



Standard Test Methods of Qualitative Examination of Mineral Filler and Mineral Coating of Paper¹

This standard is issued under the fixed designation D 686; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover two procedures for the qualitative determination and identification of the mineral constituents of filled and coated papers.

1.2 Due to the similarity in chemical composition and physical size and shape of some of the various possible constituents contained in a given paper specimen, more precise, quantitative methods may at times be required for positive identification.

1.3 It is recommended that one become thoroughly familiar with these test methods by analyzing paper samples of known mineral component content.

1.4 The test methods appear as follows:

Method A—Chemical Analysis	Sections 4 to 11
Method B—Microscopical Identification	2 to 19

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—These test methods are technically equivalent to TAPPI T 421 – 83.

2. Referenced Documents

2.1 ASTM Standards:

- D 585 Practice for Sampling and Accepting a Single Lot of Paper, Paperboard, Fiberboard, and Related Products²
- D 586 Test Method for Ash in Pulp, Paper, and Paper Products²
- D 921 Test Method for Titanium Dioxide in Paper³
- D 1030 Test Method for Fiber Analysis of Paper and Paperboard²

¹ These test methods are under the jurisdiction of ASTM Committee D06 on Paper and Paper Products and are the direct responsibility of Subcommittee D06.92 on Test Methods.

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² *Annual Book of ASTM Standards*, Vol 15.09.

³ Discontinued, see 1981 *Annual Book of ASTM Standards*, Part 20.

2.2 TAPPI Standards:

- T 401 Fiber analysis of paper and paperboard⁴
- T 438 Zinc and cadmium in paper and pigments⁴

Test Method A—Qualitative Chemical Analysis

3. Significance and Use

3.1 Qualitative chemical analyses of the mineral component of a paper specimen, Test Method A, serve to identify the ions of any such minerals. The results may then be interpreted in terms of the minerals themselves. Direct identification of some of these minerals or their ions is frequently possible using optical microscopical examination, Test Method B. For additional information, see the annex.

3.2 The analysis can be considerably simplified if it is desired only to establish the presence or absence of a particular filler.

3.3 A microscopical examination of the ash usually proves to be a useful adjunct to chemical analysis, and if possible should be attempted (see Sections 12 to 18).

4. Apparatus

4.1 *Crucible*, platinum, with lid, for use in 9.7.1 and in ashing the sample that is being examined. Porcelain or silica crucibles may be used if their weight does not change under the ignition conditions.

4.2 *Muffle Furnace*, electric, controlled to maintain a temperature of $525 \pm 25^\circ\text{C}$.

4.3 *Laboratory Oven*, electric, controlled to maintain a temperature of $150 \pm 3^\circ\text{C}$.

4.4 *Blowpipe*.

4.5 *Wire Loop*, platinum.

4.6 *Spot Plate*, black, glazed.

⁴ Available from the Technical Association of the Pulp and Paper Industry, Technology Park/Atlanta, P.O. Box 105113, Atlanta, GA 30348.



4.7 *Other Apparatus*—Beakers, 250-mL; watch glass; volumetric flasks, 100-mL; filter funnels and fairly rapid, low-ash filter paper,⁵ and Bunsen burner.

5. Reagents

5.1 *Acetic Acid, (Glacial, 99.7 % CH₃-COOH, sp gr 1.05)*, approximately 1 N solution. Add approximately 11.5 mL glacial acetic acid to 50 mL water in a volumetric flask and dilute to 100-mL mark.

5.2 *Ammonium Chloride Solution (NH₄OH, 10 %)*.

5.3 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH₄OH).

5.4 *Ammonium Oxalate Solution ((NH₄)₂-C₂O₄H₂O, 3.5 %)*.

5.5 *Ammonium Sulfate, (NH₄)₂SO₄*.

5.6 *Barium Chloride Solution (BaCl₂, 10 %)*.

5.7 *Charcoal Black*.

5.8 *Cobalt Nitrate Solution*—Dissolve 8 g of cobalt nitrate (Co(NO₃)₂·6H₂O) in 100 mL of water.

5.9 *Diphenylthiocarbazone (Dithizone) Solution*—Dissolve 10 mg dithizone in 100 mL carbon tetrachloride, (CCl₄).

5.10 *Hydrochloric Acid (2 N, sp gr 1.19)*—Concentrated hydrochloric acid (HCl). Add 15 mL of concentrated HCl to approximately 75 mL water in a 100-mL volumetric flask, cool, and dilute to 100-mL mark.

5.11 *Hydrogen Peroxide (30 % H₂O₂)*, or a solution of 3 % H₂O₂ used in proportionately greater quantities. Extreme caution should be used when handling 30 % H₂O₂ solution as it is very active when in contact with skin. Eye protection should be worn.

5.12 *Iodine Solution (0.1 N)*.

5.13 *Lead Acetate Paper*—Immerse strips of filter paper in a saturated solution of lead acetate (Pb(C₂H₃O₂)₂·3H₂O); withdraw from solution and allow to air dry.

5.14 *Lime Water*, saturated solution. Dissolve about 0.2 g of calcium hydroxide (Ca(OH)₂) in 100 mL of water and filter.

5.15 *Magnesium Reagent*—Dissolve 0.5 g of para-nitrobenzeneazoresorcinol in 100 mL of sodium hydroxide (NaOH) solution (1 %).

5.16 *Microcosmic Salt Solution*—Dissolve 5 g of sodium ammonium phosphate (NaNH₄HPO₄·4H₂O) in water and dilute to 100 mL.

5.17 *Morin (3,5,7,2',4'-pentahydroxyflavanone)*—Saturated solution of morin in methyl alcohol.

5.18 *Potassium Dichromate Solution (K₂Cr₂O₇, 4 %)*.

5.19 *Potassium Ferrocyanide Solution*—Dissolve 15 g of (K₄Fe(CN)₆·3H₂O) in 1000 mL of water.

5.20 *Potassium Hydroxide Solution (2 N)*—Dissolve 11.2 g of potassium hydroxide (KOH) in 75 mL water; cool and dilute to 100 mL.

5.21 *Sodium Carbonate*—Powdered sodium carbonate (Na₂CO₃).

5.22 *Sodium Hydroxide Solution (2 N)*. Dissolve 8 g (NaOH) in 75 mL water; cool and dilute to 100 mL.

5.23 *Sulfuric Acid (5 %, sp gr 1.84)*—Concentrated sulfuric acid (H₂SO₄). Add 3 mL of concentrated H₂SO₄ to 75 mL of water, cool, dilute to 100 mL.

6. Purity of Reagents

6.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Test Method A—Qualitative Chemical Analysis

7. Sampling

7.1 Obtain a sample of the paper to be tested in accordance with Methods D 585.

8. Test Specimens

8.1 From each test unit, for each complete determination, cut test specimens of sufficient size to yield at least 0.15 g of ash.

8.2 An additional specimen of each test unit should be available for testing without previous ashing.

9. Procedure

9.1 An outline scheme of the qualitative procedure is given in Fig. 1.

9.2 *Sulfite, Sulfide, and Carbonate (Unignited Coating or Paper Sample)*:

9.2.1 Treat a portion of the unignited coating or paper sample in a small beaker or test tube with 2 N HCl. Note whether effervescence takes place and the odor of any escaping gas. Liberation of SO₂ and H₂S indicates the presence of sulfites and sulfides, respectively. Warm the contents of the beaker and test the vapor with moistened lead acetate paper. The development of a metallic gray or black color confirms the presence of sulfide. In the absence of sulfides, add either a small crystal of potassium dichromate or a few drops of a 4 % dichromate solution to a small portion of the HCl solution of the sample. A green coloration indicates the presence of a reducing agent, in this case probably a sulfite.

NOTE 2—Mixtures of sulfites and sulfides are not known to be used in loading or coating paper.

9.2.2 If sulfites and sulfides are absent, effervescence alone is a good indication of the presence of a carbonate, which may be confirmed by holding a glass rod with a drop of saturated lime water just above the solution. Cloudiness (milky) appearance of the supported drop indicates the presence of CO₂. This precipitate may later dissolve. A confirmatory test of CO₂ in

⁵ Whatman No. 40, available from A. H. Thomas Co., P. O. Box 779, Philadelphia, PA 19105, or its equivalent, has been found satisfactory for these test methods.

⁶ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

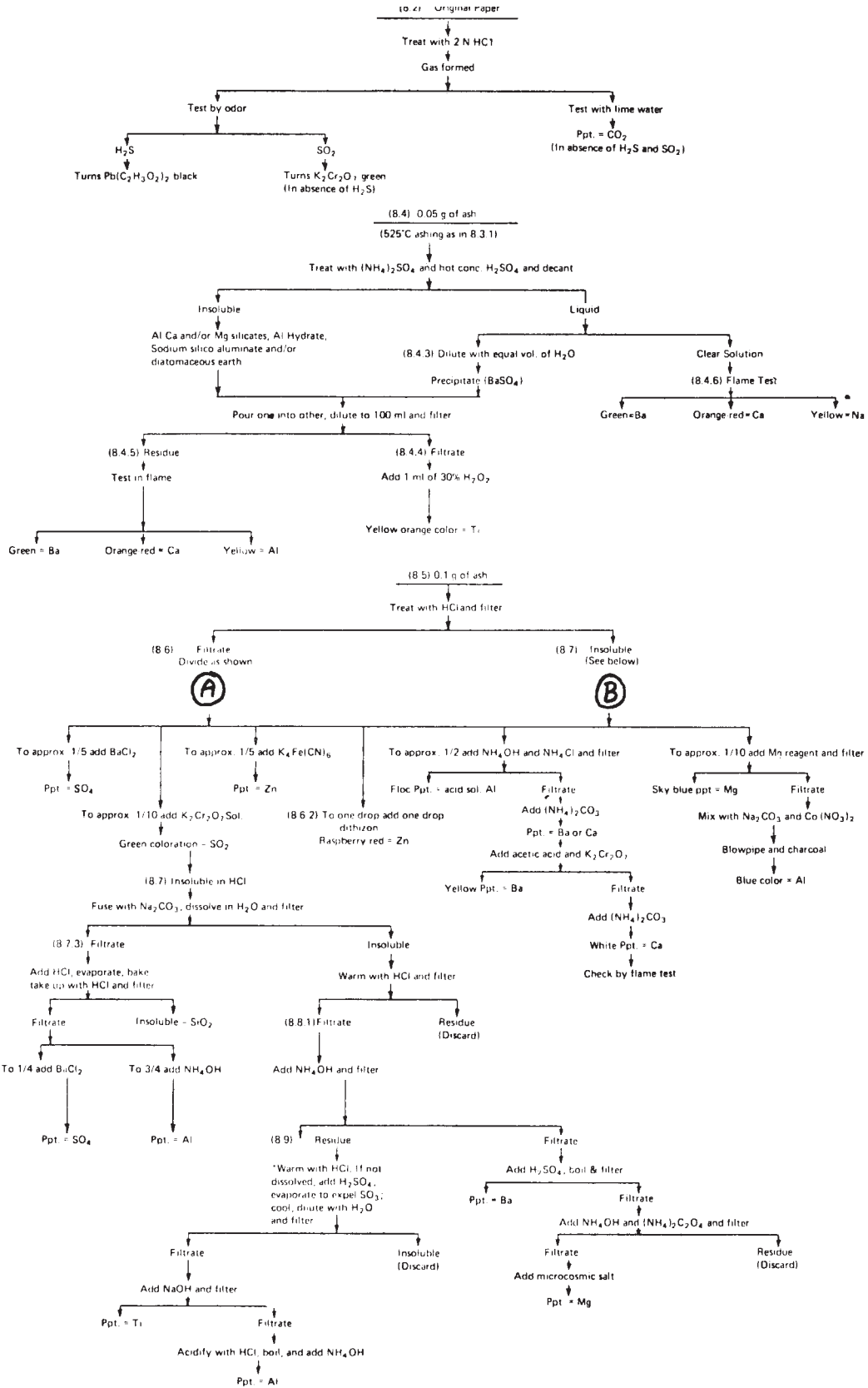


FIG. 1 Qualitative Analysis of Mineral Filler and Mineral Coating of Paper



the presence of sulfites is to oxidize the sulfites to sulfates by adding to the contents of the beaker, a weak solution of iodine (about 0.1 *M*), drop by drop, until the entire liquid is colored yellow. Then test with lime water on a glass rod as described previously in this paragraph.

9.3 Ashing:

9.3.1 Ash the specimen at a temperature of 525°C (lower than the 925°C temperature used in Test Method D 586 (see also 9.3.2)). This lower temperature is used to prevent or minimize the alteration of the composition of various coating or filling components.

9.3.2 For coated paper where separate analyses of filling material and coating minerals are desired, remove the coating by an enzymatic stripping procedure. Evaporate to dryness the aqueous mixture containing the coating minerals and ash this residue as well as the base stock in accordance with 9.3.1.

NOTE 3—If synthetic coating adhesives have been used in place of starch or casein, enzymatic stripping will not be effective. In this case, scrape the coating from the surface with a razor blade.

9.4 Aluminum Hydrate: Sodium Silicoaluminate; Al, Ca, or Mg Silicates; Ca or Ba Sulfates; TiO₂:

9.4.1 To approximately 0.05 g of ash add 10 g of (NH₄)₂SO₄ and 20 mL of concentrated H₂SO₄. Cover with a watch glass and boil vigorously for at least 3 min.

9.4.2 Considerable undissolved matter indicates the presence of one or more of the following: sodium silicoaluminate; Ca, Al, or Mg silicate; aluminum hydrate or diatomaceous earth. If this strongly acidic, hot solution is clear, the absence of these materials is confirmed. Calcium or barium sulfate, or both, will be dissolved unless the specimen being tested weighs more than 0.05 g; TiO₂ will be in the solution.

9.4.3 Decant some of the supernatant liquid into a small beaker, cool, and cautiously dilute it with a portion (up to about five times its volume) of cold water. The formation of a precipitate on dilution indicates the presence of barium sulfate, which is relatively soluble in hot concentrated H₂SO₄.

9.4.4 Mix the diluted acidic mixture (9.4.3) with the remainder of the undiluted strongly acidic mixture (9.4.2) from the concentrated H₂SO₄ treatment and add sufficient water to make the ratio of H₂O to H₂SO₄ about 5:1. If the original H₂SO₄ solution (9.4.1) was clear, dilute it 5:1 by adding water cautiously after cooling. Filter and retain any residue for examination under 9.4.5. To the cooled filtrate add 1 mL of 30 % H₂O₂. A deep yellow or orange color indicates the presence of titanium, the depth of color being proportional to the amount of titanium present. If only a very light yellow color is produced, it may be caused by titanium from clay, or derived from dissolved titanium in the mill water.

9.4.5 The presence of barium or calcium in any insoluble residue (9.4.4) can be determined by a flame test as follows: Dip a clean platinum wire into the moist residue, retained on the filter paper, and hold it in a Bunsen flame. A green flame indicates the presence of barium, a red flame indicates calcium, and a yellow to colorless flame indicates aluminum or magnesium silicates, or both, or aluminum hydrate.

NOTE 4—Calcium sulfate (CaSO₄) is quite soluble in diluted H₂SO₄ and may not be observed at this step.

9.4.6 The flame test can be used to detect soluble calcium, barium, and sodium in the clear solution obtained in 9.4.3. Cautiously dilute a small portion of the solution with an equal volume of water. Dip a clean platinum wire into the solution and hold it in a Bunsen flame. A green flame indicates barium, a red flame indicates calcium, and a strong yellow flame indicates sodium.

9.5 Sulfide, Sulfite, and Carbonate (Ash Sample Ignited at 525°C):

9.5.1 Treat 0.1 g of ash (9.3.1) with 10 mL of water and 5 mL of concentrated HCl in a small-sized beaker. Effervescence, as in 9.2.1, indicates the presence of a carbonate or sulfite. Withdraw 1 or 2 mL of the solution and add 2 drops of 4 % K₂Cr₂O₇ solution. A green coloration indicates sulfite.

9.5.2 Heat the contents of the beaker to boiling and test the fumes with moistened lead acetate paper; the development of a metallic gray or black color indicates the presence of sulfides. These tests should be checked by tests made on the original specimen of paper since carbonates may be lost. Sulfates may be reduced to sulfites or sulfides, or sulfites and sulfides oxidized to sulfates, depending on the temperature and oxidizing conditions during ignition.

NOTE 5—If the temperature of ashing is around 925°C as specified in Test Method D 586, no carbonates are present and any sulfites probably would have been oxidized to sulfates.

9.5.3 Boil the mixture for at least 5 min unless complete solution occurs sooner. Add 35 mL of water, and again heat to boiling. If this solution is not clear, filter through a fairly rapid, low-ash filter paper and wash twice with water, reserving the filtrate for analysis of the acid-soluble portion. Wash the insoluble residue thoroughly and discard the washings. Reserve the acid-insoluble portion retained on the filter paper for later treatments in accordance with 9.7.

9.6 Sulfate, Zn, Mg, Al, Ba, Ca:

9.6.1 To approximately one fifth of the acid-soluble portion from 9.5.3 add 1 mL of CaCl₂ solution. A precipitate that appears immediately or after heating for 10 min shows the presence of sulfates. To another one-fifth portion add a few millilitres of potassium ferrocyanide solution. A heavy white precipitate indicates the presence of zinc. The presence of zinc may be confirmed by the red color produced in the following dithizone test.

9.6.2 Place 1 drop of the acid-soluble portion from 9.5.3 on a watch glass and add 1 drop of 2*N* NaOH and a few drops of dithizone solution. The carbon tetrachloride (CCl₄) is evaporated by gentle blowing while stirring with a glass rod. A raspberry-red solution confirms the presence of zinc. The color of any precipitate can be disregarded.

9.6.3 To a small portion of the remaining three fifths of the filtered solution (9.5.3) (about one tenth of the total) add 1 or 2 drops of the magnesium reagent and render alkaline with NaOH solution; a sky blue precipitate indicates the presence of magnesium. However, other minerals commonly used in paper give a violet (distinguished from sky-blue) coloration to the solution. Take care not to add an excess of the reagent, because it may mask the blue precipitate if magnesium is present. If in doubt, filter the solution and examine the filter paper for the presence of a blue precipitate.



9.6.4 Mix a small portion of the filtered solution (9.5.3) with an excess of Na_2CO_3 on a charcoal block, and moisten with a very small amount of $\text{Co}(\text{NO}_3)_2$ solution. A permanent blue coloration of the melted solids upon heating with a blowpipe flame confirms the presence of aluminum. Exercise care to avoid masking the blue coloration by using an excess of $\text{Co}(\text{NO}_3)_3$ solution.

9.6.5 A more precise test for aluminum is made by adding an excess of 2N KOH to 1 mL of the acid-soluble filtrate (9.5.3) and filtering. A drop of this filtrate is acidified on a black spot plate with 2 N acetic acid and a drop of morin solution added. A green fluorescence appears in the presence of aluminum when the mixture is examined in daylight or ultraviolet light.

9.6.6 To the remainder of the filtered solution (9.5.3) add an excess of NH_4OH and NH_4Cl solutions. Aluminum will appear as a white floc if it is present in acid-soluble form. Filter any precipitate and add $(\text{NH}_4)_2\text{CO}_3$ solution to the filtrate. A white precipitate indicates the presence of barium and calcium. Without filtering, make the solution acidic with acetic acid (which dissolves the precipitate) and add $\text{K}_2\text{Cr}_2\text{O}_7$ solution. If barium is present in an acid-soluble form, a yellow precipitate occurs. Filter any precipitate (yellow) and add an excess of $(\text{NH}_4)_2\text{CO}_3$ solution. A white precipitate indicates calcium (barium having been removed during the preceding step). Check the precipitate for calcium in accordance with 9.4.5.

9.7 Silicate, Sulfate, Al:

9.7.1 Place the filter paper containing the remainder of the acid-insoluble portion from 9.5.3 in a platinum crucible. Dry, char, and ignite with free access to air until all organic matter is removed. Cool and add 1 to 2 g of Na_2CO_3 and fuse until a clear melt is obtained or until all reaction has ceased. Decompose the melt in 25 mL of hot water, heat to boiling, filter, and wash the precipitate retained on the filter paper thoroughly with water. Reserve the filtrate and the first two washings for the analyses of the water-soluble portion for silicate and aluminum (9.7.3).

9.7.2 Transfer the bulk of any insoluble portion retained on the filter paper back into the original beaker with a small jet of water. By appropriate manipulation, dissolve any precipitate, catching the acidic washings in the original beaker containing the bulk of the precipitate remaining on the filter paper by passing 10 mL of hot, dilute 1:1 HCl through it. Reserve the contents of the beaker for analysis of the water-insoluble portion in accordance with 9.8.

9.7.3 Transfer the filtrate (9.7.1) to a suitable-sized platinum dish and slightly acidify with HCl. Evaporate to dryness and bake at $150 \pm 3^\circ\text{C}$ for $\frac{1}{2}$ to 1 h. Moistened the residue with concentrated HCl, let stand a few minutes, then add 5 to 10 mL of dilute HCl, and warm. A light, flocculated, insoluble residue in the solution indicates the presence of silicate, which is best observed by viewing against a dark background. Filter off any precipitate, and to one fourth of the filtrate add BaCl_2 solution. A precipitate indicates the presence of sulfate. To the remainder of the filtrate add BaSO_4 . A white gelatinous precipitate indicates the presence of aluminum.

9.8 Al, Fe, Ba, Mg:

9.8.1 Warm the acid solution of the water-insoluble portion from 9.7.2 until no more material dissolves, add 50 mL of water, boil, and add a very slight excess of NH_4OH to precipitate aluminum (and iron). Filter any precipitate and wash; reserve the precipitate for analysis in accordance with 9.9.1. To the filtrate add 5 mL of 5 % H_2SO_4 to precipitate barium, then boil and filter. Render the filtrate ammoniacal, add a little ammonium oxalate solution to ensure the absence of calcium, filtering if any precipitate appears; then add to the cold solution 5 mL of NH_4OH and an excess of microcosmic salt solution and stir well. A precipitate appearing in 15 min indicates the presence of magnesium compounds.

9.9 Ti and Al:

9.9.1 The following is necessary only if both titanium and HCl-insoluble aluminum compounds are present and it is desired to estimate the relative proportions of titanium and aluminum. Wash the insoluble precipitate obtained by addition of NH_4OH in 9.8.1 with water, and then transfer it to the original beaker with a fine jet of water. Add 5 mL of concentrated HCl and warm. If the solution is not complete, add 4 mL of concentrated H_2SO_4 and heat until solution occurs, then drive off the SO_3 fumes over a free flame in an efficient fume hood. Cool and dilute to 35 mL with water. Any barium sulfate (BaSO_4) not decomposed by the Na_2CO_3 fusion will be insoluble at this point and should be removed by filtration. Neutralize the solution with 10 % NaOH and add an additional volume equal to that of the neutralized solution. Heat to boiling, cool, and filter. Titanium hydroxide remains insoluble. Neutralize the filtrate with HCl, heat to boiling and render slightly ammoniacal. If any precipitate forms, it is alumina trihydrate ($\text{Al}(\text{OH})_3$).

NOTE 6—Prolonged heating and boiling in this strong alkaline medium may attack the beaker slightly and dissolve silica. Any such silica at this point would lead to erroneous conclusions regarding appraisal of the aluminum content.

10. Interpretation of Observations

10.1 For the fillers listed, positive tests will be obtained in the sections indicated:

Calcium carbonate—Ca(9.6.6), CO_2 (9.2.29.2.2);

Calcium carbonate with magnesium hydroxide or carbonate—Ca (9.6.6) Mg (9.6.3) CO_2 (9.2.2);

Calcium sulfate—Ca (9.6.6), SO_4 (9.6.1);

Calcium sulfite—Ca (9.6.6), SO_2 (9.2.1);

Barium carbonate—Ba (9.6.6), CO_2 (9.2.2);

Barium sulfate—Ba (9.8.1), SO_4 (9.7.3);

Lithopone—Sulfide (9.2.1), Zn (9.6.1 and 9.6.2), Ba (9.8.1), SO_4 (9.7.3);

Zinc oxide—Zn (9.6.1 and 9.6.2);

Zinc sulfide—Zn (9.6.1 and 9.6.2), sulfide (9.2.1);

Titanium dioxide-barium sulfate—Ti (9.4.4 or 9.9.1); Ba (9.8.1), SO_4 (9.7.3);

Titanium dioxide-calcium sulfate—Ti (9.4.4 or 9.9.1), Ca (9.6.6), SO_4 (9.6.1);

Satin white (coating)—Al (9.6.4 and 9.6.5), Ca (9.6.6), SO_4 (9.6.1);

Sodium silicoaluminate—Na (9.4.6), Al (9.6.4), (9.6.5) (9.7.3), SiO_2 (9.7.3);

Aluminum hydrate—Al (9.6.4) (9.6.5) (9.6.6) (9.7.3), CO_2 (9.2.2);

Clay—Al (9.7.3 and 9.9.1), SiO_2 (9.7.3);

Diatomaceous earth— SiO_2 (9.7.3)

10.2 The use of sulfides as filling or coating materials in the paper industry is restricted to zinc sulfide alone or in combination with Ba SO_4 (lithopone). A positive test for zinc in the absence of sulfide indicates the use of zinc oxide in the paper.



A combination of the oxide and sulfide cannot be identified as such. The amount of zinc pigments in paper can be determined in accordance with TAPPI T438. The use of sulfites is restricted to calcium sulfite.

10.3 Most commercial fillers contain impurities that may lead to incorrect conclusions if only small amounts or traces of constituents are found. For example, satin white may contain carbonate; clays, especially domestic clays, contain a small quantity of titanium and clays may also contain calcium and magnesium; titanium dioxide may contain small amounts of aluminum and sulfate; calcium fillers may contain magnesium; sulfide and sulfite fillers usually contain sulfates.

10.4 The common use of alum in papermaking leads to the presence of aluminum compounds in appreciable quantities, even when fillers are absent. Small quantities or traces of calcium, magnesium sulfates, etc., are observed in many papers containing no filler and are derived from the mineral constituents of the pulp or left in the paper before drying, particularly from a mill in which the water is hard.

10.5 Carbonates together with considerable acid-soluble calcium indicate the presence of calcium carbonate that may exist as chalk or whiting. If HCl-soluble magnesium is also present, a mixture of calcium and magnesium carbonates is indicated. A combination of barium and carbonate may exist as witherite. Barium in this form will be shown in the HCl-treated portion of the ash, since barium sulfate is insoluble in dilute HCl.

10.6 A positive test for acid-soluble sulfates and calcium indicates the use of calcium sulfate as crown filler, gypsum, satin white, etc. If considerable HCl-soluble aluminum is also present in the coating, the mineral used may be satinwhite or aluminum hydrate. If carbonates are used in conjunction with sulfides, there may be a positive test for sulfates when none are present.

10.7 A positive test for calcium and sulfite indicates the presence of calcium sulfite.

10.8 The presence of considerable magnesium and silicate indicates the use of talc, agalite, or asbestine. Silica may also indicate the presence of clay or diatomaceous earth. The characteristic diatom forms may be readily recognized on microscopic examination.

10.9 The residue from the portion of the ash treated with concentrated H_2SO_4 (9.4.1) may be clay, talc, sodium silicoaluminate, calcium silicate, diatomaceous earth, aluminum hydrate, or a mixture of these substances. A positive test for aluminum indicates that clay, sodium silicoaluminate, or aluminum hydrate was used.

10.10 Barium sulfate (barytes or blanc fixe) is indicated by the formation of a precipitate on the dilution of the H_2SO_4 solution and by a positive flame test for barium on the residue.

10.11 Titanium may be present as titanium dioxide alone or mixed with barium or calcium sulfates. Titanium-barium mixtures are not likely to be found in papers made in North America after about 1960, but may be found in papers made earlier. Titanium-calcium mixtures may be found in papers made in North America and abroad.

10.12 Any of these materials may be used in conjunction with other fillers, for example, with clay. The quantitative determination of titanium pigments in paper is given in Test Method D 921.

11. Report

11.1 Report all cations and anions found, and indicate their relative amounts present such as trace, slight, considerable, large, etc. It is desirable also to interpret and report results of the analysis in terms of the fillers or mineral coating materials indicated to be present.

Test Method B—Microscopical Identification

12. Scope

12.1 This test method covers the identification of the mineral constituents of paper products by means of the optical microscope.⁷

12.2 Procedures are given for the recognition of diatomaceous earth, talc, calcium sulfate, calcium carbonate, and compounds of Ca, Zn, Ba, and Ti. Less common mineral fillers may sometimes be detected by other chemical and optical tests found in the literature.

13. Summary of Test Method

13.1 The ashing of test specimens at temperatures of around 925°C, as called for in Test Method D 586 can result in phase changes of some mineral fillers and coating pigments. Such changes may prevent direct microscopical identification of ashed samples. For this reason it is suggested that specimens be ashed at 525°C in accordance with 9.3. In addition, unashed samples should be examined for the presence of carbonates, sulfides, or sulfites in accordance with 9.2.

13.2 Before applying the method, the analyst should examine paper having a known filler content so as to become familiar with the techniques. Particular care should be taken when examining fillers containing titanium dioxide. Titanium dioxide is frequently used in combination with other fillers and because of its high index of refraction and small particle size, it sometimes masks small quantities of other fillers, such as clay or some of the precipitated fillers or pigments, making it difficult to identify them separately.

13.3 The use of waste papers in the test paper furnished may at times be determined using Test Method D 1030.

14. Significance and Use

14.1 Only very small specimens are required and tests for the presence of any one constituent can be made without preparatory separations. In many cases, the actual compounds can be recognized at once without the need to assume theoretical combinations of the cations and anions found by chemical analysis. In addition, information is also obtained as to particle size and shape.

⁷ Charmot, E. M., and Mason, C. W., *Handbook of Chemical Microscopy*, 2nd Edition, Vols I and II, New York, NY, John Wiley & Sons, Inc., 1938. Koch, H. C., Brandon, C. E., and Geohegan, K. P., "The Microscopic Identification of Paper Fillers," *Tappi*, Vol 34, No. 6, 1951, pp. 265-269. The photomicrographs in the test method are taken from this paper.



15. Apparatus

15.1 *Microscope*—A compound microscope to give magnifications between 40 and 100 diameters and between 200 and 300 diameters. More elaborate instruments with polarizers and analyzers are not essential for the procedures given, but may provide useful additional information.

15.2 *Black Light Source*, having a wavelength of 300 to 400 nm.

15.3 *Slides and Cover Glasses*—Standard slides of clear colorless glass about 25 by 75 mm with No. 2 cover glasses.

15.4 *Glass Rods*—Thin glass rods, or glass rods drawn out to tapered ends.

15.5 *Micro Burner*—A Bunsen burner equipped to give a microflame.

15.6 *Reagent Bottles*—Small bottles with droppers for solutions and small bottles with glass stoppers for solid chemicals. The hydrogen peroxide should be in a dark-colored bottle.

16. Reagents

16.1 *Acetic Acid (1 + 4)*—Add 1 part of glacial CH_3COOH (99.7 %) to 4 parts of water by volume.

16.2 *Ammonium Sulfate*, solid $(\text{NH}_4)_2\text{SO}_4$.

16.3 *Hydrochloric Acid (1 + 4)*—Add 1 part HCl (sp gr 1.19) to 4 parts water by volume.

16.4 *Hydrogen Peroxide Solution*, 3 % H_2O_2 .

16.5 *Iodic Acid*, solid HIO_3 .

16.6 *Potassium Mercuric Thiocyanate*, solid $\text{K}_2\text{Hg}(\text{SCN})_4$.

16.7 *Nitric Acid (1 + 4)*—Add 1 part HNO_3 (sp gr 1.42) to 4 parts water by volume.

16.8 *Mineral Oil*.

16.9 *Sulfuric Acid (1 + 4)*—Add 1 part H_2SO_4 (sp gr 1.84) to 4 parts water by volume.

17. Test Specimens

17.1 Ash a sample of the paper in accordance with 9.3. Use small amounts of the ash as required. Reserve a portion of the paper specimen for an unashed examination.

18. Procedure and Interpretation of Results

18.1 *Diatomaceous Earth, Talc, Clay*:

18.1.1 These materials can usually be recognized by the appearance and size of the particles.

18.1.2 Transfer a small amount of the ash to a drop of water on the slide, cover with a cover glass, and move it around with gradually increased pressure to separate the particles.

18.1.3 Diatomaceous earths are the fossil remains of microscopic plants. Chemically they are nearly pure silica (SiO_2). They are recognized by their characteristic shapes and symmetrical markings. The rods and honeycomb-like sections are often the first particles to be recognized at low magnification (Fig. 2). Higher magnifications may be necessary to show the details of some of the more intricate designs (Fig. 3 and Fig. 4).

18.1.4 Some talcs used in modern paper making are very small irregular shaped plates, sufficiently small to prevent identification based on the shape by most light microscopy techniques. Thus positive identification by observation of particle shape, etc., in this case is only available through electron microscopy.

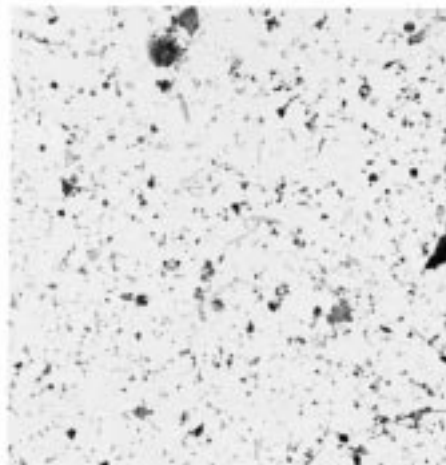


FIG. 2 Diatomaceous Earth ($\times 75$)

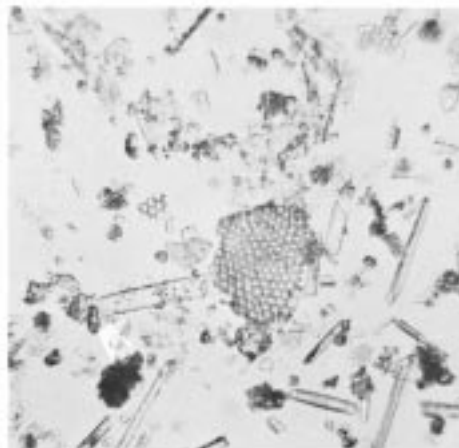


FIG. 3 Diatomaceous Earth ($\times 400$)

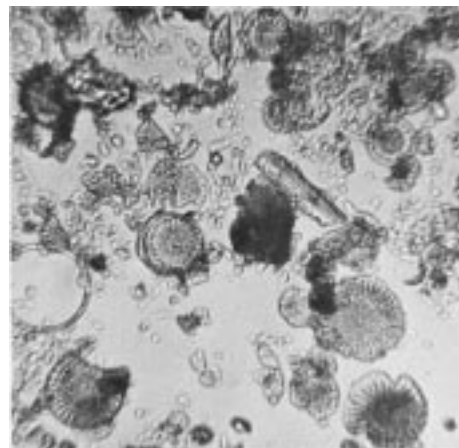


FIG. 4 Diatomaceous Earth ($\times 400$)

18.1.5 Fig. 5 gives a low magnification view of agalite talc (that is, a fibrous form of talc) which is now restricted for use in food board (paper) by the FDA. Other fibrous materials that are restricted similarly and which may be present as a major constituent or as an impurity in talc from various sources are

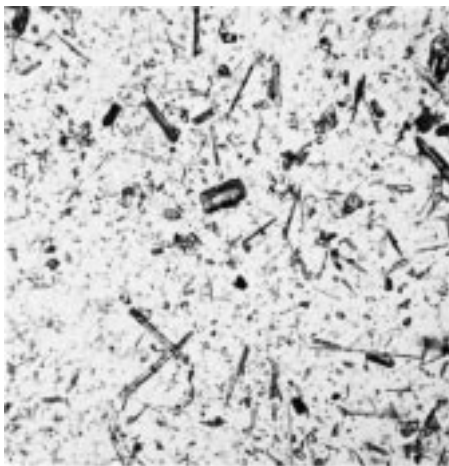


FIG. 5 Fibrous Agalite Talc ($\times 75$)

chrysotile, anthophyllite, and tremolite. Talc does not necessarily contain these fibrous materials. The absence of these allows compliance with FDA and OSHA requirements.

18.1.6 If the majority of the particles on the slide are too small to be resolved at low magnification, either clay, ultrafine talc, or a chemically precipitated filler is indicated. Any of these three are usually too small to characterize at any magnification with a light microscope. Electron micrography or X-ray diffraction gives the only positive means of identification. The particles of natural fillers are usually irregular and non-uniform in size while those of precipitated fillers are more uniform in size and shape and usually much finer.

18.1.7 Clay may sometimes be identified in the light microscope by the presence of characteristic flat plates of daolinite and mica, which are comparatively large (Fig. 6). Slowly raising the microscope tube slightly out of focus will cause some of these plates to stand out as bright areas in the field and so help to locate them. The outlines of small particles of clay, which comprise the bulk of the material, can be discerned only at higher magnifications (Fig. 7).

18.2 Calcium Compounds:

18.2.1 The presence of calcium compounds is recognized by the formation of characteristic crystals of calcium sulfate

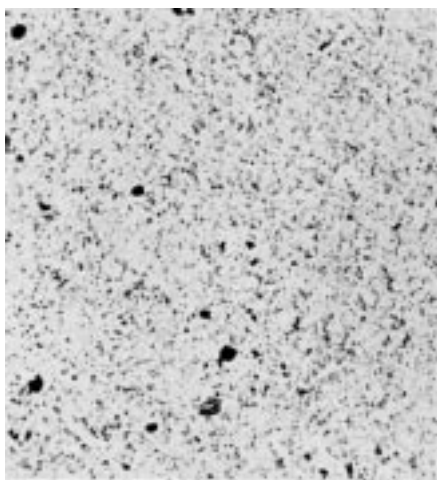


FIG. 6 Clay ($\times 75$)

(CaSO_4) or of calcium iodate ($\text{Ca}(\text{IO}_3)_2$). The more common ones used as paper fillers are calcium carbonate (CaCO_3) and CaSO_4 . The following tests will differentiate between these and also show the presence of calcium in the fillers.

18.2.2 If any effervescence occurs upon the addition of acids when preparing the slides, the presence of a carbonate, sulfide, or sulfite is indicated. Ashing at 525°C minimizes the possibility of the alteration of carbonates to oxides. In the event that effervescence is noted at this point and the presence of calcium, barium, or zinc is indicated in 18.2, 18.3, or 18.4, or any combination thereof, the observer may wish to make confirmatory tests in accordance with 9.2.

18.2.3 Treat a small portion of ash with a drop of phenolphthalein solution. A strong alkaline reaction (pink to red color) indicates the presence of calcium carbonate in the original specimen; and that the heat of ashing liberated carbon dioxide, leaving CaO .

18.2.4 To detect CaSO_4 , if present, form crystals by placing a drop of dilute HCl on one corner of a slide and add a small quantity of the specimen to it. Evaporate the drop to complete dryness above a micro-burner flame. Hold the slide slightly inclined downwards toward the drop and apply the heat near the top edge of the drop to prevent it from spreading upwards across the slide. Add a drop of water to the cooled residue. If individual and radiating clusters of needle-like crystals form, the specimen contains CaSO_4 . If the concentration of CaSO_4 happens to be low, warming the solution will hasten the crystallization. Examine the edges of the drop first—it is there that the crystallization will start. The crystals grow rapidly and as they do so, some of the needles will be seen to grow in width and finally form overlapping arrow-tail formations. These are a positive identification of calcium. A photomicrograph of CaSO_4 at low magnification is shown in Fig. 8. A group of arrow-tails appears near one corner of the field. Fig. 9 and Fig. 10 are photomicrographs at high magnification showing masses of needle-like crystals with arrow-tails fully formed, and several others in the process of forming. If the characteristic crystals do not form, prepare a new slide and add dilute H_2SO_4 directly to the evaporated residue. If the characteristic crystals then form, the presence of calcium is indicated.

18.2.5 To determine the presence of calcium ions by the iodate method, mix a small quantity of ash with a drop of water on a slide and add a small quantity of HIO_3 . The HIO_3 is dissolved in a separate drop of water, which is caused to flow into the specimen by drawing a glass rod from 1 drop into the other, accompanied by a slight tilt of the slide. The $\text{Ca}(\text{IO}_3)_2$ forms as distinctive, odorless diamond-shaped crystals (Fig. 11). It may be necessary to start crystallization by scratching the slide lightly with a glass rod, as the $\text{Ca}(\text{IO}_3)_2$ tends to form supersaturated solutions. Since the crystals may form slowly, lay aside the slide and examine it again from time to time while preparing other slides.

18.2.6 If care is taken to use only a small quantity of the HIO_3 , it may be dissolved directly in the drop of water containing the unknown. A short cut, used by experienced analysts, is to add HIO_3 to the original suspension prepared for examination for diatomaceous earth, talc, and clay. This procedure serves a threefold purpose. The HIO_3 immediately

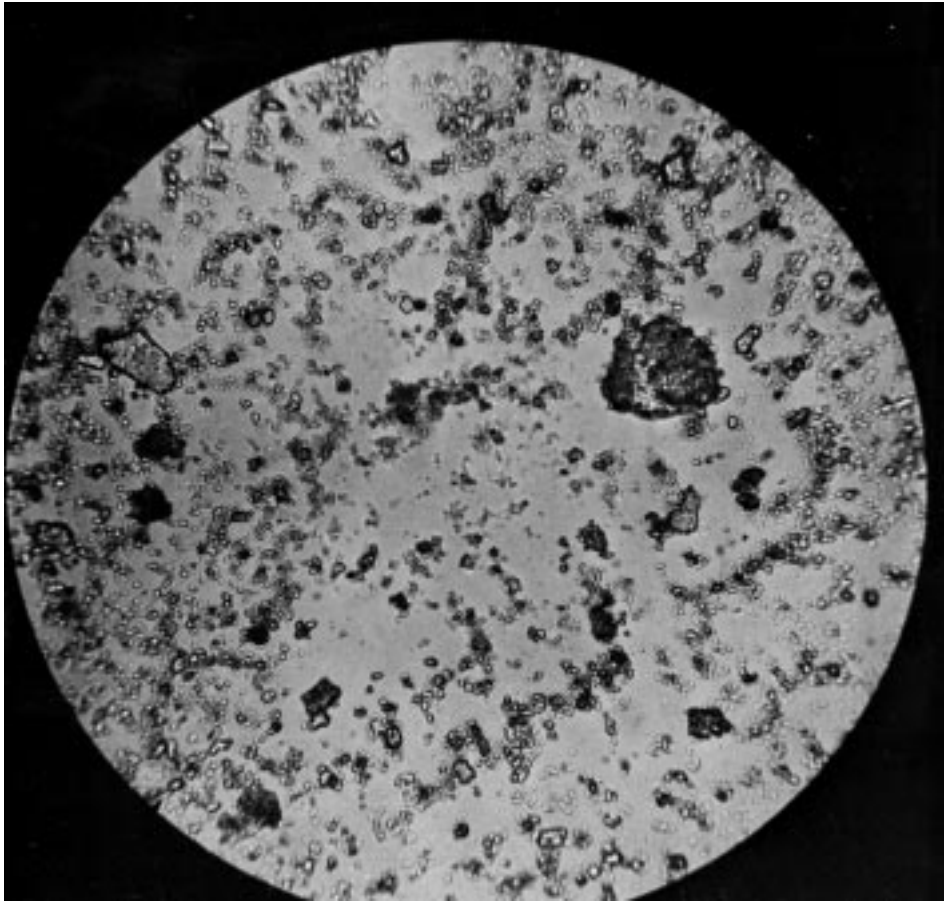


FIG. 7 Clay ($\times 400$)

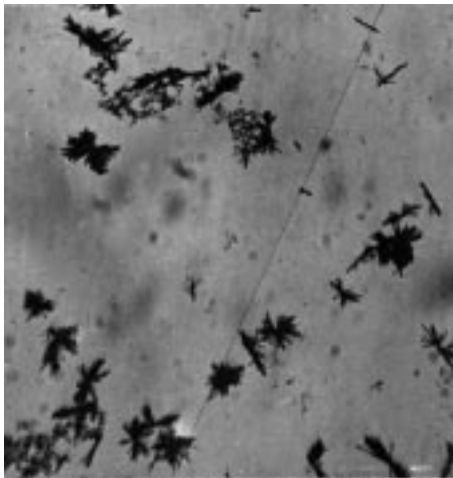


FIG. 8 Recrystallized Calcium Sulfate ($\times 75$)

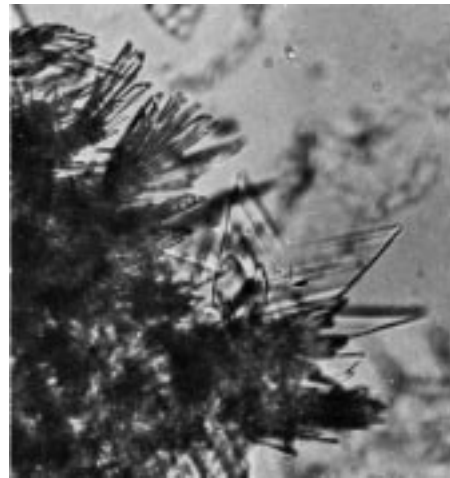


FIG. 9 Recrystallized Calcium Sulfate Showing Arrow Tails Fully Formed ($\times 400$)

indicates the presence of carbonates by causing them to effervesce; it aids in dispersing the filler particles; and it reacts as described to confirm the presence of calcium if this ion is present.

18.3 *Zinc Compounds:*

18.3.1 The presence of zinc is confirmed by the formation of characteristic crystals of zinc mercuric thiocyanate. To dissolve the zinc compounds and to avoid the possible interference by

strong acids, the sample is repeatedly evaporated to dryness with HNO_3 and is then acidified with acetic acid.

18.3.2 Add a small quantity of ash to a drop of dilute HNO_3 on one corner of a slide and evaporate to complete dryness, using the procedure described earlier. When the residue is dry and cool, add a second drop of HNO_3 and again evaporate. Repeat a third time, and then add a drop of water and acidify slightly with acetic acid. Stirring the water drop with a thin

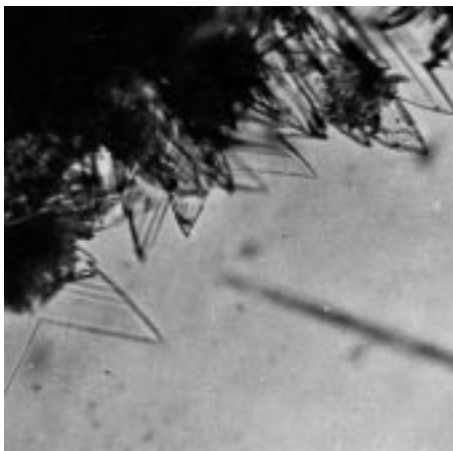


FIG. 10 Recrystallized Calcium Sulfate Showing Arrow Tails Fully Formed ($\times 400$)



FIG. 12 Zinc Mercuric Thiocyanate Crystals ($\times 75$)

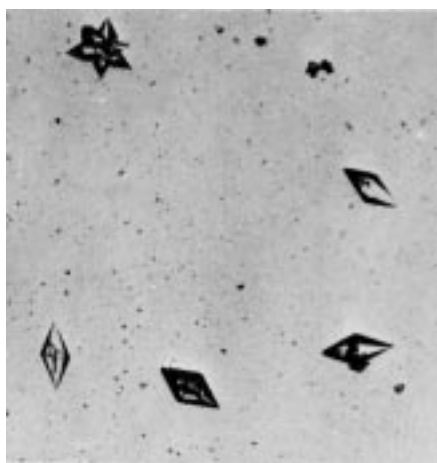


FIG. 11 Calcium Iodate Crystals ($\times 75$)

glass rod moistened with acetic acid gives good results. The right amount of acetic acid can be obtained by allowing a drop of acetic acid to run down the bottom inch or so of the rod and then shaking off any free drops.

18.3.3 In a second small drop of water on the slide, dissolve some potassium mercuric thiocyanate. Use several times as much of this reagent as that of the ash and flow this drop into it. If zinc is present, colorless crystals in the shape of feathery crosses will form (Fig. 12). Those crystals appear black by transmitted light, but white on a black background by reflected light. If numerous prisms and square tablets are obtained, repeat the test, paying more attention to the completeness of the evaporations, the concentrations of acetic acid, and the concentrations of the unknown and reagent solutions.

18.4 *Barium Compounds:*

18.4.1 Confirmation of the presence of barium compounds depends on the formation of characteristic $BaSO_4$ crystals by recrystallization from H_2SO_4 .

18.4.2 Add a very small quantity of ash to a large drop of dilute H_2SO_4 on one corner of a slide and concentrate by heating over the burner until strong white fumes appear. Do not heat the slide too rapidly. When the slide is partly cool, breathe on it a few times to start recrystallization. If barium is present,

it will be indicated by the formation of barium sulfate ($BaSO_4$) crystals, which appear as feathery crosses having a marked tendency for two of the adjacent arms to be longer than the other two (Fig. 13). These crystals may develop slowly, and considerable time should be allowed for their appearance.

18.4.3 This procedure also provides another indication of the presence of calcium. From the concentrated acid, $CaSO_4$ recrystallizes as very small rounded grains with short hairlike projections on either end.

18.5 *Titanium Compounds:*

18.5.1 The presence of TiO_2 may be indicated by the appearance of the sample when it is examined under the microscope for clay or talc. Under transmitted light, TiO_2 appears as minute pitch-black particles.

18.5.2 The addition of a small drop of mineral oil to a portion of the specimen ash on a clear glass slide, with thorough mixing of the two with a thin glass rod, greatly improves the observers' ability to detect TiO_2 particles under transmitted light by rendering other fillers having low refractive indexes, transparent. Examination of this same slide under black light of 300 to 400 nm assists in distinguishing anatase, which appears as reddish bright, from rutile, which is dull

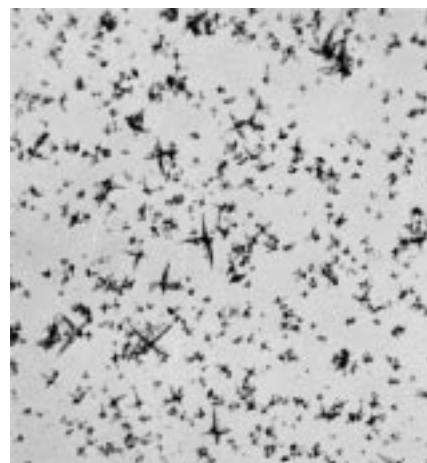


FIG. 13 Recrystallized Barium Sulfate ($\times 75$)



yellow-brown in color. Precise confirmation of the presence of rutile or anatase TiO_2 requires X-ray spectrophotometric analysis.

18.5.3 The confirming test for titanium is an adaptation of the qualitative color reaction. The microscope is not used for this test. Place a fairly large quantity of the unknown in a drop of diluted H_2SO_4 on one corner of the slide. Add solid $(\text{NH}_4)_2\text{SO}_4$ and slowly evaporate the drop until strong white fumes have appeared for several seconds. After the slide has cooled, add sufficient water to bring the drop back to approximately its original volume. Upon adding H_2O_2 to the drop on the slide, the characteristic, yellow-to-orange color will appear if titanium is present.

18.5.4 If a relatively large quantity of the ash was used and the yellow color developed is very weak, repeat the test with a lesser quantity of the ash and compare with a known sample of clay. Some clays contain sufficient titanium to show by this test when a large sample is used. Varying the quantity of sample

will, however, distinguish between the titanium naturally in the clay and that which has been added as filler.

19. Report

19.1 Report the mineral fillers present and any additional data that might be of value, such as particle size, shape, and color.

20. Precision and Bias

20.1 No statement is made about either precision or bias of these test methods since the qualitative result merely identifies the material present and its specific characteristics based on qualitative examination.

21. Keywords

21.1 aluminum; ash; barium; calcium; carbonate; chemical analysis; clay; diatomaceous earth; magnesium; microscopical examination; mineral coatings; mineral fillers; silicates; sulfates; sulfide; sulfite; talc; zinc

ANNEX

(Mandatory Information)

A1. ADDITIONAL INFORMATION

A1.1 The presence of mineral matter is indicated by the amount and appearance of the ash content of the specimen being tested. If the ash content is less than 1 % (or only slightly above), and is light and fluffy in character, added mineral filler is probably absent. If more than 1 %, and the ash is dense and compact, added filler is likely, unless waste papers have been used in the furnish. At times this may be determined microscopically as outlined in TAPPI T 401.

A1.2 Some mineral fillers or coating pigments, or both, are altered chemically during specimen ashing. Carbonates, sulfites, and sulfides are examples of those that are quite susceptible to such changes. For this reason, unashed specimens should be examined for such components.

A1.3 In order to interpret qualitative ash tests with greater assurance, it is important to estimate the relative amounts of various constituents found. In this connection, for example, the light voluminous character of an aluminum hydroxide precipitate should be taken into account when relating its quantity to that of a heavy, dense precipitate like barium sulfate. With flame and colorimetric tests, it is particularly difficult to judge the relative quantities of the constituents present and these should be interpreted with special care.

A1.4 Although the wet methods described are basic to the

technology, it is now common in many instances to use techniques based on X-ray diffraction, X-ray fluorescence, and electron microscopy to determine the pigment content of various papers. X-ray methods can be used, for example, to identify the crystal form of titanium dioxide (TiO_2 , anatase or rutile) and to estimate the amount present (using known standards for calibration). Also diffraction patterns of minerals such as clay and talc can be helpful.

A1.5 More recent developments in the field include the use of infrared techniques, especially internal reflectance methods and emission spectroscopy, as tools to identify the inorganic constituents of paper and paper coatings. Newer electron microscopy techniques including scanning electron microscopy, electron microprobe, and Auger analysis are useful additions to the list, as are atomic absorption and flame emission spectroscopy.

A1.6 The electron microscope can provide clearly identifiable pictures of the pigment in a redispersed paper sample allowing an experienced operator to distinguish among the various natural and precipitated fillers and coating pigments in use today.

A1.7 For those having access to such equipment, analysis procedures and techniques are available from the equipment manufacturers and from the literature.



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