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WI _____ 220802.10 _____

T _____ 621 _____

BALLOT NO. _____ 3 SARG _____

DRAFT NO. _____ 02 _____

DATE _____ 06/01/2023 _____

WORKING GROUP
CHAIR _____ To Be Determined _____

SUBJECT
CATEGORY _____ Chemical Properties _____

RELATED
METHODS _____ See "Additional Information" _____

CAUTION:

This method may require the use, disposal, or both, of chemicals which may present serious health hazards to humans. Procedures for the handling of such substances are set forth on Safety Data Sheets which must be developed by all manufacturers and importers of potentially hazardous chemicals and maintained by all distributors of potentially hazardous chemicals. Prior to the use of this test method, the user should determine whether any of the chemicals to be used or disposed of are potentially hazardous and, if so, must follow strictly the procedures specified by both the manufacturer, as well as local, state, and federal authorities for safe use and disposal of these chemicals.

Analysis of Rosin

Proposed RECONFIRMATION of Classical Method T 621 cm-10

1. Scope and significance

Rosin is a natural resin obtained as a vitreous water-insoluble material from pine oleoresin by removal of the volatile oils from tall oil by the removal of its fatty-acid components. It consists primarily of tricyclic monocarboxylic acids having the general empirical formula $C_{20}H_{30}O_2$, with small quantities of compounds saponifiable with a boiling alcoholic solution of potassium or sodium hydroxide and some unsaponifiable matter. The three general classifications of rosin in commerce are: (1) gum rosin, obtained from the oleoresin collected from living trees; (2) wood rosin, obtained from the oleoresin contained in dead wood, such as stumps and knots; and (3) tall-oil rosin, obtained from tall oil.

2. Sampling

2.1 Rosin is delivered in commercial bags, wooden barrels, metal drums, and tank cars. For the sampling of bags, barrels, and drums, strip off the container, leaving a solid block of rosin, and take the sample for analysis in the form of two or more lumps 76 to 102 mm (3 to 4 in.) in diameter from approximately the center of the block.

2.2 As rosin has a marked tendency to oxidize rapidly, samples should be kept in lump form. Portions for the various determinations shall be taken from the original sample lumps, crushed, and pulverized immediately before the analysis.

2.3 A preliminary sampling of 20% of the entire lot or shipment shall be made. If the color grades of 85% or more of the number of such preliminary samples agree, with none of the samples disagreeing by more than one grade, the finding shall be accepted as the grade. If the grades of more than 15% of the preliminary samples are in disagreement, or if any are under grade by more than one grade, additional packages in the lot to make up a total equal to not less than 50% of the entire shipment (preferably the entire shipment, if accessible and not too great) shall be sampled. The findings on such larger quantity shall be accepted as the grade.

NOTE 1: The packages comprising a lot of rosin which is moving or has moved in commerce from a large concentration and distributing point may represent the production of a number of different producers from widely separated localities and from gum collected at different seasons of the year and may also have been graded by a number of different graders. The difficulty of obtaining a correct appraisal of the grading of an entire lot of rosin from a too limited number of samples is thus apparent.

3. Reagents

3.1 *Neutral alcohol.* Neutralize 95% (by volume) ethyl alcohol, or Formula 30 or 3A denatured alcohol, by adding a few drops of phenolphthalein solution and then 0.5N NaOH, drop by drop until permanently faintly pink.

3.2 *Standard NaOH solution, 0.5N.* Dissolve 22.2 g of NaOH in water, dilute to 1 L, and standardize.

3.3 *Phenolphthalein indicator solution.* Dissolve 1 g of phenolphthalein in 100 mL of neutral alcohol.

3.4 *Alcoholic KOH solution, approximately 0.5N.* Dissolve 33.3 g of stick or pellet KOH in neutral alcohol and dilute to 1 L with more alcohol. Filter off any insoluble matter.

3.5 *Standard acid, 0.5N.* Accurately standardized 0.5N solution of H₂SO₄ or HCl.

3.6 *Ethyl ether, anhydrous.*

3.6.1 CAUTION! The presence of peroxides in ether constitutes an extreme safety hazard as serious explosions have resulted from laboratory work with ether containing peroxides.

3.6.2 Test for presence of peroxides using **one** of the following procedures, the first one being highly preferred and the second being used only by well trained personnel:

3.6.2.1 Peroxide test strips for determining the presence of peroxides are available from various chemical supply houses. When ordering, specify that what is required are test strips for use in detecting organic peroxide in ether.

3.6.2.2 Mix 5 mL of an aqueous solution of benzidine, saturated in the cold, with 5 mL of a saturated NaCl solution.

CAUTION: Benzidine is a recognized hazardous chemical both as a toxicant in various body organs or systems and as a carcinogen. It should be used only under supervision of persons trained in the use of such chemicals, and following all applicable safety precautions including but not limited to those in the caution statement at the beginning of this test method. Add a few drops of an extremely dilute, freshly prepared ferrous sulfate solution (a particle of FeSO_4 the size of a pinpoint dissolved in 5 mL of water). Then add 3 to 5 drops of ether to this mixture. The development of a clear blue coloration after a few minutes indicates the presence of peroxides.

3.6.2.3 Add 0.5–1.0 mL of the sample solvent to an equal volume of glacial acetic acid containing about 0.1 g of sodium iodide or potassium iodide crystals. A yellow color indicates iodine formation via iodide oxidation by sample peroxide; a brown color indicates high concentration. A blank determination should be made particularly when color development is faint since iodide/acetic acid mixtures will, over time, turn a yellow-brown color due to air oxidation.

3.7 *NaOH solution*, approximately 1%.

3.8 *Standard alcoholic KOH solution*, 0.1N. Dilute 200 mL of the 0.5N KOH solution to 1 L with neutral alcohol, mix well, filter off any insoluble matter, and standardize.

3.9 *Thymol blue or phenolphthalein indicator solution*. Dissolve 0.1g of dry indicator in 100 mL of neutral alcohol.

4. Color grade

4.1 Rosin is graded according to color. The common commercial grades, as established by the U.S. Department of Agriculture, are, in order of increasing color: X, WW, WG, N, M, K, I, H, G, F, E, D, and B. All rosin sold in interstate commerce must be described by reference to the above U.S. Standards for Rosin and is therefore subject to grading prior to such sale. Since rosin darkens on remelting, its color must be determined on a cube of the material cut from a solid lump as follows:

4.2 Cut or cleave a 22-mm (7/8-in.) cube from the original sample lump and polish the faces by a light application of a clean, heated, smooth surface (a large spatula or a heating iron). The final specimen shall have two smooth, parallel surfaces 22 mm (7/8 in.) apart. Compare the color of the prepared cube with the Official U.S. Rosin Color Standards (obtainable on security loan from the U.S. Department of Agriculture, Naval Stores Section, Production and Marketing Administration, Washington, D.C.) or with U.S. Rosin Types (obtainable from American Turpentine Farmers Association, Valdosta, Ga., at a nominal fee). Make the comparison preferably against an open, direct-north skylight or in a direction which excludes direct rays from the sun from passing through the rosin to the eye. The grade of rosin shall be considered that of the highest or lightest color standard which the sample equals or excels (is lighter than) in color.

5. Acid number

5.1 Acid number is defined as the amount in milligrams of NaOH required to neutralize 1 g of the sample. It is determined by dissolving the sample in neutral alcohol and titrating the acidity with NaOH solution to a visual phenolphthalein end point. Potentiometric titrations may be made if desired, particularly for the darker-colored rosins.

5.2 Weigh 3.95 to 4.05 g of freshly crushed rosin, to the nearest milligram, into a 250-mL Erlenmeyer flask and add 100 mL of neutral alcohol. Swirl to dissolve, warming if necessary. Cool the solution to room temperature, add 1 mL of phenolphthalein solution, and titrate with 0.5*N* NaOH to a pink color. Calculate and report the acid number to the nearest whole unit:

$$\text{Acid number} = \frac{\text{mL NaOH} \times N \times 56.1}{\text{grams of sample}}$$

where *N* = normality of the NaOH solution.

6. Saponification number

6.1 Saponification number is defined as the amount in milligrams of KOH reacting with 1 g of the sample when it is dissolved in neutral alcohol, a definite volume of alcoholic KOH solution added, the mixture refluxed for approximately 1 h, cooled, and the excess KOH titrated with standard acid. Potentiometric titrations may be made if desired, particularly for the darker-colored rosins.

6.2 Weigh duplicate portions of 3.95 to 4.05 g of the freshly crushed rosin, to the nearest milligram, into a 250-mL Erlenmeyer flask with a ground-glass joint. Add 50 mL of neutral alcohol and swirl to dissolve, warming if necessary. Pipet 50 mL of 0.5*N* alcoholic KOH solution into the flask, allowing the pipet to drain for a definite time. Connect the flask to a reflux condenser with a ground-glass joint and boil the solution gently for 50 to 60 min, starting with the point of incipient boiling. Run two blank determinations simultaneously, following the same procedure and using 50-mL portions of neutral alcohol and 50-mL portions of 0.5*N* alcoholic KOH solution measured from the same pipet, allowing it to drain for the same length of time as for the sample.

6.3 Cool the solutions, add 1 mL of phenolphthalein solution, and titrate with 0.5*N* acid to the disappearance of the pink color. Calculate and report the saponification number to the nearest whole unit:

$$\text{Saponification number} = \frac{(B - S)N \times 56.1}{\text{grams of sample}}$$

where

B = standard acid required by blanks, mL

S = standard acid required by sample, mL

N = normality of acid

7. Unsaponifiable matter

7.1 **Caution:** Because of the explosive hazard attending the use of ether, procedures involving its use should be carried out under a hood with adequate ventilation, away from open flames and exposed heating element. Be certain that the ether is free of peroxides (see 3.6).

7.2 Weigh 3.95 to 4.05 g of the sample, to the nearest milligram, into a 250- to 300-mL Erlenmeyer flask (alkali-resistant glass preferred) with ground-glass joint, add 50 mL of 0.5*N* alcoholic KOH solution, connect to a reflux condenser, and boil gently for at least 30 min. Evaporate to about 15 mL, add 10 mL of water, and boil gently until the odor of alcohol is gone. Transfer the solution while hot to a 250-mL separatory funnel, A, rinsing three times with 20-mL portions of hot water. Cool the funnel and contents under tap water and add 50 mL of ether. Shake well, and allow the layers to separate. Draw off the aqueous layer into a second separatory funnel, B. Then add 5 mL of water to Funnel A, without shaking, and again draw the aqueous layer into Funnel B.

7.3 Extract the solution in Funnel B with 50 mL of fresh ether, with thorough shaking, and, after separation, draw off the aqueous layer into a third separatory funnel, C. Add 5 mL of water to Funnel B, without shaking, and again draw the aqueous layer into Funnel C. Run the ether extract in Funnel B into Funnel A, washing Funnel B and stem with 5 mL of ether.

7.4 Extract the aqueous solution in Funnel C a third time with 50 mL of ether, as before. Draw off and discard the aqueous portion and add the ether to that in Funnel A. Add 50 mL of 1% NaOH solution to the combined ether extracts, shake thoroughly, let separate, and discard the aqueous layer. Finally, wash the ether with two 50-mL portions of water, discarding these wash solutions.

7.5 Draw the combined ether extracts into a 400-mL beaker containing about 10 g of powdered anhydrous Na₂CO₃. Rinse the funnel with 10 mL of ether, adding this ether to the beaker. Allow the solution to stand for 10 to 25 min with occasional stirring. Decant about two thirds of the ether into a clean, dried, and weighed 250-mL Soxhlet flask. Connect the flask to a water condenser by means of a one-hole rubber stopper and glass tube and distill off most of the ether on a steam bath. (The ether may be recovered for further use). Let the flask cool and decant into it the rest of the ether from the beaker. Then break up the caked Na₂CO₃ with a stirring rod, wash it with two 15-mL portions of ether, and decant them into the flask. Again connect the flask to the condenser and distill off the ether. Disconnect the flask and let it stand on the steam bath until the odor of ether is gone. Dry the flask and contents to constant weight (30 min is usually sufficient) in an oven at 100 to 105°C. Remove from the oven, cool to room temperature in a desiccator, and weigh. Calculate the percentage of dry extracted matter.

7.6 Dissolve the extract in 50 mL of neutral alcohol, add 1 mL of phenolphthalein or thymol blue indicator solution, and titrate the acidity with 0.1*N* alcoholic KOH solution. Calculate and report the percentage of unsaponifiable matter to the nearest 0.1.

7.7 *Calculation:* Let E = per cent of dry extract; C = alcoholic KOH required for titration, mL; N = normality of alcoholic KOH, R = percent of rosin acid in extract; and U = percent of unsaponifiable matter. Then,

$$R = \frac{C \times N \times 30.2}{\text{grams of sample}}$$

and

$$U = E - R$$

8. Ash

Ignite a porcelain, a vitreosil, quartz, or platinum dish with a capacity of about 100 mL, cool in a desiccator, and weigh to 0.001 g. Add about 10 g of the sample, weighed to the nearest 0.1 g, place on a ring stand in a hood, and heat gently with a Bunsen burner until the rosin can be ignited at the surface. Remove the burner and allow the rosin to burn, reheating only as necessary to maintain a moderate flame. When the flame finally dies out, increase the heat and burn off the bulk of the carbon. Finally, ignite in a muffle at 500 to 550°C until the carbonaceous matter has been consumed. Carefully transfer the dish from the muffle to a desiccator, cover with a platinum cover, cool, remove the cover, and weigh the dish and contents to the nearest 0.001 g. Calculate the percentage of residue and report as ash to the nearest 0.01.

9. Toluene-insoluble matter

9.1 **CAUTION! This procedure requires the use of toluene, also known as methyl benzene. Toluene is reported to be a toxicant in several body organs and systems, and is a possible developmental and reproductive toxicant. Toluene, even in the reagent grade form, may contain traces of benzene, which is a reported carcinogen, as well as a toxicant in various body organs and systems. This procedure should only be performed by qualified personnel in a hood with adequate ventilation. Safety precautions including but not limited to those found at the beginning of this test method should be reviewed and carefully followed.**

9.2 This determination indicates the amount of sand, chips, dirt, bark, etc. Pulverize about 200 g of the representative material to pass a 10-mesh sieve immediately before the determination is made, and mix thoroughly. Weigh about 50 g, to the nearest 0.1 g, of the pulverized sample into a 400-mL beaker, add 150 mL of reagent grade toluene and dissolve by warming and swirling. When the rosin has dissolved, filter at once by suction through a dried and weighed Gooch crucible containing an asbestos mat. Wash the crucible and contents thoroughly with fresh, hot toluene, dry to constant containing an asbestos mat. Wash the crucible and contents thoroughly with

fresh, hot toluene, dry to constant weight at 105 to 110°C (1 h usually suffices), cool, and weigh. Calculate the percentage of toluene-insoluble matter and report to the nearest 0.1.

10. Keywords

Rosin, Color, Saponification number, Ash, Sand, Dirt, Bark, Chips, Solubility, Toluene

11. Additional information

11.1 Effective date of issue: To be Assigned

11.2 This method, formerly T 621 m-55, has been reclassified as a Classical Method. Such procedures are no longer in common use or have been superseded by advanced technology; they are technically sound, have a history of use, and contain a body of literature references that make their preservation valuable.

11.3 The primary change in the 2010 edition was to improve the safety caution information.

Your comments and suggestions on this procedure are earnestly requested and should be sent to the TAPPI Standards Department. ■