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Limit of harmful substances of interior floor coatings

室内地坪涂料中有害物质限量

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Limit of harmful substances of interior floor coatings

1 Scope

This Standard specifies the terms and definitions, product classification, requirements, test methods, inspection rules and package marks etc. involved in the allowable limits of substances harmful to humans and the environment in interior floor coatings.

Note: Interior refers to the inside of places where the top is blocked or the top and the surroundings are blocked, such as industrial plants, underground parking lots, hospitals, schools, gymnasiums and other places. It is relative to places where the top and the surroundings are not blocked.

This Standard applies to various interior floor coatings with organic polymers as the main adhesives, which are painted on the base surface of floors such as cement mortar, concrete, stone, plastic or steel, for decorating and protecting the ground and other special functions (such as antistatic, corrosion resistance, anti-skid, etc.); including primers, mid-coats, topcoats and finishes.

2 Normative references

The following documents are indispensable for the application of this document. For the dated references, only the editions with the dates indicated are applicable to this document. For the undated references, the latest edition (including all the amendments) are 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 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 and expression and judgement of limiting values

GB/T 9750 Marks for package of coating products

6.2 Test methods

6.2.1 The test of the volatile organic compounds content in water-based floor coatings shall be carried out in accordance with the provisions of Appendix A and Appendix B. The calculation of the test results shall be carried out in accordance with A.7.1. The moisture content test in Appendix B may use gas chromatography or Karl Fischer method. Gas chromatography is the arbitration method.

6.2.2 The test of the total content of benzene, toluene, ethylbenzene and xylene and the total content of glycol ethers and ether esters in water-based floor coatings shall be carried out in accordance with Appendix A. The calculation of the test results shall be carried out in accordance with A.7.2.

6.2.3 The test of the volatile organic compounds (VOC) content in solvent-based and solvent-free floor coatings shall be carried out in accordance with Appendix C.

6.2.4 The test of the benzene content, the total content of toluene, ethylbenzene and xylene, and the total content of glycol ethers and ether esters in solvent-based and solvent-free floor coatings shall be carried out in accordance with Appendix D.

6.2.5 The test of formaldehyde in water-based floor coatings is carried out according to the provisions of GB/T 23993-2009.

6.2.6 The total content of free diisocyanates (TDI and HDI) is tested in accordance with GB/T 18446-2009.

6.2.7 For the sum of phthalates, prepare mixed samples according to the construction proportion indicated by the product; then test according to the provisions of Appendix C in GB 24613-2009; convert it to the content in the dry coating film.

6.2.8 The content of soluble heavy metals (lead, cadmium, chromium, mercury) is tested according to the provisions in GB/T 23991-2009. USE inductively coupled plasma atomic emission spectrometer (ICP-OES) or other suitable analytical instruments for testing.

7 Inspection rules

7.1 Type inspection items

7.1.1 All the requirements listed in this Standard are type inspection items. Under normal production conditions, type inspection shall be carried out at least

Appendix A

(Normative)

Test of volatile organic compounds content, total content of benzene, toluene, ethylbenzene and xylene, and total content of glycol ethers and ether esters in water-based floor coatings - gas chromatography

A.1 Scope

This appendix specifies the test method for the volatile organic compounds (VOC) content, the total content of benzene, toluene, ethylbenzene and xylene, and the total content of glycol ethers and ether esters in water-based floor coatings.

This method is suitable for the testing of coatings and their raw materials with VOC content (mass fraction) greater than or equal to 0.1% and less than or equal to 15%.

A.2 Principle

After the sample is diluted, the various volatile organic compounds in the sample are separated by gas chromatography analysis. After the compound under test is qualitatively identified, use the internal standard method to test its content.

A.3 Materials and reagents

A.3.1 Carrier gas: nitrogen or helium; purity is ≥99.995%.

A.3.2 Fuel gas: hydrogen; purity is ≥99.995%.

A.3.3 Combustion-supporting gas: air.

A.3.4 Auxiliary gas (septum purge and makeup gas): nitrogen with the same properties as the carrier gas.

A.3.5 Internal standard substance: a compound that does not exist in the sample and can be completely separated from other components on the chromatogram. The purity is at least 99% (mass fraction); or the purity is known. For example, isobutanol, ethylene glycol monobutyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, etc.

A.3.6 Calibration compounds: including methanol, ethanol, n-propanol,

A.4.3 Sample preparation bottle: about 20 mL glass bottle with a sealable cap.

A.4.4 Balance: Accuracy is 0.1 mg.

A.5 Test conditions of gas chromatography

A.5.1 Gas chromatographic condition 1:

- Chromatographic column (basic column): 6% cyanopropyl phenyl/94% polydimethylsiloxane capillary column; 60 m×0.32 mm×1.0 μm;
- Injection port temperature: 250 °C;
- Detector: FID; temperature: 260 °C;
- Column temperature: temperature programming. KEEP at 80 °C for 1 min; then increase to 230 °C at 10 °C/min and keep for 15 min;
- Split ratio: split injection. Split ratio is adjustable;
- Injection volume: 1.0 μL.

A.5.2 Gas chromatographic condition 2:

- Chromatographic column (confirmation column): polyethylene glycol capillary column; 30 m×0.25 mm×0.25 μm;
- Injection port temperature: 240 °C;
- Detector: FID; temperature: 250 °C;
- Column temperature: temperature programming. KEEP at 60 °C for 1 min; then increase to 240 °C at 20 °C/min and hold for 20 min;
- Split ratio: split injection. Split ratio is adjustable;
- Injection volume: 1.0 μL.

A.6 Test procedures

A.6.1 General

All tests are carried out in two parallel determinations.

A.6.2 Density

The density test is carried out according to GB/T 6750-2007. The test temperature is (23±2)°C.

test conditions as the test sample, optimize the instrument parameters according to A.6.4.1. Inject an appropriate amount of calibration compound into the gas chromatograph and record the chromatogram. According to formula (A.1), calculate the relative correction factor of each compound respectively:

$$R_i = \frac{m_{ci} \times A_{is}}{m_{is} \times A_{ci}} \qquad \cdots\cdots (A.1)$$

Where:

R_i - The relative correction factor of compound i;

m_{ci} - The mass of compound i in the calibration mixture, in grams (g);

A_{is} - The peak area of internal standard substance;

m_{is} - The mass of internal standard substance in the calibration mixture, in grams (g);

A_{ci} - The peak area of compound i.

The value of R_i is the average of two test results. The relative deviation shall be less than 5%. The result retains 3 significant digits.

A.6.4.3.3 If there is a chromatographic peak of an unknown compound other than the calibration compound in A.3.6, it is assumed that its correction factor relative to isobutanol is 1.0.

A.6.4.4 Test of sample

A.6.4.4.1 Sample preparation: WEIGH about 1 g (accurate to 0.1 mg) of the sample after being evenly stirred and the internal standard substance (A.3.5) approximately equal to the mass of the test substance INTO the sample preparation bottle (A.4.3). ADD 10 mL of dilution solvent (A.3.7) to dilute the sample; SEAL the sample preparation bottle (A.4.3) and shake it well.

A.6.4.4.2 According to the optimized conditions during calibration, set the instrument parameters.

A.6.4.4.3 Inject the marker (A.3.8) into the gas chromatograph; RECORD its retention time on the 6% cyanopropyl phenyl/94% polydimethylsiloxane capillary column; in order to determine the integration end point in the chromatogram according to the VOC definition given in 3.1.

A.6.4.4.4 Inject 1 μL of the sample prepared according to A.6.4.4.1 into the gas chromatograph. RECORD the chromatogram and the peak area of various

1000 - Conversion factor.

Detection limit of test method: 2 g/L.

A.7.2 Calculation of the total content of benzene, toluene, ethylbenzene and xylene and the total content of glycol ethers and ether esters in coating products

A.7.2.1 First, according to formula (A.2), calculate the respective contents w_i of benzene, toluene, ethylbenzene and xylene; then, according to formula (A.4), calculate the total content of benzene, toluene, ethylbenzene and xylene in the product:

$$w_e = \sum_{i=1}^{n} w_i \times 10^6 \qquad \cdots\cdots (A.4)$$

Where:

w_e - The total content of benzene, toluene, ethylbenzene and xylene or the total content of glycol ethers and ether esters in the product, in milligrams per kilogram (mg/kg);

w_i - The content of component i under test in the sample (benzene, toluene, ethylbenzene, xylene, glycol methyl ether, ethylene glycol methyl ether acetate, glycol ethyl ether, ethylene glycol ethyl ether acetate or diethylene glycol butyl ether acetate), in grams per gram (g/g);

10^6 - Conversion factor.

A.7.2.2 First, according to formula (A.2), calculate the respective contents w_i of glycol methyl ether, ethylene glycol methyl ether acetate, glycol ethyl ether, ethylene glycol ethyl ether acetate and diethylene glycol butyl ether acetate; then, according to formula (A.4), calculate the total content of five glycol ethers and ether esters in the product.

A.7.2.3 Detection limit of test method: The detection limit of benzene, toluene, ethylbenzene, xylene, glycol methyl ether, ethylene glycol methyl ether acetate, glycol ethyl ether, ethylene glycol ethyl ether acetate and diethylene glycol butyl ether acetate is all 10 mg/kg.

A.8 Precision

A.8.1 Repeatability

The relative deviation of the two test results of the same operator shall be less than 10%.

Appendix B

(Normative)

Test of moisture content

B.1 Gas chromatography

B.1.1 Reagents and materials

B.1.1.1 Distilled water: It shall meet the requirements of grade 3 water in GB/T 6682.

B.1.1.2 Dilution solvent: anhydrous dimethylformamide (DMF); analytically pure.

B.1.1.3 Internal standard substance: anhydrous isopropanol; analytically pure.

B.1.1.4 Carrier gas: hydrogen or helium; purity is ≥99.995%.

B.1.2 Instruments and equipment

B.1.2.1 Gas chromatograph with the following configuration:

- Thermal conductivity detector;
- Temperature programmed controller;
- Chromatographic column: stainless steel column filled with porous polymer beads, CP7354 styrene-divinylbenzene porous polymer column or equivalent chromatographic column.

B.1.2.2 Injector: micro-syringe. The capacity is at least twice the injection volume.

B.1.2.3 Sample preparation bottle: about 10 mL glass bottle with a sealable cap.

B.1.2.4 Balance: Accuracy is 0.1 mg.

B.1.3 Test conditions of gas chromatography

B.1.3.1 Gas chromatographic condition 1:

- Chromatographic column: a stainless steel column with a column length of 1 m, an outer diameter of 3.2 mm, and filled with 177 μm~250 μm porous polymer beads;

calibrations and input the calibration result into the titrator (B.2.1.1).

When the relative humidity of the detection environment is less than 70%, it shall be calibrated once a week. When the relative humidity is greater than 70%, it shall be calibrated twice a week; when necessary, it shall be calibrated at any time.

B.2.3.2 Sample treatment

If the sample to be tested has a high viscosity and cannot be dispersed well in Karl Fischer solvent, the sample needs to be diluted appropriately. WEIGH 20 g (accurate to 1 mg) of the evenly-stirred sample in the beaker (B.2.1.6); then add about 20% distilled water (B.2.2.1) to the beaker (B.2.1.6); accurately record the amount of sample weighing and the amount of water added. COVER the beaker with a petri dish (B.2.1.7); STIR on a magnetic stirrer (B.2.1.5) for 10 min~15 min. Then pour the diluted sample into the dropping bottle (B.2.1.4) for later use.

Note: For samples that can be well dispersed in Karl Fischer solvent, the moisture content in the sample can be directly tested. For samples that are still not well dispersed in Karl Fischer solvent after adding 20% water, the amount of dilution water can be gradually increased.

B.2.3.3 Test of moisture content

ADD fresh Karl Fischer solvent (B.2.2.2) to the titration cup of the titrator (B.2.1.1), until the liquid surface covers the electrode tip; USE Karl Fischer titrant (B.2.2.2) to titrate to the end point. ADD 1 drop of the sample treated in accordance with B.2.3.2 to the titration cup; USE the decrement method to weigh the added sample mass (accurate to 0.1 mg); INPUT the sample mass into the titrator (B.2.1.1). USE Karl Fischer titrant (B.2.2.2) to titrate to the end point; RECORD the test result displayed by the instrument.

TEST twice in parallel and average the test results. The relative deviation of the two test results is less than 1.5%.

After 3~6 tests, the Karl Fischer solvent in the titration cup shall be replaced in time.

B.2.3.4 Data processing

The moisture content of the sample after dilution treatment is calculated according to formula (B.4):

$$w_w = \frac{w'_w \times (m_s + m_w) - m_w \times 100}{m_s} \quad \text{.....(B.4)}$$

Appendix C

(Normative)

Test of volatile organic compounds (VOC) content in solvent-based and solvent-free floor coatings

C.1 Principle

The volatile-matter content tested for solvent-based and solvent-free floor coatings (if water is contained, deduct the water content) is their VOC content.

C.2 Test procedures

C.2.1 General

All tests are carried out in two parallel determinations.

C.2.2 Density

Prepare the mixed sample according to the construction proportion indicated by the product. After stirring well, according to the regulations of GB/T 6750-2007, determine the density of the sample. Test temperature: (23±2)°C.

C.2.3 Volatile-matter content

Prepare the mixed sample according to the construction proportion indicated by the product. After stirring evenly, according to GB/T 1725-2007, determine the non-volatile-matter content of the sample, expressed in mass fraction (%). USE 100 minus the non-volatile-matter content to get the volatile-matter content of the sample, expressed in mass fraction (%). Test conditions for solvent-based floor coatings: The sample weighing amount is (1±0.1)g; the baking condition is (105±2)°C/1 h. Test conditions for solvent-free floor coatings: The sample weighing amount is (1±0.1)g; the baking conditions are: first place it at (23±2)°C and relative humidity (50±5)% for 24 h; then bake it at (105±2)°C for 1 h.

C.2.4 Moisture content

If the sample contains moisture, according to the method in Appendix B, test the moisture content w_w.

C.2.5 Volatile organic compounds (VOC) content

If there is no moisture in the sample, according to formula (C.1), calculate the

Appendix D

(Normative)

Test of benzene content, toluene, ethylbenzene and xylene content, as well as glycol ethers and ether esters content in solvent-based and solvent-free floor coatings - gas chromatography analysis

D.1 Principle

After the sample is diluted, it is directly injected into the gas chromatograph; separated by the chromatographic column; detected by a hydrogen flame ionization detector; and quantified by the internal standard method.

D.2 Materials and reagents

D.2.1 Carrier gas: nitrogen; purity is ≥99.995%.

D.2.2 Fuel gas: hydrogen; purity is ≥99.995%.

D.2.3 Combustion-supporting gas: air.

D.2.4 Auxiliary gas (septum purge and makeup gas): nitrogen with the same properties as the carrier gas.

D.2.5 Internal standard substance: a compound that does not exist in the sample and can be completely separated from other components on the chromatogram. The purity is at least 99% (mass fraction); or the purity is known. For example, n-heptane, n-pentane, etc.

D.2.6 Calibration compounds: benzene, toluene, ethylbenzene, xylene, glycol methyl ether, ethylene glycol methyl ether acetate, glycol ethyl ether, ethylene glycol ethyl ether acetate, diethylene glycol butyl ether acetate. The purity is at least 99% (mass fraction); or the purity is known.

D.2.7 Dilution solvent: an organic solvent used to dilute the sample, which does not contain any substances that interfere with the test. The purity is at least 99% (mass fraction); or the purity is known. For example, ethyl acetate, butyl acetate, n-hexane, etc.

D.3 Instruments and equipment

D.3.1 Gas chromatograph with the following configuration:

D.5.2 Optimization of chromatograph parameters

According to the chromatographic test conditions in D.4, the known calibration compound shall be used to optimize the instrument each time; so that the sensitivity, stability and separation effect of the instrument are in the best state.

The injection volume and split ratio shall be matched, to avoid exceeding the capacity of the chromatographic column; and within the linear range of the instrument detector.

D.5.3 Qualitative analysis

D.5.3.1 Optimization of instrument parameters

According to the provisions of D.5.2, optimize the instrument parameters.

D.5.3.2 Determination of the retention time of the compound under test

Inject 1.0 μL of the standard mixed solution containing the compounds under test shown in D.2.6 into the chromatograph; RECORD the retention time of each compound under test.

D.5.3.3 Qualitative analysis

According to the construction proportion indicated by the product, prepare mixed sample. After stirring evenly, weigh about 1 g of sample and use an appropriate amount of dilution solvent (D.2.7) to dilute the sample; USE the injector (D.3.2) to take 1.0 μL of the well-mixed sample into the chromatograph; RECORD the chromatogram. And compare it with the standard retention time of the compound under test determined by D.5.3.2, to determine whether the compound under test exists.

Note: For solvent-based and solvent-free coatings that use isocyanate as a curing agent, as well as coatings that react quickly, the mixed samples shall be analyzed as soon as possible after preparation. For coatings that react quickly, the sample to be mixed each time shall not be less than 200 g; the stirring time is about 3 min.

D.5.4 Calibration

D.5.4.1 Preparation of calibration sample

Respectively weigh a certain amount (accurate to 0.1 mg) of various calibration compounds in D.2.6 into the sample preparation bottle (D.3.3). The weighed mass shall be in the same order of magnitude as the content of the various compounds contained in the sample to be tested. Then weigh the internal standard substance (D.2.5) of the same order of magnitude as the compound to be tested into the same sample preparation bottle. USE an appropriate

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