

Method of Test for
DETERMINATION OF AMINE VALUE OF CATALYST RESINS
DOTD Designation: TR 519-92

I. Scope

This method of test determines the amine value of catalyst resins for use with epoxy resins and solutions. The amine value is defined as the resins' equivalent weight per amine group.

II. Health Precautions

This procedure utilizes hazardous chemicals and solutions. Proper handling procedures and ventilation are mandatory.

III. Apparatus

- A. Adjustable speed magnetic stirrer
- B. Analytical balance - accurate to 0.0001 g
- C. Glass beakers - 150 mL, 250 mL, and 500 mL in size
- D. Graduated cylinders - 50 mL and 100 mL in size
- E. Magnetic stirring bars
- F. Microburette - 10 mL
- G. Volumetric flask - 1000 mL
- H. Hot plate
- I. Oven - capable of maintaining 100°C (212°F)
- J. Worksheet (Figure 1)

IV. Reagents and Solutions

A. Reagents

1. Glacial acetic acid (CH_3COOH)
2. Acetonitrile (CH_3CN)
3. Crystal violet indicator ($\text{C}_{25}\text{H}_{30}\text{ClN}_3$)
4. Perchloric acid (HClO_4) 72%
5. Potassium hydrogen phthalate ($\text{HOOC}_6\text{H}_4\text{COOK}$)
6. Acetic anhydride (CH_3CO)₂O

B. Solutions

1. Crystal violet indicator solution - Prepare a 0.1% solution of crystal violet in glacial acetic acid by dissolving 0.1 g of crystal violet in 100 mL of glacial acetic acid in a 250 mL beaker.

2. Perchloric acid solution - Prepare a 0.1N solution of perchloric acid in glacial acetic acid by adding 8.5 mL of 72% perchloric acid and 20 mL of acetic anhydride to 400 mL of glacial acetic acid in a 1000 mL volumetric flask. Shake well and dilute to full mark with glacial acetic acid.

V. Test Samples and Specimens

- A. Samples - shall consist of small amounts of the cure portion of paint or epoxy systems.
- B. Specimens - shall be approximately 1 g.

VI. Solution Standardization and Procedure

A. Standardization of Perchloric Acid Solution

1. Weigh approximately 0.2 g of potassium hydrogen phthalate which has been previously dried overnight at 100°C (212°F) into a 150 mL beaker on an analytical balance.
2. Record the weight to 0.0001 g as K on the worksheet (Figure 1).
3. Add 50 mL of glacial acetic acid and warm on low heat until the sample is dissolved.
4. Allow to cool and use an additional 50 mL of glacial acetic acid to wash down the side of the beaker.
5. Add 3-5 drops of crystal violet indicator.
6. Insert a stirring bar into the beaker and stir while titrating with the perchloric acid to a yellow green end point and record the amount of titrant added as P.

B. Procedure for Determining Amine Value

1. Weigh approximately 0.5 g of the test specimen in a 150 mL beaker.
2. Record the specimen weight to 0.0001 g as C (Figure 1).
3. Add 60 mL of glacial acetic acid and 40 mL of acetonitrile to the nearest 0.05 mL.

4. Add 5-6 drops of crystal violet indicator.
5. Insert a magnetic stirring bar into the beaker and stir while titrating with the standardized perchloric acid until the color changes from crystal violet to the first permanent blue that has no red tint.
6. Record the volume of titrant used to reach the end point as A.

VII. Calculations

- A. Calculate the normality of the perchloric acid solution (N) using the following formula:

$$N = \frac{K \times 1000}{204.2 \times P}$$

where:

K = weight of potassium hydrogen phthalate, g

P = volume of perchloric acid solution, mL

1000 = constant

204.2 = constant

example:

K = 0.2156 g

P = 6.25 mL

$$\frac{0.2156 \times 1000}{204.2 \times 6.25}$$

N = 0.169

- B. Calculate the amine value (V) for the cure solution using the following formula:

$$V = \left(\frac{A \times 56.1 \times N}{C \times D} \right) \times 100$$

where:

A = volume of perchloric acid solution, mL

N = normality of perchloric acid solution (from above)

C = specimen wt, g

D = % cure solids (determined by other test procedures)

56.1 = constant

100 = constant

example:

A = 3.00 mL

N = 0.169

C = 0.4327 g

D = 27.1%

$$\left(\frac{3.00 \times 56.1 \times 0.169}{0.4327 \times 27.1} \right) \times 100$$

V = 243

VIII. Report

Report the amine value to the nearest whole number.

NOTE: Due to the variations in titrations, color indications and solids determinations, the repeatability of this test method should be considered suspect only for amine value deviations of more than five.

IX. Normal Test Reporting Time

Normal test reporting time is 3 days.

1/92

EPOXY EQUIVALENT CALCULATION (TR 518)

Normality of Perchloric Acid, $N = \frac{K \times 1000}{204.2 \times P}$

Potassium hydrogen phthalate wt. + tare wt., g _____
 Tare wt., g _____
 Potassium hydrogen phthalate wt., g (K) _____
 Perchloric acid volume, ml (P) _____

Epoxy Equivalent, $E_w = \left(\frac{A \times 1000}{B \times N} \right) \times \frac{D}{100}$

Sample wt. + tare wt., g _____
 Tare wt., g _____
 Sample wt., g (A) _____
 Perchloric acid titer volume, ml (B) _____
 Normality of perchloric acid, N (N) _____
 Non-volatile vehicle, % _____
 from Base p. 1 of 5, (D) Worksheet 209 _____

AMINE VALUE CALCULATION (TR 519)

Normality of Perchloric Acid, $N = \frac{K \times 1000}{204.2 \times P}$

0.169

Potassium hydrogen phthalate wt. + tare wt., g 60.8581
 Tare wt., g 60.6425
 Potassium hydrogen phthalate wt., g (K) .2156
 Perchloric acid volume, ml (P) 6.25

Amine Value, $V = \left(\frac{A \times 56.1 \times N}{C \times D} \right) \times 100$

243

Perchloric acid titer volume, ml (A) 3.00
 Normality of perchloric acid, N (N) 0.169
 Sample wt. + tare wt., g 10.9028
 Tare wt., g 10.4701
 Sample wt., g (C) 0.4327
 Solids, %, from Cure p. 2 of 5 (D) 27.1
 Worksheet 209

Tested by: IV Date: 11-6-91

Checked by: KAC Date: 11-6-91

Project No. MATLAB Lab No. 22-999999

Figure 1