



# Standard Test Methods for Sampling and Testing Lac Resins<sup>1</sup>

This standard is issued under the fixed designation D 29; 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.

*This standard has been approved for use by agencies of the Department of Defense.*

## 1. Scope

1.1 These test methods cover procedures for sampling and testing orange shellac, button lac, garnet lac, and bleached lac.

1.2 The sampling procedures and test methods appear in the following order:

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Sampling:	
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1.3 *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. Specific hazard statements are given in Note 1.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

- D 304 Specification for *n*-Butyl Alcohol (Butanol)<sup>2</sup>
- D 331 Specification for 2-Ethoxyethanol<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- D 1544 Test Method for Color of Transparent Liquids (Gardner Color Scale)<sup>4</sup>
- D 1545 Test Method for Viscosity of Transparent Liquids

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and are the direct responsibility of Subcommittee D 01.33 on Polymers and Resins.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 06.04.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 06.01.

by Bubble Time Method<sup>5</sup>

D 1959 Test Method for Iodine Value of Drying Oils and Fatty Acids<sup>5</sup>

E 11 Specification for Wire-Cloth Sieves for Testing Purposes<sup>6</sup>

## SAMPLING

### 3. Orange Shellac, Button Lac, and Garnet Lac

3.1 *Lot Size*—For the purpose of sampling, the quantity of a lot of any one of these types of lac resin shall not exceed 500 bags or packages. The net weight of lac resin in each bag or package shall not exceed 75 kg.

3.2 *Source and Number of Samples*—Only original unopened bags or packages shall be sampled. Ten percent of the containers in every lot of lac resin shall be taken at random, but not less than 5 nor more than 25 containers shall be taken.

3.3 *Free-Flowing Lac Resins*—In sampling free-flowing lac resins, samples shall be drawn from different places in each container in double handfuls or by means of a suitable sampler such as a grain sampler. A total of approximately 2.7 kg shall be taken.

3.4 *Blocked or Matted Lac Resin*—Pieces of blocked or matted lac resin shall be chipped with an axe, pick, or other suitable instrument from each container taken for sampling. Approximately the same amount shall be taken from each container and the total amount taken shall be about 2.7 kg. The pieces of lac resin shall then be ground to pass a No. 4 (4.75-mm) sieve. All sieves referenced must conform to the requirements of Specification E 11 .

3.5 *Preparation of Samples for Observation or Analysis*—Whether free-flowing or rough ground, as in the case of blocked lac resin, the entire sample representing any lot shall be thoroughly mixed and divided into halves. The use of a mechanical mixer is recommended for mixing the resin and a riffle sampler for dividing it into quarters. When these devices are not available for use, the entire sample shall be mixed, heaped, and quartered along two diameters that intersect at right angles and the opposite quarters combined. One half the sample, thus obtained, shall then be mixed and divided into quarters as before. Each quarter shall be placed in an airtight

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 06.03.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 14.02.

container, sealed, labeled (Section 5), and sent to the interested parties as the “original observation sample.” When agreed upon between the seller and the purchaser, the “original observation sample” shall be used for the determination of volatile matter (moisture) (Sections 14 to 15, as applicable). The other half of the sample shall be ground to pass a No. 10 (2.00-mm) sieve, mixed thoroughly, and divided into two equal portions A and B. Portion A shall be labeled the “reserve sample.” Portion B shall then be ground to pass a No. 25 (710- $\mu$ m) sieve, mixed thoroughly, and quartered as described above. Each quarter shall be packaged in an airtight container, sealed, labeled “prepared sample,” and sent to the testing laboratory for analysis.

#### 4. Bleached Lac

4.1 *Lot Size*—For the purpose of sampling, the quantity of a lot shall not exceed 200 packages.

4.2 *Source and Number of Samples*—Only original unopened packages shall be sampled. Twenty percent of the containers in every lot shall be taken at random, but not less than two containers in any lot shall be taken, except in the case where the entire lot is packaged in a single container.

4.3 *Dry Bleached Lac (Free-Flowing)*—Samples shall be drawn with a scoop or suitable sampler from different parts of each container directly after the packages are opened or bored. Approximately 450 g shall be drawn from each container. The samples shall be combined, mixed thoroughly, and where larger than 1.4 kg, shall be reduced by quartering as prescribed in 3.5 to a sample of this size.

4.4 *Dry Bleached Lac (Blocked or Matted)*—Samples aggregating at least 450 g shall be chopped or chiseled from different parts of each container. The composite sample from all the containers shall be quickly crushed to lumps about 25 mm square or smaller. The crushed lac resin shall be well mixed and where the amount is larger than 1.4 kg, it shall be reduced by quartering, as prescribed in 3.5, to a sample of approximately this size.

4.5 *Hanks, Bars, or Crushed Free-Ground Bleached Lac*—This material, which generally contains approximately 25 % moisture, shall be sampled by the procedures described in 4.3 or 4.4, as applicable.

4.6 *Preparation of Samples for Analysis*—The composite sample obtained as described in 4.3 or 4.4 shall be mixed thoroughly and divided into two equal portions A and B as prescribed in 3.5. Each portion shall be placed in a clean, dry glass jar provided with a rubber-sealed cap or an airtight friction-top tin can. Portion A shall be labeled “reserve sample.” Portion B obtained in accordance with 4.3 or 4.4 shall be further ground to pass a No. 20 (850- $\mu$ m) sieve, thoroughly mixed and replaced in the jar, sealed and labeled “prepared sample.” Portion B obtained in accordance with 4.5 shall be further ground to pass a No. 10 (2.00-mm) sieve, thoroughly mixed, replaced in the jar, sealed, labeled “prepared sample,” and sent to the laboratory for analysis.

#### 5. Identification of Samples

5.1 The following information shall be legibly placed on the label, which shall be securely attached to each sample container: date of the sampling, number of bags, barrels or

packages sampled, total number of containers in the lot, condition of the containers and their contents, manufacturer’s name, lot and code numbers of the containers, and the purpose identification, namely “original observation sample” or “sample for determination of volatile matter (moisture)”, “reserve sample” or “prepared sample” as may apply.

### TEST METHODS

#### 6. Reagents

6.1 *Purity of Reagents*—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 American Chemical Society, where such specifications are available.<sup>7</sup> 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

#### 7. Source and Preparation of Specimens for Tests

7.1 Each portion of sample for use in a given test shall be taken from the sample of lac resin only after it has been mixed, either by rolling on paper or by rolling and tumbling in its airtight container, as the condition of the sample requires, a sufficient number of times to ensure uniformity of the specimen taken. The test specimens shall be taken from the “prepared sample” (3.5 or 4.6), as received, except in the following cases:

7.1.1 When it has been previously agreed upon between the seller and the purchaser that the “original observation sample” shall be used for the determination of volatile matter (moisture). In this case, the “original observation sample” shall be mixed, quartered, ground, and sieved in accordance with the procedure described in 3.5 for obtaining the “prepared sample.” All operations shall be done as expeditiously as possible and the test specimen taken immediately after the sieved sample has been thoroughly mixed, to avoid any possible loss by evaporation.

7.1.2 When the “prepared sample” is known to have a high moisture content, as in the case of certain forms of bleached lac (4.5), it shall be dried to a moisture content of 6 % before the test specimens are taken. The lac resin shall be dried by placing it in a thin layer in a flat-bottom dish (loosely covered to prevent dust contamination) and exposing it to the atmosphere at room temperature for 24 h and then desiccating it over anhydrous calcium chloride. The partially dried lac resin shall be kept in a clean, dry, airtight container, and shall be thoroughly mixed by rolling and tumbling in the container before the specimens are taken for analysis.

<sup>7</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

INSOLUBLE MATTER

8. Test Method A—For Orange Shellac, Button Lac, Garnet Lac, and Regular Bleached

8.1 Apparatus:

8.1.1 *Condenser*—A four-bulb Allihn condenser of the dimensions and design shown in Fig. 1.

8.1.2 *Siphon Tube*—A Knoefler siphon tube of the dimensions shown in Fig. 1.

8.1.3 *Filter Tube*—A carbon filter tube of the dimensions shown in Fig. 1.

8.1.4 *Flask*—A borosilicate glass Erlenmeyer flask  $176 \pm 3$  mm in height and  $48 \pm 1.5$  mm in inside diameter at the top.

8.1.5 *Flask Support*—A suitable ring support with an iron clamp and a Nichrome or iron wire gauze square without an asbestos center.

8.1.6 *Extraction Thimble*—Extraction thimble  $26 \pm 1$  mm in diameter and  $60 \pm 1$  mm in height.

8.1.7 *Water Bath*—A metal container with cover of the size and design shown in Fig. 2. The container and cover shall be made of 26-oz copper sheet. The cover shall have a flanged hole  $57 \pm 1$  mm in diameter for a 200-mL beaker and also a hole  $35 \pm 1$  mm in diameter for the carbon filter tube. Directly below this hole in the bottom of the container shall be a flanged hole  $25 \pm 1$  mm in diameter.

8.1.8 *Heating Device*—An electric hot plate or bunsen burner equipped with a draft shield.

8.1.9 *Weighing Bottle*—A glass-stoppered weighing bottle of the dimensions shown in Fig. 1.

8.2 *Solvent*—Specially denatured 95 % (190 proof) ethyl alcohol conforming to Formula No. 1 or No. 3A of the Alcohol, Tobacco and Firearms Division of Internal Revenue Service, U.S. Treasury Department.

NOTE 1—**Precaution:** The reagents and samples used in these methods may, under some conditions, be hazardous. Refer to the supplier's Material Safety Data Sheet for specific handling and safety precautions.

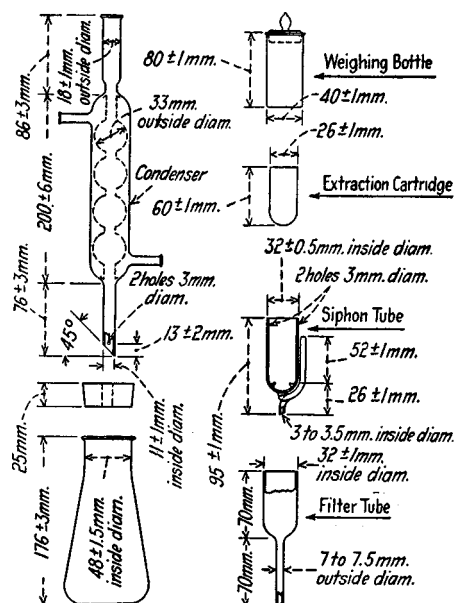


FIG. 1 Extraction Apparatus for Insoluble Matter, Test Method A

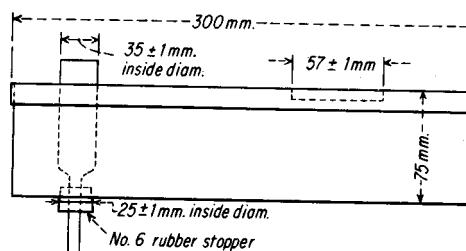


FIG. 2 Hot-Water Bath for Insoluble Matter, Test Method A

Safe laboratory handling procedures and all applicable OSHA regulations are to be followed.

8.3 Preparation of Extraction Thimble:

8.3.1 Pass the stem of the condenser through a hole cut in the center of a cork stopper of such size that it will tightly fit the flask. Adjust the cork on the stem so that the bottom of the cork is just above the holes in the stem. Place an extraction thimble (use new thimbles only) in the siphon tube. Suspend the siphon tube from the stem of the condenser by passing a piece of copper wire through the holes in the stem and fastening the ends of the wire through the holes in the siphon tube. The wire shall be sufficiently long to leave about 6-mm space between the tip of the condenser and the top of the siphon tube.

8.3.2 Place 125 mL of ethyl alcohol in the flask and attach the flask to the condenser by means of the cork stopper. Place the flask on an electric hot plate or a flask support. Run a steady stream of cold water through the condenser. Adjust the flame of the burner or the hot plate setting so as to give a cycle of filling and emptying of the siphon tube every 2 min, and extract the thimble for 30 min. Remove the extraction thimble from the siphon tube and allow to drain and air-dry for several minutes.

8.3.3 Place the thimble in a weighing bottle and dry in an oven for 2 h at  $105 \pm 2^\circ\text{C}$ . Remove and stopper the weighing bottle and cool in a desiccator. Weigh the bottle and thimble lifting the stopper momentarily before weighing. Continue drying and weighing as before after each hour of drying until the loss in weight between successive weighings does not exceed 2 mg.

8.3.4 A number of thimbles may be extracted and kept in weighing bottles or a desiccator until needed.

8.4 Procedure:

8.4.1 Weigh to 1 mg  $5 \pm 0.2$  g of the mixed sample (Section 7) and place in a 200-mL tall-form beaker. Add 125 mL of ethyl alcohol to the beaker and place it in the hot-water bath (Fig. 2), which has been previously heated to not less than  $90^\circ\text{C}$ . Maintain the bath at this temperature, or above, during the solution and filtration of the sample. Boil the solution for 30 min, keeping the volume of alcohol constant to ensure complete solution of the lac resin.

8.4.2 Place an extracted, weighed extraction thimble (8.3) in the carbon filter tube (Fig. 2). Wet the thimble with hot alcohol and decant the boiling solution into the warm thimble until the beaker is nearly empty. Wash the remaining solution and insoluble matter into the thimble with a stream of hot alcohol from a wash bottle using a "policeman" if necessary. Finally, wash the thimble from the top down. The transfer of the

insoluble matter from the beaker and the washing down of the thimble will require at least 75 mL of hot alcohol.

8.4.3 Transfer the thimble with the insoluble matter to the siphon tube of the extraction apparatus (Fig. 1). Place 125 mL of alcohol in the flask and attach the condenser. Adjust the heating device so that a complete filling and emptying of the siphon tube with hot alcohol requires 2 min or 30 cycles per hour (Note 2), and extract for exactly 1 h (Note 3). Remove the thimble, and allow it to drain in an upright position.

NOTE 2—Occasionally, lac resins are encountered that will not yield the required 30 siphons per hour due to slow filtration. In these instances the extraction shall be continued until 30 cycles have occurred and the determination reported as abnormal or slow filtering.

NOTE 3—During the 1-h extraction, all the remaining soluble matter should be extracted by the hot alcohol, leaving only the insoluble matter in the thimble.

8.4.4 Place the thimble in the weighed weighing bottle and dry in an oven at  $105 \pm 2^\circ\text{C}$  for 2 h. Remove the weighing bottle from the oven, insert its stopper, cool in a desiccator, and weigh, lifting the stopper momentarily to break the vacuum before weighing. Continue drying and weighing as before after each hour of heating until the loss in weight between successive weighings does not exceed 2 mg.

8.5 Calculation—Calculate the percent of matter insoluble in hot alcohol as follows:

$$\text{Insoluble matter, \%} = [R/S(1 - M)] \times 100 \quad (1)$$

where:

$R$  = insoluble matter obtained, g,

$S$  = sample used, g, and

$M$  = volatile matter (moisture) content of the sample, expressed as a decimal fraction.

## 9. Test Method B—For All Grades of Lac Resins Including Refined Bleached Lac<sup>8</sup>

### 9.1 Apparatus (Fig. 3):

9.1.1 *Crucible*—A borosilicate glass Gooch crucible having a capacity of 30 mL with a fritted-glass filter disk having a medium porosity.

<sup>8</sup> Hartman, C. C., "Determination of Insoluble Matter in Shellac," *Journal of Research, Nat. Bureau Standards*, Vol 7, No. 6, 1931, p. 1105.

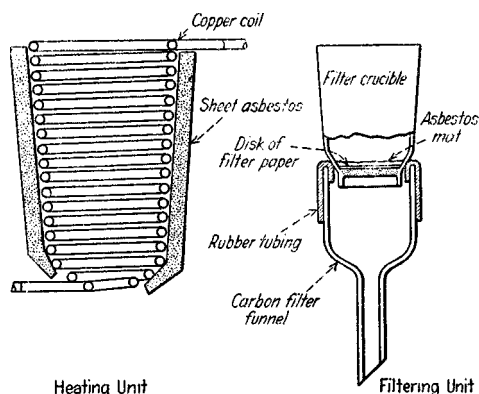


FIG. 3 Apparatus for Insoluble Matter, Test Method B

9.1.2 *Filter Tube*—A carbon filter tube made of borosilicate to fit the crucible.

9.1.3 *Heating Coil*—A heating coil made of 3-mm diameter copper tubing of such size and shape that the filter crucible and the large part of the carbon tube will fit snugly within it. The outside shall be insulated with sheet asbestos paper.

9.2 *Solvent*—Either of the following materials may be used as the solvent for the lac resin:

9.2.1 *2-Ethoxyethanol*, conforming to the requirements of Specification D 331.

9.2.2 *Normal Butyl Alcohol (n-Butanol)*, conforming to the requirements of Specification D 304.

### 9.3 Preparation of Filtering Unit:

9.3.1 Cut a disk of rapid, ashless filter paper to fit inside the crucible and place it on top of the glass filter. Introduce upon the filter paper, in the customary manner, an asbestos mat approximately 3 mm in thickness. Dry the crucible at  $105 \pm 2^\circ\text{C}$ ; then cool in a desiccator to constant weight. Weigh the prepared crucible and place it within the carbon tube, using thin rubber tubing to form an airtight connection. Place the combined filtering unit within the heating unit, attach to a suction flask, and pass a current of steam through the coil.

### 9.4 Procedure:

9.4.1 Weigh to 1 mg  $5 \pm 0.2$  of the mixed sample (Section 7 and Note 4) into a 200-mL beaker. Add 75 mL of the solvent (9.29.2) and bring the solution to boiling on an electric hot plate. Keep the solution boiling slowly for 5 min to ensure complete solution.

NOTE 4—For refined bleached shellac and other shellacs having a very low insoluble matter content take a 10 to 20-g specimen using proportionally more solvent.

9.4.2 Pour about 10 mL of the boiling solvent from a wash bottle into the heated crucible. Gently apply suction and immediately pour the boiling solution into the crucible so as to retain as much as possible of the insoluble residue in the beaker. Wash the insoluble residue successively with three 20-mL portions of the solvent, boiling the solution on the electric hot plate for about 1 min before each filtration.

9.4.3 Transfer the residue from the beaker to the crucible with a stream of the boiling solvent from a wash bottle, using a policeman when necessary. Wash down the inner walls of the crucible with the boiling solvent. The total volume of the solvent used will be approximately 175 mL. It is advisable to keep the crucible covered with a small watch glass at all times, except when actually transferring the solution from the beaker to crucible, or when washing down the inside walls of the crucible to maintain a higher temperature within the crucible. Allow the crucible to remain inside the heating coil with the suction on for a few minutes, so as to suck it as dry as possible.

NOTE 5—The insoluble matter can be easily removed together with the asbestos mat and filter paper. The crucible may be used several times without further cleaning. Additional cleaning when necessary is easily accomplished by immersing the crucible in a hot mixture of sulfuric and nitric acids for a few minutes.

9.4.4 Remove the crucible and wash the outside with boiling solvent. Dry in an oven at  $105 \pm 2^\circ\text{C}$  for 2 h, cool in a desiccator, and weigh.

9.5 Calculation—Calculate the percent of matter insoluble

in the hot solvent as follows:

$$\text{Insoluble, \%} = [R/S(1 - M)] \times 100 \quad (2)$$

where:

$R$  = insoluble matter obtained, g,

$S$  = sample used, g, and

$M$  = volatile matter (moisture) content of the sample, expressed as a decimal fraction.

## 10. Iodine Value

### 10.1 Reagents:

10.1.1 *Potassium Iodide Solution* (100 g/L)—Dissolve 10 g of iodate-free potassium iodide (KI) in water and dilute to 100 mL.

10.1.2 *Reference Standard Shellac*—Pure shellac of known iodine value.<sup>9</sup>

10.1.3 *Sodium Thiosulfate, Standard Solution* —(0.1  $N$ )—Prepare and standardize in accordance with Section 5 of Method D 1959.

10.1.4 *Starch Indicator Solution*—Prepare in accordance with Test Method D 1959.

10.1.5 *Wijs Solution*—Prepare in accordance with Test Method D 1959. The Wijs solution should be tested against an orange shellac the iodine value of which is accurately known. The iodine value thus obtained should be within  $\pm 0.5$  of the known iodine value.

### 10.2 Procedure:

10.2.1 Weigh to 0.1 mg about 0.2 g of the mixed sample (Section 7 and Note 6 and Note 7) into a 250-mL dry, clear glass bottle having a ground-glass stopper. Add 20 mL of glacial acetic acid and heat at 65 to 70°C on a hot-water bath, gently swirling the contents of the bottle occasionally, until solution is complete, except for the wax. This should not require more than 15 min. Add 10 mL of chloroform and cool at 21.5 to 22.5°C for ½ h in an insulated, thermostatically controlled water bath.

NOTE 6—In the case of grossly adulterated samples, a smaller quantity (0.15 or 0.1 g) should be used instead of 0.2 g of the material in order that the excess of iodine monochloride may not be too greatly reduced, since the excess of halogen is one of the factors in determining the amount of absorption. In case less than 25 mL of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution is required, another test should be made using a smaller quantity of the lac resin.

NOTE 7—In weighing lac resin some difficulty is at times experienced on account of its electrical resistance properties. In very dry weather it may be found that the necessary handling to prepare it for weighing has electrostatically charged it, and that it may be necessary to leave it in the balance pan at rest for a few minutes before determining the weight.

NOTE 8—If a number of samples are being run, allow at least 5 min between the additions of the Wijs solution.

10.2.2 Add 20 mL of the Wijs solution to the bottle, using a pipet. Replace the stopper and half immerse the bottle in the water bath held from 21.5 to 22.5°C for exactly 1 h (Note 8).

<sup>9</sup> The sole source of supply of Standard samples of pure orange shellac, rosin-free of accurately known iodine known to the committee at this time is the U. S. Shellac Importers Assn., Inc., 425 Park Ave., New York, NY 10022. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,<sup>1</sup> which you may attend.

Gently swirl the contents of the bottle occasionally during the hour. Remove the bottle from the bath and add 10 mL of the KI solution washing into the bottle any Wijs solution on the stopper with the same.

10.2.3 Immediately titrate with the standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution, allowing the solution to run rapidly and swirling the contents of the bottle vigorously and continuously until the solution becomes a straw color. Add 5 mL of the starch indicator solution and continue the titration dropwise until the blue color just disappears. The end point is sharp and any blue color returning after 30 s should be disregarded.

10.2.4 *Blank*—Run a blank determination on the reagents at the same time and through the entire procedure. The blank is necessary because of the effect of temperature changes on volume and possible loss in strength of the Wijs solution.

10.2.5 *Reference Standard*—Run a determination on a sample of pure shellac of known iodine value (10.1.2) with each set of test specimens.

10.3 *Calculation*—Calculate the iodine value as follows:

$$\text{Iodine value} = [(B - V)N \times 12.69]/S \quad (3)$$

where:

$V$  =  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the specimen, mL,

$B$  =  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the blank, mL,

$N$  = normality of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution, and

$S$  = sample used, g.

## PURITY

### 11. Qualitative Test for Rosin

#### 11.1 Reagents:

11.1.1 *Acetic Acid (Glacial)*.

11.1.2 *Ethyl Alcohol (Absolute)*.

11.1.3 *Halphen-Hicks Reagent*<sup>10</sup>—Prepare the following two solutions:

11.1.3.1 *Solution A*—One part by volume of phenol dissolved in 2 parts by volume of carbon tetrachloride.

11.1.3.2 *Solution B*—One part by volume of bromine dissolved in 4 parts by volume of carbon tetrachloride.

#### 11.2 Procedure:

11.2.1 Weigh  $2 \pm 0.1$  g of the mixed sample (Section 7) into a 2-L Florence flask and dissolve in 20 mL of either absolute ethyl alcohol or glacial acetic acid, warming on a steam bath if necessary. Cool, add 100 mL of petroleum ether, and mix thoroughly.

11.2.2 Add sufficient water to bring the petroleum ether layer into the neck of the flask when separated. Add the water portionwise, shaking the flask between additions to prevent coagulation of the precipitated lac resin. Allow to stand until the petroleum ether separates into a distinct layer.

11.2.3 Siphon off at least 50 mL of the petroleum ether solution, filter if cloudy, and heat on an electric hot plate or steam bath until the petroleum ether is completely removed.

<sup>10</sup> For more detailed information, reference may be made to Hicks, E. F., "New Color Reactions for Some of the Resins with Halphen's Reagent for Colophony," *Industrial and Engineering Chemistry*, Vol 3, 1911, p. 86.

11.2.4 Dissolve the residue in several millilitres of Solution A, and transfer 1 to 2 mL of the mixture to one of the cavities of a white porcelain spot plate. Immediately fill an adjacent cavity with Solution B. Cover the plate with an inverted watch glass and note the color developed in the Solution A mixture by the bromine vapors from Solution B. The development of a fugitive violet color, best observed on the flat portion of the spot plate, indicates the presence of rosin. A control sample containing rosin should be run simultaneously, as a guide in judging the color developed with the test specimen.

## 12. Qualitative Test for Copal

### 12.1 Reagents:

12.1.1 *Ethyl Alcohol, Denatured*—(See 8.2).

12.1.2 *Methyl Alcohol (99 %)*.

### 12.2 Procedure:

12.2.1 Weigh to 0.1 g about 15 g of the mixed sample (Section 7) into an Erlenmeyer flask. Add twice its weight of the denatured alcohol, stopper the flask and let stand with periodic shaking until the sample is in the solution. Filter the solution through a folded filter paper, discarding the first 5 mL of filtrate.

12.2.2 Transfer 10 mL of the filtrate to a large test tube (6 by ¾ in.) (150 by 20 mm) and nearly fill the tube with methyl alcohol. Stopper the tube and mix its contents thoroughly. Immediate formation of a cloudiness or precipitate indicates the presence of copal. Lac resin free of copal should remain clear.

## 13. Estimation of Adulteration

13.1 Since the variation between the highest and lowest iodine values of a pure lac resin is not great, it is recommended that the following assumptions (Note 9) be made:

Type of Lac Resin	Assumed Iodine Value
Rosin-free and copal-free shellac, button lac, and garnet lac	15
Rosin-free and copal-free bleached lac	10
Rosin	228
Copal	130

13.2 Calculate the percent of adulteration as follows:

$$\begin{aligned} &\text{Percent of rosin in orange shellac, button lac, and garnet lac} \\ &= [(x - 15)/(228 - 15)] \times 100 \end{aligned} \quad (4)$$

$$\text{Percent of rosin in bleached lac} = [(x - 10)/(228 - 10)] \times 100$$

$$\begin{aligned} &\text{Percent of copal in orange shellac, button lac, and garnet lac} \\ &= [(x - 15)/(130 - 15)] \times 100 \end{aligned}$$

$$\text{Percent of copal in bleached lac} = [(x - 10)/(130 - 10)] \times 100$$

where:

$x$  = iodine value of the sample under test, determined in accordance with 10.2.

NOTE 9—The results obtained by assuming the values of 15 and 10 as the iodine value of orange and bleached shellac, respectively, and 228 as the iodine value of rosin may give a slightly lower percent rosin, under some circumstances, than that which is actually present.

## VOLATILE MATTER (MOISTURE)

### 14. Test Method A—For Orange Shellac, Button Lac, Garnet Lac, and Dry Bleached Lac

#### 14.1 Procedure:

14.1.1 Weigh to 0.1 mg approximately 2 g of the mixed sample from the air-tight container (7.1.1 or 7.1.2) into a weighed, clean, dry, flat-bottom glass dish about 4 in. (100 mm) in diameter and provided with a ground-glass cover. Place the dish, with the cover removed, in a well-ventilated oven maintained at  $40 \pm 1^\circ\text{C}$  for 6 h.

14.1.2 Transfer the dish and cover to a vacuum desiccator containing concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp gr 1.84). Immediately evacuate the desiccator and keep the specimen uncovered in the vacuum for 18 h. Release the vacuum, replace the cover on the dish, and weigh immediately.

14.2 *Calculation*—Calculate the percent volatile matter (moisture) in the sample as follows:

$$\text{Volatile matter (moisture), \%} = [1 - (S_2/S_1)] \times 100 \quad (5)$$

where:

$S_1$  = sample used, g, and

$S_2$  = dried specimen, g.

### 15. Test Method B—For Bleached Lac in Form of Hanks, Bars, and Crushed Fresh-Ground

#### 15.1 Procedure:

15.1.1 Thoroughly mix the “original observation” sample in its original airtight container by rolling and tumbling. Transfer 25 to 50 g to a mortar and crush as rapidly as possible into fine granules. Keep the mortar covered as well as possible to avoid any loss of moisture. Immediately transfer approximately 10 g of the crushed lac to a weighed, clean, dry, flat-bottom glass dish about 100 mm in diameter, provided with a ground-glass cover, and weigh to 0.1 mg. Record the weight of the lac taken for use as  $S_1$ .

15.1.2 Place the dish and contents in a vacuum desiccator containing  $\text{H}_2\text{SO}_4$ (sp gr 1.84). Remove the cover from the dish and immediately evacuate the desiccator. Keep the dish in the vacuum at room temperature for 18 to 24 h. Replace the cover on the dish, remove from the desiccator, and weigh. Record the weight of the partially dried lac for use as  $S_2$ .

15.1.3 Grind the partially dried lac resin until it entirely passes a No. 40 (425- $\mu\text{m}$ ) sieve. Thoroughly mix the sieved lac on a mixing sheet (7.1). Transfer approximately a 2-g specimen of it from the mixing sheet to a weighed, covered dish of the type described in 15.1.1, and weigh to 0.1 mg. Record the weight of the specimen taken for use as  $S_3$ .

15.1.4 Heat the dish with cover removed in a well-ventilated oven at  $40 \pm 1^\circ\text{C}$  for 18 h. Replace the cover on the dish, cool in a desiccator, and weigh. Record the weight of dried lac obtained for use as  $S_4$ .

15.2 *Calculation*—Calculate the percent of volatile matter (moisture) in the original lac sample as follows:

$$\text{Volatile matter (moisture), \%} = [1 - (S_4 \times S_2)/(S_3 \times S_1)] \times 100 \quad (6)$$

where:

- $S_1$  = crushed wet lac taken for drying in vacuum, g, (15.1.1)  
 $S_2$  = partially dried lac, g, (15.1.2),  
 $S_3$  = partially dried, sieved lac used as specimen for final oven drying, g, (15.1.3), and  
 $S_4$  = completely dried lac specimen obtained in 15.1.4, g.

## 16. Wax

### 16.1 Apparatus:

16.1.1 *Extraction Apparatus*—An assembly suitable for continuous extraction with hot solvent, such as that used for the determination of insoluble matter (Section 8).

16.1.2 *Filtering Medium*—A Büchner funnel, having an inside diameter of 55 to 90 mm, and prepared just before use in the following manner. Fit a disk of filter paper snugly over the bottom of the funnel and then with the suction on pour over the filter paper in a layer of uniform thickness 1 g of filter aid (16.2.3) suspended in water.

16.1.3 *Extraction Thimble*—A thimble, such as prescribed in 8.1.6, that has been previously extracted with chloroform by the procedure given in 8.3.

### 16.2 Reagents:

16.2.1 *Chloroform*, redistilled, free of nonvolatile residue.

16.2.2 *Ethyl Alcohol, Denatured*, as prescribed in 8.2.

16.2.3 *Filter Aid*—A suitable filter aid, extracted with chloroform and dried before using.

16.2.4 *Sodium Carbonate* ( $\text{Na}_2\text{CO}_3$ ).

### 16.3 Procedure:

16.3.1 Weigh to 1 mg approximately 10 g of the mixed sample (Section 7) into a 200-mL tall-form beaker. Dissolve 2.5 g of  $\text{Na}_2\text{CO}_3$  in 150 mL of hot water and add to the beaker. Immerse the beaker in a boiling water bath and stir until the lac resin is in solution. Cover the beaker with a watch glass and allow to remain in the bath for 2 to 3 h, without agitation.

16.3.2 Remove the beaker from the bath and place it in cold water. The wax will come to the top of the solution where it will solidify as a layer or float as small, hard particles. Add 0.5 g of the filter aid to the lac solution and filter through the Büchner funnel with the aid of suction. Transfer all of the wax from the beaker to the filter with a stream of water from a wash bottle, using a policeman if necessary. Finally pour a few millilitres of the alcohol over the filter to facilitate drying. Place the funnel in an oven and dry its contents at  $60 \pm 2^\circ\text{C}$  for several hours.

16.3.3 Insert a thin spatula under the edge of the filter paper and transfer the contents of the funnel to a sheet of filter paper. Securely wrap the transferred material in the filter paper, and bind it firmly with fine copper wire. Place the packet in the prepared extraction thimble. Wash out both the beaker in which the lac resin was originally dissolved and the Büchner funnel with portions of hot chloroform, filtering the chloroform solutions through the extraction thimble into the flask to be used in the extraction. Place the thimble in the extraction apparatus, and extract with hot chloroform for 2 h.

16.3.4 Transfer the chloroform extract to a weighed beaker and heat on a steam-bath until most of the chloroform has been evaporated. Finally heat the residue in the beaker in an oven at  $105 \pm 2^\circ\text{C}$  to constant weight (within 10 mg). Cool in a

desiccator and weigh.

16.4 *Calculation*—Calculate the percent of wax in the lac resin as follows:

$$\text{Wax, \%} = [R/S(1 - M)] \times 100 \quad (7)$$

where:

$R$  = wax obtained, g,

$S$  = sample used, g, and

$M$  = volatile matter (moisture) content of the sample, expressed as a decimal fraction.

## 17. Matter Soluble in Water

### 17.1 Procedure:

17.1.1 Weigh to 0.1 g 10 g of the mixed sample (Section 7) into a 400-mL beaker. Add 200 mL of water and stir thoroughly. Cover the beaker with a watch glass and let stand with occasional stirring for 4 h at  $25 \pm 2^\circ\text{C}$ .

17.1.2 Filter the water solution through a filter paper into a 400-mL beaker. Transfer all the lac resin from the beaker to the filter paper with a stream of water from a wash bottle using a policeman if necessary. Finally wash the lac resin and filter paper with approximately 100 mL of water.

17.1.3 Evaporate the filtrate almost to dryness in a weighed evaporating dish on a steam bath. Dry the extracted residue for 1-h periods in an oven maintained at  $105 \pm 2^\circ\text{C}$  until the difference in successive weighings does not exceed 1 mg. Cool in a desiccator and weigh.

17.2 *Calculation*—Calculate the percent of matter soluble in water as follows:

$$\text{Matter soluble in water, \%} = [R/S(1 - M)] \times 100 \quad (8)$$

where:

$R$  = residue obtained, g,

$S$  = sample used, g, and

$M$  = volatile matter (moisture) content of the sample, expressed as a decimal fraction.

## 18. Ash

### 18.1 Procedure:

18.1.1 Weigh to 1 mg between 3 and 5 g of the mixed sample (Section 7) into a weighed porcelain crucible. Place the crucible in a hood and heat with a low flame until the contents of the crucible are a dry, charred mass. Transfer to a muffle furnace and ignite the residue at a dull red heat (not exceeding  $600^\circ\text{C}$ ) until the ash is free of carbon. Cool in a desiccator and weigh. Repeat the ignition, cooling and weighing until the difference between successive weighings does not exceed 1 mg.

18.1.2 If a carbon-free ash cannot be obtained in this manner, add water to the crucible, bring the water to a slow boil and digest the ash for 5 to 10 min. Filter through an ashless filter paper, washing out the crucible with a stream of hot water from a wash bottle using a policeman if necessary. Retain the filtrate. Transfer the filter paper with the insoluble residue to the crucible and ignite at a dull red heat in a muffle furnace until all the carbon is consumed. Then add the filtrate to the crucible and evaporate to dryness over a low flame or hot plate. Finally ignite the crucible and its contents at dull red heat to constant weight (within 1 mg) as prescribed in 18.1.1.

18.2 *Calculation*—Calculate the percent ash of the lac resin as follows:

$$\text{Ash, \%} = [R/S(1 - M)] \times 100 \quad (9)$$

where:

$R$  = ash obtained, g,

$S$  = sample used, g, and

$M$  = volatile of matter (moisture) content of the sample, expressed as a decimal fraction.

## 19. Color

### 19.1 Apparatus:

19.1.1 *Glass Tubes*—Clear glass tubes with closed, flat, even bottom, an external length of approximately 114 mm, and a uniform internal diameter of  $10.65 \pm 0.025$  mm throughout the length of the tube. Viscosity tubes described in Test Method D 1545 are satisfactory.

19.1.2 *Glass Plate*—White Carrara or Vitrolite glass plate approximately 150 by 200 mm, one side of which has been polished to a smooth, high gloss surface.

19.1.3 *Film Applicator*—Film applicator to case a film 50-mm wide and 50- $\mu$ m thick. A clearance of 4 mils should provide the required thickness.

19.2 *Reagent*—Ethyl Alcohol, Denatured, as prescribed in 8.2.

19.3 *Color Comparison Material*—The lac resin mutually agreed upon by the purchaser and the seller for the color comparison.

### 19.4 Procedure:

19.4.1 Weigh  $10 \pm 0.1$  g each of the mixed sample (Section 7) and the comparison lac resin, which shall have been similarly prepared, into separate Erlenmeyer flasks. Add to each flask an amount of alcohol equal to twice the weight of the resin and stopper the flasks. Keep the flasks at 21 to 32°C and shake at frequent intervals until the resins are completely dissolved (cut). Allow the flasks to stand undisturbed for ½ h. Compare the color of the lac solutions by one or both of the following procedures as agreed upon between the purchaser and the seller.

19.4.2 *Comparison of Solutions*—Fill separate glass tubes to their bottom lines with each of the solutions, being careful not to disturb any settlement that may have occurred in either flask. Place the tubes side by side and make the color comparison by viewing the liquids while they are held against a background substantially equal in illumination to that of a fairly light overcast northern sky.

19.4.3 *Comparison of Films*—Without disturbing any settlement that may have occurred in the flask, decant a suitable portion of the solution of the sample and draw down on the white glass plate with a film, 50-mm wide and 50- $\mu$ m thick, using the apparatus described in 19.1.3. In a similar manner, draw down a film of the comparison solution on the same plate keeping the films as close together as possible. Air-dry the films at 21 to 32°C for 24 h. Compare the color of the dried films by viewing them by reflected light at an illumination substantially equal to that of a fairly overcast northern sky.

## 20. Color of Orange Shellac

### 20.1 Apparatus:

20.1.1 *Funnel*—Porcelain No. 1 Büchner funnel 55 mm in inside diameter.

20.1.2 *Colorimetric Tubes*—Nessler color comparison tubes, approximately 20 mm in diameter and 300 mm in length.

20.1.3 *Standard Light Source*—A light source consisting of a 100-W frosted daylight bulb mounted at the center of the back wall of a 255-mm cubic box so that the tip of the bulb faces the front. The front opening of the box shall be covered with a white opaque paper or a ground-glass plate. The lamp shall be inserted in a socket which just protrudes through the wall of the box so that the distance from the tip of the lamp to the paper or glass is approximately 115 mm. The five inside walls of the box shall be painted white. Any other suitable apparatus or standard daylight lamp may be used, provided it produces light of the same characteristics as specified above. See Test Method D 1544 for using the Gardner Color Scale.

### 20.2 Reagents:

20.2.1 *Ethyl Alcohol*—Specially denatured 95 % (190 proof) ethyl alcohol; either formula No. 1 or formula No. 30 of the U.S. Internal Revenue Bureau.

20.2.2 *Filter Aid*—Any high-grade analytical filter aid for rapid flow.

20.2.3 *Ferric Sulfate*— $(\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O})$ —Any hydrated analytical reagent.

20.2.4 *Sodium Hydroxide, Standard Solution (1N)*—Dissolve 40 g of pure NaOH in 500 mL of distilled water and dilute to 1 L in a volumetric flask. Standardize against pure oxalic acid dihydrate.

20.2.5 *Sodium Thiosulfate, Standard Solution (0.2N)*—Dissolve 49.66 g sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in distilled water that has been previously boiled to free it from carbon dioxide and dilute to 1 L of the solution. It is best to let this solution stand about 2 weeks before standardizing with pure resublimed iodine or potassium bi-iodate. Preserve in a brown stock bottle with a guard tube filled with soda lime.

20.2.6 *Starch Solution*—Make a paste of 0.2 g of soluble starch (potato starch) in cold water and pour into 100 mL of boiling water, cool and bottle or use the solution prepared for the iodine number determination (10.1.5).

20.2.7 *Potassium Iodide (KI)*—Iodate-free crystal.

20.2.8 *Nickel Sulfate*—Reagent grade ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ).

### 20.3 Preparation of Color Standards

20.3.1 *Ferric Sulfate*—Dissolve 400 g of  $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$  in about 600 mL of water by heating to boiling while stirring constantly. After complete solution, cool to room temperature and dilute to 1 L in a volumetric flask. Standardize this stock solution by titrating with iodine in the following manner: Dissolve 20 g of KI in 30 mL of water and add 5 mL of the stock solution. Add to this approximately 2 weight % of  $\text{H}_2\text{SO}_4$  (sp gr 1.84). Allow to stand for 5 min and titrate with 0.2 N sodium thiosulfate solution in the usual manner, not adding the starch indicator until near the end of the titration. Run at the same time a blank determination on the KI solution and correct for any nonuniformity of this reagent. Adjust the stock solution to approximately 0.725 M  $\text{Fe}_2(\text{SO}_4)_3$  solution (Note 10); 5 mL of the stock solution should then be equivalent to  $36.2 \pm 0.8$



mL of 0.2 *N* sodium thiosulfate solution.

**NOTE 10**—The amount of coordinated water in ferric sulfate may vary, and has to be taken into account in weighing out the required amount of ferric salt. It is usually about 6 mols per mol of ferric sulfate for the powdered analyzed reagent.

**20.3.2 Nickel Sulfate**—Dissolve 50 g of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in about 300 mL of water. After complete solution, dilute to 500 mL in a volumetric flask.

**20.3.3 Reference Standard for All Grades<sup>11</sup>**—Transfer exactly 20 mL of the stock ferric sulfate solution (20.3.1) to a 100-mL volumetric flask. Add 11.5 mL of the 1.0 *N* NaOH solution from a buret, and shake until all the precipitate formed has dissolved. Then, add 10 mL of the nickel sulfate solution and dilute to 100 mL with distilled water. If any of the solutions show permanent precipitates, prepare fresh solution.

#### 20.4 Procedure:

**20.4.1** Transfer exactly 5 g of the sample to a clean 120-mL wide-mouth bottle and add exactly 50 mL of alcohol. Shake until solution is complete and then cool to 10°C.

**20.4.2** Place a 55-mm tough, hard, close texture filter paper or its equivalent in the Büchner funnel which has been mounted in the neck of a 2-L suction flask with a rubber stopper. Pour evenly upon the filter paper a 1-g suspension of filter aid in 50 mL of alcohol, and suck completely dry with a partial vacuum, using a water suction pump. Remove the funnel and add about 400 mL of alcohol to the flask. (**Note 11**) Place an 200-mm test tube in the suction flask, supporting, if necessary, with filter paper, so that the tip of the Büchner funnel when inserted in the neck of the flask will come well within the open test tube. Reinsert the funnel in the flask.

**20.4.3** Add 1 g of filter aid to the cold shellac solution and stir thoroughly. Transfer completely to the Büchner funnel and filter at the rate of 2 drops per second by means of a carefully regulated vacuum. This may be conveniently done by the use of a water pump to which has been attached a trap carrying a stopcock to admit air. Slowly increase the amount of vacuum toward the end of the filtration in order to maintain a constant filtration rate until the filtration is practically complete, and then suck dry. The final volume in the test tube should be 49 to 50 mL. If it is less than 48 mL, repeat the procedure.

**NOTE 11**—The method used in preparing the solution for comparison is very important. A slight loss in alcohol will materially affect the color when diluted for comparison. Alcohol is placed in the flask to avoid undue evaporation of the solution during filtration. The rate of filtration is an important factor.

**20.4.4** Transfer 10 mL of filtered solution to one of the colorimetric tubes, and compare with 10 mL of the standard color solution by viewing the tubes transversely in front of the standard light source. Dilute the shellac solution with alcohol until it matches the reference standard color. Report the volume in millilitres of the diluted solution; this is taken as the color number of the sample. Determine the color of the filtered solution the same day upon which the samples are dissolved.

<sup>11</sup> This standard color solution was designed to match the No. 5 iodine color standard of the Angelo color method which has been used by various laboratories for obtaining numerical color values for lacs. It is closer in hue to most lacs than the iodine solution and hence easier to match.

**NOTE 12**—Most filtered solutions made by dissolving shellac that has been ground for analysis will darken appreciably in color if allowed to stand for periods longer than 12 h.

## 21. Acid Value

### 21.1 Definition:

**21.1.1 acid value**—the number of milligrams of potassium hydroxide required to neutralize 1 g of moisture-free lac resin.

### 21.2 Reagents:

**21.2.1 Neutral Ethyl Alcohol**—Alcohol, as described in Section 8, that has been neutralized with standard KOH or NaOH solution, using the phenolphthalein indicator to a faint but persistent pink color just prior to use.

**21.2.2 Phenolphthalein Indicator Solution**—Dissolve 1 g of phenolphthalein in 100 mL of ethanol (8.2), methanol, or isopropanol.

**21.2.3 Potassium Hydroxide or Sodium Hydroxide Solution, Standard Aqueous or Alcoholic (0.1 *N*):**

**21.2.3.1 Preparation of Aqueous Solution**—Prepare a stock concentrated solution by dissolving potassium hydroxide (KOH) or sodium hydroxide (NaOH) in water in the proportion of 112 g of KOH, or 85 g of NaOH in 200 mL of water. Allow the solution to cool and settle in a stoppered bottle for several days. Decant the clear liquid from the carbonate precipitate into another clean bottle. Add clear barium hydroxide ( $\text{Ba}(\text{OH})_2$ ) solution until no further precipitate forms. Again allow to settle until clear. Draw off 175 mL and dilute to 10 L with water. Preserve in a stock bottle provided with a guard tube filled with soda-lime.

**21.2.3.2 Preparation of Alcoholic Solution**—Place 5 to 10 g of KOH in a 2-L flask and add 1 to 1.5 L of alcohol prescribed in 8.2. Boil on a water bath under a reflux condenser for 30 to 60 min. Distill and collect the alcohol. Dissolve 5.6 g of KOH or 4 g of NaOH in 1 L of the distilled alcohol, keeping the temperature below 15.5°C while the alkali is being dissolved. This solution should remain clear.

**21.2.3.3 Standardization of Solution**—Standardize either solution by titrating against pure potassium acid phthalate,<sup>12</sup> using phenolphthalein indicator. The solution will be approximately 0.1 *N*. Determine its exact normality to  $\pm 0.001$  *N*.

**21.2.4 Thymol Blue Indicator Solution**—Dissolve 0.04 g of thymol blue (thymol sulfonphthalein) in 100 mL of the alcohol prescribed in 8.2.

### 21.3 Procedure:

**21.3.1** Weigh to 1 mg approximately 2 g of the mixed sample (Section 7) into a 250-mL Erlenmeyer flask and add 100 mL of the neutral alcohol. The sample should completely dissolve at room temperature within a few hours with the aid of periodic gentle swirling. Titrate in accordance with 21.3.2 or 21.3.3.

**21.3.2** In case of bleached lac, add 1 mL of the phenolphthalein indicator solution and titrate with 0.1 *N* KOH or NaOH solution, with constant swirling of the contents of the flask. Take as the end point when a faint pink color remains after continuous swirling for 30 s.

<sup>12</sup> National Institute of Standards and Technology standard reference material No. 84d is recommended for this purpose and should be handled as directed in the certificate of analysis accompanying the sample.

21.3.3 In case of orange shellac, place several drops of the thymol blue indicator solution on a white porcelain spot plate. Titrate the solution with 0.1 *N* KOH or NaOH solution, with constant swirling, and determine the end point by transferring 1 or 2 drops of the solution on a glass rod to the indicator. The end point is reached when the first blue color is developed in the indicator.

21.4 *Calculation*—Calculate the acid value as follows:

$$\text{Acid value} = (VN \times 56.1)/S(1 - M) \quad (10)$$

where:

*V* = KOH or NaOH solution required for the titration, mL

*N* = normality of the KOH or NaOH solution,

*S* = sample used, g, and

*M* = volatile matter (moisture) content of the sample expressed as a decimal fraction.

## 22. Orpiment

### 22.1 Reagents and Materials:

22.1.1 In addition to conforming to the requirements of Section 6, all reagents shall be free of arsenic.

22.1.2 *Ammonium Hydroxide* (NH<sub>4</sub>OH)—Concentrated ammonium hydroxide (sp gr 0.90).

22.1.3 *Carbon Disulfide* (CS<sub>2</sub>).

22.1.4 *Carbon Tetrachloride* (CCl<sub>4</sub>).

22.1.5 *Ethyl Alcohol, Denatured*, as prescribed in 8.2.

22.1.6 *Ferrous Sulfate or Ferrous Ammonium Sulfate* (FeSO<sub>4</sub> or FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>).

22.1.7 *Hydrochloric Acid* (HCl)—Concentrated hydrochloric acid (sp gr 1.19).

22.1.8 *Hydrogen Peroxide* (H<sub>2</sub>O<sub>2</sub>)—Concentrated hydrogen peroxide 30% .

22.1.9 *Hydrogen Sulfide* (H<sub>2</sub>S)—A supply or source of gaseous hydrogen sulfide.

22.1.10 *Nitric Acid* (HNO<sub>3</sub>)—Concentrated nitric acid (sp gr 1.42).

22.1.11 *Sulfuric Acid* (H<sub>2</sub>SO<sub>4</sub>)—Concentrated sulfuric acid (sp gr 1.84).

### 22.2 Apparatus:

22.2.1 *Filter Paper*—Ashless, medium-porosity filter paper.

22.2.2 *Funnel*—A jacketed-glass funnel or funnel about which has been wound a coil of copper or tin tubing through which steam may be passed to heat it.

22.2.3 *Gooch Crucible*—A Gooch crucible that has been prepared with an asbestos mat in the usual manner, ignited, cooled, and stored in a desiccator.

22.2.4 *Distillation Assembly*—A 300-mL Kjeldahl flask, fitted with a 2-hole rubber stopper, and attached to a bulb-type glass condenser by a U-tube having about 6.4-mm bore and a distance of 205 mm between arms. Through the other hole in the stopper a double-bulb safety tube or a small separatory funnel with a long, slim stem is inserted. The tip of the safety tube or funnel is bent to form a short U, the orifice of which points upward. The tube or funnel is fitted into the flask so that the U tip nearly touches the bottom of the flask. A 250-mL beaker, which serves as a receiver, is held on a movable support, immediately under the condenser tip.

### 22.3 Procedure:

22.3.1 Weigh to 0.1 g approximately 50 g of the mixed

sample (Section 7) into a 500-mL Kjeldahl flask. Add 450 mL of the alcohol to the flask and heat its contents in a hot water bath at a gentle boil until the lac resin is completely dissolved.

22.3.2 Remove the flask from the bath and wait just long enough to permit settlement of the bulk of the insoluble matter from the solution. Decant the solution from the flask to the filter paper held in the jacketed funnel which must be kept hot during the entire filtration by passing steam through the coil or jacket. Keep a watch glass over the funnel when not pouring the solution into it (Note 13).

22.3.3 Wash the sediment layer in the flask with four successive 50-mL portions of boiling alcohol, and decant the washings through the filter. Finally wash the filter paper with 50 mL of the boiling alcohol. Continue heating the funnel to drive off most of the alcohol. Pour slowly over the entire surface of the filter paper approximately 200 mL of boiling carbon tetrachloride to dissolve any of the lac wax that may have remained on the filter paper (Note 14). Now leave the watch glass off and continue passing the steam through the funnel jacket to dry the solvent from the paper.

NOTE 13—If the funnel and its contents are not kept hot the wax will congeal and clog the filter paper, thus slowing up the filtration.

NOTE 14—All wax should be removed from the filter paper and inside of the flask, as otherwise the subsequent digestion procedure may be materially prolonged.

22.3.4 Carefully transfer the filter paper and its contents to the flask. Add 25 mL of HNO<sub>3</sub> (sp gr 1.42) to the flask, and apply gentle heat, digesting the contents of the flask for 20 min. Cool, add 25 mL of H<sub>2</sub>SO<sub>4</sub> and again heat gently until most of the nitrous fumes have been driven off. Increase the heat and continue boiling until the evolution of sulfur trioxide (SO<sub>3</sub>) fumes occurs.

22.3.5 If organic matter or charring is evident at this point, allow the flask to cool to room temperature. Rinse down the inside of the flask with a small amount of water and carefully add 3 to 4 mL of H<sub>2</sub>O<sub>2</sub>. After any initial violent gas evolution has subsided again heat to SO<sub>3</sub> fumes. If discoloration reappears, repeat the hydrogen peroxide treatment and heating until a clear carbon-free solution is obtained.

22.3.6 Transfer the clear solution to the 300-mL Kjeldahl flask, rinsing the flask thoroughly with small portions of water until the volume of the solution and washing is between 125 and 150 mL. Heat the solution rapidly to boiling and evaporate just short of fuming to ensure complete removal of both HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>.

22.3.7 Add 20 g of either ferrous sulfate or ferrous ammonium sulfate to the flask and connect the flask to the distillation assembly. Place 50 mL of water in the beaker, serving as receiver, and raise the beaker on its support until the end of the condenser is immersed in the water. Start H<sub>2</sub>S bubbling into the water in the beaker (Note 15) and cold water flowing through the condenser. Place 50 mL of HCl in the safety tube or separatory funnel and adjust the stopcock so that the acid runs in a slow stream into the flask. Apply gentle heat and bring the solution to a steady boil. If orpiment is present a yellow precipitate will appear in the receiver when distillation starts. Discontinue the distillation when bumping begins.

22.3.8 Remove the flame, change the receiver, add another

50-mL portion of the HCl to the contents of the flask and repeat the distillation procedure (Note 16). When the second distillation is completed, lower the receiver, and wash down the inside of the condenser and the outside of the condenser tip with water. If any orpiment adheres to the walls of the condenser, wash it off with a small amount of NH<sub>4</sub>OH, allow it to drain into the receiver, and then rinse again with water. Check the contents of the beaker for acidity, adding more acid if necessary, and allow the H<sub>2</sub>S to bubble through the solution for a few minutes longer.

NOTE 15—The H<sub>2</sub>S supply should be of sufficient amount to afford a uniform and good rate of flow during the entire distillation.

NOTE 16—With a properly prepared specimen, practically all of the arsenic comes over in the first distillation, the second one serving mainly as a safeguard.

22.3.9 Filter the contents of both beakers through the prepared and weighed Gooch crucible. Wash all of the precipitate from each beaker into the crucible with a stream of hot water from a wash bottle, using a policeman if necessary. Next, wash out the beaker with two 50-mL portions of alcohol followed by two 50-mL portions of boiling CS<sub>2</sub> (Note 17). When filtering these washings, adjust the suction so that each portion will be retained in the crucible for approximately 5 min (Note 18). Dry the crucible and its contents at 105 ± 2°C for 2 h. Cool in a desiccator and weigh.

NOTE 17—Bring the CS<sub>2</sub> to a boil on a steam bath, making sure there is no gas flame or electric arc in the immediate area in which the CS<sub>2</sub> is being used.

NOTE 18—This treatment ensures complete removal of all traces of sulfur that may have precipitated with the orpiment and which, if left in, would materially affect the final result, especially with a sample quite low in arsenic.

22.3.10 If there is any reason for believing that the reagents used are not arsenic-free, run blank determinations concurrently, using the same reagents in the same amounts and make the proper correction for the amount of orpiment thus found.

22.4 *Calculation*—Calculate the percentage of orpiment (As<sub>2</sub>S<sub>3</sub>) as follows:

$$\text{Orpiment, \%} = [(R - B)/S(1 - M)] \times 100 \quad (11)$$

where:

*R* = residue from specimen, g (22.3.9),

*B* = residue from blank, g (if any) (22.3.10),

*S* = sample used, g, and

*M* = volatile matter (moisture) content of the sample, expressed as a decimal fraction.

## 23. Saponification Value

### 23.1 *Definition:*

23.1.1 *saponification value*—the number of milligrams of potassium hydroxide that react with 1 g of the moisture-free sample. It is a measure of the alkali reactive groups in lac resins.

### 23.2 *Reagents:*

23.2.1 *Hydrochloric Acid, Standard (0.5 N)*—Add 45 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to about 900 mL of water, cool, and dilute to 1 L. Standardize against freshly standardized NaOH solution or by any other accurate method.

23.2.2 *Neutral Alcohol*, as prescribed in 21.2.1.

23.2.3 *Phenolphthalein Indicator Solution*, as prescribed in 21.2.2.

23.2.4 *Potassium Hydroxide, Alcoholic Solution (0.5 N)*—Prepare the solution as prescribed in 21.2.3, Item 2, except use 33 g of KOH in 1 L of the alcohol.

23.2.5 *Thymol Blue Indicator Solution*, as prescribed in 21.2.4.

### 23.3 *Procedure:*

23.3.1 Weigh to 1 mg approximately 1 g of the mixed sample (Section 7) into an alkali-resistant, standard-taper, ground-glass joint, 250-mL Erlenmeyer flask. Using a constant volume pipet, add 25 mL of the alcoholic KOH solution to the flask containing the specimen and to a second flask for use as a blank. Add 25 mL of the neutral alcohol to each flask and attach a standard-taper, ground-glass joint condenser to each flask. Connect the condensers with soda-lime tubes and reflux on a steam bath for at least 1 h. Wash down the condensers and the sides of the flasks with 20 mL of the neutral alcohol and titrate in accordance with 23.3.2 or 23.3.3.

23.3.2 In the case of bleached lac, add several drops of the phenolphthalein solution to each flask and titrate with 0.5 *N* HCl, with constant swirling of the contents of the flask, until the pink color just disappears.

23.3.3 In the case of orange shellac place several drops of the thymol blue indicator solution on a white porcelain spon plate. Titrate the solutions with 0.5 *N* HCl, with constant swirling, and determine the end point by transferring one or two drops of the solution on a glass rod to the indicator. The end point is when the color of the indicator changes to red.

23.4 *Calculation*—Calculate the saponification value as follows:

$$\text{Saponification value} = [(B - V)N \times 56.1]/S(1 - M) \quad (12)$$

where:

*V* = HCl required for titration of the specimen, mL,

*B* = HCl required for titration of the blank, mL,

*N* = normality of the HCl,

*S* = sample used, g, and

*M* = volatile matter (moisture) content of the sample expressed as a decimal fraction.

## 24. Keywords

24.1 bleached lac; button lac; insoluble content; matted lac; orange lac; saponification value; shellac; volatile content

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