SCANDINAVIAN PULP, PAPER AND BOARD
TESTING COMMITTEE

SCAN-T 13:74

Accepted – January 1974

DENMARK · FINLAND · NORWAY · SWEDEN · DENMARK · FINLAND · NORWAY · SWEDEN · DENMARK · FINLAND · NORWAY · SWEDEN · DENMARK · FINLAND · NORWAY · SWEDEN

UNSAPONIFIABLE MATTER IN TALL OIL

Definition

In this standard unsaponifiable matter is defined as the substance that remains unsaponified when a sample of tall oil is treated with alkali as specified (Note 1).

Scope

This standard applies in the first place to distilled tall oil and tall oil fatty acids. For other tall oil products, such as crude tall oil, tall oil rosin, tall oil pitch and tall light oil, the results of the determination may be less accurate (Note 1).

Apparatus

1. Erlenmeyer flasks, capacity 100 ml, with ground joints.
2. Reflux condensers with ground joints to fit the flasks.
3. Separating funnels, pear-shaped, 500 ml.
4. Erlenmeyer flasks, capacity 250 ml, with ground joints.
5. Condenser for distillation to fit the 250 ml flasks, water-cooled and with receiver.
6. Drying oven, ventilated, capable of maintaining an air temperature of 103°C ± 2°C.

Reagents

1. Ethanol, C_2H_5OH, 95 per cent by volume.
2. Benzene, C_6H_6.
3. Ethanolic potassium hydroxide solution, 2.0 mol/l. Dissolve 130 g of KOH in 1 litre of ethanol and adjust the molarity to 2.0 mol/l ± 0.1 mol/l. Ethanolic potassium hydroxide solution darkens when stored and has a limited shelf-life.
4. Petroleum ether, boiling point range 40°C to 60°C. If, on evaporation, 100 ml of the petroleum ether gives more than 2 mg of dry residue, it must be redistilled.
5. Ethanol, 50 per cent by volume. Dilute 500 ml of C_2H_5OH, 95 per cent, with 500 ml of distilled water.
6. Phenolphtalein indicator solution, 1 per cent. Dissolve 1 g of phenolphtalein in 100 ml ethanol.
7. Acetone, $(CH_3)_2CO$.

All reagents should be of analytical grade (*pro analysi*).

Procedure

Mix the sample thoroughly and weigh 5 g of it to the nearest milligramme in a 100-ml Erlenmeyer flask. If the sample consists of crude tall oil or if there is reason to believe that it contains more than a trace of water, weigh another sample for a determination of the water content as described in SCAN-T 7.

Add 25.0 ml of the ethanolic potassium hydroxide solution with a pipette and swirl the flask gently to dissolve the sample. If it does not dissolve completely (as in the case of, for instance, pitch samples) add about 5 ml of benzene. Connect the reflux condenser to the flask, heat on a water-bath and boil for 45 min ± 1 min. Raise the flask and condenser, cover the bath and let the reflux from the condenser drain before removing the flask. If the sample has formed sticky patches on the glass walls, discard it and repeat the procedure, adding benzene to dissolve the sample.

Add 25 ml of distilled water to the flask and mix. Transfer the mixture to a separating funnel, rinse the flask three times with portions of 50 per cent ethanol, 50 ml in all, and transfer the rinsings quantitatively to the funnel.

Add 50 ml of petroleum ether to the funnel and shake to extract the unsaponified part of the sample. When the phases have separated, run off the lower layer, which contains the saponified substances, into a second funnel. Cut the two liquid layers as exactly as possible. To the solution in the second separating funnel add another 50-ml portion of petroleum ether and extract the remaining unsaponified matter. After separation run off the lower layer into a third separating funnel. Extract it with a third 50-ml portion of petroleum ether and, after separation, run off the lower layer from the funnel and discard it.

Make the cuts as exact as possible, while taking care not to lose any petroleum ether with the lower layer. Collect the petroleum ether solutions in the first separating funnel in the following way: Transfer the contents of the second funnel to the first one. Rinse the second funnel with the contents of the third and then pour this solution into the first funnel. To remove any contaminants in the combined petroleum ether solutions, add 25 ml of 50 per cent ethanol and shake the funnel. After separation discard the lower layer. If the meniscus is not sharply defined, leave a little of the lower phase. Repeat the washing procedure twice and add to the lower layer from the third wash three times its volume of distilled water. Check that the solution is neutral by adding a few drops of phenolphthalein indicator solution. If it is not, repeat the washing procedure.

Weigh a 250-ml flask to the nearest milligramme. Transfer the washed petroleum ether solution from the funnel to the flask. Rinse the funnel with a few 10-ml portions of petroleum ether and add the rinsings to the flask. Place the flask on a boiling water-bath, attach the condenser and receiver and distil off the petroleum ether.

When all of the petroleum ether has been distilled off, remove the flask from the water-bath, add 2 ml of acetone, and dry at 103°C ± 2°C for 1 h. Allow to cool in a desiccator and weigh to the nearest milligramme.

Dry for a further 30 min and weigh again. Record both weights.

Calculation and report

Carry out two determinations and calculate the unsaponifiable matter content from the expression

$$X = 100\ (a - b)/m$$

where

a = weight of the flask with the dried residue, mean of the two weighings, g.
b = weight of the empty flask, g.
m = amount of sample taken, calculated on an water-free basis, g.
X = unsaponifiable matter, %.

If the weight change during the second drying period was less than ± 1 mg (a small increase in weight is not unusual, *e.g.* in the case of products that have been exposed to air during storage), report the result to the second decimal place. Such a weight change is usual for tall oil fatty acids and other distilled tall oils with a low unsaponifiable matter content.

If the weight change (usually a weight loss) was between 1 and 10 mg, report the result to the first decimal place. This is generally the case for crude tall oils, tall oil rosin and distilled tall oils containing a moderate amount of unsaponifiable matter, *i.e.* 2 to 10 per cent.

If the weight change exceeds 10 mg report the result to the nearest whole number. This is very often the case for tall light oils or crude tall oils containing much easily oxidized unsaponifiable matter.

Additional information

This method is based on CCA 15 and should give equivalent results. Other similar methods are ASTM D 1965—67 (2) and AOCS Ca 6a-40 (3). The methods ASTM D 803-65 (4), ASTM D 1065-56 (5) or British Standard 684 (6) use ethyl ether for the extraction and therefore generally give higher values for unsaponifiable matter in tall oils than this standard.

Note 1

Unsaponifiable matter as determined by this method includes a wide range of substances of different kinds. Compounds in, for example, crude tall oil and tall oil pitch or volatile matter in tall light oil that are insoluble in petroleum ether under the conditions of the test will be lost and will thus not be included in the value obtained as the result of the test, although they may be unsaponifiable in the true sense of the word.

Other compounds, though not actually unsaponifiable, may be difficult to saponify, and if the sample contains a large amount of such substances, the values obtained may be too high.

These facts should be borne in mind when appraising the results of the test.

Literature

1. CCA 15, Svensk Papperstidn. *49*(1946):5, 102—103.
2. American Society for Testing and Materials, 1973 Book of ASTM Standards, Part 20, p. 761—762.
3. American Oil Chemists' Society, AOCS Official method Ca 6a-40.
4. American Society for Testing and Materials, 1973 Book of ASTM Standards, Part 20, p. 318—320.
5. *ibid.* Part 20, p. 418—421.
6. British Standards Institution, British Standard 684: 1958.

This method has been published in:

Norsk skogindustri 28 (1974):3, 74—77. (English, Norwegian)
Paperi ja Puu — Papper och Trä 56 (1974):3, 218—219, 221—222, 225—226. (English, Finnish, Swedish)
Svensk papperstidning 77 (1974):3, 102—105. (Swedish, English)

SCAN testing methods 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.

1500 - 5-74 - J.N.