Method of determining acid number of tall oil using a potentiometric end point

Scope

This method is used to determine the acid number of crude tall oil using the potentiometric technique for determining the equivalence point of the titration.

The test is used to determine the acid number of crude tall oil (CTO) and other related products. The potentiometric method yields a more accurate value with better precision compared to the colorimetric indicator method.

The sample is dissolved in an isopropyl alcohol/toluene solvent and titrated with a standardized alcoholic potassium hydroxide to a potentiometric equivalence point.

Apparatus

1. Glass electrode pH meter. Use either standard or alkali-resistant electrodes for this test. An automatic potentiometric titrator may be used in place of a pH meter.
2. Burette, 50-mL with 0.1 mL divisions.
3. Stirrer, variable-speed with PTFE coated magnetic stir bar or other type mechanical stirrer.
4. Beaker, 400-mL.

Reagents

1. Standard alcoholic alkali (potassium hydroxide) solution, 0.5N - Purchase or prepare by dissolving 33 g of potassium hydroxide (pellets or sticks) in methyl alcohol or 39 mL of 45% KOH solution in a one liter bottle, and dilute to approximately one liter with the alcohol. Standardize to t 0.001N by dissolving approximately 2.5 g of potassium acid phthalate (KHP) in 60 mL of water followed by the addition of 40 ml. of isopropyl alcohol once the KHP has dissolved; 2.553 g of KHP will be neutralized by 25.0 mL of 0.5N KOH solution. Protect the standardized solution against evaporation and absorption of carbon dioxide (CO_2) from the air. The solution should be standardized weekly potentiometrically. The standardization should use the same equipment and techniques as used in the actual acid number determination.
2. Methanol, reagent grade.
3. Isopropanol, reagent grade.
4. Toluene, reagent grade.
5. Potassium acid phthalate (KHP), primary standard grade.
6. Buffer, pH 10, commercially available.

Procedure

1. Accurately weigh 3-5 g of sample to the nearest 0.001 g, and transfer it to a 400-mL beaker. Add 25 mL of toluene and swirl to dissolve.
2. Add 75 mL of isopropanol and swirl to mix.
3. Adjust the beaker so the lower half of each electrode of the pH meter is immersed in the solution. Add the stir bar. Start the stirrer and adjust the speed so that there is vigorous stirring without spattering.

NOTE 1: If an autotitrator is employed, follow the manufacturer's operating instructions.

NOTE 2- Glass *electrodes* read to dehydrate in nearly anhydrous solvent medium. Condition the electrode in water between tests and check with known pH buffers frequently.

4. Titrate with the standard alkali solution, recording the burette and pH meter readings. Sufficient alkali may be added initially to bring the pH of the solution to approximately 8. Allow sufficient time for the electrode system to reach equilibrium. Add alkali in 1.0 mL portions until the change in pH per increment added amounts to about 0.3 pH unit. Reduce the additions of alkali to 0.1 mL or smaller until the end point has been passed, as indicated by a significant decrease in pH units per 0.1 mL added. Continue the titration with 1.0 mL ,portions until it becomes apparent that the inflection point has been well defined.

Determine the inflection point (point of maximum change in pH per milliliter of alkali solution) to the nearest 0.05 mL by plotting the pH readings against the milliliters of alkali used. For greater accuracy, a plot may be made of the change in pH per milliliter of alkali, against the pH. The peak of this curve will indicate the exact inflection point The inflection point is considered the end point of the titration. Alternatively, if an automatic titrator is used, the end point is either the inflection point from the plotted curve or the pH determined to coincide with the inflection point in the laboratory performing the analysis.

NOTE 3: The valued 10.8 is the average pH encountered at the inflection point by the above procedure using closely controlled conditions, solvent, etc. For less accurate work, a titration directly to the pH of 10.8 may be used.

Calculation

Calculate the acid number of the sample, expressed as milligrams of KOH per gram of sample as follows, and report the value to the nearest whole number.

$$\textit{Acid number} = \frac{(A \times N \times 56.1)}{B}$$

where:

A = volume of alkali solution required for titration of the specimen, mL
N = normality of the alkali solution
B = sample weight, g
56.1 = equivalent weight of KOH and is used in the equation to express the acidity based on an equivalent amount of milligrams of KOH.

Precision Statement

Based on an ASTM round-robin study, the within laboratory (repeatability) standard deviation for this test is 0.41 and the between laboratory (reproducibility) standard deviation for this test is 1.18.

Reference

ASTM D465 "Acid Number of Naval Stores Products Including Tall Oil and Other Related Products. “

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