Organic Chemical

Hydroxyl value of Polyether polyol

Acid-Base Titration by
Automatic Potentiometric Titrator

<table>
<thead>
<tr>
<th>Standard</th>
<th>JIS</th>
<th>K 1557-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO</td>
<td>14900</td>
<td></td>
</tr>
<tr>
<td>JIS</td>
<td>K 0070</td>
<td></td>
</tr>
</tbody>
</table>

1. Abstract

Hydroxyl value is obtained from a sample of pyridine containing acetic anhydride, which is first acetylated, of which excessive acetylated reagent then hydrolyzes with water, and thus generated acetic acid is titrated with potassium hydroxide up to the endpoint. The endpoint is determined by the inflexion point on titration curve. Hydroxyl value of polyether polyol is calculated from titration volume.

2. Reference

2) ISO 14900:2001 Plastics · Polyols for use in the production of polyurethane · Determination of hydroxyl number
3) JIS K 0070-1992 Test Method for Acidity, Saponification value, Ester value, Iodine value and Hydroxy value of Chemical products and Unsaponifiables

3. Cautions in measurement

1) If the sample contains excessive water, normal acetylation may not be obtained.
2) Pyridine and acetic anhydride are harmful and inflammable. Acetic anhydride is corrosive. Caution must be taken when handle these chemicals.
### 4. Post measurement care

Clean the electrode with pure water each time after measurement is finished.

### 5. Test equipment

- **Main unit**: Automatic potentiometric titrator (Standard preamplifier: STD—)
- **Electrode**:
  - Option: Glass electrode
  - Option: Cork type reference electrode

### 6. Reagent

- **Titrant**: 0.5mol/L Potassium hydroxide Ethanol solution \((f=1.00)\)
- **Reagent**: Pure water, Pyridine, Acetic ether, Perchloric acid (78%), Acetic anhydride

### 7. Measurement procedure

**—Pretreatment—**
1. Add 4.0g (2.35mL) perchloric acid to 400mL acetic ether.
2. Add 8mL acetic anhydride, and leave at room temperature for 30 minutes.
3. Cool it to 5°C, and add 42mL chilled acetic anhydride. Leave at 5°C for one hour.
4. The solution warmed at room temperature is the acetic anhydride solution.
5. Add 100mL water to 300mL pyridine to make pyridine + water \((3+1)\).

**—Measurement—**
1. Sample 3g in a 100mL beaker.
2. Add 10.0mL acetic anhydride, and stir for 15 minutes.
3. Add 2mL water and 10.0mL pyridine + water \((3+1)\), and stir for 5 minutes.
4. Add 10.0mL pyridine.
5. Titrate with 0.5mol/L potassium hydroxide ethanol to obtain hydroxyl value.
6. Perform blank test likewise.

### 8. Formula

Hydroxyl value \( (\text{mg/g}) \) = \(( BL1 - EPl ) \times TF \times Cl \times K1 / \text{SIZE} \)

- **EPl**: Titration volume \((\text{mL})\)
- **BL1**: Blank level \((56.1542\text{mL})\)
- **TF**: Factor of titrant \((1.00)\)
- **Cl**: Concentration conversion coefficient \((28.05\text{mg/mL})\)
  - (Formula mass of potassium hydroxide: 56.11×1/2)
- **K1**: Unit conversion coefficient \((1)\)
- **SIZE**: Sample size \((\text{g})\)
9. Example of measurement

-Ambient condition-
<table>
<thead>
<tr>
<th>Room temperature</th>
<th>Humidity</th>
<th>Weather</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.9 °C</td>
<td>48 %</td>
<td>Cloudy</td>
</tr>
</tbody>
</table>

-Titration parameter-

-Model: AT-510  
-Method No.: 12  
-Titr. mode: Auto Titration  
-Titr. form: EP Stop

[Titration parameter]

-Form: EP Stop  
-APB No.: 1  
-Unit No.: 1  
-Detector No.: 1  
-Unit: mV  
-Max. Volume: 80.0mL  
-Wait Time: 0s  
-Direction: Auto

[Result parameter]

-<Calculation>
  
  Calc.Type: Sample  
  Conc.1: Set  
  CO1 = (BL1·EP1)·TF·C1·K1·SIZE

-<Constant>
  
  C1(mg/mL): 28.05  
  K1: 1

-<Blank list>
  
  Blank1: 56.1542

-The above printout data were obtained from titration by AT-510 unit

-Titration curve-

-*** Result ***
  
  Sample No.: 03-08  
  Date: 1999/10/26 10:42  
  Sample ID: Method 12

-Method No.: 12  
-Method Name: Auto Titration

-Dose Reagent Name:

-Titr. Reagent Name:

-<Blank>
  
  Blank 1: 56.154
  
  Init.Level: 69.2mV  
  Fin.Level: 204.4mL  
  Fin.Volume: 80.9mL  
  Tit.Time: 00:00:20

-<Size>
  
  Size: 3.0154g  
  MW: 1,000  
  EGN: 1,000

-Conc 1: 143.57mg/g

-End Point:
  
  Volume: 49.755mL  
  Potential: 236.1mV

-300 [mV]  
-100  
-0.000  

-64,000  
-64,000 [mL]

(Blank 1: 56.1542

-Titration parameter-

-Form: of titration  
-APB No.: the burette used in titration / Unit No.: APB Unit File number

-Detector No.: the detector used in titration / Unit of potential / Max Volume: of titration

-Wait Time: before titration starts / Direction: of titration

-Control parameter-

-End Point No.: number of EPs / End sense: of EP detection / End Point Area: EP detection area


-Data samp.Pot.: potential change of sampling signal / Data samp.Vol.: titration volume of sampling signal

-Control Speed: control mode of titration speed

-Calculation parameter-

-Calc.Type: of formula / Conc.1 formula 1 / Unit: of results

-EP No. of calculation / Temp.Comp.: temperature compensation / C1(mg/mL): concentration conversion coefficient

-K1: unit conversion coefficient / TF: factor of titration liquid / Blank1: blank level 1

TIR-99386 Ver.01 3/4
### Measurement results

<table>
<thead>
<tr>
<th>n</th>
<th>Sample (g)</th>
<th>Titration (mL)</th>
<th>Hydroxyl value (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0134</td>
<td>40.7515</td>
<td>143.37</td>
</tr>
<tr>
<td>2</td>
<td>3.0427</td>
<td>40.8803</td>
<td>140.81</td>
</tr>
<tr>
<td>3</td>
<td>3.0127</td>
<td>40.9781</td>
<td>141.30</td>
</tr>
</tbody>
</table>

*The above test results were obtained by 3 tests of the same sample.

*Red underline shows the data from page 3/4.

### 10. Summary

Hydroxyl value is expressed by potassium hydroxide in mg required to neutralize acetic acid coupled with hydroxyl group when 1 gram of sample is acetylated.

Hydroxyl value of polyol is important for quality control in production of polyurethane.

The sample measurement this time shows a good repeatability with 1% of relative standard deviation.

Precise and reliable measurement is assured by the automated potentiometry.

Hydroxyl value of polyether polyol can be perfectly measured by any of the following titration systems manufactured by Kyoto Electronics (KEM).

**[AT-610]**
- Awarded Product of Supreme Technology from Kyoto City
- Easy key entry by touch panel of large color LCD (8-inch wide)
- Simultaneous titration in parallel
- Both potentiometric and Karl Fischer moisture titration (coulometric・volumetric) can be performed at a time.

**[AT-510]**
- Compact and cost performance model
- PC card expands data memory for convenience and versatility.

**[AT-500N-1]**
- Low cost and high performance
- Easy view with back light LCD
- GLP/GMP conformed model

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