Kentucky Method 64-263-08
Dated 03/31/08

TEST METHOD FOR ANALYSIS OF CALCIUM SULFONATE

1. SCOPE

1.1 This method is designed for the determination of the calcium sulfonate content of the resin system found in calcium sulfonate structural steel coatings.

2. MATERIALS AND REAGENTS

2.1 Balance accurate to 0.001g.

2.2 High speed centrifuge

2.3 Centrifuge tubes, plastic (polypropylene) with screw caps, 50 ml

2.4 Syringes, 10 ml with slip tips

2.5 Burette, 50 ml capacity with 0.1 ml graduations

2.6 Erlenmeyer flasks, 250 ml wide-mouth

2.7 Volumetric flasks, 50 ml and 1000ml

2.8 Class A pipets: 1,2,3,4,5 and 10 ml (See 7.3)

2.9 Graduated cylinder, 50 ml

2.10 Sulfuric acid, 2.5M

2.11 Acid indicator solution (See 3.1)

2.12 Standard Sodium Dodecyl Sulfate solution

2.13 Prepared Hyamine solution (See 3.3)

2.14 Methylene Chloride, reagent grade

2.15 1:1 Heptane:Isopropyl Alcohol solution, reagent grade

2.16 Distilled water, ASTM D1193 Type II

3. PREPARATION OF STANDARD SOLUTIONS

3.1 Acid indicator solution
Dilute 40 ml of stock solution (Solution for anionic surfactant determination, formerly known as dimidium bromide-disulphine blue, BDH, see 7.4) with 400 ml of distilled water in a 1L volumetric flask and add 40 ml 2.5M sulfuric acid. Dilute to mark with distilled water and mix well.

3.2 Standard sodium dodecyl sulfate solution
Dry the sodium dodecyl sulfate @ 60•C for 2 hours, then cool in a dessicator. Accurately weigh 1.9-2.0 g sodium dodecyl sulfate to the nearest 0.001g and record weight. Dissolve in 500 ml distilled water in a 1L volumetric flask. Dilute to mark with distilled water and mix well.

3.3 Prepared Hyamine solution
Dissolve 1.37g Hyamine 1622 (benzethonium chloride) cationic surfactant (BDH, see 7.4) in 500 ml distilled water in a 1 L volumetric flask. Dilute to mark with distilled water and mix well.

4. STANDARDIZATION OF PREPARED HYAMINE SOLUTION

4.1 Pipet 10 ml of the standard sodium dodecyl sulfate solution into a 250 ml Erlenmeyer flask.

4.2 Add 20 ml methylene chloride and 40 ml acid indicator solution.

4.3 Titrate with the prepared Hyamine solution as described in Section 6.

4.4 Calculate and record the molarity of the prepared Hyamine solution (see 8.1).

5. SAMPLE PREPARATION

5.1 To analyze a calcium sulfonate coating the pigment must first be removed.

5.2 Using a syringe weigh a 5g sample of the coating to the nearest 0.001 g into a centrifuge tube. Add 15 ml 1:1 heptane:isopropyl alcohol.

5.3 Tap tube on counter or use stir rod to disperse the coating into the solvent mixture. If a stir rod is used, rinse any residue back into the tube using 1:1 heptane:isopropyl alcohol.

5.4 Centrifuge the sample to produce a minimum relative centrifugal force (RCF) of 4200 until the pigment and resin system have been completely separated (approximately 30 min). See 8.2 for calculation of RCF.

5.5 Pour the separated resin system into a labeled 50 ml volumetric flask.

5.6 Repeat the extraction procedure using only 10 ml heptane:isopropyl alcohol. Add the separated resin system from these extractions to the volumetric flask.

5.7 Gently warm volumetric flask on a hotplate to ensure solubility of the resin system. DO NOT BOIL. Stopper and mix well.

5.8 Cool flask to room temperature. Fill to mark with the solvent mixture, stopper and mix well.

5.9 Prepare samples in duplicate.

6. TITRATION PROCEDURE

6.1 Pipet 3 ml of the prepared sample into a 250 ml Erlenmeyer flask (see 7.3).

6.2 Add 20 ml methylene chloride and 40 ml acid indicator solution to the flask.

6.3 Using a burette titrate the prepared sample solution with prepared Hyamine solution (see 7.1).

6.4 Swirl flask vigorously after each titrant addition. The lower solvent layer will be pink prior to the end point.

6.5 Titrate to a pale gray end point (see 7.2).

6.6 Record mls of prepared Hyamine solution used.

6.7 Calculate % active calcium sulfonate (8.3).

6.8 Calculate relative percent difference (RPD)(8.4).

7. NOTES

7.1 To start the titration , add about ½ of the expected volume of the prepared Hyamine solution needed to complete the titration from the burette. After

a few titrations, you will know about how much to add. After this large initial addition dispense prerpare Hyamine solution in 1 ml increments.

7.2 As the end point is approached the pink color will become fainter. Reduce additions of prepared Hyamine solution to 0.1 ml. Titrate to a pale gray end point. The solvent layer will turn blue if the end point is exceeded.

7.3 The end point can be best observed and is sharpest when the volume of the prepared Hyamine solution used to reach the endpoint is between 10 and 20 ml. Since different coatings contain different amounts of active calcium sulfonate, you may have to pipet a larger or smaller aliquot from the diluted sample for titration. After the first titration, if the endpoint lies outside the optimal range alter the volume aliquoted for titration accordingly.

7.4 These specialty chemicals can be obtained through British Drug House (BDH).

8. CALCULATIONS

8.1 Calculation for Molarity of prepared Hyamine solution:

$$M = \frac{W \times 10}{V \times 288.38}$$

Where: M = Molarity of the prepared Hyamine solution (to 5 decimal places)
W = grams of sodium dodecyl sulfate used to prepare the standard solution
10 = volume in mls of standard sodium lauryl sulfate solution titrated
V = volume in mls of prepared Hyamine solution used

8.2 Calculation for Relative Centrifugal Force (RCF):

$$RCF = 0.00001118 \times r \times N^2$$

Where: RCF = Relative Centrifugal Force
r = Rotating Radius
N = Revolutions Per Minute

8.3 Calculation for % Active Calcium Sulfonate:

$$\% ACS = \frac{V1 \times M \times 50 \times 470 \times 100}{W \times V2 \times 1000}$$

Where: V1 = volume in mls of prepared Hyamine solution used to titrate standard sodium dodecyl sulfate solution
M = molarity of the Hyamine solution (to 5 decimal places)
50 = dilution volume
470 = equivalent weight of calcium sulfonate
100 = factor to convert to percent
W = sample weight
V2 = volume in mls of the prepared sample
1000 = factor to convert liters to milliliters

8.4 Calculation for Relative Percent Difference (RPD):

Reported %Active Calcium Sulfonate(ACS) = (ACS a + ACS b)/2

Where: ACSa = %ACS from duplicate a
ACSb = %ACS from duplicate b
ACS = Average of duplicate results

Calculation for Relative Percent Difference:

$$RPD = [(ACSa-ACSb)/ACS] (100)$$

9. REPORT

9.1 Report the weights of the duplicate coating samples to the nearest 0.001g.

9.2 Report the %ACS in duplicate to the nearest 0.01%. Results should be considered suspect if duplicate analyses differ by more than 5% RPD when performed by a single analyst.

APPROVED _____
DIRECTOR
DIVISION OF MATERIALS

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