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BALLOT NO. _____ 03 SARG _____

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DATE _____ 6/1/2023 _____

WORKING GROUP
CHAIR _____ Don Guay _____

SUBJECT
CATEGORY _____ Pulp 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.

Specific external surface of pulp (Proposed Re-affirmation of Classical Method T 226 cm-11)

1. Scope

This method, based on the silvering method devised by Clark (1), is used to determine the specific exposed surface of unbeaten, or only slightly beaten, chemical pulps, groundwood, wood flour, and similar materials. It is not suitable for finely fibrillated or well-beaten fibers, since the silvering step causes some of the finest fibrils to collapse and hence lowers the exposed area (2).

2. Significance

2.1 Presently this is the most direct method of measuring the exposed surface of fibers. It may be used to determine the value of the constants in the formulas for quicker but less direct methods, such as those based on the Kozeny equation.

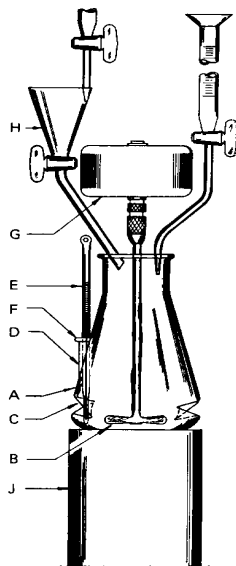
2.2 This method provides a measure of the degree of the average fineness of the material and, consequently, is greatly influenced by the quantity of debris present.

3. Definition

Specific external surface of pulp is defined as the exposed area in square centimeters per gram of moisture-free pulp.

4. Apparatus

4.1 *Reaction apparatus*¹, as shown in Fig. 1. The reaction vessel (A) is made from a 500-mL wide-mouthed Erlenmeyer flask. Two indentations (C) are made in opposite sides near the bottom to direct the swirling liquid downward. A glass tube (D) is inserted tangentially near the bottom at an angle of about 45° to hold a thermometer (E) in position so that its bulb is immersed during the reaction. Thermometer (E) is graduated from 0° to 50°C so as to permit estimation to 0.1°C. A tight rubber washer (F) on the stem of the thermometer prevents the bulb from touching the bottom, which would thus trap and hold the fibers.



¹Names of suppliers of testing equipment and materials for this method may be found on the Test Equipment Suppliers list, available as part of the CD or printed set of Standards, or on the TAPPI website general Standards page.

Fig. 1. Reaction apparatus.

4.1.1 A small vertical motor and chuck (G) is mounted to rotate the glass propeller shaft at 600 ± 50 rpm. The shaft carries a two-bladed glass propeller (B), 40 mm diameter, with blades set at an angle. It is important that the direction of rotation of the propeller be such as to cause a downward deflection of the liquid as it flows past the indentation in the reaction flask.

4.1.2 Also included are two burets of 25 mL capacity, preferably of the automatic zero type with bell mouths for easy filling, one with an extension to the delivery top; a removable support (J) for the flask; and a funnel (H) having a capacity of 30 mL or more, with a large-bore stopcock, or a funnel fitted with a short piece of plastic tubing and a pinch clamp, so that the contained liquid can be delivered quickly.

4.2 *Hot plates*, two, with analog or digital temperature control.

4.3 *Stirrer*, with a motor-driven, small glass propeller, mounted above one of the hot plates with its speed adjusted to approximately 300 rpm.

4.4 *Crucibles*, two 30-mL Jena I-I or Pyrex fritted-glass crucibles, of coarse porosity.

4.5 *Container*, for pulp suspension, 4000-mL beaker or a plastic bucket or bowl of similar capacity.

4.6 *Dipper*, approximately 200-mL capacity. Use a porcelain casserole if the container is a plastic bucket or bowl, or a plastic dipper if the glass beaker is used.

4.7 *Stopwatch or stopclock*, preferably 100 s/revolution.

4.8 *Dissecting needle*, of platinum or iridium.

4.9 *Other apparatus*: beakers, two 250-mL; rubber policeman; graduated cylinders, 25-, 100-, and 500-mL; thermometer, 0-120°C; dark-stoppered bottle, 2000-mL capacity.

5. Reagents

CAUTION: As this method is based on a catalytic reaction, scrupulous cleanliness is essential. Distilled water of unquestionable purity must be used for preparation of all reagents and of the pulp suspension. The ordinary laboratory distilled water has been found unsuitable in many instances. Impurities in the distilled water are evidenced in formation of debris on heating the diluted silvering solution in the absence of fibers (a blank test) and in excessive clumping of fibers during silvering. If redistillation is required, add a small quantity of KMnO_4 to the water in the glass distilling flask prior to distillation. Precautions should be taken that none of the KMnO_4 is carried over in the spray by using a distilling column or a flask with a long neck in which a loose plug of glass wool is inserted.

5.1 *Silvering solution*. Dissolve 200 g of reagent grade silver nitrate (AgNO_3) in 1500 mL of water. Add, with stirring, 160 mL of concentrated ammonia solution, NH_4OH . Then slowly add dilute NH_4OH (1: 9) until the brown precipitate first formed just disappears, avoiding addition of an excess. If the silvering solution is too alkaline (i.e., perfectly clear), very troublesome debris will be formed during the silvering, so that any excess ammonia should be neutralized by adding a little more AgNO_3 solution until a very faint cloudiness is visible. It is most important to prepare the solution correctly. Dilute with water to 2000 mL and store in a dark glass-stoppered bottle. This solution may be kept for periods up to 1 month.

5.2 *Potassium permanganate, 0.5N*: Dissolve 31.6 g of reagent grade KMnO_4 in about 1500 mL of water. Heat the solution at slightly below the boiling point for about an hour. Filter through glass wool to remove any manganese dioxide and dilute to 2000 mL. This solution need not be accurately standardized.

5.3 *Hydrogen peroxide, 0.5N*: Measure 25 mL of 30% H_2O_2 solution into about 750 mL of water containing 4 mL of 2N H_2SO_4 . Dilute to approximately 1000 mL. Adjust the concentration so that 24.5-25.0 mL of H_2O_2 solution are equivalent to 25.0 mL of KMnO_4 solution. This adjustment must be made daily.

5.4 *Sulfuric acid, approximately 2N*: Dilute 53 mL of concentrated H_2SO_4 to 1000 mL.

5.5 *Sodium borate buffer solution*. Add 25 g sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) to 400 mL of warm water containing 20 mL of 1N NaOH and dilute to 500 mL. Dilute 100 mL of this solution to 2000 mL.

5.6 *Nitric acid, 1 + 1 solution, HNO_3* .

5.7 *Binder-free glass microfiber filters type 934-AH*, made into a slurry with water to a consistency of approximately 3 g of glass filter/100 mL.

6. Sampling and test specimen

6.1 For air-dry pulp, weigh out a portion of approximately 1 g. Completely defiber in distilled water with a minimum amount of agitation and stirring. It is recommended that the weighed sample be soaked for an hour or more and then defibered by gently rubbing moist portions between the palms of the hand covered with rubber gloves or by stirring as gently as possible.

6.1.1 If the sample is received in slush form, defibering is unnecessary.

6.2 Filter an amount of slush pulp equivalent to approximately 1 g of moisture-free material through a coarse-porosity, fritted-glass crucible (do not apply suction until a mat is formed); wash the residue thoroughly with boiling hot, distilled water.

6.3 Remove as much as possible of the pulp pad from the crucible with the platinum needle. Add this to a beaker containing 100-150 mL distilled water, and boil for 5 min. Filter the suspension again through the crucible, wash the pad again with the hot distilled water, then place it in a 4000-mL beaker or plastic container.

6.4 Add enough distilled water to the part of the pulp in the container to give a consistency such that a volume of 110-140 mL will require 3-8 mL of KMnO_4 solution for the back titration. This volume is the most suitable for the reaction vessel. The proper consistency should be determined by making a preliminary specific surface determination by the procedure outlined below. It is desirable to have the volume of the pulp suspension about 2000 mL at this point, adjusting the concentration by adding more water or moist pulp. Table 1 may be used as a guide in estimating the approximate dilution of the pulp suspension.

Table 1. Estimates of dilution.

<i>Approximate area, cm^2/g</i>	<i>Desired consistency, grams of moisture- free pulp/1000 mL</i>
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Unbeaten pulp	7,000 - 15,000	0.25 - 0.15
Groundwood or slightly beaten pulp	15,000 - 35,000	0.15 - 0.05

6.5 Using the dipper, agitate the suspension vigorously, and quickly remove a test specimen consisting of a single portion of at least 110 but no more than 140 mL. Transfer the entire portion to a graduated cylinder and record the volume to the nearest milliliter.

6.5.1 Alternatively, add the specimen to a tared 250-mL beaker and weigh it.

7. Procedure

7.1 If not weighed in the beaker, pour the specimen into it and rinse the graduate into the beaker with a few milliliters of distilled water.

7.2 Heat to boiling by placing the beaker on a hot plate set at "high." When the liquid is boiling, place the beaker on the second hot plate positioned for using the stirrer. Introduce the stirrer and start the motor rotation at about 300 rpm.

7.3 Add 15-16 mL of silvering solution from a Mohr pipet or a 25-mL graduated cylinder. Keep the temperature of the solution during the silvering operation close to 100°C. Record the time at the addition of the silvering solution.

NOTE 1: Although the effect of light has not been established, it is desirable to avoid exposure of the solution to strong light during the silvering procedure; otherwise some debris of reduced silver may be formed.

7.4 After a total silvering period equivalent to about three times that from the addition of silvering solution to the change in color of the fibers to a dark reddish brown, remove the beaker from the hot plate. Add about 10 mL of the glass filter slurry, mix by swirling, then filter immediately on a Gooch crucible containing a 3-mm-thick glass filter mat.

NOTE 2: The time required for silvering depends upon the nature of the pulp and may vary from 5 to 60 min. In case of doubt or in testing a pulp of unusual character, it is recommended that several samples be silvered for different times. The results obtained when silvering is continued beyond a certain minimum time, unless unduly prolonged, will be found essentially identical. Microscopic examination of a few fibers removed from the suspension with a dissecting needle will be found helpful in judging the course of silvering. When complete, all elements of the fibers should appear black or very dark orange. The time of silvering beyond the minimum necessary to completely cover the fibers with a black coating of silver is not critical. However, silvering times much beyond this result in a slow decrease in area, caused by filling up of crevices in the fibers, and should be avoided; also, the fibers may become brittle and break into fine fragments during the stirring.

NOTE 3: The silvering solution should form no debris, and the silvering beaker should show only a smoky haze upon dilution of 15 mL of the solution with distilled water and heating for approximately 15 min as in the actual silvering of fibers. If the silvering solution has been properly prepared otherwise, and a troublesome debris still forms during this blank test, it may be found helpful to reflux the stock solution before use. Boil gently for 2 h under a water-cooled reflux condenser, cool, and filter through a plug of glass wool inserted in the cone of a filtering funnel.

7.5 Rinse the beaker with distilled water to transfer all the silvered fibers to the crucible, and, with the rubber policeman, push any fibers clinging to the sides of the crucible to the bottom. Add to the crucible an additional 10 mL of the glass filter slurry to form a mat on the fibers. Wash thoroughly with distilled water, taking care to wash all the soluble silver salts from the inside wall of the crucible.

7.6 When the washing is complete, remove the mat together with all silvered fibers to the reaction flask with the dissecting needle. Wipe out any fibers adhering to the crucible with a small quantity of moist glass filter on the needle. Attach the flask to the stand and add 100 mL of the diluted buffer solution.

7.7 Turn on the stirrer (previously adjusted to rotate at about 600 rpm) and stir for 15-20 s to break up the pad. During this period, add a volume of 0.5N H₂O₂ equivalent to 25.0 mL of 0.5N KMnO₄ to the special funnel after having adjusted its temperature so that the final solution is preferably 20-23°C.

7.8 Simultaneously open the funnel stopcock and start the timer at the moment the peroxide enters the solution. Rinse the funnel with 2 to 3 mL of distilled water. At the end of 20 s, record the temperature and remove the thermometer to prevent an accumulation of fibers against it. Close the funnel stopcock and place 15 mL of 2N H₂SO₄ in the funnel.

7.9 At the end of exactly 100 s from the peroxide addition, open the stopcock so as to run the acid from the funnel into the reaction flask. This will stop the reaction. Finally, rinse the funnel with water. Titrate the remaining undecomposed H₂O₂ with KMnO₄ solution. From the amount of KMnO₄ used, determine the surface area (*A*) of the sample from the calibration chart (Fig. 2) as modified by McEwen (3).

NOTE 4: If the consistency of the suspension, i.e., the weight of the specimen tested, is either too low or too high as indicated by the permanganate titration, adjust the consistency of the sample in the 4000-mL flask and repeat the procedure.

NOTE 5: To facilitate cleaning the flask later, because MnO₂ is absorbed by the glass surface and constitutes a potent catalytic inhibitor, it is advisable to run a few extra milliliters of H₂O₂ after equivalence has been reached and later to tip and rotate the flask, so as to bathe the sides of the flask with the excess peroxide.

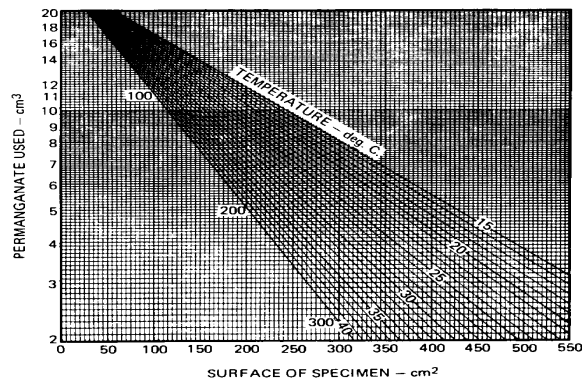


Fig. 2. Calibration chart for specific surface.

- NOTE 6:** Between determinations, the reaction flask, propeller, funnel, and thermometer should be rinsed thoroughly with distilled water. To remove deposited material from the reaction flask, treat with hot dilute HNO_3 (1:0).
- NOTE 7:** If the H_2O_2 buret does not drain cleanly, treat it with 50% NaOH solution, afterward washing it thoroughly with distilled water.
- NOTE 8:** The silvering beakers and propeller should be washed after each test with HNO_3 (1:1) to remove deposited silver.
- CAUTION:** Special care should be used in cleaning the reaction vessel, propeller, and thermometer after each test. The presence of a single drop of the end product of the previous reaction will cause a substantial reduction in the succeeding test.

7.10 Determine the consistency of the sample by filtering off the fibers contained in about 500 mL of suspension on a weighed Gooch crucible with a glass filter mat, drying to constant weight at 100-105°C, and weighing. Measure the consistency specimen with the same care used in measuring the test specimen. Thoroughly stir the pulp suspension, dip out portions with the casserole, and transfer the whole of each portion to a 500-mL graduated cylinder. Record the exact volume (V), which should be less than 500 mL.

- NOTE 9:** To obtain an accurate consistency of the pulp suspension, do not try to adjust the volume measured to a predetermined value because the pulp is usually dewatered when only a portion of the suspension is poured out of the dipper.

8. Calculations

8.1 For each of two determinations, calculate the consistency (C) of the pulp suspension, in grams per 1000 mL, from the formula:

$$C = \frac{1000 \times \text{weight of dry fibers, g}}{\text{Total volume of suspension (V)}}$$

8.2 Calculate the specific external surface from the formula:

$$S = \frac{1000 A}{CD}$$

where:

S = specific external surface, cm^2/g of moisture-free pulp

A = surface area, cm^2

C = average consistency of pulp suspension, $\text{g}/1000 \text{ mL}$

D = amount of pulp suspension tested, mL or g

9. Report

Report the specific external surface in square centimeters, or square meters, per moisture-free gram of pulp, to three significant figures. To express the result in SI units of m^2/kg , divide cm^2/g by 10.

10. Precision

10.1 Repeatability: 3%;

10.2 Reproducibility: not known;

10.3 The repeatability value was calculated from data obtained from Table J of Reference (3), based on 12 sample sizes from 11.70 through 33.10 mg of unbeaten sulfite pulp.

11. Keywords

Pulp, Specific surface, Beater, Fineness, Groundwood, Wood flour

12. Additional information

12.1 Effective date of issue: **To be assigned.**

12.2 A wide latitude in the choice of equipment, procedure, time of reaction, and strength of reacting solutions appears possible if the same conditions are followed when the calibration chart is prepared, but the adopted conditions should be meticulously followed once they have been established.

12.3 There is evidence (4) that the values obtained are likely to be satisfactory for comparative purposes, but the absolute calibration of the method with cellophane squares is somewhat uncertain.

12.4 A nomograph alignment chart somewhat simpler than Fig. 2 has been published by Davis (5) and will be found convenient where a considerable number of determinations are run.

12.5 It is suggested that if the pulp is suspected of containing impurities affecting the test, boil the sample for a half-minute successively in very dilute NaOH, very dilute HCl, and finally in water, before proceeding to step 6.2.

12.6 There have been some favorable indications that by a new technique involving the preliminary treatment of the specimen with stannous chloride, the fibers can be silvered in cold, thus avoiding coagulation of the finer elements of the fibers with boiling; however, details of the technique have not been established.

12.7 For some purposes, the specific surface of the pulp without its fine material may be of interest. Some difficulties with the procedure are obviated if this debris is first removed. The result then will be sensitive to the actual quantity eliminated, because the specific surface of the fines is relatively very large.

12.8 This 2010 revision differs from the 1965 revision in that a precision statement has been added in a previous review and the use of asbestos has been replaced with glass microfiber filters.

12.9 This method, formerly T 226 os-74, 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. An example of the advanced technology now available for determining the effective surface area of solid materials is the B.E.T (Brunauer, Emmett, and Teller) method utilizing gas adsorption and desorption isotherms.

Literature cited

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2. Emerton, H. W., Mattocks, R. E., and Blanchard, D. M. W., "A Direct Comparison of the Silvering and Permeability Methods of Determining Specific External Surface," *Tappi* **37** (2):55 (1954).
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4. Hyttinen, A., and Simonds, F. A., "A Study of the Clark Method of Determining the External Surface Areas of Pulps," U. S. Department of Agriculture, Forest Products Lab., Report on Job 1011, Project 01-7006, Oct. 10, 1952.

5. Davis, D. S., *Paper Industry - Paper World* **25** (10):1109 (1944).

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