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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Methods for Acid and Base Milliequivalent Content of Electrocoat Bath[1]

This standard is issued under the fixed designation D 4370; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the determination of acid and base milliequivalent contents of anodic and cathodic electrocoat baths and their ultrafiltrates.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification For Reagent Water[2]

3. Summary of Test Methods

3.1 Specimens are titrated with standard acid and alkali solutions respectively. Alternative procedures are given for determining acid and base concentrations potentiometrically or using a pH meter.

4. Significance and Use

4.1 The acid and base concentrations are a measurement of the titratable acidic and alkaline components in the electrocoat baths. These measurements are used for research, production or electrocoat bath process control.

5. Apparatus

5.1 *Automatic Potentiometric Titrator with Stirrer and Recorder*, any model.

5.2 *Analytical Balance*, with sensitivity of 0.1 mg.

5.3 *pH Meter*, any model.

5.4 *Glass and Saturated Calomel Electrodes.*

5.5 *Syringes*, 5-mL disposable.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3]

Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—References to water shall be understood to mean water conforming to Type II of Specification D 1193.

6.3 *Potassium Hydroxide Solution in Methanol*, 0.1 *N*—Prepare by dissolving 5.6 g of potassium hydroxide (KOH) pellets in 1 L of methanol. Standardize against NIST standard reference material of acid potassium phthalate No. 84 using an automatic potentiometric titrator[4] to a given end point or, alternatively, to a phenolphthalein end point.

6.4 *Hydrochloric Acid Solution*, 0.1 *N*—Prepare by mixing about 8.50 mL of concentrated hydrochloric acid (HCl) (1.19 sp gr) into a mixture of 600 mL water and 400 mL methanol. Standardize against 0.1 *N* potassium hydroxide solution (see 6.3).

6.5 *1,3-Propanediol* (Propylene Glycol) (PG).

6.6 *Tetrahydrofuran* (THF).

6.7 *Reference pH Standard Solutions*—Commercial standards of pH 4.0, 7.0, and 10.0.

7. Sampling and Sample Preparation

7.1 The sample should be obtained while the electrocoat bath is under proper circulation such that a uniform material is obtained. In case of an ultrafiltrate, the material should be thoroughly mixed or stirred prior to sampling to assure uniformity.

7.2 After sampling and prior to removing a test specimen, it is mandatory that the samples be shaken or stirred until they are homogeneous and free of any settled material. This is particularly important if there is a delay between sampling the bath and performing the test. The absence of settled material can be ascertained visually (in a transparent container) or by inserting a spatula, scraping the bottom of the container, and making sure that there is no settled matter. The shaking or stirring of

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[1] These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paint and Paint Materials.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[3] Svehla, G., *Automatic Potentiometric Titration*, Pergamon Press, 1978, p. 187.

the samples should be carried out up to the moment of taking a specimen; *this Point is Very Important.*

8. Base Concentration Content

8.1 Stir the sample very thoroughly to disperse materials that might have settled to the bottom of the container. With the aid of a syringe, withdraw approximately 5 mL of the sample quickly, weigh the full syringe to 0.1 mg, and record this weight as W_1. Transfer the entire contents of the syringe into a 100-mL beaker. Reweigh the empty syringe to 0.1 mg and record as W_2. Duplicate the procedure using a second specimen.

8.2 Add approximately 40 mL of THF/PG 80/20 mixture to the specimens in the beakers and cover, preferably with aluminum foil, to minimize evaporation of the solvent mixture.

NOTE 1—In cases where the recommended THF/PG 80/20 mixture causes precipitation of the material, substitute the same amount of an appropriate solvent or solvent mixture to a new specimen. The formation of a precipitate during the titration might foul the electrode system and mask potentiometric changes. Other solvents suitable for dilution are acetone, dimethylformamide, toluene, or methanol. Any other solvent or solvent mixture that does not cause the formation of a precipitate throughout the titration is suitable. In certain instances it may be necessary to run a titration blank and to make the appropriate corrections for the solvent.

8.3 Titrate both specimens with 0.1 *N* HCl solution using the automatic potentiometric titrator until an end point "break" is reached.[4] Add approximately 5 mL of additional titrant to complete the curve. A typical titration curve is shown in Fig. 1. Record as V_1 the volume of titrant needed for the end point.

NOTE 2—If the titration curve does not show an inflection point (end point), back titration with 0.1 *N* KOH will give an acceptable result.

9. Base Content Calculation

9.1 Calculate the base content as follows:

$$A = \frac{(V_1 \times N_1) \times 100}{(W_1 - W_2)M}$$

where:

A = milliequivalents of base per gram of nonvolatile matter,
V_1 = volume of HCl titrant used, mL,
N_1 = normality of HCl titrant,
W_1 = mass of the syringe filled with sample, mg,
W_2 = mass of the empty syringe after delivery of the specimen, mg, and
M = nonvolatile matter content, % .

10. Acid Concentration Content

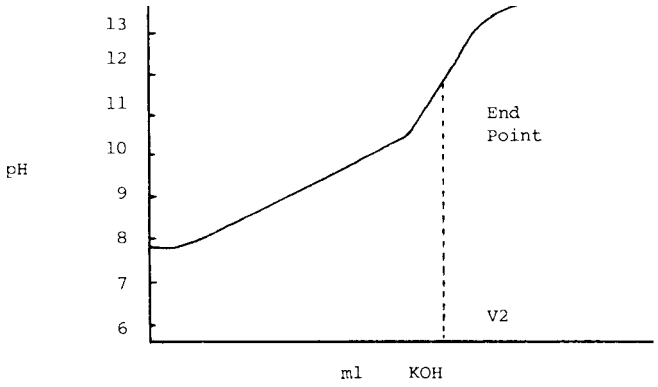
10.1 Using a fresh portion of the sample, follow 8.1 and 8.2.

10.2 Titrate both specimens with 0.1 *N* KOH solution using the automatic potentiometric titrator until an end point break is reached. Add about 5 mL more of titrant to complete the curve. From the curve, determine and record, as V_2, the volume of titrant needed for the end point.[4]

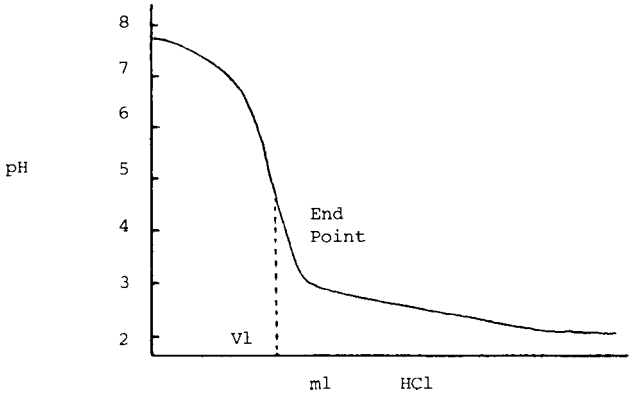
11. Acid Content Calculation

11.1 Calculate the acid content as follows:

$$A = \frac{(V_2 \times N_2) \times 100}{(W_3 - W_4)M}$$



(*a*) Acid Milliequivalent Content Titration



(*b*) Base Milliequivalent Content Titration

FIG. 1 Potentiometric Titration Curves for the Acid and Base Milliequivalent Content

where:

A = milliequivalents of acid per gram of nonvolatile matter,
V_2 = volume of KOH titrant used, mL,
N_2 = normality of KOH titrant,
W_3 = mass of the syringe filled with sample, mg,
W_4 = mass of the empty syringe after delivery of the specimen, mg, and
M = nonvolatile matter content, %.

12. Base Concentration Content Using a pH Meter

12.1 Proceed in accordance with 8.1 and 8.2.

12.2 Standardize the pH meter at 4.0 and 7.0.

12.3 Titrate both specimens with 0.1 *N* HCl until a pH of 4.0 is obtained. Make certain that the solutions are well agitated during titration (a magnetic stirrer is recommended). Record volume of titrant, as V_1, used for each titration. Because electrocoating paints vary greatly, it might be advisable to titrate to a pH value agreed upon between the producer and the user.

13. Base Content Calculation

13.1 Calculate the base content as described in Section 9.

14. Acid Concentration Content Using a pH Meter

14.1 Proceed in accordance with 8.1 and 8.2.

14.2 Standardize the pH meter at 7.0 and 10.0.

14.3 Titrate both specimens with 0.1 *N* KOH until a pH of 10.0 is obtained. Make certain that solutions are well agitated during titration (a magnetic stirrer is recommended). Record volume of titrant, as V_2 used for each.

15. Acid Content Calculation

15.1 Calculate the acid content as described in Section 11.

16. Precision

16.1 In an interlaboratory study of the test methods, in which six laboratories measured in duplicate on two days four electrocoat samples with acid and base milliequivalents ranging from 0.2 to 0.8, the within-laboratory coefficient of variation, after discarding one result, was found to be 1.4 % relative at 23 df and the between-laboratory coefficient of variation 5.7 % relative at 19 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

16.1.1 *Repeatability*—Two results, each the mean of duplicate determination, obtained by the same operator on different days should be considered suspect if they differ by more than 4.1 % relative.

16.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 17 % relative.

17. Keywords

17.1 acid content; base content; electrocoat baths