Method to determine unsaponifiables in tall oil

Scope

This method is used to determine the amount of unsaponifiable matter in tall oil. It is a gravimetric test for constituents which cannot be saponified by potassium hydroxide.

Apparatus

1. Erlenmeyer flask, 250-mL flat-bottom fitted with a condenser.
2. Erlenmeyer flask, wide-mouth, 300-mL capacity.
3. Separatory funnel, 500-mL capacity with glass stopper.

Reagents

1. Alcoholic potassium hydroxide solution, -2N - Dissolve 132 g of KOH in 150 m, of water and dilute to 1 L with ethanol.
2. Alcoholic potassium hydroxide solution, 0.1N - Dissolve 6.6 g of KOH in ethanol and dilute with ethanol to 1 L. Standardize against a known standard to ± 0.001N. The solution should be standardized frequently.
3. Ethyl ether - reagent grade.
4. Ethanol, 95%.
5. Isopropanol, reagent grade.
6. Phenolphthalein indicator solution, 1% in ethanol.

Procedure

1. Weigh a 5 g * 0.5 g sample to the nearest 0.001 g into a 300-mLErlenmeyer flask, add 15 mL of the alcoholic potassium hydroxide (2N).
2. Attach condenser and reflux for 90 minutes.
3. Allow the flask to cool to approximately room temperature, and add 50 mL of water.
4. Transfer the solution into a separatory funnel. Rinse the flask with 40 mL of ether, and add to the funnel.
5. Shake the funnel well, and allow to stand until the ether layer separates.
6. Draw off the aqueous soap solution (lower layer) into a second separatory funnel allowing a few drops of the water to remain above the stopcock to prevent loss of the ether layer by creeping through the ground-glass joint.
7. To the soap solution in the second separatory funnel add 30 n1L of ether and extract as before, drawing off the soap layer into the original Erlenmeyer flask. Add the ether in the second funnel to the ether in the first funnel; extract the soapy water again with 30 mL of the ether.
8. Draw the soap layer off into the Erlenmeyer flask again and add the ether layer to the first separatory funnel as before. At this time draw off all but a few drops of the soap solution which has collected below the combined ether layers in the first funnel and add to the soap solution before the final ether extraction.
9. Extract the combined soap solutions for the fourth time with 30 mL of ether and again add the ether layer to the first separatory funnel. The soap layer may now be discarded.
10. To the first separatory funnel containing the four combined ether extracts, add 2 mL of water after first drawing off any soap solution that may again have collected above the stopcock. Swirl the funnel gently and draw off the water, which may be discarded. Wash the ether layer by shaking with 5 mL of water and then with two 30 mL water washes.
11. Draw off the washed ether extract into a dry, tared wide-mouth Erlenmeyer flask. Rinse the funnel with 15 mL of ether and add to the flask. Evaporate the solvent on a steam bath. If water droplets are observed, add a few milliliters of

methanol, and continue to evaporate until a clean, dry residue is obtained.

12. Place the flask in an oven at 100° to 105°C for 10-15 minutes, or longer, if necessary. Cool in a desiccator, and weigh to the nearest 0.001 g.

Calculation

$$\textit{Unsaponiftables, \%} = \frac{A \times 100}{W} - \frac{B \times N \times 30.2}{W}$$

where:

A	=	dried residue, g
B	=	KOH solution used, mL
N	=	normality KOH solution
W	=	sample used, g
30.2	=	equivalent weight of abietic acid, a typical rosin acid/10

Report the unsaponifiable results to nearest 0. 1 %.

References

ASTM D 1065-92 "Unsaponifiable Matter in Naval Stores, Including Rosin, Tall Oil and Related Products."

TAPPI Method T 621 cm-82

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