Technical requirement for environmental labeling products

Gravure ink and flexographic ink

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This document is a translation of a Chinese original. In case of dispute, the original document should be taken as authoritative.
Foreword

This standard is formulated for the purposes of implementing the Environment Protection Law of the People's Republic of China, reducing adverse impacts of gravure ink and flexographic ink on the environment and human health in the processes of production and use and disposal.

This standard identifies environmental protection requirements for toxic and harmful substances in raw material, production process and products of gravure ink and flexographic ink.

This standards revises the Technical Requirement for Environmental Labeling Products—Gravure Ink and Flexographic Ink (HJ/T 371-2007) with the following major amendments:

-- Adjust applicable scope, terms and definitions;
-- Add restricted varieties of heavy metals and harmful elements and adjusted limit requirements;
-- Adjust restricted varieties of phthalate and ketone substances;
-- Enhance the restrictions on hydroquinone, mequinol and alkylphenol ethoxylates (APEOs);
-- Increase restrictions on dyes;
-- Add restrictions on photoinitiator in energy curing ink;
-- Adjust the restrictions on halogenated hydrocarbons;
-- Adjust restrictions on volatile organic compounds (VOCs), benzene, toluene, xylene, ethylbenzene, methanol and ammonia in the products;
-- Increase restrictions on styrene and free formaldehyde in the products;
-- Adjust the requirements for product packaging and instructions.

The development of this standard is under the organization of the Department of Science and Technology and Standards of the Ministry of Ecology and Environment of China.

The main organizations drafting this standard are Sino-Japan Friendship Center for Environment Protection, Plastic Products Packaging Commission of China Packaging Federation, National Food Soft Package Products & Equipment Quality Supervision and Inspection Center (Guangdong).

This standard was approved by the Ministry of Ecology and Environment of China on July 12, 2018.
This standard takes effect as of October 1, 2018.

This standard shall be interpreted by the Ministry of Ecology and Environment of China.

The previous version replaced by this standard is HJ/T 371-2007.
Technical requirement for environmental labeling products

Gravure Ink and Flexographic Ink

1 Applicable Scope

This standard stipulates the terms and definitions, basic requirements, technical contents and test methods for gravure ink and flexographic ink environmental labeling products.

This standard is applicable to the assessment of environmental characteristics of gravure ink and flexographic ink products.

2 Normative References

This standard contains references to the following documents. The latest version of any quoted document without a marked date shall be applicable to this standard.

- GB 18581 Indoor Decorating and Refurbishing Materials – Limit of Harmful Substances of solvent-based wood coating
- GB/T 15962 Terminology of Printing Ink
- GB/T 16483 Safety Data Sheet for Chemical Products—Contents and Order of Sections
- GB/T 23986 Paints and Varnishes – Determination of Volatile Organic Compound (VOC) Content - Gas Chromatographic Method
- GB/T 23993 Determination of Formaldehyde Content of Waterborne Coatings Spectrophotometric Method with Acetylacetone
- GB/T 26395 Water Based Gravure Ink for Cigarette Packing
- HJ 2546 Technical Requirement for Environmental Labeling Products—Textile Products
- QB 2930.1 Limit and Determination Method for Toxic Elements in Printing Ink—Part 1 Soluble Elements

3 Terms and Definitions

The terms and definitions given in GB/T 15962 and the followings shall be applicable to this standard.

3.1 Gravure ink

It is the general name of printing ink suitable for all kinds of gravure printing.

3.2 Flexographic ink
It refers to the printing ink applicable for flexographic printing.

4 Basic Requirements

4.1 The products shall meet the requirements of relevant quality and safety standards.
4.2 Product manufacturers shall obtain pollutant discharging licenses, and discharge pollutants in accordance with the requirements of the licenses.
4.3 Product manufacturers shall strengthen clean production in the process of production.

5 Technical Contents

5.1 Methanol, formaldehyde, halogenated hydrocarbon, acetone, butanone, cyclohexanone, methyl isobutyl ketone, isophene, hydroquinone, p-methoxyphenol and benzene solvents shall not be added to the products.
5.2 Alkylphenol ethoxylates (APEOs) and glycol ether substances listed in Annex A shall not be added to the products.
5.3 Phthalate plasticizers listed in Annex B shall not be added to the products.
5.4 Azo dyes, carcinogenic dyes and sensitized disperse dyes specified in Annex A, B and C of HJ 2546-2016 shall not be added to the products.
5.5 Photoinitiators such as benzophenone (BP), isopropylthioxanthone (ITX), 2-methyl -1-(4-methoxyphenyl) -2-morpholinyl - 1-acetone (907) shall not be added to the products.
5.6 The limits of hazardous substances in the products shall meet the requirements of Table 1 and 2.

<table>
<thead>
<tr>
<th>Item</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs, %</td>
<td>≤ 5</td>
</tr>
<tr>
<td>Gross of benzene, toluene, xylene, ethylbenzene, tritoluene, and styrene, mg/kg</td>
<td>≤ 100</td>
</tr>
<tr>
<td>Methanol, %</td>
<td>≤ 0.3</td>
</tr>
<tr>
<td>Free formaldehyde, mg/kg</td>
<td>≤ 50</td>
</tr>
<tr>
<td>Ammonia and its compounds, %</td>
<td>≤ 2</td>
</tr>
</tbody>
</table>

Table 2 The limit of soluble elements in the product

<table>
<thead>
<tr>
<th>Item</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stibium (Sb), mg/kg</td>
<td>≤ 60</td>
</tr>
</tbody>
</table>
### Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Limit, mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>≤ 25</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>≤ 1000</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>≤ 75</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>≤ 60</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>≤ 90</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>≤ 60</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>≤ 500</td>
</tr>
</tbody>
</table>

#### 5.7 Packaging and instruction requirements

5.7.1 Polybrominated biphenyl (PBBs), polybrominated diphenyl ether (PBDEs) and chlorinated paraffin wax (chain carbon number 10-13, containing chlorine concentration of more than 50%) shall not be added to plastic packaging containers of the products.

5.7.2 No plastic additives containing lead, cadmium, mercury, hexavalent chromium and other elements shall be added to the plastic packaging containers of the products.

5.7.3 The theoretical content of volatile organic compounds (VOCs) in the product should be marked, with suggestion of no adding diluent containing VOCs in use process.

5.7.4 Enterprise shall provide users with product safety technical specifications conforming to the requirements stated in GB/T 16483.

### 6 Test Methods

6.1 The test of VOCs content in Table 1 of Technical Content 5.6 shall be conducted based on the methods specified in GB/T 23986-2009.

6.2 The test of benzene, methylbenzene, xylene, trimethylbenzene, ethylbenzene and styrene in Table 1 of Technical Contents Clause 5.6 shall be conducted based on the methods specified in GB/T 26395-2011.

6.3 The test of methanol content in Table 1 of Technical Content 5.6 shall be conducted based on the methods specified in GB 18581-2009.

6.4 The test of free formaldehyde content in Table 1 of Technical Content 5.6 shall be conducted based on the methods specified in GB/T 23993-2009.

6.5 The test of ammonia and its compounds content in Table 1 of Technical Content 5.6 shall be conducted based on the methods specified in Annex C.

6.6 The test of soluble elements in Table 2 of Technical Content 5.6 shall be conducted based on the methods specified in QB 2930.1-2008.
6.7 Other requirements in the Technical Contents shall be verified by document review combined with site inspection.
Annex A
(Normative Annex)

**Glycol Ether**

<table>
<thead>
<tr>
<th>Chinese Name</th>
<th>English Name</th>
<th>CAS No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>乙二醇甲醚</td>
<td>2-methoxyethanol</td>
<td>109-86-4</td>
</tr>
<tr>
<td>乙二醇甲醚醋酸酯</td>
<td>2-methoxyethyl acetate</td>
<td>110-49-6</td>
</tr>
<tr>
<td>乙二醇乙醚</td>
<td>2-ethoxyethanol</td>
<td>110-80-5</td>
</tr>
<tr>
<td>乙二醇乙醚醋酸酯</td>
<td>2-ethoxyethyl acetate</td>
<td>111-15-9</td>
</tr>
<tr>
<td>二乙二醇丁醚醋酸酯</td>
<td>2-(2-butoxyethoxy)ethyl acetate</td>
<td>124-17-4</td>
</tr>
</tbody>
</table>
### Annex B
(Normative Annex)

**Phthalates**

<table>
<thead>
<tr>
<th>Chinese Name</th>
<th>English Name</th>
<th>Abbreviation</th>
<th>CAS No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>邻苯二甲酸二甲酯</td>
<td>Dimethyl phthalate</td>
<td>DMP</td>
<td>131-11-3</td>
</tr>
<tr>
<td>邻苯二甲酸二乙酯</td>
<td>Diethyl phthalate</td>
<td>DEP</td>
<td>84-66-2</td>
</tr>
<tr>
<td>邻苯二甲酸二烯丙酯</td>
<td>Diallyl phthalate</td>
<td>DAP</td>
<td>131-17-9</td>
</tr>
<tr>
<td>邻苯二甲酸二异丁酯</td>
<td>Diisobutyl phthalate</td>
<td>DIBP</td>
<td>84-69-5</td>
</tr>
<tr>
<td>邻苯二甲酸二丁酯</td>
<td>Dibutyl phthalate</td>
<td>DBP</td>
<td>84-74-2</td>
</tr>
<tr>
<td>邻苯二甲酸二（2-甲氧基）乙酯</td>
<td>Bis(2-methoxyethyl) phthalate</td>
<td>DMEP</td>
<td>117-82-8</td>
</tr>
<tr>
<td>邻苯二甲酸二（4-甲基-2-戊基）酯</td>
<td>Bis(4-methyl-2-pentyl) phthalate</td>
<td>BMPP</td>
<td>146-50-9</td>
</tr>
<tr>
<td>邻苯二甲酸二（2-乙氧基）乙酯</td>
<td>Bis(2-ethoxyethyl) phthalate</td>
<td>DEEP</td>
<td>605-54-9</td>
</tr>
<tr>
<td>邻苯二甲酸二戊酯</td>
<td>Dipentyl phthalate</td>
<td>DPP</td>
<td>131-18-0</td>
</tr>
<tr>
<td>邻苯二甲酸二己酯</td>
<td>Dihexyl phthalate</td>
<td>DHXP</td>
<td>84-75-3</td>
</tr>
<tr>
<td>邻苯二甲酸丁基苯基酯</td>
<td>Benzyl butyl phthalate</td>
<td>BBP</td>
<td>85-68-7</td>
</tr>
<tr>
<td>邻苯二甲酸二（2-丁氧基）乙酯</td>
<td>Bis(2-n-butoxyethyl) phthalate</td>
<td>DBEP</td>
<td>117-83-9</td>
</tr>
<tr>
<td>邻苯二甲酸二环己酯</td>
<td>Dicyclohexyl phthalate</td>
<td>DCHP</td>
<td>84-61-7</td>
</tr>
<tr>
<td>邻苯二甲酸二（2-乙基）己酯</td>
<td>Bis(2-ethylhexyl) phthalate</td>
<td>DEHP</td>
<td>117-81-7</td>
</tr>
<tr>
<td>邻苯二甲酸二苯酯</td>
<td>Diphenyl phthalate</td>
<td>DPhP</td>
<td>84-62-8</td>
</tr>
<tr>
<td>邻苯二甲酸二正辛酯</td>
<td>Di-n-octyl phthalate</td>
<td>DNOP</td>
<td>117-84-0</td>
</tr>
<tr>
<td>邻苯二甲酸二异壬酯</td>
<td>Diisononyl ortho-phthalate</td>
<td>DINP</td>
<td>68515-48-0</td>
</tr>
<tr>
<td>邻苯二甲酸二壬酯</td>
<td>Dinonyl phthalate</td>
<td>DNP</td>
<td>84-76-4</td>
</tr>
</tbody>
</table>
Annex C
(Normative Annex)

Determination of Ammonia and Its Compounds in Printing Ink – Titration after Distillation

C.1 Principle
Distill ammonia from alkaline solution, absorb by excessive sulfuric acid standard solution, adopt methyl red-methylene blue mixed indicator as the indicator, and titrate the excessive sulfuric acid by sodium hydroxide reference titration solution.

C.2 Reagents
C.2.1 The water involved in this method is distilled water or water of the same purity.
C.2.2 The chemical reagents involved in this method are all analytical pure chemical reagents, unless otherwise specified.
C.2.3 Hydrochloric acid: 1+1.
C.2.4 Sulfuric acid stand solution: \( c(1/2H_2SO_4) = 0.1\text{mol/L} \).
C.2.5 Sodium hydroxide standard titration solution: \( c(\text{NaOH}) = 0.1\text{mol/L} \).
C.2.6 Methyl red-methylene blue mixed indicator: mix 50mL methyl red ethanol solution (2g/L) with 50mL methylene blue methyl red-methylene blue mixed indicator (1g/L).
C.2.7 Universal pH test paper.
C.2.8 Sodium hydroxide.

C.3 Instrument and Equipment
C.3.1 Analytical balance with precision 0.0001g
C.3.2 500mL glass distiller
C.3.3 300mL beaker
C.3.4 300mL conical flask
C.3.5 25mL test tube
C.3.6 10mL transfer pipette
C.3.7 50mL alkali burette
C.3.8 1000W electric stove

**C.4 Determination Steps**

**C.4.1 Sample treatment**

Stir the sample evenly, weigh two samples with weight at about 1-2g each, accurate to 0.0001g, and put them into two 300mL beakers (C.3.3), dissolve it with water and transfer it into a 500mL glass distiller (C.3.2), control the total volume of 200mL ready for distillation.

**C.4.2 Distillation**

Add several pieces of sodium hydroxides (C.2.8) into the solution for distillation, test by universal pH test paper (C.2.7), adjust the solution pH >12, add several explosion-proof glass beads.

Accurately transfer 10mL standard sulfuric acid solution (C.2.4) into a 25mL test tube (B.3.5), add 3-4 drops of mixed indicator (C.2.6), place the test tube (C.3.5) in 300mL conical flask (C.3.4), and then insert the outlet glass tube of distillate of the distiller into the sulfuric acid solution at the bottom of the test tube.

Check and ensure that the distiller is properly connected and sealed. Then heat it for distillation. Stop heating after collecting 180mL distilled liquid, remove the distillation flask, rinse condensing pipe with water, and collect the washing liquid in the conical bottle.

**C.4.3 Titration**

Transfer the solution in the test tube into a 300mL conical flask, wash the test tube, and collect the washing solution into the conical flask. Use sodium hydroxide reference titration solution (C.2.5) to re-titrates the excessive sulfuric acid standard solution until the indicator changes from bright purple to grayish green, and the volume of the sodium hydroxide reference titration solution is expressed as V1.

**C.4.4 Blank test**

At the same time of the above measurement, conduct parallel operation without adding test materials by the same analysis steps, reagent and dosage, and determine the consumption volume V2 of reference titration solution of sodium hydroxide in the blank test.
C.5 Calculation

The content of ammonia and its compounds in printing ink shall be expressed by NH₃ mass fraction, and is calculated with Formula C.1

\[
X_{\text{NH}_3} = \frac{(V_2-V_1) \times 0.01703}{m} \times 100
\]  \hspace{1cm} (C.1)

Where \(X_{\text{NH}_3}\) —— mass fraction of NH₃ in printing ink, \(\%\);

c —— accurate concentration value of the standard sodium hydroxide solution, mol/L;

\(V_1\) —— value of standard sodium hydroxide solution volume consumed by titration of the sample solution, mL;

\(V_2\) —— value of sodium hydroxide reference solution volume consumed by blank test, mL;

0.01703 —— ammonia mass equivalent to 1.00 mL sodium hydroxide reference solution \([c(\text{NaOH})=1.000\text{mol/L}]\), g;

\(m\) —— mass of the sample, g.

Take the arithmetic mean value of the two parallel measurement data as the measurement results, when the absolute difference of the two parallel measurement results is greater than 0.01%, the measurement should be redone.