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**AMERICAN WOOD-PRESERVERS' ASSOCIATION
STANDARD**

A3-91

**STANDARD METHODS FOR DETERMINING PENETRATION OF
PRESERVATIVES AND FIRE RETARDANTS**

Note: Standard A3-90 consists of five pages dated as follows: Pgs. 1-5, 1990.

Scope

These are the methods for determining the depth of preservative penetration in treated wood in order to decide whether the treated product meets acceptance levels as prescribed in treatment standards.

The methods appear in the following order:

1. Method for Determining Penetration of Boron-Containing Preservatives and Fire Retardants.
2. Method for Determining Penetration of Copper-Containing Preservatives.
3. Procedure for Determining Penetration of Pentachlorophenol Using 4, 4'-Bis-Dimethyl-amino-Triphenylmethane (DMTM).
4. Procedure for Determining Penetration of Pentachlorophenol Using a Silver-Copper Complex Known as Penta-Check.
5. Determination of Penetration of Solvent Used with Oil-Soluble Preservatives.
6. Method for Determining Penetration of Zinc-Containing Preservative.
7. Method for Determining Penetration of Fluoride in Wood.
8. Method for the Determination of Copper In Wood Using Rubeanic Acid.
9. Standard Visual Penetration Test for Phosphorus Containing Fire Retardants.
10. Colorimetric Analysis of Copper.
11. Method for Determination of the Presence of Hexavalent Chromium in Treated Wood.
12. Method for the Determination of Penetration In Wood of Zinc-Containing Preservatives.
13. Method for the Determination of Pentachlorophenol Penetration In Poles By X-Ray Fluorescence

1. METHOD FOR DETERMINING PENETRATION OF BORON-CONTAINING PRESERVATIVES AND FIRE RETARDANTS

Reagents

Solution 1. Extract 10 grams turmeric with 90 grams ethyl alcohol. Decant or filter to obtain clear solution.

Solution 2. Dilute 20 ml. of concentrated hydrochloric acid diluted to 100 ml. with ethyl alcohol and then saturate with salicylic acid (about 13 grams per 100 ml.).

Procedure

A smooth surface shows the results of the spot test better than a rough surface. The surface must be dry, otherwise the test will not be satisfactory.

Solution 1 is applied, preferably by spraying, or with a dropper, to the surface to be treated. The surface being treated is then allowed a few minutes to dry.

Solution 2 is then applied in a similar manner to the areas that have been colored yellow by the application of Solution 1. The color changes should be observed carefully and will show up a few minutes after application of the second solution. In the presence of boron, the yellow color of the turmeric solution is turned red.

After reagent application, placing wood in warm oven accelerates and intensifies the color reaction to better differentiate between treated and untreated wood.

2. METHOD FOR DETERMINING PENETRATION OF COPPER-CONTAINING PRESERVATIVES

Reagent

Dissolve 0.5 gram Chrome Azurol S¹ concentrate and 5.0 grams sodium acetate in 80 ml. water and dilute to 500 ml.

Procedure

Spray the solution over split borings or freshly cut surfaces of treated wood. A deep blue color reveals the presence of copper.

¹Chrome Azurol S, Color Index No. 43825, also known as Mordant Blue 29.

3. PROCEDURE FOR DETERMINING PENETRATION OF PENTACHLOROPHENOL, USING 4, 4'-BIS-DIMETHYLAMINO-TRIPHENYLMETHANE (DMTM)¹

Scope

By using 4, 4'-bis-Dimethylamino-Triphenylmethane it is possible to detect the presence of pentachlorophenol in treated wood. The test will readily detect quantities of 0.05 pounds per cubic foot and frequently will detect 0.01 pound.

The test may become less selective as a solution of DMTM in acetone ages. Therefore, only freshly prepared solutions should be used.

¹DMTM is also known as Leucomalachite Green or P,p' Benzyldiene bis-(N,N-dimethylaniline)

The method is *not* suitable for determining penetration in wood treated with pentachlorophenol dissolved in P9 heavy solvents.

Apparatus and Chemicals

Balance, accurate to 0.1 gram
125 ml. flask
100 ml. graduate cylinder
Spatula
Infra red lamp (115–125 V, 250 W Westinghouse clear glass heat lamp has been found satisfactory)
Support for lamp
Eye dropper
4, 4'-bis-Dimethylamino-Triphenylmethane (DMTM)
CP acetone

Make-up of Stain Solution

Stain consists of 0.5 g. DMTM dissolved in 75 ml. CP acetone. When stain solution is to be made the solid dye is weighed on a balance into a 125 ml. Erlenmeyer flask. Acetone is poured into the flask and the dye dissolved by swirling gently. Solution should be made up fresh each day unless it is stored under refrigeration. Since the solution is basically a stain, any unused portion should be disposed of out doors. If kept in the laboratory it will dry, becoming a greenish dust which may stain clothing, equipment, etc.

Procedure

With an eye dropper¹ place several drops of freshly prepared stain on a cross section or the end grain of an increment borer core. Usually 4 to 6 drops of stain per inch length of core is sufficient to thoroughly soak the surface of the boring.

Allow the surface of the samples to dry for 10 to 15 seconds, then place samples under an infra red lamp at a distance of 3 to 4 inches beneath the lamp. The test may be conducted without the use of a lamp.

After an exposure period of 2 to 3 minutes under a lamp, maximum reaction will have taken place. If no lamp is used, maximum reaction will take place in 5 to 10 minutes.

The presence of pentachlorophenol is indicated by the development of a green color on the surface of the wood.²

¹ An eye dropper is recommended rather than dipping the sample in stain solution. If samples are dipped, there is a possibility of solution contamination by pentachlorophenol from one sample to the next. This will not occur if a dropper is used.

² When freshly prepared solutions are used, the reaction is positive. If old solutions are used (24 hours or older) a faint greenish cast appears even on the surface of untreated wood.

4. PROCEDURE FOR DETERMINING PENETRATION OF PENTACHLOROPHENOL USING A SILVER-COPPER COMPLEX KNOWN AS PENTA-CHECK

Penta-Check is a special blend of copper and silver ions for the determination of pentachlorophenol and distribution in wood. Reddish colored copper pentachlorophenate is formed where pentachlorophenol is present thus indicating the exact location of pentachlorophenol. Untreated springwood and heartwood of southern yellow pine and Ponderosa are colored green. Untreated Douglas fir is colored yellowish to olive.

The exact mechanism of the silver ions is not known, but in their presence, a redder color is formed than with copper alone.

This method is recommended for determining the penetration of pentachlorophenol in wood using light-colored Hydrocarbon Solvent Type A, Hydrocarbon Solvent Type B, or Hydrocarbon Solvent Type C of Standard P9. The penetration of pentachlorophenol dissolved in dark-colored Hydrocarbon Solvent Type A should be judged by visual examination without staining. The method is not suitable for determining the penetration in the heartwood of redwood.

Reagents

Cupric acetate $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$
Silver acetate $\text{CH}_3\text{COO Ag}$
Triton X-100
Distilled Water

Stock Blends

I		II	
Cupric Acetate	4.0 grams	Silver Acetate	0.4 grams
Triton X-100	0.5 grams	Distilled Water	100.0 grams
Distilled Water	100.0 grams		

Mix cupric acetate and distilled water until dissolved and then add the Triton X-100 and blend until solution clears. Reserve as Blend I. Mix silver acetate and distilled water until dissolved and reserve as Blend II. Aspirate each stock solution to the treated wood, split borings, or cross-sectional slabs of penta treated wood and observe the rapid formation of the reddish colored copper pentachlorophenate. Excessively dark penta treatments tend to obscure the color.

SPECIAL NOTE: This methodology usually detects penta to 0.04 pcf, but certain cases have been documented to indicate non-detection at retentions up to 0.22 pcf.

NOTE: Triton X-100 is manufactured by Rohm & Haas Chemical Co. and is a 9-10 mole iso-octyl phenol. Commercial grade 9-mole nonyl-phenol has also proved to work with satisfactory results. Cupric acetate should be reagent grade quality.

5. DETERMINATION OF PENETRATION OF SOLVENT USED WITH OIL-SOLUBLE PRESERVATIVES

Scope

The method is designed exclusively for determining the penetration in wood of pentachlorophenol dissolved in light-colored Hydrocarbon Solvent Type A of Standard P9. The penetration of pentachlorophenol in dark-colored Hydrocarbon Solvent Type A should be judged by visual examination without staining.

Reagents

1. 20 parts 'Speedex' filter aid powder, or calcium carbonate.
2. 1 part Oil Red 0.*

Weigh dry powders and grind together with mortar and pestle.

Basis of Test

The dry powdered oil red dyestuff dissolves in petroleum solvent producing bright red color.

Method of Application

Must be used on freshly made and split borings or wood cross sections.

Apply very light (invisible) coating of mixed powders to wood samples with a small brush. The portions of wood containing petroleum solvent in which pentachlorophenol is carried will turn bright red within 5 minutes. Untreated portions of wood sample retain their normal color.

Notes as to penetration must be made immediately as the borings cannot be saved as a permanent record. The petroleum solvent tends to bleed along freshly exposed surfaces. However, the line of demarcation between treated and untreated wood is very sharp for first few minutes.

Important: Brush and powder which is dusted on wood surfaces must be kept dry and free of petroleum.

NOTE: This powder has also been successfully used by dusting from a small hand spray gun.

*Oil Red 0, Color Index No. 26125, also known as Calco Oil Red, Solvent Red 27, and Oil Red 235

6. METHOD FOR DETERMINING PENETRATION OF ZINC-CONTAINING PRESERVATIVES

Reagents

1. 1 gm. of potassium ferricyanide in 100 ml. of water.

2. 1 gm. of potassium iodide in 100 ml. of water.

3. Starch indicator solution. Make a paste of 1 gm. of soluble starch in about 5 ml. of distilled water, add 100 ml. of distilled water, and boil for 1 minute with constant stirring. Cool. This solution is subject to decomposition and therefore should not be used longer than three days before a new batch is prepared.

Method of Application.—The boring or cross-section of wood to be tested should be reasonably dry. Mix 10 ml. each of the 3 stock solutions, and pour into a good atomizer. A DeVilbiss No. 30 atomizer has been found satisfactory. Spray the boring or cross-section of wood evenly all over. The reaction between the zinc chloride and the spraying solution will cause the treated wood to turn a deep blue instantly, while the untreated part will retain its original color. This method is a positive test. Should the color fade, repeat the process.

7. METHOD FOR DETERMINING PENETRATION OF FLUORIDE IN WOOD

Solution 1. Sodium alizarin sulfonate.....	0.50 gms.
Water.....	100. gms.
Solution 2. Zirconyl chloride (Fisher Z-80).....	0.50 gms.
Hydrochloric acid, sp. gr. 1.19.....	30. gms.
Water.....	70. gms.

Procedure

1. The surface of the boring or cross section of the timber to be tested is allowed to dry thoroughly before testing. (Results are not so reliable with wet surfaces.)

2. Mix equal quantities of Solutions No. 1 and No. 2 by adding No. 1 to No. 2 (red to white). It is important to add the alizarin solution to the zirconyl chloride; otherwise a proper reaction will not take place.

These two solutions must be *mixed fresh* before using, as the mixture will not work satisfactorily after standing one hour. It is normal to mix up the minimum quantities in order to avoid wastage.

3. Spray the surface to be tested with the mixture. The atomizer should be held about three inches away from the surface under test and the spray is added until the surface can be seen to be wetted. No running of the solution must take place.

As the wood again dries, the red color of the sprayed surface will change to yellow where the preservative has penetrated. The reaction is comparatively slow and the color will be developed fully after 15 minutes.

A second application of spray can be made when the surface has dried again to obtain a clearer definition.

8. METHOD FOR THE DETERMINATION OF COPPER IN WOOD USING RUBEANIC ACID

Reagents

1. Rubenic Acid Solution. Dissolve 0.5 rubenic acid (dithio oxamide) in 100 ml ethanol.
2. Sodium Acetate Solution. Dissolve 5 g sodium acetate in 100 ml distilled water.

Procedure

Spray the core or wood section with Rubenic acid solution, then the sodium acetate solution. A dark green color indicates the presence of copper, the untreated wood being colored pale yellow.

Comments

The rubenic acid has approximately the same sensitivity as Chrome Azurol S, at ca. 25 ppm copper. Chrome Azurol S is the preferred reagent for freshly treated wood because of its stronger reaction. Rubenic acid is, however, more specific to copper and is less subject to interference reactions. Therefore, it is the preferred reagent for measuring CCA penetration in wood that has been in service for some time in ground contact.

9. STANDARD VISUAL PENETRATION TEST FOR PHOSPHORUS CONTAINING FIRE RETARDANTS

Solution A

Dissolve 3.5 gm ammonium molybdate in 90 ml distilled water. Add 9 ml concentrated nitric acid and mix.

Solution B

Dissolve .15 gm stannous chloride in about 75 ml 1 to 1 hydrochloric acid and water, make-up with 1 to 1 hydrochloric acid to 100 ml.

Note: The most satisfactory results are obtained by using freshly prepared Solution A. Solution B is stable for one month.

Test Procedure:

1. Apply Solution A to the wood surface with a medicine dropper. Saturate the wood surface—don't merely wet the surface.

Let stand for at least 2 minutes to give chemicals time to react.

2. Shake off any excess liquid and apply Solution B. Color change will appear immediately; maximum effect is within 5 minutes. The color reaction is permanent and becomes more distinct after 1 hour.

3. The treated portion will appear dark blue—the untreated portion will remain a natural color or

acquire a green tinge. A green color indicates an area of no treatment.

Warning:

The two solutions are acidic and can cause burns. Avoid contact with skin and eyes. In case of contact, immediately flush skin or eyes with plenty of water. For eyes, get medical attention.

10. COLORIMETRIC ANALYSIS OF COPPER

Scope

This method provides for the colorimetric determination of copper in copper naphthenate-treated wood or in copper naphthenate solutions. It measures the total copper in the sample.

1. Equipment and Chemicals

Analytical Balance
Crucibles for igniting samples
Bunsen Burner
Hood
Nitric Acid, concentrated
Distilled water
Aqueous Ammonium Hydroxide, concentrated
Volumetric Flasks, 25 ml and 50 ml
Spectrophotometer (610 nm)
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, reagent grade

2. Standard Graphs

- a) Accurately weigh about 0.8 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ into a bottle and add about 49 grams of water to make exactly 50.00 grams of dilute copper standard stock solution. (Alternatively, dilute to 50 ml in a volumetric flask.)
- b) Accurately weigh about 0.5 grams of the stock solution into a 25 ml volumetric flask, add about 10 ml of ammonium hydroxide, dilute to the mark with water, and mix well. (Alternatively, measure exactly 0.50 ml of the stock solution instead of weighing it.)
- c) Place a portion of the 25 ml blue solution into a clean spectrometer cell and measure the % Transmittance at 610 nm. (The instrument should be warmed up and zeroed with air and water.)
- d) Repeat (b) and (c) six times using six different sample sizes: 0.5, 1, 2, 3, 4, 5 grams.
- e) Plot the grams of copper vs. the absorbance. $\text{Absorbance} = -\log(\%T/100)$. All six points should lie on the straight line per Beer's Law. (Alternatively, semi log paper may be used to plot % Transmittance directly vs. the grams of copper.)

3. Sample Analysis

- a) Accurately weigh a sample of copper naphthenate treating solution or copper naphthe-

nate-treated wood into a crucible. Use a sample size so as to provide about 0.01 grams of copper (0.002 to 0.02 grams).

NOTE: Wet wood may be analyzed by weight but this should be so stated. Alternatively, the % moisture may be cited or the wet density. Or, simply the volume of the wood can be measured and the copper concentration in the wood may be expressed in weight per volume units such as g./cu.in. or pcf. These approaches avoid the need to dry the samples. If a drying step is used the evaporation of both water and organic solvent should be accounted for.

- b) Carefully ignite the sample until the organic matter is burned off. Cool and add about 3 ml of nitric acid. Carefully heat and boil the acid. This ensures that the copper is in the cupric state.
 - c) Cool and quantitatively transfer the solution to a 25 ml volumetric flask, washing the crucible out with small portions of distilled water. Leave room in the flask for about 10 ml of ammonium hydroxide. Dilute to the mark with water.
 - d) Measure the % Transmittance of 610 nm. Read the corresponding grams of copper from the Standard Graph.
4. Calculations
- a) Calculate the grams of copper in each of the six standard test solutions:

$$\text{g. of Cu} = \text{g. of CuSO}_4 \cdot 5\text{H}_2\text{O} \times \frac{63.54}{249.6} \times \frac{\text{g. of stock sol'n}}{50.00}$$

Alternatively,

$$\text{g. of Cu} = \text{g. of CuSO}_4 \cdot 5\text{H}_2\text{O} \times \frac{63.54}{249.6} \times \frac{\text{ml. of stock sol'n}}{50.00 \text{ ml.}}$$

- b) Calculate the weight % copper in the sample:
- $$\% \text{ Cu in sample} = \frac{\text{g. of Cu from Standard Graph}}{\text{g. of sample}} \times 100$$

Alternatively,

$$\text{pcf Cu in wood} = \frac{\text{g. of Cu from Standard Graph}}{\text{cu.in. of wood sample}} \times 3.810$$

11. METHOD FOR DETERMINATION OF THE PRESENCE OF HEXAVALENT CHROMIUM IN TREATED WOOD

Scope

When chromotropic acid is complexed with chromium (VI), a pink to purple color is formed. Such

visible color does not occur with chromium (III). This method indicates, by the absence of the colored chromotropic acid complex, the presence of 15 ppm or less chromium (VI).

Reagent

Dissolve 0.5 grams of chromotropic acid (4,5-dihydroxy-2,7-naphthalene disulfonic acid) or its disodium salt in 100 ml. of 1N (approx. 5 wgt.%) sulfuric acid. This solution should have a shelf life of at least 2 months.

Procedure

Borings for testing should be taken by hand, split and the bit thoroughly rinsed in water between borings. Borings should be allowed to come to room temperature before testing.

Place the freshly cut boring on a white blotter paper surface, such as filter paper or a white index card. With a medicine dropper, apply several drops of the chromotropic acid solution to wet the core. Usually 5 to 7 drops per a one-inch length of core is sufficient for a core still wet from treatment. If the core is dry, it is helpful to apply 2 or 3 drops of the solution carefully and allow the surface of the core to become saturated before applying the remaining drops.

Allow the reaction to continue for at least 10 minutes. Then remove the core and observe the colored complex that has leached onto the blotter; if the blotter is not wet, insufficient solution was applied and the test must be repeated. Any pink to purple color on the blotter indicates the incomplete conversion of chromium (VI) to chromium (III).

Sensitivity for Color

The minimum detection limit for the method is 15 ppm chromium (VI).

12. METHOD FOR THE DETERMINATION OF PENETRATION IN WOOD OF ZINC-CONTAINING PRESERVATIVES

Reagents

0.1 grams of Dithizone (Dimethylthiocarbazone) dissolved in 100 ml of chloroform (or other available chlorocarbon solvent).

Application

Drop, brush, spray this reagent solution onto the treated wood. The green solution will immediately (1–5 seconds) turn red on the wood if zinc is present. It will stay green if zinc is absent. (The red color will remain for over 30 minutes, but eventually will slowly fade.)

13. METHOD FOR THE DETERMINATION OF PENTACHLOROPHENOL PENETRATION IN POLES BY X-RAY FLUORESCENCE

1.0 X-ray (ASOMA) determination of penetration of pentachlorophenol in wood borings

1.1 Scope: Following is a method utilizing the ASOMA x-ray fluorescence analyzer and split-borings to determine penetration of Pentachlorophenol.

2.0 Sample Borings

When penetration of preservative cannot be detected visually, then the subject method could be utilized for the questionable boring(s).

3.0 Instrument Preparation

3.1 Make sure that the ASOMA x-ray unit has been turned on and is warmed up. This takes approximately 15 minutes.

3.2 The unit must be STABILIZED and STANDARDIZED before any meaningful results can be obtained. These functions shall be performed in accordance with the ASOMA instructions prior to each analysis.

4.0 Boring Preparation

4.1 ASOMA instructions caution relative to the drying of borings; DO NOT OVEN DRY—PENTA CAN BE DRIVEN OFF BY HIGH TEMPERATURES.

4.2 Weigh the total boring ($\pm .01$ grams) and record the weight and length.

4.3 Cut boring into the appropriate zone as shown below:

Required Depth of Penetration (in)	Boring Segment (inches from surface)
2.5	2.25–2.75
3.0	2.75–3.25
3.5	3.25–3.75

If the sapwood depth is less than the penetration requirement (inches), then the 1/2 inch segment to be analyzed would be centered around a point at which the minimum percent sapwood requirement is satisfied (i.e. 85% for 0.30 PCF, 90% for 0.38 PCF, and 90% for 0.45 PCF retentions).

4.4 Section the boring into 1-1/2 inch lengths, centering the 1/2 inch zone to be tested. Split the boring into two halves along the grain direction. Suggest using a boring splitter.

5.0 Analysis

5.1 Stabilize the machine (see paragraph 3.0 above).

5.2 Analyze untreated ground boring sample (blank) and set ground boring zero.

5.3 Analyze untreated split boring sample (blank) and set split boring zero only if necessary.

5.4 Insert the split boring sample to be tested (determined in paragraph 4.3) and close shield cup.

5.5 Determine density of PCF.

5.6 ID if desired.

5.7 Press "ANLYZ" and the unit will perform the analysis, calculate, and print the results.