ISONATE
Pure and Modified Test Procedures

Pure and Modified
This bulletin describes the non-standard test methods used to determine values for several physical properties of Isonate Pure and Modified MDI products.

Test procedures included are those for the determination of isocyanate equivalent weight, NCO content by weight, viscosity and acidity (as percent HCl).

NOTICE: The procedures described herein should not be considered validated test methods with supporting precision and bias data. Recipients of this document are cautioned to confirm the reliability of the procedures for the intended use in their own laboratory. Additionally, the information herein is presented in good faith, but no warranty, express or implied, is given, nor is freedom from any patent owned by The Dow Chemical Company or others to be inferred.

Each analyst should be acquainted with the potential hazards of reagents, products and solvents before commencing laboratory work.

SOURCES OF INFORMATION INCLUDE: MATERIAL SAFETY DATA SHEETS, LITERATURE, AND OTHER RELATED DATA. Safety information on non-Dow products should be requested from the supplier. Disposal of reagents, reactants and solvents must be in compliance with local, state and federal laws and regulations.

Contents
Determination of Isocyanate Equivalent Weight ..............2 (in toluene solution)
Determination of NCO Content by Weight ..................3
Determination of Kinematic and Absolute Viscosities .......3
Determination of Acidity (as % HCl) .........................5 (cold method)

Determination of Isocyanate Equivalent Weight (in toluene solution)
The isocyanate is reacted with dibutyl amine to form a urea. Unreacted (excess) amine is determined by backtitration with hydrochloric acid.

Equipment
1. 250-ml Erlenmeyer flasks, narrow-mouth, Pyrex brand, equipped with solid penny-head stoppers.
2. 20-ml pipet, volumetric, Class “A”, inserted through a hole in a size 9 1/2 or 10 rubber stopper up to the middle of the pipet bulb (see Figure 1).
3. 2- or 3-oz. rubber pipet bulb.
4. 50-ml buret, Class “A”.
5. Plastic transfer pipet (medicine dropper type).
6. Vacuum-insulated flask, narrow-mouth, Pyrex, 845 ml capacity. The vacuum flask should be insulated with an approximately 1 1/2-inch thickness of a rigid polyurethane foam (see Figure 1).
7. Magnetic stirrer.
9. Hot plate set at 230° ± 2°C.
10. Analytical balance, 1 milligram sensitivity.
11. Bottle-top dispenser, 1.0 to 5.0 ml delivery.
12. Fume hood.
13. Drying oven, forced-draft type, set at 65°-70°C.
14. Glassine weighing paper. Cut the paper into approximately 1/2-inch by 2-inch strips.

Chemicals
1. 2N di-n-butylamine (high-purity organic reagent) in toluene (reagent grade) solution (<300 ppm water in the solution). Preparation procedure attached.
2. Standardized 1N hydrochloric acid. The use of prestandardized 1.0000 N HCl can introduce error of 0.2 I.E. units. This effect can be neglected as long as proper care is taken to ensure the normality does not change.
3. 0.04 percent (w/v aqueous solution) bromophenol blue (as the sodium salt), reagent grade.
4. Methanol, technical grade.
Procedure

1. Dry an adequate number of clean 250-ml Erlenmeyer flasks for the sample(s) and a reagent “blank” solution in the drying oven for at least 30 minutes. Remove the flasks from the oven and stopper them. Allow the stoppered flasks to cool to room temperature.

2. With aid of transfer pipet, weigh the sample to the nearest milligram into a dry flask(s) from step 1. Sample size should be:

<table>
<thead>
<tr>
<th>Product</th>
<th>Sample (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>125M</td>
<td>2 ± 0.3</td>
</tr>
<tr>
<td>143L</td>
<td>2 ± 0.3</td>
</tr>
<tr>
<td>181</td>
<td>3 ± 0.3</td>
</tr>
<tr>
<td>240</td>
<td>4 ± 0.3</td>
</tr>
</tbody>
</table>

Note: Keep the flask(s) stoppered after the insertion of the sample(s) and during the sample weighing. Sample transfers of volatile isocyanates must be made in a fume hood.

3. Record the sample weight(s) in grams.

4. In a fume hood, with the aid of a rubber pipet bulb:
   A. Pipet 20 ml of the 2N di-n-butylamine solution into the Erlenmeyer flask(s) containing the sample(s). Place a strip of glassine weighing paper next to the inner wall of the ground glass joint of the sample flask(s) and stopper the flask(s). Gently swirl the contents of the flask(s) in order to dissolve as much of the sample(s) as possible.
   B. Pipet 20 ml of the 2N di-n-butylamine solution into another one of the dry flasks from step 1. This solution will be used as the reagent “blank.” Stopper the flask in the same way as the sample flask(s) in step 4A.

5. Place the sample solution flask(s) and the “blank” solution flask on the hot plate. The solution should start to boil in approximately two minutes. Allow the boiling to continue in each flask until the reflux line of the vapor condensate extends one inch above the liquid level.

6. Remove the flasks from the hot plate and gently swirl the contents of each flask several times.

7. Allow the flasks and contents to cool to room temperature.

8. Remove the stopper and strip of paper from each flask. Wash each stopper several times with methanol and allow each wash to drain into its respective flask. Discard the strips of paper.

9. Using the bottle top dispenser (item 11), place 1 ml of 0.04 percent bromophenol blue indicator solution into each flask.

10. By measuring with the volume graduations on the flasks, fill each flask with methanol to the 150 ml mark.

11. Carefully place a stirring bar in each flask.

12. Place the “blank” solution flask on the magnetic stirrer. Start the magnetic stirrer and set the stirring speed as high as possible without causing splashing of the solution.

13. Titrate the “blank” solution with standardized 1N HCl to the first appearance of a stable yellow color. The solution will change from a blue color at the start of the titration, to a bluish-green intermediate color, to a yellow color at the end point. Recognition of the end point is a matter of experience, but better-defined color changes are obtained when the standard 1N HCl is titrated rapidly into the solution until the first flash of yellow color is observed. This flash of yellow color will appear within a few tenths of a milliliter from the end point.

14. Record the volume of the 1N HCl used to the nearest 0.01 ml (“blank” titration).

15. Repeat steps 12 and 13 for the sample solution(s). Record the volume of the 1N HCl used to the nearest 0.01 ml (sample titration).

Calculations

1. Isocyanate Equivalent Weight (I.E.) = \( \frac{(W)(1000)}{(V_1 - V_2)(N)} \)

Where: 
- \( W \) = weight in grams of sample from step 3
- \( V_1 \) = ml of standard HCl solution from step 14 ("blank" titration)
- \( V_2 \) = ml of standard HCl from step 15 (sample titration)
- \( N \) = normality of 1N HCl

Report the result to the nearest 0.1 I.E. units.

Note: Only one “blank” titration needs to be made for the calculation of I.E.’s of groups of samples that are analyzed at the same time.

2. If the purity of the sample(s) is required:

\[ \% \text{ Purity} (w/w) = \left( \frac{\text{I.E.} \cdot N \cdot (V_1 - V_2)}{W} \right) \]

Where: 
- I.E. = Theoretical isocyanate equivalent weight of the sample
- \( N \) = normality of 1N HCl
- \( V_1 \) = ml of 1N HCl from step 14 ("blank" titration)
- \( V_2 \) = ml of 1N HCl solution from step 15 (sample titration)
- \( W \) = weight in grams of sample from step 3

Report the result to the nearest 0.1 percent.
PREPARATION OF DI-N-BUTYLAMINE

Preparation

1. **Summary:** Add 1020 ml of di-n-butylamine (DNBA) and 70 grams of molecular sieves into a 4-liter brown glass bottle. Dilute the bottle contents to 3 liters with toluene. Decant the DNBA solution into another bottle.

2. **Chemicals:**
   A. Toluene, reagent grade
   B. Di-n-butylamine, 98 percent minimum purity
   C. Molecular sieves, Type 4A, 1/16-inch pellets

3. **Procedure for preparing 3 liters of solution:**
   (PERFORM THIS PROCEDURE IN A FUME HOOD)
   A. Obtain two 4-liter brown glass bottles equipped with screw caps.
   B. Determine and mark the 3-liter level on one of the bottles.
   C. Rinse both bottles and caps three times each with practical-grade acetone and dry them in a 65°-70°C (149°-158°F) oven for 24 hours.
   D. Remove the bottles and caps from the oven and set a cap on each bottle. Let the bottles and caps cool for a minimum of five minutes. Cap one bottle tightly and set it aside for use in Step 3J.
   E. Add 1020 ml (775.3 grams) of DNBA into the bottle with 3-liter calibration.
   F. Dilute to the mark with toluene.
   G. Add approximately 70 grams of molecular sieves into the bottle contents.
   H. Cap the bottle tightly and mix the contents by shaking the bottle vigorously for five minutes.
   I. Let the bottle stand for 24 hours.
   J. Carefully decant the toluene-DNBA solution into the other brown bottle. Cap the bottle tightly.
   K. Transfer a portion of this solution to the equipment shown in Figure 1 for use in the analytical procedure.

**DETERMINATION OF NCO CONTENT BY WEIGHT**

This value is determined by conversion of the isocyanate equivalent weight.

\[
\text{% NCO (w/w)} = \frac{\text{I.E.}}{100}
\]

Where: I.E. = Determined isocyanate equivalent weight from calculation no.1, Determination of Isocyanate Equivalent Weight procedure.

Report the result to the nearest 0.1 percent.

**DETERMINATION OF KINEMATIC AND ABSOLUTE VISCOSITIES**

The viscosity of a liquid is calculated from the time it takes a fixed volume of the liquid to flow by gravity through a capillary.

**Equipment**

1. Constant temperature bath, suitable for immersion of the viscometer tube so that the reservoir at the top of the capillary is at least five centimeters below the upper bath level. The device must be capable of maintaining the bath temperature within ±0.1°C (±32°F) of test temperature.
2. Cannon-Fenske viscosity tubes (Fig. 2). Select the size according to the expected viscosity range in the following table:
4. Electric timer or stopwatch, 0.1 second readability.

**Procedure** (Refer to Fig. 2)
1. Clean the viscometer tube with acetone or any other suitable solvent. Dry the viscometer by passing clean, dry, filtered air through the tube to remove the final traces of the solvent. Periodically, traces of organic deposits should be removed with chromic acid cleaning solution.
2. To charge the sample into the viscometer, invert the tube and apply suction with a rubber bulb to tube D, immerse tube A in the liquid sample and draw the liquid to etch mark C. Wipe clean arm A and turn the tube to its normal vertical position.
3. Place the viscometer in the holder and insert it into the constant temperature bath which is maintained at test temperature, ± 0.1°C (± 32°F).
4. Allow 30 minutes for temperature equilibrium.
5. Apply suction to tube A and draw the liquid slightly above mark B.
6. To measure the efflux time, allow the liquid sample to flow freely down past the etch mark B, measuring the time for meniscus to pass from mark B to C.

**Calculations**
1. \( V_K = (c)(t) \)
2. \( V_A = (V_K)(D) \)

Where:
- \( V_K \) = Kinematic viscosity in centistokes at test temp.
- \( V_A \) = Absolute viscosity in centistokes at test temp.
- \( c \) = Viscometer constant, centistokes/second (each tube is calibrated)
- \( t \) = Efflux time in seconds
- \( D \) = Density (g/ml) of the test material at test temp.

125M ......1.180 @ 43°C
143L .......1.214 @ 25°C
181 .........1.221 @ 25°C
240 .........1.220 @ 25°C

### Range of Viscosity in Centistokes for 35 to 100 seconds efflux time (as calculated with the approximate viscometer tube constant)

<table>
<thead>
<tr>
<th>Range of Viscosity</th>
<th>Viscometer Tube Size</th>
<th>Approximate Viscometer Tube Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5 to 10</td>
<td>200</td>
<td>0.1</td>
</tr>
<tr>
<td>8.8 to 25</td>
<td>300</td>
<td>0.25</td>
</tr>
<tr>
<td>17.5 to 50</td>
<td>350</td>
<td>0.5</td>
</tr>
<tr>
<td>42 to 120</td>
<td>400</td>
<td>1.2</td>
</tr>
<tr>
<td>87.5 to 250</td>
<td>450</td>
<td>2.5</td>
</tr>
<tr>
<td>280 to 800</td>
<td>500</td>
<td>8</td>
</tr>
<tr>
<td>1400 to 4000</td>
<td>600</td>
<td>40</td>
</tr>
<tr>
<td>3500 to 10,000</td>
<td>700</td>
<td>100</td>
</tr>
</tbody>
</table>
DETERMINATION OF ACIDITY (as percent HCl)(cold method)

This method is to be used only to test ISONATE 125M pure MDI. No method has been developed for ISONATE 181 or 240 MDI prepolymer, or for 143L MDI derivative.

Equipment

1. 250-ml Griffin beakers (graduated low form).
3. Magnetic stirrer hot plate and stirring bar coated with Teflon resin.
4. 60-minute timer.
5. Metrohm automatic titrator Model E-436, or equivalent, equipped with a 5-ml buret and a combination pH electrode.

Reagents

1. N-propanol, reagent grade.
2. Tetrabutylammonium hydroxide, 0.01N in methanol.

Procedure

1. Weigh to the nearest mg approximately 10 grams of sample into the 250-ml Griffin beaker.
2. Add 20 ml of n-propanol, and stir for 10 minutes.
3. Use the Metrohm automatic titrator and titrate with methanolic 0.01N tetrabutylammonium hydroxide using the following instrument conditions:
   A. pH control on 14 pH full scale.
   B. Titration speed 2.
   Note: Always use the automatic slope control for all titrations.
4. Titrate enough to get a complete S-curve. The inflection at the equivalence point is very sharp and should have an m.v. reading of approximately 5.3.
5. Run a blank under the same conditions as the sample, following steps 2-4.

Calculations

1. Using the evaluating ruler, determine the end-point of the titration. (The end point can also be determined by drawing tangents).
2. Read the volume of titrant from the chart, noting that this is a 5-ml buret.
   \[ \% \text{HCl} = \frac{V \times N \times 3.65}{S} \]
   \[ V = \text{ml of KOH titrant} \]
   \[ N = \text{normality of KOH titrant} \]
   \[ S = \text{sample weight in grams} \]
   Note: If an automatic titrator is not available, use a pH meter, adding titrant in increments and plotting pH versus volume. A curve can be drawn from these points and the end point determined.
FOR MORE INFORMATION
For additional information about PAPI polymeric MDI products, consult the brochure, Safe Handling and Storage of MDI-Based Isocyanates (Form No. 109-01224), or contact Dow's Customer Information Center at 1-800-441-4369. Also review the current MSDS for this product.

References
1. ASTM D-445-61-T.

Customer Notice
Dow encourages its customers to review their applications of Dow products from the standpoint of human health and environmental quality. To help ensure that Dow products are not used in ways for which they were not intended or tested, Dow personnel are willing to assist in dealing with ecological and product safety considerations. Your Dow representative can arrange the proper contacts.

For additional information in the U.S. and Canada, call 1-800-441-4DOW (4369).

Notice: No freedom from any patent owned by Seller or others is to be inferred. Because use conditions and applicable laws may differ from one location to another and may change with time, Customer is responsible for determining whether products and the information in this document are appropriate for Customer’s use and for ensuring that Customer’s workplace and disposal practices are in compliance with applicable laws and other governmental enactments. Seller assumes no obligation or liability for the information in this document. NO WARRANTIES ARE GIVEN; ALL IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE ARE EXPRESSLY EXCLUDED.

Published June 2000.