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Tall oils

Resin Acids

1. Scope and field of application

This SCAN-test Standard specifies a method for the determination of resin acids. It applies to crude and distilled tall oils, tall oil rosins, tall oil fatty acids, tall light oils and tall oil pitch.

2. References

SCAN-T 11, Acid number of tall oil.

3. Definitions

Resin acid: A group of monocarboxylic organic acids with a skeleton formed by the combination of four isoprene molecules. Most resin acids have three six-membered carbon rings (phenanthrene configuration) and two double bonds and thus correspond to the general formula $C_{19}H_{29}COOH$. This is the case for the most abundant acids in Scandinavian coniferous trees.

Resin acids content (of tall oil): The quotient of the mass of the resin acids and the mass of the whole sample, excluding water. The quotient is normally expressed as a percentage.

4. Principle

The procedure described in this Standard depends on acidimetric titration of the free acids remaining after a pretreatment in which fatty acids, but not resin acids, are esterified.

The esterification procedure is that described by Linder and Persson (10). To a very small extent resin acids will be esterified and to a similar small extent fatty acids will escape esterification. This is corrected for in the calculation.

5. Apparatus

5.1 *Esterification apparatus,* consisting of the following parts:

5.1.1 *Conical flasks,* 250 ml capacity and having a standard tapered ground joint (B 29 or equivalent).

5.1.2 *Water trap,* in principle as shown in Figure 1, having standard tapered joints (B 29 or equivalent) at both ends.

5.1.3 *Condenser,* water cooled, 300 mm long, having a standard tapered joint to fit the water trap.

5.2 *Titration equipment,* including:

5.2.1 *Burette,* 50 ml capacity, suitable for use with ethanolic potassium hydroxide solution and readable to the nearest 0.1 ml.

5.2.2 *Magnetic stirrer* with a coated magnet.

5.2.3 *pH-meter,* with an alkali-resistent glass electrode, readable to the nearest 0.05 pH unit. Calibrate and check the pH-meter as described in SCAN-T 11.

6. Reagents

6.1 *Esterification solution.* In a distillation flask, mix 500 ml of n-butanol, C_4H_9OH, 500 ml of toluene, $C_6H_5CH_3$, and 6 g (3.3 ml) of concentrated sulphuric acid (H_2SO_4, density 1840 kg/m^3). Connect the water trap (5.1.2) and the condenser (5.1.3) to the flask. Boil the mixture under reflux until no more water can be collected in the water trap, which normally takes about 30 min.

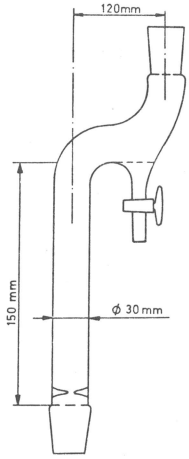

Figure 1.
Water trap (5.1.2)

6.2 *Ethanolic potassium hydroxide solution,* 0.5 mol/l, prepared and standardized as described in SCAN-T 11.

6.3 *Ethanol,* about 95 per cent C_2H_5OH.

7. Procedure

Shake the gross sample in its storage bottle and weigh a sample in a conical flask (5.1.1) to the nearest milligram. The size of the sample is chosen as indicated in the table below:

Expected resin acids content, per cent	< 2	2–5	5–50	> 50
Recommended sample size, grams	8–10	5–8	2–5	2

Add 50.0 ml of the esterification solution and a few boiling stones.

Connect the water trap and the reflux condenser to the flask, place it on a hot plate, heat to boiling and reflux for 20 min.

Allow the apparatus to cool somewhat. Remove the flask and cool it under running tap water to room temperature.

Transfer the contents of the flask to a 300 ml beaker, using a total of 100 ml ethanol for at least 5 successive rinsings.

Ensure that the pH-meter (5.2.3) is in calibration. Rinse the electrodes, first with distilled water and then with a mixture of 10 ml of distilled water and 100 ml of ethanol.

Fill the dry burette with the standardized potassium hydroxide solution (6.2) and place it so that the tip is close to the surface of the sample solution. Immerse the electrodes in the solution, and adjust the magnetic stirrer (5.2.2) to mix well without splashing.

Record the initial pH. Add portions of the potassium hydroxide solution, allowing the pH reading to stabilize and recording it and the burette reading after each addition. Plot the pH-readings against the added volume of potassium hydroxide solution. Two inflection points will be obtained, the first in the pH range 3.0–5.5 and the second in the range 10.0–11.5. Decrease the size of the portions when near an equivalence point. Record the potassium hydroxide consumption at the two inflection points as b and a millilitres, respectively.

NOTE. – An automatic titrator may be used provided it gives accuracy as good as or better than as the manual titration described above. The same titrator should then be used when standardizing the ethanolic potassium hydroxide solution.

8. Calculation

Calculate the resin acids content of the sample from the following expression

$$X = 31.51\ c\ (a-b)/w - 0.1$$

where

a = volume of ethanolic potassium hydroxide solution consumed at the second inflection point, in millilitres.
b = volume consumed at the first inflection point, in millilitres.
c = concentration of the ethanolic potassium hydroxide solution, in moles per litre.
w = mass of sample, in grams.
X = the resin acids content expressed as a percentage.

The numerical factor 31.51 contains the relative molecular mass of the resin acids, 302.4, an empirical factor 1.042 to correct for unwanted esterification of resin acids and the factor 0.1 required to express the result as a percentage.

The term 0.1 subtracted to correct for the error due to incomplete esterification of fatty acids.

9. Report

The test report should include reference to this SCAN-test Standard and the following particulars:

(a) date and place of testing,
(b) identification mark of the material tested,
(c) the results,
(d) any departure from the standard procedure or any other circumstances that may have affected the results.

10. Literature

Linder, Å. and Persson, U.: Determination of Rosin Acids in Mixture with Fatty Acids. J. Am. Oil Chem. Soc. *34*(1957), 24–27.

APPENDIX

In routine a titration with phenolphthalein indicator is sometimes used instead of the potentiometric titration in the standard procedure. It is not applicable to samples of dark colour.

When this procedure is used, a blank should be run. The blank is prepared by treating 50.0 ml of the esterification solution in exactly the same manner as a sample solution.

The esterification is carried out as described under Procedure. When the flask has been cooled to room temperature, add a few drops of phenolphthalein indicator (1 per cent ethanolic solution). Titrate with the ethanolic potassium hydroxide solution (6.2) to a pink end point.

Calculate the result using the same expression as given in Section 8. Let a represent the volume of ethanolic potassium hydroxide solution consumed in the sample titration and b that of the blank.

This modified procedure should give results similar to those obtained by the standard method, but it cannot be considered as complying with the Standard and if it is used this should be stated in the report.

SCAN testing standards are issued and recommended by the Central Laboratories of the Pulp, Paper and Board Industries in Denmark, Finland, Norway and Sweden. Distribution: Secretariat, Scandinavian Pulp, Paper and Board Testing Committee, Box 5604, S-114 86 Stockholm, Sweden.