Humectants for Toothpastes  Glycerine and Macrogol

(Draft for Approval)

(Draft Completion Date: 1 August 2007)
Preface

The content highlighted in bold characters in Table 1 and Table 2 of this standard is mandatory while the rest is recommended.

This standard is compiled in reference to the US Pharmacopoeia (USP30/NF25) and integrated with regards to the particular situation of our toothpaste industry.

This standard is proposed by China Light Industry Association.

This standard is under the jurisdiction of National Toothpaste and Wax Product Standardisation Centre.

The main drafting organisations of this standard include: National Light Industry Toothpaste and Wax Product Quality Supervision and Test Centre, Beijing Procter & Gamble Technology Co. Ltd, Liuzhou LMZ Co., Ltd, Masson Group Co. Ltd, Shanghai Toothpaste Factory of Shanghai White Cat Co. Ltd, Chongqing Dencare Oral Care Co., Ltd, Guangzhou Colgate-Palmolive Co. Ltd, Unilever (China) Co. Ltd.

The main drafters of this standard were: Zou Bin, Ye Tingting and Ma Xuan.

This standard was issued on ... for the first time.
Humectants for toothpastes  Glycerine and macrogol

1  Scope

This standard sets the requirements, test methods, and rules for the inspection, packaging, labelling, transportation and storage of glycerine and macrogol in the humectants used in toothpaste.

This standard is applicable to glycerine and macrogol humectants used in toothpaste.

2  Normative References

The provisions of the following documents become provisions of this standard after being referenced. For dated reference documents, all later amendments (excluding corrigenda) and versions do not apply to this standard; however, the parties to the agreement are encouraged to study whether the latest versions of these documents are applicable. For undated reference documents, the latest versions apply to this standard.

GB/T 191-2000  Packaging - Pictorial Marking for Handling of Goods
GB/T 601     Chemical Reagent - Preparations of Standard Volumetric Solutions
GB/T 602     Chemical Reagent - Preparations of Standard Solutions for Impurity
GB/T 603     Chemical Reagent - Preparations of Reagent Solutions for use in Test Methods
GB/T 6682    Water for Analytical Laboratory Use - Specification and Test Methods
GB/T 6678    General Principles for Sampling Chemical Products
GB/T 13216.2 – 1991 Test Methods for Glycerines - Determination of Transparency
GB/T 13216.3 –1991 Test Methods for Glycerines - Determination of Odour
GB/T 13216.4 –1991 Test Methods for Glycerines - Determination of Colour (Hazen Unit-Platinum-Cobalt Scale)
GB/T 13216.5 –1991 Test methods for Glycerines - Determination of Density at 20ºC
GB/T 13216.6 –1991 Test Methods for Glycerines - Determination of Glycerol Content
GB/T 13216.7 –1991 Test Methods for Glycerines - Limit Test for Chloride
GB/T 13216.8 –1991 Test methods for Glycerines - Determination of Sulphated Ash - Gravimetric Method
GB/T 13216.9 – 1991 Test methods for Glycerines - Determination of Acidity or Alkalinity - Titrimetric Method
GB/T 13216.10 – 1991 Test methods for Glycerines - Determination of Saponification Equivalent
GB/T 13216.13 – 1991 Test methods for Glycerines - Test of Reducing Substances
JJF1070—2005  Rules of Metrological Testing for Net Quantity of Products in Pre-packages with Fixed Content
Decree No 75 of the General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic of
3 Requirements

3.1 Glycerine

The sensory characters, physical and chemical elements and the limits of toxic substances of glycerine should meet the requirements set out in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Item</th>
<th>Character</th>
<th>Saponification</th>
<th>Zymotechnics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sensory Character</strong></td>
<td><strong>Appearance (transparency)</strong></td>
<td>Transparent, no suspended substance or sedimentation</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Smell</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Colour (hazen)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Glycerine content / %</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Density (20°) / (g/ml)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Chloride (calculated by Cl)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Sulphated ash / %</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Acidity or alkalinity / (mmol/100g)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Physical &amp; Chemical Character</strong></td>
<td><strong>Reducing substance</strong></td>
<td>No sedimentation or silver mirror reaction</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Saponification equivalent / (mmol/100g)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Molysite (calculate by Fe) (mg/kg)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Limits of Toxic Substance</strong></td>
<td><strong>Diglycol and related compounds %</strong></td>
<td>1.0 (total of diglycol and related impurities, other impurities • 0.1 respectively)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Heavy metal content (calculate by Pb) / (mg/kg)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Arsenic content (calculated by As) / (mg/kg)</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 Macrogol

The sensory characters, physical and chemical elements and the limits of toxic substances of macrogol should meet the requirements set out in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Item</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sensory Character</strong></td>
<td>Appearance</td>
</tr>
<tr>
<td><strong>Physical &amp; Chemical Elements</strong></td>
<td>Average molecular weight</td>
</tr>
<tr>
<td></td>
<td><strong>pH</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Burning residue %</strong></td>
</tr>
<tr>
<td><strong>Limits of Toxic Substance</strong></td>
<td><strong>Diglycol and glycol %</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Heavy metal (calculated by lead) / (mg/kg)</strong></td>
</tr>
<tr>
<td></td>
<td><strong>Arsenic / (mg/kg)</strong></td>
</tr>
</tbody>
</table>

3.3 Net Content

The net content of packaged humectants in toothpastes should conform to the
requirements stipulated in *JJF1070–2005*.

4 **Test Methods**  
With the exception of any special requirements, the reagents and water of this standard are all pure analytic reagents and water that conform with the stipulations of GB/T6682.

With the exception of any special requirements, the standard solution for the titration analysis, the standard solution for the impurity measurement and for the preparation and products used the test in this standard are all prepared according to the provisions of GB/T601, GB/T602 and GB/T603.

4.1 **Test Methods for Glycerine in Toothpaste**

4.1.1 **Appearance**  
Test according to the provisions of GB/T 13216.2.

4.1.2 **Odour**  
Test according to the provisions of GB/T 13216.3.

4.1.3 **Colour**  
Test according to the provisions of GB/T 13216.4.

4.1.4 **Glycerine Content**  
Test according to the provisions of GB/T 13216.6.

4.1.5 **Density**  
Test according to the provisions of GB/T 13216.5.

4.1.6 **Chloride**  
Test according to the provisions of GB/T 13216.7.

4.1.7 **Sulphated Ash**  
Test according to the provisions of GB/T 13216.8.

4.1.8 **Acidity or Alkalinity**  
Be tested according to the provisions of GB/T 13216.9.

4.1.9 **Reducing Substance**  
Be tested according to the provisions of GB/T 13216.13.

4.1.10 **Saponification Equivalent**  
Be tested according to the provisions of GB/T 13216.10.

4.1.11 **Molysite**  
Test according to the provisions of Appendix VIIIG to Pharmacopoeia of the People’s Republic of China, 2005 Edition (Part Two).

4.1.12 **Diglycol and Related Compounds**
4.1.12.1 Apparatus

Gas phase chromatography: with a flame ionisation detector, chromatographic column G43 (6% cyanopropylphenyl, 94% p-methylpolysiloxane - substance quantity in percentage) (0.53 mm × 30m × 3 • m) as the fused silica capillary column, sample entry lining tube type as inward warping cup. Chromatography settings as follows: initial chromatographic column temperature of 100°C; after injecting the sample increase the temperature to 220°C at a speed of 7.5 /min and maintain for 4 min. Maintain a temperature of 220°C at the sample entry area and maintain the temperature of the detector at 250°C. Use helium as carrier gas. Diversion ratio as 10:1, linear speed: 38 cm / s. After entry of the resolution fluid, record the peak chromatogram response according to the specified conditions of the test method. The separation of the two peaks between the diglycol and glycerine should not be less than 7.0. Repeat by injecting the standard solution, and record the chromatographic peak area. The relative deviation to the standard should not exceed 15%.

4.1.12.2 Reagent

a) Glycerine and glycol: chromatographic pure;

b) Resolution fluid: weigh the chromatographic pure diglycol and glycerine accurately, dissolve them in water, diluting them quantitatively - step by step diluting if necessary - and create diglycol and glycerine solutions with a concentration of around 0.5 mg / ml;

c) Standard solution: weigh the chromatographic pure diglycol accurately, dissolving it in water, diluting it quantitatively - step by step diluting if necessary - and create a diglycol solution with a concentration of around 0.05 mg / ml;

d) Testing solution: accurately add 5g of glycerine in a 100 ml measuring flask, dilute with water to the scale and shake it evenly.

4.1.12.3 Test procedure

Conduct the test with the same volume (about 0.5 • L) of the standard solution and test the solution respectively. Record the chromatograms and measure the peak area. Calculate the diglycol content (C₁) in the glycerine sample using the formula (1):

\[ C_1 = \frac{C_s \times r_u}{C_u \times r_s} \times 100 \]  

In the formula:

\( C_1 \)  – diglycol content, %;

\( C_s \)  – diglycol concentration in the standard solution, unit as mg/ml;

\( C_u \)  – diglycol concentration in the testing solution, unit as mg/ml;

\( r_u \)  – chromatograph peak area of diglycol in the testing solution;

\( r_s \)  – chromatograph peak area of diglycol in the standard solution.

Calculate the other impurity (without the solution peak) content (C₂) in the glycerine sample using the formula (2):
\[ \frac{r_i}{r_s} \times 100 \quad \text{……………………………………(2)} \]

In the formula:
- \( C_2 \) – impurity (without the solution peak) content in the glycerine sample, \%;
- \( r_i \) – peak area of each impurity in the tested solution;
- \( r_s \) – total peak areas measured from the test solution.

4.1.13 Arsenic
Test according to the provisions on the silver diethyldithiocarbamate spectrophotometric method of Appendix VIIIJ to the Pharmacopoeia of the People’s Republic of China, 2005 Edition (Part Two).

4.1.14 Heavy Metal
Test according to the provisions on the first method of Appendix VIIIH to the Pharmacopoeia of the People’s Republic of China, 2005 Edition (Part Two).

4.2 Macrogol

4.2.1 Appearance
Test according to the provisions regarding Macrogol set out in the Pharmacopoeia of the People’s Republic of China, 2005 Edition (Part Two).

4.2.2 Average Molecular Weight

4.2.2.1 Main Apparatus
Heat resistance pressure bottle

4.2.2.2 Reagent
a) Phthalic anhydride solution: place 49.0g phthalic anhydride in a brown bottle, dissolve it in 300 ml distilled pyridine or 300 ml pyridine from a newly opened bottle, fully oscillate until it completely dissolves. Add 7g imidasole, carefully shake to dissolve and leave for 16 hours before use.
b) Macrogol testing solution: carefully place 25.0 ml phthalic anhydride solution into a dry heat resistance pressure bottle. Add an accurately weighed sample of macrogol with the mass of its expected average molecular weight at around 1/160. Wrap the pressure bottle tightly with a cloth.
c) Sodium hydroxide: 0.5 mol/l.

4.2.2.3 Test Procedure
Immerge the bottle in a 96°C-100°C water bath; the immersing depth of the bottle should be at fluid level in the pressure bottle. Remove the bottle after 5 minutes and shake it evenly without unwrapping the cloth. Continue to heat the water bath for 30 minutes then remove it, allowing it to cool to room temperature. Remove the pressure bottle from the cloth bag, carefully opening the cap to release the pressure, add 10 ml water and shake thoroughly. Leave for 2 minutes and add 0.5 ml phenolphthalein. With 1 +100 pyridine solution, titrate with 0.5 mol/l sodium hydroxide until a sustained pink colour initially appears for 15 seconds. Record the consumption of the titration liquid volume.
as S. Using the same method, carry out a blank test in 25.0ml phthalic anhydride solution and pyridine, recording the volume of consuming 0.5 mol / L of sodium hydroxide as B.

4.2.2.4 Average Molecular Weight Calculation
Calculate the average molecular weight (M) of macrogol using the formula (3):

\[
M = \frac{2000 \times W}{N \times (B - S)} \times 100
\]  

(3)

In the formula:
M – average molecular weight of macrogol;
W – macrogol mass of the prepared testing solution, unit as g;
B – blank consuming 0.5 mol/l sodium hydroxide, unit as ml;
S – sample consuming 0.5 mol/l sodium hydroxide, unit as ml;
N – molar concentration of the sodium hydroxide solution, unit as mol/L.

4.2.3 pH
Tested according to the provisions stipulated in Appendix VIH to the Pharmacopoeia of the People’s Republic of China, 2005 Edition (Part Two).

4.2.4 Diglycol and Glycol

4.2.4.1 Diglycol and glycol measurement of the macrogol sample with an average molecular weight of less than 450

4.2.4.1.1 Main Apparatus
Gas phase chromatography: with a flame ionisation detector, the 3mm × 1.5m stainless steel chromatographic column filled with untreated diatomite bearing 12% sorbitol. Use nitrogen as the carrier gas or another suitable inert gas with a flow rate of 50 ml/min. The column temperature should be maintained at 140 ºC. Maintain the sample entrance at 250ºC and the flame ionisation detector temperature at 280ºC.

4.2.4.1.2 Reagent
a) Diglycol and glycol: chromatographic pure;
b) Standard solution: make up the standard solution with chromatographic pure diglycol and glycol both with a concentration of 500 g / ml; 
c) Testing the solution: place the accurately weighed 4g macrogol into a 10 ml measuring flask; dilute it to the scale and shake evenly.

4.2.4.1.3 Test Procedure
Add 2.0 ml standard liquid sample, record its chromatogram and adjust operating conditions so as to make the peak height not less than 100 mm. Measure the first chromatographic peak height (glycol) and the second peak height (diglycol) and record as P1 and P2 respectively. Put in 2.0 L testing solution sample, record its chromatogram in the same operating condition. Measure the first chromatographic peak height (glycol) and the second peak height (diglycol) and record as p1 and p2 respectively.
4.2.4.1.4 Calculation of Diglycol and Glycol

The glycol content in the sample (C₃) is calculated using the formula (4):

\[
C_3 = \frac{c_1 \times p_1}{p_1 \times \#} \times 100 \quad (\text{4})
\]

In the formula:
- \(C_3\) – glycol content, %;
- \(c_1\) – glycol concentration of the standard solution, unit as mg / ml;
- \(p_1\) – glycol peak height of the testing solution, unit as mm;
- \(P_1\) - glycol peak height of the standard solution, unit as mm;
- \(W\) – glycol mass used in the test, unit as mg.

The diglycol content in the sample (C₄) is calculated using the formula (5):

\[
C_4 = \frac{c_2 \times p_2}{p_2 \times \#} \times 100 \quad (\text{5})
\]

In the formula:
- \(C_4\) – diglycol content, %;
- \(c_2\) – diglycol concentration of the standard solution, unit as g / ml;
- \(p_2\) – diglycol peak height of the testing solution, unit as mm;
- \(P_2\) - diglycol peak height of the standard solution, unit as mm;
- \(W\) – diglycol mass used in the test, unit as mg.

4.2.4.2 Diglycol and glycol measurement of the macrogol sample with average molecular weight of higher than 450 and lower than 1000

4.2.4.2.1 Main Apparatus:
- a) distillation flask;
- b) spectrophotometer.

4.2.4.2.2 Reagent:
- a) nitrate: 0.25 mol/l;
- b) ceric ammonium nitrate: dissolve 6.25g ceric ammonium nitrate in 100 ml 0.25 mol/l nitrate solution and use within three days;
- c) standard solution: place 62.5 mg diglycol in a 25 ml measuring flask. Dissolve the diglycol by the solution, which is mixed by the same voluminal newly-distilled acetonitrile and water, and then dilute the solution to scale;
- d) testing solution: dissolve 50.0g macrogol into 75 ml diphenyl ether in a 250 ml distillation flask. If any crystallisation occurs, preheat the solution to dissolve the crystals. Slowly distil under a pressure of 1-2 mm mercury column; collect the distillation in a 100 ml container with 1 ml graduation until the distillation reaches 25 ml. Add 20.0 ml water into the distillation, fully oscillate, and then keep still for delamination. Place the mixture in an ice bath to solidify the diphenyl ether and separate the two-phase solid-liquid. Filter the separated water layer and collect the filtrate. Wash the diphenyl ether with 5.0 ml ice water, filter and collect the washing fluid. Mix the filtrate and washing fluid in a 25 ml conical flask and add water to
dilute to the scale, and then shake evenly. Heat the solution to room temperature, if necessary. Mix this solution evenly with 25.0 ml newly distilled acetonitrile in a 125 ml conical flask with a glass plug.

4.2.4.2.3 Test Procedure
Separately place 10.0 ml standard solution and 10.0 ml testing solution into two 50 ml flasks with 15.0 ml ceric ammonium nitrate solution in each and mix evenly. Within 2 to 5 minutes use 1 cm cells and spectrophotometers with a maximum absorption wavelength of 450 nm to simultaneously measure the absorbency of the two solutions. Blank contrast 15.0 ml ceric ammonium nitrate solution and 10.0 ml mixture solution with the same voluminal newly distilled acetonitrile and water. The absorbency of the testing solution should not exceed the absorbency of the standard solution, i.e. the total content of the glycol and diglycol should not exceed 0.25%.

4.2.5 Burning Residue
Test according to the provisions set out in Appendix VIIIIN to the Pharmacopoeia of the People’s Republic of China, 2005 Edition (Part Two).

4.2.6 Heavy Metal
Test according to the provisions set out in the first method of Appendix VIIIH to the Pharmacopoeia of the People’s Republic of China, 2005 Edition (Part Two).

4.2.7 Arsenic
Test according to the provisions on silver diethyldithiocarbamate spectrophotometric method set out in Appendix VIIIJ to the Pharmacopoeia of the People’s Republic of China, 2005 Edition (Part Two).

4.3 Net Content
The net content of packaged humectants for toothpaste should be tested according to the provisions stipulated in JJF1070-2005.

5 Inspection Rules

5.1 Inspection Classification

5.1.1 Final Factory Inspection
Items inspected in the final factory inspection for glycerine are sensory characters, physical and chemical elements and requirements for “diglycol and related compounds”.

Items inspected in the final factory inspection for macrogol are sensory characters, physical and chemical elements and requirements for “diglycol and glycol”.

5.1.2 Type Inspection
All items specified in the technical requirements of this standard are type inspection items. A type inspection should be conducted every three months.
under normal conditions. A type inspection must be carried out if one of the following conditions occur:
   a) modification made to a key production process;
   b) modification made to main raw materials;
   c) production resumed after a suspension;
   d) if required by national quality supervision authorities or buyers.

5.1.3 Acceptance Inspection
The buyer is entitled to perform an acceptance inspection on the received goods according to the relevant terms of the contract signed by the supplier and buyer and in accordance with the provisions set out in this standard. The acceptance inspection should be carried out within 15 days from the date of delivery.

5.2 Batching and Sampling Rules

5.2.1 Products of the same specification supplied in one delivery are considered as one batch.

5.2.2 A product may only be released from the factory after being inspected by the quality control department of the production enterprise in accordance with this standard and when issued with an inspection report; the recipient also conducts an acceptance inspection in accordance with this standard.

5.2.3 Sampling of glycerine and macrogol should be conducted according to GB/6678 and the sample quantity should not weigh less than 500g.

5.3 Determination Rules
If the test result does not meet the requirements of the standard, new samples should be taken and the test should be repeated. If the repeated test result still does not meet the requirements, the entire batch of the product shall be considered as unqualified.

5.4 Archiving Sample and Sample Preserving
In each batch of inspected products, a sample should be preserved for 30 days as an archiving sample.

6 Packaging, Labelling, Transportation and Storage

6.1 Packaging
As a kind of oral product with a high level of cleanliness, it should be ensured that the container of this product is clean, and inside coated steel barrels, polyethylene plastic buckets, square polyethylene plastic cans, containers with polyethylene plastic lining, galvanised buckets, stainless steel buckets or tankers could be selected as the packaging.

Packaging should conform to the provisions set out in GB 191.

6.2 Labelling
The contents of the packaged product should be clearly labelled with the product name, name and address of the manufacturer, trade mark, production batch or production date, shelf life and serial numbers of applied standards.

6.3 Transportation
This product should not be transported together with any toxic or harmful substances, and should be loaded and unloaded with care so as to avoid causing deformation or rupture to the packaging.

6.4 Storage
This product should be stored in a dry and ventilated store; it should not be stored outdoors; should avoid being stored where dust and water may be collected on the package; and should not be stored together with any toxic, harmful or contaminating goods, and a ‘first come, first go’ principle should be applied in the store so as to cut the storage time down to as short a length as possible.