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**Test methods of hexavalent chromium in automotive
materials**

汽车材料中六价铬的检测方法

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Test methods of hexavalent chromium in automotive materials

1 Scope

This document specifies the terms and definitions of hexavalent chromium detection in automotive materials, X-ray fluorescence spectroscopy, qualitative test of hexavalent chromium in metal anti-corrosion plating, determination of hexavalent chromium content in metal anti-corrosion plating, determination of hexavalent chromium in polymer materials and electronic materials, determination of hexavalent chromium content in leather materials (colorimetric method), determination of hexavalent chromium content in leather materials (chromatographic method), test reports, etc.

This document applies to qualitative and quantitative testing of hexavalent chromium, in automotive materials.

2 Normative references

The contents of the following documents constitute essential provisions of this document through normative references in the text. Among them, for dated references, only the version corresponding to the date applies to this document; for undated references, the latest version (including all amendments) is applicable to this document.

GB/T 8170 Rules of rounding off for numerical values & expression and judgement of limiting values

GB/T 30512 Requirements for prohibited substances on automobiles

QB/T 2262 Terms of leather industry

QB/T 2706 Leather - Chemical physical and mechanical and fastness tests - Sampling location

3 Terms and definitions

The terms and definitions, which are defined in GB/T 30512 and QB/T 2262, as well as the following terms and definitions, apply to this document.

3.1

Homogeneous material

4.2.2 Boric acid: Excellent grade pure, which is dried at 105 °C for 1 h, then stored in a desiccator.

4.2.3 Anhydrous lithium tetraborate: Excellent grade pure, which is calcined at 700 °C for 4 hours, then stored in a desiccator.

4.2.4 Liquid nitrogen: Industrial grade.

4.2.5 Standard material containing chromium element.

4.2.6 Polyester film.

4.3 Instruments and equipment

4.3.1 X-ray fluorescence spectrometer.

4.3.2 Cutting machine.

4.3.3 Liquid nitrogen cryogenic pulverizer.

4.3.4 Grinding machine: Abrasives with tungsten carbide (WC).

4.3.5 Tablet press: The working pressure is not less than 20 MPa.

4.3.6 Fusion machine: The working temperature is not lower than 1150 °C.

4.4 Samples

4.4.1 Principles of sample preparation

4.4.1.1 The sample, which is used for analysis, must cover the measurement window of the spectrometer.

4.4.1.2 The irradiated surface of the sample shall be able to represent the whole sample.

4.4.1.3 Care shall be taken, to prevent contamination during sample preparation.

4.4.2 Sample preparation method

4.4.2.1 Solid parts

Homogeneous material part, which has flat surfaces and sizes suitable for X-ray fluorescence spectrometer requirements, is subject to direct analysis. Small parts, which have flat surfaces, can be pooled together for analysis. For thin parts, that can be stacked together to be thick enough (at least 5 mm thick and maintain thickness consistency and compositional uniformity) for analysis. In order to spread the sample flat, during analysis, a lining material can be added as a support. It shall select the lining material, which has a low background, as much as possible.

For various blocks, plates, other indeterminate parts, parts that are too large, cutting machines and grinders, etc. can also be used to process them to appropriate sizes. For small parts, which have uneven surfaces (such as plastic particles, etc.), they can be frozen by liquid nitrogen, pulverized mechanically, then pressed by a tablet press, to prepare analytical samples. For fragile parts, such as glass and ceramics, they are first crushed into small pieces; then ground into powders of less than 200 mesh. After mixing evenly, use boric acid (see 4.2.2) as base, to press it into sample, which has a thickness of not less than 1 mm. OR use anhydrous lithium tetraborate (see 4.2.3), to prepare glass melt, for analysis of samples. For heterogeneous parts, which are composed of heterogeneous materials AND do not require or are difficult to further mechanically disassemble, cut the parts into pieces; freeze them in liquid nitrogen; use a grinder to grind the broken samples into powders with a particle size of not more than 1 mm. After mixing the sample, use boric acid (see 4.2.2) as base to press it, to prepare the sample, which has a thickness of not less than 1 mm. OR use anhydrous lithium tetraborate (see 4.2.3) to make a glass melt, to analyze the sample.

4.4.2.2 Liquid parts

Pipette a certain volume of liquid part. Add it to the special sample cup for liquid (the thickness of the sample is not less than 15 mm). The bottom of the cup is supported by 6 μm thick polyester film; the top of cup is covered by a cap with holes.

4.5 Test procedure

4.5.1 Preparation of instrument

Turn on the instrument, according to the instrument's operating procedures. Warm up the instrument, until the instrument is stable.

4.5.2 Analytical spectrum

For the X-ray fluorescence spectrometry analysis of chromium element, it is recommended to select the $K\alpha$ analytical spectrum.

4.5.3 Drawing of working curve

Select a reference material, which contains chromium that matches the matrix of the sample to be tested (see 4.2.5), to measure the fluorescence intensity of chromium in the reference material, according to the measurement conditions of the X-ray fluorescence spectrometer. According to the standard value given by the reference material AND the intensity measured by the spectrometer, draw a working curve.

4.5.4 Verification

Before each test of sample, use a standard material, which contains chromium (see 4.2.5), to calibrate the working curve.

corrosion plating

5.1 Principle

Under acidic conditions, the hexavalent chromium in the metal anti-corrosion plating reacts with diphenylcarbazide. The diphenylcarbazide is oxidized to diphenylcarbazone, whilst the hexavalent chromium is reduced to trivalent chromium. The trivalent chromium further reacts with diphenylcarbazone, to form a red or purple complex, which can be used to qualitatively judge whether there is hexavalent chromium in the metal anti-corrosion plating.

This method is suitable for qualitative determination of hexavalent chromium in automotive metal anti-corrosion plating.

5.2 Reagents and materials

5.2.1 Unless otherwise stated, only reagents confirmed to be analytically pure and distilled or deionized water or water of equivalent purity are used, in the analysis.

5.2.2 Diphenylcarbazide.

5.2.3 Potassium dichromate.

5.2.4 Acetone.

5.2.5 Ethanol.

5.2.6 Orthophosphoric acid solution (mass fraction 75%).

5.2.7 Hexavalent chromium stock solution: Weigh 0.1414 g of potassium dichromate (see 5.2.3), which was dried to constant weight. Dissolve it in water. Transfer it into a 100 mL volumetric flask. Dilute to the mark. The hexavalent chromium content of this solution is 500 µg/mL. Cap the container tightly. This solution is valid for 12 months. Or use the national standard solution.

5.2.8 Hexavalent chromium standard solution: Pipette 0.50 mL of hexavalent chromium stock solution (see 5.2.7), into a 250 mL volumetric flask. Dilute to the mark. The content of hexavalent chromium in this standard solution is 1 µg/mL. Close the container tightly. The validity period of this solution is 24 h. Or use the national standard solution.

5.2.9 Color developing solution A: Weigh 0.4 g of diphenylcarbazide (see 5.2.2). Dissolve it in a mixture of 20 mL of acetone (see 5.2.4) and 20 mL of ethanol (see 5.2.5). After dissolution, add 20 mL of orthophosphoric acid solution (see 5.2.6) and 20 mL of water. The validity period of this solution is 8 h.

5.3 Instruments and equipment

Analytical balance: The accuracy is 0.1 mg.

5.4 Samples

5.4.1 The part storage environment shall prevent trivalent chromium from being oxidized to hexavalent chromium. Parts shall be stored in an environment, at a relative humidity range of 45% ~ 75% and a temperature of 15 °C ~ 35 °C, prior to testing.

5.4.2 The sample shall meet the requirements of homogeneous material (see 3.1). It shall be obtained by suitable physical disassembly and other methods.

5.4.3 Contamination, fingerprints, stains on the sample surface need to be cleaned before testing. If the surface of the sample is covered with oil stains, THEN before the test of sample, it shall be cleaned by a suitable less reducing solvent, such as acetone and absolute ethanol. Samples shall be dried below 35 °C. It shall not be handled in alkaline solutions, which will destroy the anti-corrosion protective plating.

5.4.4 If there is a polymer layer on the surface of the sample, fine sandpaper (such as 800-mesh SiC sandpaper) can be used for light grinding; OR it may use other methods to remove the surface polymer, etc., so that the anti-corrosion plating is exposed, to facilitate testing.

5.4.5 The samples, that may contain hexavalent chromium, AND the reagents used in the test, shall be carefully handled and stored; they shall not be disposed of arbitrarily.

Note: For the new off-line metal anti-corrosion plating part, it shall be sealed for at least 5 days, to make the plating stable before testing.

5.5 Test procedure

5.5.1 For flake or block samples, add 1 ~ 5 drops of color developing solution A (see 5.2.9) on the surface of the sample. If there is hexavalent chromium, the surface of the sample will appear red or purple, within a few minutes. If the color develops after a long time (e.g., after drying), ignore it.

5.5.2 For fasteners (such as small bolts), the sample can be placed in a small container (such as a test tube). Add 1 ~ 5 drops of color developing solution A (see 5.2.9) to the container. If hexavalent chromium is present, the surface of the sample will appear red or purple, within a few minutes. It is easier to observe the color of the color developing solution, after removing the fastener sample from the container AND placing the container on a white background.

5.5.3 If the surface of the sample appears red or purple, it is considered that the plating contains hexavalent chromium, then the test result is recorded as positive; otherwise, the test result is recorded as negative.

5.5.4 If the test result is negative, the following tests can be continued, for further

diphenylcarbazide; the diphenylcarbazide is oxidized to diphenylcarbazone, whilst the hexavalent chromium is reduced to trivalent chromium; the trivalent chromium and diphenylcarbazone further react, to form a red or purple complex, which can be quantitatively determined by a colorimeter at 540 nm; then the content of hexavalent chromium in the metal plating is quantitatively determined.

This method is suitable for quantitative determination of hexavalent chromium content, in automotive metal anti-corrosion plating, including no additional covering layers (e.g., oil films, water-based or solvent-based polymers or wax films).

Note: For the new off-line metal anti-corrosion plating part, it shall be sealed for at least 5 days, to make the plating stable, before testing.

6.2 Reagents and materials

6.2.1 Unless otherwise stated, only reagents confirmed to be analytically pure and distilled or deionized water or water of equivalent purity are used, in the analysis.

6.2.2 Diphenylcarbazide.

6.2.3 Potassium dichromate.

6.2.4 Acetone.

6.2.5 Orthophosphoric acid solution (mass fraction 75%).

6.2.6 Hexavalent chromium stock solution: Weigh 0.113 g of potassium dichromate (see 6.2.3, dry at 100 °C for 1 h before use) in a glass vessel. Add water to make the volume reach to 1000 mL. The hexavalent chromium concentration, in this solution, is 40 µg/mL. Cap the container tightly. This solution is valid for 12 months. OR use national standard solution.

6.2.7 Equivalent standard solution of hexavalent chromium: Pipette 3.3 mL of hexavalent chromium stock solution (see 6.2.6), into a volumetric flask. Dilute it to 1000 mL. The concentration of this equivalent standard solution of hexavalent chromium is 0.13 µg/mL, which is equivalent to 0.13 µg/cm². Cap the container tightly. This solution is valid for 24 hours. OR use the national standard solution.

6.2.8 Color developing solution B: Weigh 0.5 g of diphenylcarbazide (see 6.2.2). Dissolve it in 50 mL of acetone (see 6.2.4). Use 50 mL of water to dilute it, under stirring (quick mixing may produce diphenylcarbazide precipitates). This solution shall be refrigerated at 7 °C ± 2 °C in brown glass bottles. It shall not be used, if discolored.

6.3 Instruments and equipment

6.3.1 Analytical balance: The accuracy is 0.1 mg.

6.3.2 Heating device: Keep the extract in a boiling state.

6.3.3 Colorimeter: The detection wavelength is 540 nm; it is equipped with a colorimeter of 1 cm or more. It can use other colorimeters, which have the required accuracy.

6.4 Samples

6.4.1 The part storage environment shall prevent trivalent chromium, from being oxidized to hexavalent chromium. The relative humidity of the part to be stored before testing shall be 45% ~ 75%; the temperature shall be 15 °C ~ 35 °C.

6.4.2 The sample shall meet the requirements of homogeneous material (see 3.1). It shall be obtained, by suitable physical disassembly method.

6.4.3 Contamination, fingerprints, stains on the sample surface need to be cleaned before testing. If the surface of the sample is covered with oil stain, the sample shall be cleaned, by a suitable less reducing solvent, such as acetone and absolute ethanol, before testing. Samples shall be dried below 35 °C. They shall not be processed in alkaline solutions.

6.4.4 If there is a polymer layer on the surface of the sample, fine sandpaper (such as 800-mesh SiC sandpaper) can be used for light grinding, OR other methods can be taken to remove the surface polymer, so as to expose the anti-corrosion plating, to facilitate testing.

6.4.5 Cut samples, which have a plating area of $50\text{ cm}^2 \pm 5\text{ cm}^2$. For some small parts or parts with irregular surfaces, such as fasteners, use an appropriate number of parts, to make the total surface area of the plating reach the required $50\text{ cm}^2 \pm 5\text{ cm}^2$. For the calculation of the fastener area, refer to Appendix A; OR use other calculation method. If the surface area of the sample used for the test cannot be reached, it is necessary to reduce the volume of the extraction solution, to ensure that the ratio of the sample surface to the volume of the extraction solution is (1 cm^2 : 1 mL), whilst the minimum sample surface area should not be less than 25 cm^2 . If the sample's surface area is large, a corresponding proportion of the extraction liquid is required and reflected in the final report. The sample shall not be exposed to strong alkaline solution, during cutting.

6.4.6 The samples, that may contain hexavalent chromium, and the reagents, which are used in the test, shall be carefully handled and stored. It shall not be disposed of arbitrarily.

6.5 Test procedure

6.5.1 Parallel test

Carry out two tests in parallel. Take the average value.

6.5.2 Drawing of calibration curve

Where:

C - The concentration of hexavalent chromium in the sample solution, in micrograms per milliliter ($\mu\text{g/mL}$);

B - The concentration of hexavalent chromium in the blank solution, in micrograms per milliliter ($\mu\text{g/mL}$);

V - The volume of the extract, in milliliters (mL);

A - The surface area of the sample, in square centimeters (cm^2);

F_D - The dilution factor; if not diluted, $F_D = 1$.

The calculation result must retain at least two significant figures.

6.7 Quality assurance and control

6.7.1 Use a hexavalent chromium equivalent standard solution (see 6.2.7), for performance verification tests, to ensure proper operation of the instrument. If the relative deviation, between the test results of the hexavalent chromium equivalent standard solution and the standard solution value ($0.13 \mu\text{g/mL}$), exceeds 15%, before the sample measurement, the standard curve needs to be redrawn. If after the sample measurement, the relative deviation, between the equivalent standard solution test result and the standard solution value ($0.13 \mu\text{g/mL}$), is more than 15%, THEN, the standard curve and all samples in the series need to be remeasured.

6.7.2 The absolute difference, between the two parallel samples, shall not exceed 20% of the arithmetic mean; otherwise, the measurement shall be re-measured.

7 Determination of hexavalent chromium content in polymer materials and electronic materials

7.1 Principle

After dissolving or swelling samples of various matrices, by organic solvents, use an alkaline digestion solution, to extract the hexavalent chromium in the samples. Then under acidic conditions, diphenylcarbazide reacts with hexavalent chromium; diphenylcarbazide is oxidized to diphenylcarbazone; hexavalent chromium is reduced to trivalent chromium. Trivalent chromium and diphenylcarbazone further react, to form a red or purple complex, which can be quantitatively determined, by a colorimeter, at 540 nm.

This method is suitable for the determination of hexavalent chromium content, in automotive polymer materials and electronic materials. The content of hexavalent

chromium in other automotive materials, such as glass, ceramics, fabrics, paints, is determined with reference to this method.

7.2 Reagents and materials

7.2.1 Unless otherwise stated, only reagents confirmed to be analytically pure and distilled or deionized water or water of equivalent purity are used, in the analysis.

7.2.2 N-Methylpyrrolidone (NMP): Add 10 g of active molecular sieve, to each 100 mL of newly opened NMP. Seal it. Store it in a brown bottle. Store it in the dark, at 20 °C ~ 25 °C. Shake it occasionally. It shall be stored for more than 12 hours before first use. The validity period after opening is 28 days.

7.2.3 Nitric acid (35% by volume fraction): Store it in the dark at 20 °C ~ 25 °C. Do not use yellow concentrated nitric acid when preparing it, because the contained NO_3^- will decompose into NO_2^- in light, leading to the reduction of hexavalent chromium.

7.2.4 Diphenylcarbazide.

7.2.5 Acetone.

7.2.6 Anhydrous magnesium chloride: 200 mg of MgCl_2 is equivalent to 50 mg of Mg^{2+} .

7.2.7 Phosphate buffer solution: Prepare pH = 7 buffer. Use 700 mL of water, to dissolve 87.09 g K_2HPO_4 and 68.04 g KH_2PO_4 . Transfer it into a 1 L volumetric flask. Dilute it to the mark. The prepared solution contains K_2HPO_4 of 0.5 mol/L and KH_2PO_4 of 0.5 mol/L.

7.2.8 Lead chromate: Excellent grade pure, which is sealed and stored at 20 °C ~ 25 °C.

7.2.9 Digestion solution: Use water to dissolve 20.0 g $\pm$ 0.05 g of sodium hydroxide and 30.0 g $\pm$ 0.05 g of anhydrous sodium carbonate. Place it in a 1 L volumetric flask. Dilute it to the mark. Seal it in polyethylene bottles at 20 °C ~ 25 °C, which is valid for 30 days. Check the pH value of the digestion solution, before use. If the pH value is less than 11.5, it requires preparing the digestion solution again.

7.2.10 Toluene.

7.2.11 Potassium dichromate stock solution: Dissolve 0.1414 g of $\text{K}_2\text{Cr}_2\text{O}_7$, which was dried at 105 °C, in water. Dilute it into a 1 L volumetric flask. The hexavalent chromium content of this solution is 50 $\mu\text{g/mL}$. OR use the national standard solution.

7.2.12 Potassium dichromate standard solution: Use water to dilute 10 mL of potassium dichromate stock solution (see 7.2.11), in a 100 mL volumetric flask. The hexavalent chromium content of this solution is 5 $\mu\text{g/mL}$. OR use the national standard solution.

7.2.13 Sulfuric acid (10% by volume fraction): Use water to dilute 10 mL of sulfuric acid, in a 100 mL volumetric flask.

precision, can be used.

7.3.12 Calibrated pipettes: Grade A or equivalent accuracy and precision vessels.

7.3.13 Digestion vessel: The glass bottle with screw mouth (wide neck).

7.3.14 Glass separatory funnel.

7.3.15 Filter membrane (0.45 μm): Fiber or PC filter membrane; syringe filter (0.45 μm): nylon or PVDF.

7.3.16 C18 syringe filter column or PA column.

7.3.17 Microwave digestion tank.

7.3.18 Infrared spectrometer.

7.4 Samples

7.4.1 Samples shall be taken and stored, using devices and containers that do not contain chromium elements. For soluble polymers (ABS, PC, PVC), the sample size can be larger than 250 μm ; however, it may take longer to dissolve the sample substrate. Insoluble or unknown polymers and antimony-free electronic components shall be ground to a fine powder AND 100% pass through a 250 μm sieve, before extraction. If the type of polymer substrate is unknown, an organic solvent solubility test can be performed, using a small amount of sample. Infrared spectroscopy (see 7.3.18) can also be used, to characterize polymer category. Use X-ray fluorescence spectrometer (XRF), to confirm the presence of antimony.

7.4.2 The samples that may contain hexavalent chromium AND the reagents used in the test shall be carefully handled and stored. They shall not be disposed of arbitrarily.

7.5 Test procedure

7.5.1 Drawing of calibration curve

7.5.1.1 The colorimeter shall be calibrated, by 1 blank and at least 5 standard solutions. The colorimeter shall be zero-calibrated, by a 0.0 $\mu\text{g/mL}$ standard solution blank; the standard solution blank shall be retained. Re-zero shall be performed, before testing the sample and standard solution. For the standard solution test, it takes the absorbance value as the ordinate and the hexavalent chromium standard solution concentration (including 0.0 $\mu\text{g/mL}$) as the abscissa, to establish the working curve.

7.5.1.2 The substrate of the standard solution shall be consistent with that of the test sample. After the digestion procedure (see 7.5.2.7 or 7.5.3.5), add an appropriate volume of hexavalent chromium standard solution (see 7.2.11), to prepare a standard solution, which has a concentration gradient of 0.1 $\mu\text{g/mL}$ to 1.0 $\mu\text{g/mL}$. It shall prepare 1 blank and at least 5 standard solutions. If the content of hexavalent chromium in the sample

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