GB

NATIONAL STANDARD OF THE

PEOPLE'S REPUBLIC OF CHINA

ICS 87.040

G 51

GB 24409-2020

Replacing GB 24409-2009

Limit of Harmful Substances of Vehicle Coatings

车辆涂料中有害物质限量

Issued on: March 4, 2020 **Implemented on: December 1, 2020**

Issued by: State Administration for Market Regulation;

Standardization Administration of the People's Republic of China.

Table of Contents

Foreword 3
1 Scope 5
2 Normative References 5
3 Terms and Definitions 6
4 Product Classification 10
5 Requirements 10
6 Test Methods 16
7 Inspection Rules 18
8 Packaging Marks 19
9 Implementation of Standard 19
Appendix A (normative) Determination of Moisture Content - Gas Chromatography 20
Appendix B (normative) Determination of Hexavalent Chromium (Cr^{6+}) Content - Spectrophotometry 24
Bibliography 31

Limit of Harmful Substances of Vehicle Coatings

1 Scope

This Standard stipulates the product classification, requirements, test methods, inspection rules, packaging marks and implementation of the Standard related to the allowable limits of substances harmful to humans and the environment in various types of vehicle coatings.

This Standard is applicable to various kinds of original vehicle coatings, refinish coatings, rail transit vehicle coatings, motorcycle (including electric motorcycle) coatings, bicycle (including electric bicycle) coatings, and coatings for other vehicles (special motor vehicles, low-speed vehicles and trailers) and vehicle parts.

This Standard is not applicable to coatings for tractor transport units, special wheeled mechanical vehicles and military vehicles.

2 Normative References

The following documents are indispensable to the application of this document. In terms of references with a specified date, only versions with a specified date are applicable to this document. In terms of references without a specified date, the latest version (including all the modifications) is applicable to this document.

GB/T 1725-2007 *Paints, Varnishes and Plastics - Determination of Non-volatile-matter Content*

GB/T 3186 *Paints, Varnishes and Raw Materials for Paints and Varnishes - Sampling*

GB/T 6682-2008 *Water for Analytical Laboratory Use - Specification and Test Methods*

GB/T 6750-2007 *Paints and Varnishes - Determination of Density - Pycnometer Method*

GB/T 8170-2008 *Rules of Rounding off for Numerical Values & Expression and Judgement of Limiting Values*

GB/T 9750 *Marks for Package of Coating Products*

GB/T 9754-2007 *Paints and Varnishes - Determination of Specular Gloss of Non-metallic Paint Films at 20°, 60° and 85°*

GB/T 9758.5-1988 *Paints and Varnishes - Determination of Soluble Metal Content -*

Part 5: Determination of Hexavalent Chromium Content of the Pigment Portion of the Liquid Paint or the Paint in Powder Form - Diphenylcarbazide Spectrophotometric Method

GB/T 9760-1988 *Paints and Varnishes - Preparation of Acid Extracts from Paints in Liquid or Powder Form*

GB/T 23986-2009 *Paints and Varnishes - Determination of Volatile Organic Compound (VOC) Content - Difference Method*

GB/T 23990-2009 *Determination of the Contents of Benzene Toluene Ethylbenzene and Xylene in Coatings by Gas Chromatography*

GB/T 23992-2009 *Determination of Chlor-hydrocarbon Content in Coatings - Gas Chromatographic Method*

GB/T 30647-2014 *Determination of Harmful Elements Total Content of Coatings*

GB/T 34675-2017 *Determination of Volatile Organic Compound (VOC) Content in Radiation Curable Coatings*

3 Terms and Definitions

The following terms and definitions are applicable to this document.

3.1 Road Vehicle

Road vehicle refers to vehicles that are designed and manufactured to carry passengers, transport goods or perform special operations on the road, and are legally allowed to travel on the road. Road vehicle includes motor vehicles and non-motor vehicles.

[GA 802-2014, Definition 3.1]

3.2 Rail Transit Vehicle

Rail transit vehicle refers to a means of transportation that needs to travel on a specific track. Rail transit vehicle includes powered car train-sets, passenger cars (railway vehicle), urban rail transit vehicles and wagons, etc.

3.3 Power-driven Vehicle

Power-driven vehicle refers to a wheeled vehicle that is driven or towed by a power device, and travels on the road to carry passengers or transport goods, and for special engineering operations. Power-driven vehicle includes cars, car trains, motorcycles, tractor transport units, special wheeled mechanical vehicles and trailers.

transportation tool that is, in principle, grouped to be used in passenger trains and freight trains.

[GB/T 4549.1-2004, Definition 2.1]

3.9 Carriage; Passenger Car; Coach

Railway Vehicle

Carriage (railway vehicle) refers to a vehicle used to transport passengers and operate for this service, or, in principle, grouped to be used in passenger trains.

[GB/T 4549.1-2004, Definition 2.2]

3.10 Urban Rail Transit Vehicle

Urban rail transit vehicle refers to a public transport mode with the vehicle transportation system that adopts a track structure for load-bearing and guidance; in accordance with the requirements of the overall planning of urban transportation, it sets up fully enclosed or partially enclosed exclusive track lines, and transports a large-scale passenger flow in the form of trains or single vehicles. Urban rail transit vehicle includes subway system, light rail system, monorail system, tram car, maglev system, automatic guide rail system and city rapid rail system.

3.11 Wagon; Freight Car

Wagon (freight car) refers to vehicle that is used to transport goods and serve for this purpose, or in principle, grouped to be used in freight trains. By purpose, it can be divided into general wagons and special-purpose wagons.

[GB/T 4549.1-2004, Definition 2.37]

3.12 Special Motor Vehicle

Special motor vehicle refers to vehicle that is equipped with special-purpose equipment or appliances, and designed and manufactured to be used for special engineering operations (including health and medical treatment), such as: truck cranes, fire trucks, concrete pump trucks, wreckers, aerial work vehicles, road sweeping trucks, sewage suction trucks, rig trucks, instrument trucks, inspection vehicles, monitoring vehicles, power supply vehicles, communication vehicles, television vehicles, blood collection vehicles, medical treatment vehicles and medical examination vehicles, etc. However, it does not include vehicles equipped with special-purpose equipment or appliances, and more than 9 seats (including the driver’s seat) (except fire trucks).

[GB 7258-2017, Definition 3.2.3]

3.13 Low-speed Vehicle

interference in a thin layer), with different colors (color change, color jump and color shade change) or texture.

[GB/T 5206-2015, Definition 2.91]

3.22 High Decorative Coatings Including Effect Pigment

High decorative coatings including effect pigment refers to a type of coating that contains effect pigment, and whose coated orange peel value in the medium long wave is ≤ 15 and short wave is ≤ 25.

3.23 Volatile Organic Compound

VOC

Volatile organic compound refers to organic compound participating in atmospheric photochemical reactions, or organic compound determined in accordance with relevant regulations.

3.24 Volatile Organic Compound Content

VOC Content

Volatile organic compound content refers to the mass of volatile organic compounds in the coating measured under specific conditions.

[GB/T 5206-2015, Definition 2.271]

3.25 Application Condition

Application condition refers to the condition where the application can be carried out after all the components of a product are mixed, and when the application modes and application conditions meet the requirements in the corresponding technical specifications.

4 Product Classification

In this Standard, vehicle coating is divided into: water-based coating, solvent-based coating, radiation-curing coating and powdered coating.

5 Requirements

5.1 Except for special functional coatings, the limit value of VOC content in the various types of vehicle coatings shall comply with the requirements of Table 1, Table 2 and Table 3.

NOTE: special functional coatings refer to primers for polypropylene substrates (including

accordance with a method determined through negotiation. The sampling size shall be determined in accordance with the demand of inspection.

6.2 Test Methods

6.2.1 VOC content

6.2.1.1 Density

In accordance with the stipulations of GB/T 6750-2007, conduct the test. The test temperature is (23 ± 0.5) °C.

6.2.1.2 Gloss

In accordance with the stipulations of GB/T 9754-2007, conduct the test. Use a wet film preparation device with a groove depth of (100 ± 2) μm to prepare a sample on black glass or a flat glass plate pre-coated with matte black paint on the back. The baking condition is (105 ± 2) °C/1h; use a 60° specular gloss meter for the test.

6.2.1.3 VOC content in water-based coatings

Firstly, in accordance with the stipulations of Appendix A, determine the moisture content in water-based coatings.

If the moisture content in the coatings is greater than or equal to 70% (mass fraction), then, proceed in accordance with the stipulations of GB/T 23986-2009. Weigh-take around 1 g of sample. The chromatographic column shall adopt a medium-polarity chromatographic column (6% cyanopropylphenyl / 94% polydimethylsiloxane capillary column). The label is diethyl adipate. VOC content shall be calculated in accordance with 10.4 in GB/T 23986-2009.

If the moisture content in the coatings is less than 70% (mass fraction), then, proceed in accordance with the stipulations of GB/T 23985-2009. Non-volatile-matter content shall be determined in accordance with the stipulations of GB/T 1725-2007. Weigh-take around 1 g of sample. The baking condition is (105 ± 2) °C/1h. VOC content shall be calculated in accordance with 8.4 in GB/T 23985-2009.

6.2.1.4 VOC content in solvent-based coatings

In accordance with the stipulations of GB/T 23985-2009, conduct the test. Non-volatile-matter content shall be determined in accordance with the stipulations of GB/T 1725-2007. Weigh-take around 1 g of sample. The baking condition is (105 ± 2) °C/1h. Do not determine the moisture content. The moisture content shall be set to zero.

The calculation of VOC content shall be conducted in accordance with 8.3 in GB/T 23985-2009.

6.2.1.5 VOC content in radiation-curing coatings

7.1.1 Under normal production, type inspection shall be conducted at least once a year. Type inspection items include all the requirements listed in this Standard.

7.1.2 Under one of the following circumstances, type inspection shall be conducted at any time:

---When new product is initially finalized;

---When product is produced off-site;

---When there are significant changes in the production formula, process, the source of key raw materials and application ratio under the application condition;

---When production is resumed after 3 months of suspension.

7.2 Determination of Inspection Result

7.2.1 The determination of the inspection result shall be conducted in accordance with the rounding-off comparison method in GB/T 8170-2008.

7.2.2 When reporting the inspection result, the application ratio under the expressly indicated application condition shall be simultaneously indicated.

7.2.3 When the inspection results of all items meet the requirements of this Standard, then the products comply with the requirements of this Standard.

8 Packaging Marks

8.1 The packaging marks shall comply with the stipulations of GB/T 9750. In addition, products that pass the inspection in accordance with this Standard may be expressly indicated on the packaging marks.

8.2 The packaging marks or product specification shall expressly indicate the application ratio under the application condition.

8.3 The packaging marks or product specification shall indicate the classification, category and type (or application mode) of products that comply with this Standard.

8.4 For polyurethane, epoxy and other multi-component cured coatings, the period of application shall be indicated on the packaging marks or in the product specification.

9 Implementation of Standard

When conducting spot-check of the coating products under the application condition on the site of coating, the sampling inspection of multi-component cured coatings, such as polyurethanes and epoxy resins, shall be conducted within the period of application.

A.3.1 Chromatographic column: capillary column of styrene-divinylbenzene porous polymer, 25 m × 0.53 mm × 10 μm.

A.3.2 Inlet temperature: 250 °C.

A.3.3 Detector temperature: 300 °C.

A.3.4 Split ratio: 5:1.

A.3.5 Column temperature: programmed temperature-raising, 100 °C, maintain for 2 min, then, at 20 °C/min, raise the temperature to 130 °C and maintain for 3 min; at 30 °C/min, raise the temperature to 200 °C and maintain for 5 min.

A.3.6 Carrier gas: hydrogen, flow rate: 6.5 mL/min.

NOTE: in accordance with the performance of the used gas chromatograph, the type of the chromatographic column and the actual condition of the sample to be tested, optimal gas chromatography test conditions may also be selected.

A.4 Test Procedures

A.4.1 Test the relative response factor (*R*) of water

In the same sample preparation bottle (A.2.4), weigh-take around 0.2 g of distilled water (A.1.1) and around 0.2 g of the internal standard substance (A.1.3), accurate to 0.1 mg. Record the mass of water m_w and the mass of the internal standard substance m_i, then, add 5 mL of dilution solvent (A.1.2); seal the sample preparation bottle (A.2.4) and shake it well. Use a micro-syringe (A.2.3) to draw 1 μL of the mixture in the sample preparation bottle (A.2.4); inject it into the chromatograph, record the chromatogram. In accordance with Formula (A.1), calculate the relative response factor (*R*) of water:

$$R = \frac{m_i \times A_w}{m_w \times A_i} \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (A.1)$$

Where,

R---relative response factor of water;

m_i---mass of internal standard substance, expressed in (g);

A_w---peak area of water;

m_w---mass of water, expressed in (g);

A_i---peak area of internal standard substance.

If the internal standard substance and the dilution solvent are not anhydrous reagents, then, use the same amount of internal standard substance and dilution solvent (mixed

Appendix B

(normative)

Determination of Hexavalent Chromium (Cr^{6+}) Content - Spectrophotometry

Warning -- the use of all samples and reagents that potentially contain hexavalent chromium (Cr^{6+}) in the test method shall be prevented with appropriate measures. Solutions and waste materials containing hexavalent chromium (Cr^{6+}) shall be properly handled.

B.1 Principle

If the total chromium content in the sample is less than 8 mg/kg, then, the result of hexavalent chromium (Cr^{6+}) content shall be reported as “not detected”; the detection limit is 8 mg/kg. If the total chromium content in the sample is ≥ 8 mg/kg, then, after the sample (simultaneously spiked with the matrix) is dispersed by ultrasound, use an alkaline digestion solution to extract hexavalent chromium (Cr^{6+}) compound from the sample. The hexavalent chromium (Cr^{6+}) in the extraction solution reacts with diphenylcarbazide in an acidic solution to generate a purple complex. Use spectrophotometry to determine the hexavalent chromium (Cr^{6+}) content in the test solution (wavelength at 540 nm); meanwhile, determine the non-volatile-matter content in the sample. The final result shall be reported as the hexavalent chromium (Cr^{6+}) content in the dry film.

B.2 Reagents and Materials

In the analytical tests, reagents that are confirmed to be analytically pure shall merely be used; the used water shall comply with the requirements of Level-3 water in GB/T 6682-2008.

B.2.1 *N*-Methyl-pyrrolidone (NMP): the reagent shall be stored in a brown bottle at 20 °C ~ 25 °C; kept away from direct sunlight. Before use, add 10 g of active molecular sieve to each 100 mL of reagent; store for more than 12 h. After the container is opened, the storage period is 1 month.

B.2.2 Nitric acid: about 65% (mass fraction); density is about 1.40 g/mL; yellowed nitric acid shall not be used.

B.2.3 Sulfuric acid: about 98% (mass fraction); density is about 1.84 g/mL.

B.2.4 Sodium hydroxide.

B.2.5 Sodium carbonate anhydrous.

may be added, so as to increase the wettability of the sample. Use a stopper to cover the digestion device (B.3.5); place it in the ultrasonic water bath kettle (B.3.3); at 60 °C ~ 65 °C, conduct ultrasonic treatment for 1 h.

From the ultrasonic water bath kettle (B.3.3), take out the digestion device (B.3.5); gradually cool it down to room temperature. Transfer the solution (do not filter the solution, even if the solution is turbid, or there are flocculent precipitates) in the digestion device (B.3.5) into a clean beaker (B.3.9). While stirring it, drop-wise add nitric acid (B.2.11) into the beaker. Use an acidity meter (B.3.4) to test it; adjust the pH value of the solution to 7.5 ± 0.5. Thus, obtain an extract. The extract shall develop colors and be determined as soon as possible.

B.4.3 Tests

B.4.3.1 Preparation of color-developing solution

In the extract in each beaker (B.3.9), slowly drop-wise add sulfuric acid solution (B.2.12). Use the acidity meter (B.3.4) to test it; adjust the pH value of the solution to 2.0 ± 0.5; evenly mix it. Then, use the transfer pipette (B.3.7) to accurately add 2.0 mL of diphenylcarbazide color developer (B.2.15); mix it well. Then, transfer all of it to a 100 mL volumetric flask (B.3.6); use water to dilute to the scale to obtain the test solution. Let the test solution settle for 5 min ~ 10 min, then, determine it as soon as possible; complete the on-board test within 30 min.

B.4.3.2 Preparation of series of standard working solutions

Use the transfer pipette (B.3.7) to respectively transfer-take 0.0 mL, 2.0 mL, 4.0 mL, 6.0 mL, 8.0 mL, 10.0 mL and 20 mL of hexavalent chromium (Cr^{6+}) standard solution (B.2.17) to a 100 mL volumetric flask. Use the measuring cylinder (B.3.8) to respectively add 50 mL of water; respectively drop-wise add sulfuric acid solution (B.2.12). Use the acidity meter (B.3.4) to test it; adjust the pH value of the solution to 2.0 ± 0.5. Use the transfer pipette (B.3.7) to respectively add 2.0 mL of the color developer (B.2.15); respectively use water to dilute to the scale; evenly mix it. Let it settle for 5 min ~ 10 min, then, complete the determination as soon as possible within 30 min. The mass concentration of hexavalent chromium (Cr^{6+}) in this series of standard working solutions is respectively: 0.0 mg/L, 0.1 mg/L, 0.2 mg/L, 0.3 mg/L, 0.4 mg/L, 0.5 mg/L and 1.0 mg/L.

B.4.3.3 Determination of hexavalent chromium (Cr^{6+}) content in sample

Respectively transfer an appropriate amount of the series of standard working solutions into a 10 mm colorimetric cell. On a spectrophotometer (B.3.2), at a wavelength of 540 nm, determine its absorbance. Use the absorbance value corresponding to the mass concentration value to draw a calibration curve. The correction coefficient of the calibration curve shall be ≥ 0.99. Otherwise, a new calibration curve shall be re-drawn.

$$SR = \frac{SS - US}{SA} \times 100 \qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (B.2)$$

Where,

SR---spiked matrix recovery rate, expressed in (%);

SS---hexavalent chromium (Cr^{6+}) content in spiked sample (calculated by dry film), expressed in (mg/kg);

US---hexavalent chromium (Cr^{6+}) content in un-spiked sample (calculated by dry film), expressed in (mg/kg);

SA---hexavalent chromium (Cr^{6+}) content in spiked solution converted into hexavalent chromium (Cr^{6+}) content calculated by dry film, expressed in (mg/kg).

Example: add 0.5 mL of hexavalent chromium (Cr^{6+}) standard stock solution (200 mg/L); the non-volatile-matter content in the sample is 0.50 g/g, and the weighed sample mass is around 0.1 g; then, SA = 0.5 mL × (100 mg/L)/(0.1 g × 0.50 g/g) = 1,000 mg/kg.

In accordance with the hexavalent chromium (Cr^{6+}) content in the sample being tested, other appropriate amounts of spiked solution may be selected, so as to ensure that the mass concentration of spiked solution is within the appropriate curve range.

B.4.4.3 Correction of results and detection limits

The acceptable range of the spiked matrix recovery rate shall be ≥ 50% and ≤ 125%.

When the spiked matrix recovery rate is < 50%, add a double amount of spiked solution for the test. When the spiked matrix recovery rate is > 125%, add an equal amount of spiked solution for the test. If the spiked matrix recovery rate in the re-test is still beyond the range ≥ 50% and ≤ 125%, then, the alkaline digestion method is inapplicable to the sample being tested. Then, the hexavalent chromium (Cr^{6+}) content in the sample shall be tested in this way: in accordance with Chapter 6, 8.1, 8.2.3 and 8.4 in GB/T 9760-1988, prepare the acid extract (the weighed mass of the prepared pigment is around 0.5 g), then, in accordance with GB/T 9758.5-1988, test the hexavalent chromium (Cr^{6+}) content. The result is divided by the non-volatile-matter content, then, reported as the hexavalent chromium (Cr^{6+}) content in the dry film.

If the spiked matrix recovery rate is > 75% and ≤ 125%, then, it is no need to correct the result; the detection limit is 8 mg/kg.

If the spiked matrix recovery rate is within the range ≥ 50% and ≤ 75%, in accordance with the spiked matrix recovery rate, correct the result and the detection limit. In other words: the result is multiplied by the ratio of 100% spiked recovery rate to the actual spiked matrix recovery rate; the detection limit is corrected in the same way.

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