic Emission Spectrometry)

A.1 Principles

The metal elements in the rubber were determined by inductively coupled plasma atomic emission spectrometry after the rubber was burned and dissolved with acid, the content of the metal elements could be determined quantitatively according to the characteristic spectral lines and intensity of the elements.

A.2 Instruments

A.2.1 Inductively coupled plasma Atomic Emission Spectrometer.

A.2.2 Balance, Muffle stove, crucible, water bath.

A.2.3 Pipette (5 mL, 10 mL, 20 mL), volumetric bottle (50 mL, 100 mL)

A.3 Reagents

Unless otherwise specified, the reagents used in this document are analytical pure reagents, and the experimental water used is distilled water, deionized water, or water of comparable purity.

Hydrochloric acid (1+3) solution.

A.4 Operating steps

A.4.1 Preparation of sample solution

Take sample 5.0g, cut, place in crucible, and put in the Muffle furnace 350℃ heating sample until smoke-free production (about 6h, should avoid flame generation), then heated to 550°C continue burning for 30min. Cool the crucible to room temperature, add 15mL hydrochloric acid (1+3) solution, add the crucible cover, heat it in a water bath for 30 minutes, cool to room temperature, and transfer to a 50mL volumetric bottle. Wash the crucible with hydrochloric acid (1+3) solution, 10mL each time, repeat 3 times, wash the mixture into the volumetric bottle, add hydrochloric acid (1+3) solution to the scale, mix well to obtain the sample test solution.

A.4.2 Determination of metal elements Tin, lead, copper, cadmium, chromium and barium

Take appropriate amount of test solution to determine the metal elements,such as tin (189.93 nm), lead (220.35 nm), copper (327.40 nm), cadmium (214.44 nm), chromium (267.72 nm) and barium (455.40 nm) were determined respectively.

A.5 Result

According to formula (A.1) :

$$P=C_{sample}X50mL/M_{sample}/1000000X100 \text{..............} (A.1)$$

In the formula represents:

P - Content of each metal element, %;

C_{sample} - The concentration of each metal element in the sample test solution is obtained from the standard curve, in micrograms per milliliter (μg/mL);

M_{sample} - The sample is weighed in grams (g).

Appendix B

(normative)

Determination of Oligomer Content (Gas Chromatography Method)

B.1 Principles

The raw rubber was dissolved in a mixture of cyclohexane/dichloromethane, and the oligomer and its halogenated products were dissolved in a mixture of methanol/cyclohexane/dichloromethane, and determined by gas chromatoc-hydrogen flame ionization detector (GC-FID). The internal standard method was used for semi-quantitative analysis.

B.2 Instruments

B.2.1 Gas chromatography-Hydrogen Flame ionization detector

B.2.2 Analytical balance.

B.2.3 Pipette (5 mL, 20 mL), volumetric bottle (50 mL, 200 mL), threaded sampling tube (60mL), syringe (without rubber closures), filter (0.45 μ m filter membrane).

B.3 Reagents

Unless otherwise specified, the reagents used in this document are analytically pure.

B.3.1 Benzophenone (or other validated internal standard).

B.3.2 Cyclohexane.

B.3.3 Dichloromethane.

B.3.4 Methanol.

B.4 Operating Steps

B.4.1 Preparation of internal standard solution

Accurately weigh 400 mg benzophenone, place it in a 50mL volumetric bottle, dissolve it with dichloromethane, add dichloromethane to the scale, shake well to obtain the internal standard reserve solution. Precision suction internal standard reserve solution 5 mL, to 200 mL volumetric bottle, add methylene chloride to the scale, shake well, obtain benzophenone concentration of 0.2 mg/mL internal standard solution.

B.4.2 Preparation of sample test solution

Take an appropriate amount of raw rubber, cut it into 1 mm~2 mm particles, accurately weigh 1g, place it in a 60 mL threaded sampling tube, add 5mL of internal standard solution, add 5mL of cyclohexane (in order to improve the dissolution rate, another 5mL of dichloromethane can be added), screw the cap tightly, shake for about 3h until completely dissolved, add methanol 15 mL, screw the cap tightly, shake vigorously for about 1 min, absorb part of the solution with a syringe without rubber closures, filter through 0.45 μ m filter membrane, and obtain the sample test solution.

B.4.3 Chromatographic conditions (Recommended conditions, can be adjusted according to the actual situation)

The column was polyethylene glycol capillary column (DB-WAX,30 m×0.25 mm×0.25 μm). Heating procedure: the initial temperature was 40 ℃, keep for 2 min, then heated up to 190 ℃ at 25 ℃/min, then heated up to 220 ℃ at 10 ℃/min, and finally heated up to 240 ℃ at 5 ℃/min, keep for 7 min; The carrier gas was nitrogen, and the flow rate was 2 mL/min. The detector was a hydrogen flame ionization detector

(FID), the detector temperature was 260 ℃, the hydrogen flow rate was 40 mL/min, the air flow rate was 400 mL/min, and the tail blowing flow rate was 20 mL/min. The inlet temperature was 260 ℃ and the shunt ratio was 5:1. The sample quantity was 1.0 µL. Under the above chromatographic conditions, the following substances can be determined. $C_{13}H_{24}$、$C_{21}H_{40}$、$C_{13}H_{23}Cl$、$C_{13}H_{23}Br$、$C_{21}H_{39}C1$ 和 $C_{21}H_{39}Br$.

B.4.4 Determination

Accurately absorb sample test solution 1.0 µL, inject into the gas chromatograph, record the chromatogram.

B.5 Result

Compare the ratio of chromatographic peak area of related oligomers and their halogenated products (BHT and BHT oxidation products did not participate in the calculation) with the chromatographic peak area of benzophenone.

Appendix C

(Normative)

Determination of epoxy soybean oil (ESBO) content

C.1 Method A, Determination of epoxy soybean oil (ESBO) content (gas chromatographic method)

C.1.1 Principles

The raw rubber was dissolved in a mixture of cyclohexane/dichloromethane, and the epoxy soybean oil (ESCO) in the raw rubber was methylated by transesterification with potassium hydroxide methanol solution. The raw rubber was precipitated by acetone, and the fatty acid methyl ester was dissolved in the mixture of acetone/cyclohexane/dichloromethane, and determined by gas chromatography-hydrogen flame ionization detector (GC-FID). The internal standard method was used for quantitative analysis.

C.1.2 Instruments

C.1.2.1 Gas chromatography-Hydrogen Flame ionization detector

C.1.2.2 Balance, analytical balance

C.12.3 Pipette (5mL, 20mL), volumetric bottle (25mL, 50mL, 200mL), ground flat flask (150mL), magnetic stirrer, syringe (without rubber closures), filter (0.45μm filter membrane).

C.1.3 Reagents

Unless otherwise specified, the reagents used in this document are analytically pure.

C.1.3.1 Benzophenone (or other validated internal standard).

C.1.3.2 Cyclohexane.

C.1.3.3 Dichloromethane.

C.1.3.4 Acetone.

C.1.3.5 Epoxy Soybean Oil (ESBO).

C.1.3.6 Potassium hydroxide methanol solution: 1.36g potassium hydroxide is dissolved in 1000mL methanol to prepare.

C.1.3.7 Potassium bisulfate.

C.1.4 Operating steps

C.1.4.1 Preparation of internal standard solution

Accurately weigh 400 mg benzophenone, place it in a 50 mL volumetric bottle, dissolve it with dichloromethane, add dichloromethane to the scale, shake well to obtain the internal standard reserve solution. Accurately absorb 5 mL of internal standard reserve solution into a volumetric bottle of 200 mL, add methylene chloride to the scale, and shake well to obtain an internal standard solution with 0.2 mg/mL benzophenone.

C.1.4.2 Preparation of standard test solutions

Absorb about 1.25g epoxy soybean oil , put into a 50 mL volumetric bottle containing an appropriate amount of cyclohexane, accurately weigh, add cyclohexane to the scale, and mix well to obtain a 25 mg/mL epoxy soybean oil reserve solution. Accurately absorb 5 mL, 4 mL, 3 mL, 2 mL, 1 mL of epoxy soybean oil reserve solution into different 25 mL volumetric bottles, add cyclohexane to the scale, and mix well to obtain the epoxy soybean oil standard solution with concentrations of 5 mg/mL, 4 mg/mL, 3 mg/mL, 2 mg/mL, 1 mg/mL. Absorb 5mL of each epoxide soybean oil standard solution with a series of precision absorb concentrations, place into a 150mL flat-bottom grinding flask with magnetic stirrers. Accurately add 5mL of the internal standard solution ,and 5mL of methylene chloride , stir well. under stirring condition, slowly drop 0.2mL hydrogenated potassium oxide methanol solution, stir for 10min, add 0.5g potassium bisulphate under stirring condition, stir for 15min, add 15mL acetone under stirring condition, stir for 1min ~ 2min, stop stirring. Absorb part of the solution by a syringe without rubber closures and filtered by a 0.45µm filter membrane to obtain a series of standard test solutions containing 25mg, 20mg, 15mg, 10mg and 5mg of epoxy soybean oil.

C.1.4.3 Preparation of sample test solution

Take an appropriate amount of raw rubber, cut it into 1 mm~2 mm particles, accurately weigh 1g, put it into a 150mL flat-bottom flask with magnetic stirrers, accurately add 5mL of internal standard solution, 5mL of cyclohexane, and 5mL of dichloromethane, seal with plug , shake or stir it magnetically for about 2 h~3 h until completely dissolved. Remove the plug from the bottle and slowly drop 0.2mL hydrogenated potassium oxide methanol solution under stirring condition,stir for 10 min, add 0.5g potassium bisulphate under stirring condition, stir for 15 min, add 15mL acetone under stirring condition, stir for about 1 to 2 min, then stop stirring. Absorb part of the solution by a syringe without rubber closures and filtered by a 0.45µm filter membrane to obtain the test sample solution.

C.1.4.4 Chromatographic conditions (Recommended conditions, can be adjusted according to the actual situation)

The column was polyethylene glycol capillary column (DB-WAX,30 m×0.25 mm×0.25 µm). Heating procedure: the initial temperature was 150℃, heated up to 200 °C at 25 °C/min, then heated up to 230 °C at 10 °C/min, and finally heated up to 240 °C at 5 °C/min, keep for 12 min; The carrier gas was nitrogen, and the flow rate was 2 mL/min. The detector was a hydrogen flame ionization detector (FID), the detector temperature was 260 °C, the hydrogen flow rate was 40 mL/min, the air flow rate was 400 mL/min, and the tail blowing flow rate was 20 mL/min. The inlet temperature was 260 °C and the shunt ratio was 5:1. The sample quantity was 1.0 µL. Under the above chromatographic conditions, the following five substances can be determined, methyl palmitate, methyl stearate, methyl epoxyoleate (18:1E), methyl diepoxylinoleate (18:22E) and methyl diepoxylinoleate

C.1.4.5 Determination (Unless otherwise specified, the first method is generally used)

C1.4.5.1 First Method (Control method)

The corresponding standard test solution was prepared according to the content of epoxy soybean oil in raw rubber (generally use the standard test volume solution with epoxy-soybean oil content of 10mg), and the standard test solution and sample test solution were accurately absorbed 1.0µL respectively, inject into the gas chromatograph, record the chromatogram, and record the peak area of methyl palmitate, methyl stearate and methyl epoxy-oleate respectively (18: 1E), methyl diepoxylinoleate (18:22E), methyl diepoxylinoleate (18:22E) chromatographic and compare with internal standard chromatographic peak area.

C.1.4.5.2 Second Method (Standard Curve Method)

Each standard test solution with different content is accurately absorbed 1.0µL, inject into the gas chromatograph, and record the chromatogram ,and record the peak area of methyl palmitate, methyl stearate and methyl epoxy-oleate respectively (18: 1E), methyl diepoxylinoleate (18:22E), methyl diepoxylinoleate (18:22E) chromatographic, and total chromatographic peaks of 5 epoxy-soybean oil-related substances. Compare total chromatographic peaks of 5 epoxy-soybean oil-related substances with the area of internal standard chromatographic peaks $A_{\text{stamdard}}/A_{\text{Internal standard}}$ as the X-axis, and the content of epoxy-soybean oil (mg) as the Y-axis, to make standard cureve.

Accurately absorb the sample test solution of 1.0μL and inject into the gas chromatograph, record the chromatogram. and record the peak area of methyl palmitate, methyl stearate and methyl epoxy-oleate respectively (18: 1E), methyl diepoxylinoleate (18:22E), methyl diepoxylinoleate (18:22E) chromatographic, and total chromatographic peaks of 5 epoxy-soybean oil-related substances. And calculate the content of epoxy-soybean oil (mg) in sample solution from the standard curve.

C.1.5 Results

C.1.5.1 Results of the First method

Calculate the relative percentage of epoxy soybean oil according to formula (C.1) :

$$P=(W_{st} \times R_s / R_{st}) / 1000 / M_{st} \times 100 \quad \text{...............(C.1)}$$

P--Relative percentage content of epoxy soybean oil ,%;

Wst--The content of epoxy soybean oil in the standard solution, unit is milligrams (mg);

Mst--Sample weight, in grams (g);

Rst.=Ast / Ainst, Ast is the total chromatographic peak area of five epoxy soybean oil related substances, including standard solutions of methyl palmitate, methyl stearate, methyl epoxyoleate (18:1E), methyl diethoxylinoleate (18:22E), and methyl diethoxylinoleate (18:22E). Ainst is the peak area of the internal standard chromatogram in the standard solution;

Rs.=As / Ainst., As is the total chromatographic peak area of five epoxy soybean oil related substances, including sample solutions of methyl palmitate, methyl stearate, methyl epoxyoleate (18:1E), methyl diethoxylinoleate (18:22E), and methyl diethoxylinoleate (18:22E). Ainst is the peak area of the internal standard chromatogram in the sample solution;

C. 1.5.2 Second Method Results

Calculate the relative percentage content of epoxy soybean oil according to the formula (C.2)

$$P=(W_s / 1000 / M_s \times 100 \quad \text{...............(C.2)}$$

P--Relative percentage content of epoxy soybean oil,%;

Ws --Calculate the content of epoxy soybean oil in the sample solution on the standard curve, in milligrams (mg);

Ms --Sample weight, in grams(g);

C.2 Reference method B: Determination of epoxy soybean oil (ESBO) content (potentiometric titration method)

C.2.1 Principle

This method is applicable for the determination of stabilizer content in bromobutyl rubber.

Extract stabilizers (epoxy soybean oil) from rubber by acetone and trichloromethane. In the presence of tetraethylammonium bromide, the determination of epoxyethane oxygen in epoxy soybean oil is carried out by potentiometric titration. The standard solution used for titration is a perchloric acid solution dissolved in acetic acid at a concentration of 0.02 mol/L.

C.2.2 Instrument

C.2.2.1 Automatic titrator, equipped with: glass electrode (non-aqueous electrode); Ag/AgCI reference electrode: filled with saturated lithium chloride ethanol solution inside and outside.

C.2.2.2 Electronic balance with an accuracy of 0.01 g.
C.2.2.3 Electronic balance with an accuracy of 0.1 mg
C.2.2.4 Magnetic stirrer.
C.2.2.5 High beaker: 100mL.
C.2.2.6 Volumetric bottle: 500 mL, 1000 mL.
C.2.2.7 Pipette: 10 mL, 25 mL.
C.2.2.8 Graduated cylinder: 100 mL.
C.2.2.9 Conical flask: 50mL

C.2.3 Reagents

All reagents used are analytical pure reagents.

C.2.3.1 70% perchloric acid aqueous solution.
C.2.3.2 Acetic anhydride.
C.2.3.3 Ice acetic acid.
C.2.3.4 Potassium hydrogen phthalate.
C.2.3.5 20% Tetraethylammonium Bromide Acetic Acid Solution: Weigh 2g of Tetraethylammonium Bromide Acetic Acid and dissolve it in 10mL of ice acetic acid, shake well.
C.2.3.6 Acetone.
C.2.3.7 Trichloromethane.
C.2.3.8 Anhydrous ethanol, analytical pure.

C.2.4 Solution Preparation

C.2.4.1 Equivalent 0.1 mol/L perchlorate acetic acid solution

Take 8.7 mL of perchloric acid into a 1000 mL volumetric bottle by a pipette, add 500 mL of ice acetic acid by graduated cylinder, and then add 20 mL of anhydrous acetic anhydride. Shake well and dilute to the scale with acetic acid;

This solution should be left for at least 24 hours before use.

C.2.4.2 Calibration of perchloric acid solution concentration

Potentiometric titration determination using potassium hydrogen phthalate as standard:

Weigh 0.1 g~0.2 g(accurate to 0.1 mg)105℃~110℃ constant weight reference reagent potassium hydrogen phthalate, transfer all samples to a titration beaker equipped with a magnetic stirrer, add 60mL acetic acid and stir until completely dissolved.

Immerse the electrode in the dissolved solution and titrate with perchloric acid solution of about 0.1mo1/L.

Calculation: The concentration of perchloric acid standard solution shall be calculated according to formula (C.3):

$$C=\frac{m \times 1000}{V \times 204.22} \quad ....(C.3)$$

where:

c----------Concentration of perchloric acid standard solution, unit: equivalent/L;
m ---------The amount of potassium hydrogen phthalate standard substance used, in grams (g);

V----------Volume of perchloric acid standard solution used in titration, in mL
204.22---- Molecular weight (equivalent) of potassium hydrogen phthalate

C.2.5 Operation steps

C.2.5.1 Analysis

Weigh 50 mL of conical flask mass (accurate to 0.1 mg), and then weigh 1 g ~ 1.5 g dry rubbercut which was cut into fine particles (accurate to 0.1 mg), put into a 50 mL conical flask, add 15 mL chloroform by a graduated cylinder, shake until the rubber completely dissolved.

After dissolution is complete, add 10mL acetone and 10mL tetraethyl ammonium bromide solution by graduated cylinder, weigh the mass of the mixture solution, stir by stirrer or shake, so that the rubber is completely precipitated, and then weigh about 30g of supernatant solution into a small beaker by the reduction method, immerse it into an electrode, and titrate it with calibrated perchloric acid standard solution.

C.2.5.2 Blank experiment

Mix equal volumes of 15mL chloroform, 10mL acetone and 10mL tetraethylammonium bromide solution, and titrate according to the same method as above.

Preparation of tetraethylammonium bromide solution making before titration.

Note: Polymer dissolution and potentiometric titration must be performed in a fume hood.

C.2.6 Calculation

The percentage content of stabilizer in bromobutyl rubber:w% is calculated according to formula (C.4).

$$W = \frac{(V-V_0) X\ N X 16\ X\ 10}{W\ .\ X} \quad ....(C.4)$$

where:

V-----Volume of perchloric acid standard solution used for titration of sample, unit: mL;
V_0-----Volume of perchloric acid standard solution used in blank experiment, unit: mL;
N-----Equivalent concentration of perchloric acid standard solution used, unit: equivalent/L;
16-----oxygen equivalent;
X--oxygen content of ethylene oxide in stabilizer, generally use 6.6;
W--Pipette the mass of rubber sample in part of liquid, and calculate according to formula (C.5):

$$W = \frac{m_2\ X\ m}{m_1 - m_0} \quad ....(C.5)$$

m_2--------The mass of a part of the liquid being removed, unit: g
m------mass of rubber sample, unit: g);
m_1----Mass of mixed solution + empty bottle, unit: g;
m_0-----Mass of empty conical flask, unit: g.

C.2.7 Presentation of analytical results

For each sample, take the arithmetic mean value of the two determination results as the analysis result, and keep the analysis result to two decimal places. The relative deviation of two determinations is not more than 5%

Appendix D

(Normative)

Determination of Antioxidant Content (High Performance Liquid Chromatography)

D.1 Principle

Raw rubber was dissolved in cyclohexane/methylene chloride mixed solution and precipitated with methanol. Antioxidants (antioxidant BHT, antioxidant 1010 and antioxidant 1076) in raw rubber were dissolved in methanol/cyclohexane/methylene chloride mixed solution and determined by HPLC. The internal standard method was used for quantitative analysis.

D.2 Instruments

D.2.1 Liquid chromatograph.
D.2.2 Analytical balances.
D.2.3 Pipettes (5mL, 20mL), volumetric bottles (50 mL, 100mL, 200mL) threaded sampling tubes (60mL), syringes (without rubber closures), filters (0.45μm filter membrane)

D.3 Reagents

Unless otherwise specified, the reagents used in this document are analytically pure reagents, and the experimental water used is distilled water, deionized water or water of comparable purity.

D.3.1 Methanol.
D.3.2 Cyclohexane.
D.3.3 Methylene chloride.
D.3.4 Antioxidant BHT.
D.3.5 Antioxidant 1010.
D.3.6 Antioxidant 1076.
D.3.7 Antioxidant 3114.

D.4 Operation steps

D.4.1 Preparation of internal standard solution

Take about 100mg of 1,3,5-tris (3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate (antioxidant 3114), weigh accurately, place it in a 50mL volumetric bottle, dissolve it in an appropriate amount of dichloromethane, add to scale, and shake well to obtain the internal standard stock solution. Accurately pipette 5mL of internal standard stock solution into a 200mL volumetric bottle, add dichloromethane scale, shake well, then obtain an internal standard solution with antioxidant 3114 concentration of 0.05 mg/mL.

D.4.2 Preparation of standard test solutions

Take an appropriate amount of raw rubber, cut it into 1 mm~2 mm particles, accurately weigh 1g, place it in a 60 mL threaded sampling tube, add 5mL of internal standard solution, add 5mL of cyclohexane (in order to improve the dissolution rate, another 5mL of dichloromethane can be added), screw the cap tightly, shake for about 3h until completely dissolved, add methanol 15 mL, screw the cap tightly, shake vigorously for about 1 min, absorb part of the solution with a syringe without rubber closures, filter through 0.45 μ m filter membrane, and obtain the sample test solution.

D.4.3 Preparation of sample test solution

Take a proper amount of raw rubber, shear it into particles of 1mm~2 mm, accurately weigh 1 g, put it into a 60mL threaded sample tube, accurately add 5mL of internal standard solution, add 5mL of cyclohexane (in order to improve the dissolution rate, add another 5mL of dichloromethane), tighten the screw cap, shake for about 3h until completely dissolved, add 15mL of methanol, tighten the screw cap, shake vigorously for about 1min, absorb part of the solution with a syringe without rubber seal, filter through a 0.45 m filter membrane, and obtain the sample test solution.

D.4.4 Chromatographic conditions (recommended conditions, which can be adjusted appropriately according to actual conditions)

The chromatographic column was filled with octadecylsilane bonded silica gel (Agilent XDBC 18,5μ m, 4.6 mm X 150 mm). The mobile phase A consisted of water, phase B consisted of isopropanol and acetonitrile (volume ratio 1:1), the flow rate was 1.5 mL/min, and the elution gradient was 70% at the beginning of phase B and kept for 1 min. The proportion of phase B increased linearly to 84% at 7min, and increased linearly to 95% at 18min, and increased linearly to 96% at 24min, and decreased linearly to 70% at 25min, and kept for 2 min. The injection volume was 20μL. The detector was UV detector with detection wavelength of 280nm. The sample was stored at 5°C and the column temperature was room temperature.

Under the above chromatographic conditions, three different antioxidants can be determined: antioxidant BH, antioxidant 1010 and antioxidant 1076.

D.4.5 Determination method (Unless otherwise specified, the first method is generally used)

D.4.5.1 Method I (Control Method)

According to the type and content of antioxidants in raw rubber, prepare corresponding standard test solutions, respectively accurately absorb 20μ of standard test solution and sample test solution, inject into gas chromatography and record chromatograms, respectively record the chromatographic peak areas of relevant antioxidants and internal standard.

D.4.5.2 Second method (standard curve method)

Each standard test solution with different content is accurately absorbed 20μL, inject into the gas chromatograph, and record the chromatogram , respectively record the chromatographic peak areas of relevant antioxidants and internal standard. Chromatographic peak area ratio A_{sx}/A_{Inst} as the X-axis, and content of relevant antioxidant in sample solution (mg) as the Y-axis, to make standard cureve.

Accurately absorb the sample test solution of 20 μL and inject into the gas chromatograph, record the chromatogram, respectively record the chromatographic peak areas of relevant antioxidants and internal standard. Calculate chromatographic peak arearatioAsx/Ainst, and calculate the content of relevant antioxidant in sample solution (mg) from calibration curve.

D.5 Results

D.5.1 Results of the first method

Calculate the relative percentage content of relevant antioxidants according to formula (D.1):

$$P=(Wst \times Rs / Rst) / 1000 / Ms \times 100 \quad \text{...............(D.1)}$$

where:

P----Relative percentage content of relevant antioxidants,%;

Wst -----The content of relevant antioxidants in the standard solution, in mg;

Ms---Sample weighing, unit: g;

Rst.=Ast / Ainst, Ast is the chromatographic peak area of the antioxidant related to the standard solution, Ainst is the chromatographic peak area of the internal standard of the standard solution;

Rs.=As / Ainst, As is the chromatographic peak area of the relevant antibody of the sample solution, Ainst is the chromatographic peak area of the internal standard of the sample solution.

D.5.2 Results of the second method

Calculate the relative percentage content of antioxidant according to formula (D.2):

$$P=Ws / 1000 / Ms \times 100 \quad \text{...............(D.2)}$$

where:

P------Relative percentage content of antioxidants,%;

Ws ----The content of antioxidant in sample solution was calculated from cinnamon standard curve, unit: mg.

Ms--Sample weight, unit: g.

Appendix E

(Normative)

Determination of Unsaturation

E.1 Principle

A certain amount of raw rubber was dissolved in carbon tetrachloride solution, add iodine bromide solution, add excess potassium iodide solution to react with residual iodine bromide to produce iodine, titrated with sodium thiosulfate standard solution to make a blank test and calculate.

E.2 Instruments

Thermostatic water bath, Thermostatic water bath oscillator, acid buret (25 mL), pipette (10 mL), measuring cylinder (5 mL, 10 mL, 100 mL), iodine measuring bottle (250 mL), beaker (100 mL, 400 mL), brown reagent bottle (500 mL, 1 000 mL, 5 L), transparent reagent bottle (500 mL), glass rod, ear-sucking ball.

E.3 Reagents

Unless otherwise specified, the reagents used in this document are pure analytical reagents. The experimental water used is distilled, deionized, or water of comparable purity.

E.3.1 Iodine bromide.

E.3.2 Sodium thiosulfate.

E.3.3 Carbon tetrachloride.

E.3.4 Potassium iodide.

E.3.5 Soluble starch.

E.4 Preparation of reagents

E.4.1 Preparation of iodine bromide solution (0.1 mol/L)

Take washed and dried 5L brown reagent bottle,10 bottles 500 mL carbon tetrachloride solution. Add 1000 mL carbon tetrachloride to the brown reagent bottle, take out the iodine bromide from the refrigerator, open the bottle and pour directly into the 5L brown reagent bottle, add the appropriate amount of carbon tetrachloride in to the iodine bromide reagent bottle , dissolve the remaining iodine bromide, transfer to 5L brown reagent bottle, repeat many times until all the iodine bromide in the reagent bottle is transferred to 5L brown reagent bottle, add an appropriate amount of carbon tetrachloride, cover the bottle and shake, when all the iodine bromide is dissolved, add the remaining carbon tetrachloride into 5L brown reagent bottle, stir well with a glass rod. Stand for one month away from light,wait until used.

E.4.2 Preparation and calibration of 0.1 mol/L sodium thiosulfate standard solution

E.4.2.1 Preparation of 0.1 mol/L sodium thiosulfate standard solution

Weigh 26g sodium thiosulfate ($Na2S2O3 \cdot 5H2O$)(or 16g anhydrous sodium thiosulfate), dissolve in 1000 mL water, slowly boil for 10 min, then cool. Fliter after standing for two weeks, wait until used.

E.4.2.2 Calibration of 0.1 mol/L sodium thiosulfate standard solution

Weigh 0.18 g the reference potassium dichromate which was baked at 120 ° C ±2 ° C to the constant weight, measured to 0.000 1 g. Place in iodine bottle, dissolve in 25 mL water, add 2g potassium iodide and 20 mL sulfuric acid solution (20%), shake well, place in dark place for 10 min. Add 150 mL water and titrate with prepared sodium thiosulfdate solution [$c(Na2S2O3)$=0.1 mol/L]. Add 2 mL of starch indicator solution (10 g/L) near the end and titrated until the solution changed from blue to bright green. At the same time, a blank test was performed.

The standard solution concentration of sodium thiosulfate is calculated according to formula (E.1) :

$$\text{C Na2S2O3} = \frac{\text{mK2Cr2O7}}{(\text{V-Vblank})\text{X}0.049\ 03} \quad \text{...........(E.1)}$$

Where:

C Na2S2O3 —— concentration of standard sodium thiosulfate solution(unit: mol/L)

mK2Cr2O7 —— weight of potassium dichromate(unit: g)

V —— consumption amount of standard sodium thiosulfate solution when titrating potassium dichromate, unit: mL

Vblank —— consumption amount of standard sodium thiosulfate solution when titrating blank solution, unit: mL

0.049 03 —— weight of potassium dichromate(unit: g) which is in accordance with 1.00mL standard sodium thiosulfate solution(C Na2S2O3=1.000mol/L)

E. 4.3 Preparation of potassium iodide solution (10%)

Use a balance to weigh 50g analytical iodized in 400 mL beaker, use measuring cylinder to take 450mL distilled water, dissolve and transfer all into 500 mL brown reagent bottle. Wait for use.

E4.4 Preparation of starch indicator (0.5%)

Weigh 2.5g powder and put into 50mL beaker, measure 500mL distilled water. First, use a few drops of starch to mushy, then take about 400 mL water and heat it on the electricity until it is slightly boiled, pour the paste starch, then rinse 50mL beaker by using the remaining distilled water for 3 times, pour the liquid into the beaker, and then keep slightly boiled for 3 mins. Starch indicator solution should not be stored more than 2 weeks.

E.5 Operation steps

E.5.1 Weighing rubber

Weigh 0.500g raw rubber with 0.0001g accuracy and place in 250mL iodine flask.

E.5.2 Dissolve rubber .

Measure 50mL carbon tetrachloride solution with a measuring cylinder, add it to an iodine flask and place it on a Thermostatic water bath oscillator, oscillate for 2h at the speed 100r/min and the temperature 25℃.

E.5.3 Adding iodine bromide

Use pipette to accurately remove 10mL 0.1mol/L iodine bromide solution to the iodine measuring bottle, shake well, put in thermostatic water bath for 0.5hours at 25 °C away from light (the reaction time should be strictly controlled at 0.5h. If the time is too short, addition reaction will be inadequate. If reation time is too long, side reaction replacement will happen.

E.5.4 Adding potassium iodide

Measure 10 mL of 10% potassium iodide solution by a measuring cylinder and add it to the iodine measuring bottle that has reached the reaction time. Shake well.

E.5.5 Titration

Titrate with 0.1 mol/L sodium thiosulfate standard solution, near the end, the upper layer of solution was light yellow, the lower layer was light pink, then add 5mL of 0.5% starch indicator, and then titrate until the blue disappeared, that is the end.

E.5.6 Blank test

Use a measuring cylinder to measure 50 mL carbon tetrachloride solution into an iodine measuring bottle and repeat steps E.5.3 to E.5.5

E.6 Results

E.6.1 Value

Calculate the iodine value of raw glue by the formula (E.2) :

$$I = \frac{c \cdot (V0-V)X12.69}{m} \qquad \text{..................(E.2)}$$

Where:

I —— iodine value of raw rubber(g iodine/100g rubber)

c —— the substance concentration of sodium thiosulfate standard titration of (unit: mol/L)

V0 —— the volume of sodium thiosulfate standard titration solution required for titration of blank solution(unit: mL)

V —— the volume of sodium thiosulfate standard titration solution required for titration of the sample solution(unit:mL)

m —— the weight of raw rubber sample(unit: g)

E.6.2 Unsaturation

Calculate the unsaturation of raw rubber by the formula (E.3) :

$$X= \frac{I \cdot M}{126.9X3} \qquad \text{..................(E.3)}$$

Where:

X —— unsaturation of raw rubber

I —— iodine value of raw rubber(g iodine/100g rubber)

M —— average molecular weight of butyl rubber monomer with a typical value of 56.393

126.9 —— atomic weight of iodine

The results of the test analysis are based on the arithmetic mean of the two repeated measurements. Under the condition of repeatability, the difference between the two determination results, iodine value should not be more than 0.2 gI/100 g rubber, unsaturation should not be more than 0.02.

Appendix F

(Normative)

Determination of Calcium Stearate Content

F.1 A Arbitration method: Determination of calcium stearate content (gas chromatography method)

F.1.1 Principles

The raw rubber is dissolved in cyclohexane/dichloromethane mixed solution, the calcium palmitate and calcium stearate in the raw rubber are acidified into palmitic acid and stearic acid,The raw rubber was precipitated by methanol, palmitic acid, stearic acid and methanol are formed into methyl ester under acidic conditions, methyl palmitate and methyl stearate are dissolved in methanol/cyclohexane/dichloromethane mixed solution, then determinate by gas chromatographic flame ionization detector(GCFID) . Quantitative analysis was performed by internal standard method.

F.1.2 Instruments

F.1.2.1 Gas chromatographic flame ionization detector, oven.

F.1.2.2 Analytical Balance

F.1.2.3 Pipette (5mL, 20 mL), volumetric bottle (50mL, 200mL), threaded sampling tube (60 mL), Syringe(without rubber closures), filter (0.45um filter membrane).

F.1.3 Reagents

Unless otherwise specified, the reagents used in this document are analytically pure.

F.1.3.1 Benzophenone

F.1.3.2 Cyclohexane

F.1.3.3 Methylene chloride

F.1.3.4 Methanol.

F.1.3.5 Concentrated sulfuric acid

F. 1.3.6 Calcium stearate

F.1.3.7 Sodium bicarbonate

F.1.4 Operating steps

F.1.4.1 Preparation of 10% methanol sulfate solution

Absorb 5 mL concentrated sulfuric acid and slowly drop into a 50 mL volumetric bottle containing methanol of about 30mL. When drop concentrated sulfuric acid, gently shake the volumetric bottle. After the concentrated sulfuric acid are completely added, cool to room temperature, add methanol to the scale, and mix well.

F.1.4.2 Preparation of standard solution dilution solvent

Absorb 6mL 10% methanol sulfate solution, put into a 200mL volumetric bottle, add methylene chloride to the scale, mix well to obtain the standard solution diluted solvent.

F.1.4.3 Preparation of benzophenone internal standard solution

Accurately weigh 600mg benzophenone and place it in 50 mL volumetric bottle. Dissolve with methylene chloride and dilute to scale to obtain benzophenone reserve solution; Accurately measure benzophenone cyclohexane reserve solution 10 mL, put into 200 mL volumetric bottle, add cyclohexane to the scale, to obtain the concentration of 0.6 mg/mL benzophenone internal standard solution

F.1.4.4 Preparation of standard test solutions

Accurately weigh 50mg of calcium stearate, put into a 50mL volumetric bottle, dissolve with appropriate amount of standard solution dilution solvent, add the standard solution dilution solvent to the scale, and obtain a stearic acid standard solution with a concentration of about 1mg/mL(calculated by calcium stearate); Accurately absorb 1 mg/mL(calculated by calcium stearate) stearic acid standard solution 25mL, 10mL, to 50mL volumetric bottles, and add the standard solution dilution solvent to the scale, and mix well to obtain the stearic acid standard solution with a concentration of about 0.5mg/mL and 0.2mg/mL(calculated by calcium stearate). Accurately absorb 10mL of stearic acid solution 1.0mg/mL, 0.5mg/mL and 0.2mg/mL respectively, put them into 60mL threaded sampling tubes, add 5 mL of internal standard solution precisely, drop 0.3 mL of 10% methanol sulfate solution, add 15 mL methanol, mix well, screw the cap tightly, and place them in the oven at 50 °C for 90 mins, take out the threaded sampling tubes, naturally cool to room temperature, add 0.8g~1.0g sodium bicarbonate, seal with a plug, shake violently for about 30s, let it stand until it is clarified, absorb part of the solution with a syringe without rubber closures, and filter through a 0.45μm filter membrane to obtain a system containing a series of calcium stearate with 10mg, 5mg, 2mg, 1mg concentration methyl stearate standard test solution. In addition, accurately weigh calcium stearate 20mg and 40mg respectively, and operated according to the preparation method of sample solution, then obtain the standard test solutions of series concentration methyl stearate with contents (calculated by calcium stearate) of 20mg and 40mg.

Note: Methyl stearate obtained by the standard solution dilution solvent is not more than 20mg(calculated by calcium stearate), and the standard test solution with higher content needs to be accurately weigh appropriate amount of calcium stearate and operated according to method F.1.4.5.

F.1.4.5 Sample Solution Preparation

Take 1g of the raw rubber sample, cut into small pieces, and weigh accurately. Place it in a 60 mL threaded sampling tube and add 10 mL of dichloromethane. Precision-add 5 mL of the internal standard solution. Tighten the cap and shake vigorously to dissolve the sample. Add 0.6 mL of 10% sodium methanolate solution under a vortex condition. Add 15 mL of methanol. Seal the tube tightly and shake vigorously for about 30s. Place into an oven at 50°C for 90 minutes. Take out the threaded sampling tube when its temperature drops to room temperature. Add 0.8g to 1.0g of sodium bicarbonate and shake vigorously for about 30s. let it stand until it is clarified, absorb part of the solution by a syringe without rubber closures, filter the sample test solution through a 0.45μm filter membrane to obtain a sample test solution.

Note: The maximum content of calcium stearate by this test method is about 50mg. If require higher content of calcium stearate, need reduce the sample size or appropriately increase the amount of sulfuric acid.

F.1.4.6 Chromatographic conditions (recommended conditions, can be adjusted according to the actual situation)

The column was polyethylene glycol capillary column (DB-WAX,30 m×0.25 mm×0.25 μm). Heating procedure: the initial temperature was 150°C, heated up to 200 °C at 25 °C/min, then heated up to 230 °C at 10 °C/min, and finally heated up to 240 °C at 5 °C/min, keep for 5 mins; The carrier gas was nitrogen, and the flow rate was 2 mL/min. The detector was a hydrogen flame ionization detector (FID), the detector temperature was 260 °C, the hydrogen flow rate was 40 mL/min, the air flow rate was 400 mL/min, and the tail blowing flow rate was 20 mL/min. The inlet temperature was 260 °C and the shunt ratio was 5:1. The sample quantity was 1 μL. Under the above chromatographic conditions, the chromatographic peaks of methyl palmitate, methyl stearate and benzophenone can be measured.

F.1.4.7 Determination (Unless otherwise specified, the first method is generally used)

F.1.4.7.1 First Method (Control method)

According to the different content of calcium stearate in raw rubber, the corresponding content of standard test solution is prepared [The determination of brominated butyl rubber can use the content of 20mg(calculated by calcium stearate) standard test solution, the determination of chlorinated butyl rubber, butyl rubber and brominated isobutylene - p-methylstyrene copolymer rubber can use the content of 10mg(calculated by calcium stearate) standard test solution], absorb 1μL the standard test solution and 1μL the sample test solution, inject into the gas chromatograph, and the record the chromatogram. Respectively record the chromatographic peak area of methyl palmitate, methyl stearate and benzophenone.

F.1.4.7.2 Second Method (Standard curve method)

Accurately absorb the standard test solutions of different concentrations of 1μL respectively, and inject into the gas chromatograph , record the chromatogram and record the chromatographic peak areas of methyl palmitate, methyl stearate and benzophenone ,calculate the ratio of chromatographic peak areas $(A_{sm1} + A_{sm2})/A_{inst}$ as the X-axis and calcium stearate content (mg) as the Y-axis.

Accurately absorb 1μL of the sample test solutions, and inject into the gas chromatograph , record the chromatogram and record the chromatographic peak areas of methyl palmitate, methyl stearate and benzophenone , calculate the ratio of chromatographic peak areas ratio $(A_{sm1} + A_{sm2})/A_{inst}$, calculate the calcium stearate content (mg) from the standard curve.

F.1.5 Results

F.1.5.1 Results of the first method

Calculate the relative percentage of calcium stearate by formula (F.1) :

$P=(W_{sm}\ X\ R_{sm}/R_{st})/1000/M_{sm}\ X100$ ………………………… (F.1)

Where:

P-calcium stearate relative content %;

W_{st} - Calcium stearate content in standard solution, unit:mg

M_{sm} - Sample weight, unit: g

$R_{st} = (A_{st1} + A_{st2})/A_{inst}$, A_{st1} is the chromatographic peak area of methyl palmitate in standard solution, A_{st2} is the chromatographic peak area of methyl stearate in standard solution, and A_{inst} is the chromatographic peak area of standard solution

$R_{sm} = (A_{sm1} + A_{sm2})/A_{inst}$, A_{sm1} is the chromatographic peak area of methyl palmitate in sample solution, A_{sm2} is the chromatographic peak area of methyl stearate in sample solution, and A_{inst}, is the chromatographic peak area of internal standard in sample solution

F.1.5.2 Results of the Second method

Calculate the relative percentage of calcium stearate by formula (F.2) :

$P=W_{sm} / 1000 / M_{sm}\ X\ 100$ …………… (F.2)

Where:

P-calcium stearate relative percentage content,%

W_{sm} -Calcium stearate content in sample solution was obtained in the standard curve, unit: mg.

M_{sm} -- sample weight , unit: g

F.2 Reference method B: Determination of calcium stearate content (titration method)

F.2.1 Principles

After the ash test, take the ash of rubber samples dissolve with hydrochloric acid 1:1 , and the pH value was adjusted to about 10 by 1mol/L sodium hydroxide solution. The content of total calcium stearate in butyl rubber was titrated by EDTA with chromium black T as indicator and triethanolamine as a mask agent.

F.2.2 Reagents and materials

Unless otherwise specified, the water used is tertiary water, and the reagents are analytically pure.

F.2.2.1 Triethanolamine, hydrochloric acid, sodium chloride, sodium hydroxide, ammonia water and ammonium chloride.

F.2.2.2 Conical flask :250mL.

F.2.2.3 Measuring cylinder :10 mL, 25 mL.

F.2.2.4 Pipette :2mL micro-volume pipette with a division value of 0.02 mL.

F.2.2.5 Volumetric bottle :250mL.

F.2.2.6 EDTA Standard titration solution :$c_{(EDTA)}$=0.02 mol/L.

F.2.2.7 1%　chromium black T indicator: Grind 1g chrome black T and 99g sodium chloride into fine powder with agate body and mix well.

F.2.2.8 1mol/L sodium hydroxide: Weigh 4g sodium hydroxide and dissolve in 100mL distilled water.

F.2.2.9 1:1 triethanolamine :distilled water mixed with equal volume of triethanolamine.

F.2.2.10 1:1 hydrochloric acid : distilled water mixed with equal volume of hydrochloric acid .

F.2.2.11 Buffer solution: dissolve 67.5g ammonium chloride in 300mL of distilled water in a 1000mL volumetric bottle, add 570mL of ammonium hydroxide and dilute to the scale with distilled water.

F.2.3 Instruments and equipment

Electronic balance: Accurate to 0.1 mg.

F.2.4 Operation steps

F.2.4.1 Determination of calcium stearate content in butyl rubber

Dissolve the ash which is obtained after the ash test with 5mL 1:1 hydrochloric acid, transfer to 250mL conical flask, repeatedly washed the crucible with 100mL distilled water and transfer to the conical flask, adjust the pH value to 9~10 with 1mol/L sodium hydroxide, successively added 10mL of buffer solution, 25mL of 1:1 triethanolamine, and 0.095g of working indicator, titrated with EDTA standard solution until the color change to blue.

F.2.4.2 Determination of calcium stearate content in halogenated butyl rubber

Dissolve the ash which is obtained after the ash test with 5mL 1:1 hydrochloric acid, transfer to 250mL volumetric bottle, repeatedly washed the crucible with distilled water , and dilute to scale, shake well. Transfer 100mL of the sample into a 250mL conical flask with a pipette, adjust the pH value to 9~10 with 1mol/L sodium hydroxide, successively added 10mL of buffer solution, 25mL of 1:1 triethanolamine, and 0.095g of working indicator, titrated with EDTA standard solution until the color change to blue.

F.2.5 Calculation

F.2.5.1 Calcium stearate content in butyl rubber is calculated by formula (F.3)

$$W = \frac{c \cdot V \times 60.704}{m} \quad \text{.........(F.3)}$$

Where:

W- Mass fraction of calcium stearate in sample %

c-The substance concentration of EDTA standard titrating solution, unit: mol/L

V- The volume of the EDTA standard titration solution ,unit:mL;
m- The sample mass of butyl rubber for ash determination, unit:g.
607.04- Molar mass of calcium stearate , unit: g/mol

F.2.5.2 Calcium stearate content in halogenated butyl rubber is calculated by formula (F.4) :

$$W = \frac{c \cdot V \times 60.704}{m \times 100/250} \quad \text{.........(F.3)}$$

Where:
W- Mass fraction of calcium stearate in sample,%;
c-The substance concentration of EDTA standard titrating solution, unit: mol/L
V- The volume of the EDTA standard titration solution ,unit:mL;
m-The sample mass of butyl rubber for ash determination, unit:g.
607.04- Molar mass of calcium stearate , unit: g/mol

F.2.6 Presentation of analysis results

For any sample, the results of the analysis should be expressed as the arithmetic mean of the two repeated measurements, calculated to the third decimal place, and reported to the second decimal place.

F.2.7 Repeatability

The same operator, using the same instrument, repeated determination of the same sample under the same conditions with normal and correct operation methods, and the difference between the determination results should not be more than 0.02%.

Appendix G
(Normative)
Determination of Halogen Content (X-ray Fluorescence chromatography)

G.1 Principles

The composition of a sample is determined qualitatively or quantitatively according to the sample's absorption of X-rays which will be different because of varies of the composition and content in the sample. Halogen content in rubber was determined by X-ray fluorescence spectrometry.

G.2 Instrument or equipment

X-ray fluorescence spectrometer, plate vulcanizing machine (10t), insert machine.

G.3 Preparation of rubber sheets to be inspected

Take a few of rubber samples ,put in the middle between two layers of polyester film, put into a mold matching the X-ray fluorescence spectrometer sample cup, compressed at 120℃ and 10t pressure for 5min, and then cooled and compressed at 10t pressure for 5min. Put the pressed rubber sheet in the middle between two layers of polyester film on the insert machine, heating at 130 ° C for 8min, then cooled for 7 min, wait to use.

G.4 Determination of chlorine and bromine

Put the the prepared rubber sheet into the sample box of X-ray fluorescence spectrometer, and determine the content of halogen such as chlorine and bromine .

G.5 Test results

Two parallel tests should be carried out for each measurement, calculated to the third decimal place. The difference of the twice test results should not more than 5%. The average of the two tests was taken as the final test result. The percentage by weight of bromine content of bromine in bromo-p-methylstyrene copolymer rubber is multiplied by 0.675 to get he molar percentage result.