

CS-194-53
PENTACHLOROPHENOL CONCENTRATE FOR WOOD PRESERVATION
AND SOIL POISONINGCOMMERCIAL STANDARD CS194-53
(Effective August 24, 1953)

1. PURPOSE

1.1 The purpose of this commercial standard is to provide a nationally recognized specification for pentachlorophenol concentrate for wood preservation and soil poisoning, for the guidance of producers, distributors, and users; to promote fair competition and consumer confidence in products conforming to this standard; and to provide a basis for labeling and guaranteeing the quality of the product.

2. SCOPE

2.1 This standard sets forth the minimum requirements for one type of pentachlorophenol concentrate intended for dilution with 10 parts of diluent to 1 part of concentrate before use. It specifies requirements and methods of test for flash point, weight per gallon, stability on storage, color, and active ingredients content, and includes a recommended statement for use in declaring conformance with this standard. The product covered is intended for soil poisoning or wood treatment by methods that do not require heating of the treating solution.

2.2. The requirements of this standard do not ensure a product that is suitable for treatment of wood that is to be subsequently painted or otherwise surface-finished, such as millwork, interior trim, etc. A purchaser who desires a product for use on wood that is to receive subsequent treatment should obtain assurance from the seller that the product is suitable for the specific type of application he intends to use, with instructions regarding suitable diluents.

3. REQUIREMENTS

3.1 Materials.— The concentrate shall consist of technical pentachlorophenol and such solvents as are necessary to meet the requirements of the standard. The concentrate shall be dilutable with petroleum distillates such as kerosene, Diesel fuel, mineral spirits, No. 2 fuel oil, and with heavier oils such as crank case oil; and with linseed oil, liquid resins, and other special substances for the particular usage at hand as recommended by the manufacturer.

3.2 Weight per gallon.—The concentrate shall weigh at least 9.45 pounds per gallon at 100° F when tested in accordance with par. 4.1. Lower weight per gallon is acceptable provided the technical pentachlorophenol content is not less than 3.78 lb/gal.

3.3. Flash point.—The flash point shall be not lower than 135° F by the method specified in par. 4.2.

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3.4 Pentachlorophenol content.--The concentrate shall contain not less than 40 percent by weight of technical pentachlorophenol which shall conform in all respects to Federal Specification TT-W-570 ^{1/}. Determination of technical pentachlorophenol shall be made by either Method I (par. 4.3.1) or Method II (par. 4.3.2). Method II shall be used in all cases where the presence of halogen compounds other than chlorophenols is known or suspected.

^{1/} As 10:1 concentrates are used to prepare ready-to-use solutions with varying concentrations of pentachlorophenol by percent, as the weight of pentachlorophenol per gallon of concentrate can vary, and as the weight per gallon of diluent will vary according to type, a simple formula is given to show how a ready-to-use solution of any desired specific percent of pentachlorophenol can be prepared regardless of the specific gravity or weight per gallon of the diluent. The formula for determining the volume of diluent required to yield a given percent of pentachlorophenol in the ready-to-use solution is:

$$Vd = \frac{Vc \times Wc (Cp - Dp)}{Dp \times Wd}$$

where Vd = Volume of diluent oil (cut-back oil) to be added in gallons
Vc = Volume of concentrate in gallons
Wc = Weight of concentrate in pounds per gallon
Cp = Concentration of PENTA in the concentrate expressed as a decimal fraction
Dp = Desired percent of pentachlorophenol wanted in the ready-to-use solution - expressed as a decimal fraction
Wd = Weight of diluent oil (cut-back oil) in pounds per gallon

Example: If one wanted to prepare a ready-to-use solution containing 5% by weight of pentachlorophenol from a 10:1 concentrate containing 40% by weight of pentachlorophenol, the concentrate weighing 9.4 pounds per gallon, and if the petroleum used for diluting weighed 7 pounds per gallon (the usual weight of a No. 2 fuel oil), then substituting in the above formula one would find

$$Vd = \frac{1 \times 9.4 (0.40 - 0.05)}{0.05 \times 7} = 9.4$$

or that it would take 9.4 gallons of diluent to one gallon of concentrate to give an exact 5% ready-to-use solution, and if diluted 10:1 the ready-to-use solution would be slightly under a 5% solution.

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3.5 Stability in storage.--The concentrate shall not show crystals of pentachlorophenol^{2/} at a temperature of 320 F when tested as specified in par. 4.4. Method II shall be the referee method in cases of dispute.

3.6 Odor.--The concentrate shall not have a disagreeable odor. The odor should be no more objectionable than that of a 50/50 mixture of diacetone alcohol and diesel fuel.

3.7 Staining effect.--The concentrate, on dilution with kerosene, shall not cause undue staining of wood or concrete when tested as specified in par. 4.5.

4. METHODS OF TEST

4.1 Weight per gallon.--ASTM Designation D287.

4.2 Flash point.--ASTM Designation D93.

4.3 Pentachlorophenol content.--Pentachlorophenol may be estimated by a determination of the total chlorine by Method I or other suitable method; or colorimetrically by Method II. Method II shall be used when the absence of halogens other than chlorine combined as chlorophenols cannot be established.

4.3.1 Method I.--This method is intended for the chemical analysis of oils containing pentachlorophenol. The procedure is fairly rapid, reasonably accurate, and suitable for use under conditions where limited facilities are available. It is not applicable to samples containing other halogen compounds unless the latter can be determined and a correction made.

The method is based on destroying the organic material by heating and absorbing the liberated chlorine in calcium hydroxide. The chlorine is determined by the Volhard procedure. Potassium nitrate is used as an accelerator.

The method is suitable for amounts of pentachlorophenol of .002 gm to .075 gm with the limitation of not more than 2.0 gm of organic material.

4.3.1.1 Apparatus.--

- (a) Crucibles.--100 ml iron (Armco), or No. 3 high-form porcelain.
- (b) Burners.--Fisher high temperature or equivalent, equipped with sleeve for cutting off air supply:
 - No. 3-900 for gases of 500-600 BTU per cu ft.
 - No. 3-902 for gases of approximately 1000 BTU per cu ft.
 - No. 3-902P for bottled gases, propane or butane or mixture of the two.
- (c) Balance.--Analytical balance, sensitive to 0.001 gm.
- (d) Weighing bottles, 25 ml, equipped with droppers.

^{2/} As 10:1 concentrates are prepared from technical grade pentachlorophenol and technical grade solvents, some sedimentation not due to the crystallization of pentachlorophenol may occur. Such sedimentation shall not be cause for rejection.

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4.3.1.2 Reagents.--

- (a) Calcium hydroxide.--Analytical reagent grade, chloride content less than 0.005 percent. If high purity Ca(OH)_2 is not available, the soluble chloride may be removed as follows: Make a slurry of the Ca(OH)_2 in distilled water and stir thoroughly for some time. Filter on a large suction filter and wash moderately with distilled water. Repeat the process until the water shows little or no test for chloride. 2 - 3 times will usually suffice. Dry the filter cake at 100°C and crush to pass a 30-mesh screen before using. 30 grams of the dry Ca(OH)_2 should give a blank of less than 0.1 ml of 0.1 N AgNO_3 . If a centrifuge is available it may be used in place of filtration.
- (b) Potassium nitrate.-- Analytical reagent grade, chloride content not greater than 0.002%. Grind KNO_3 in a clean agate or porcelain mortar to pass a 30-mesh screen.
- (c) Nitric acid.--Concentrated (Sp. Gr. 1.42), analytical grade, chloride content not greater than 0.00007%.
- (d) Silver Nitrate.--Standard 0.1 N solution. Purchase from a reliable supply house or prepare by dissolving 16.989 gm of reagent primary standard grade AgNO_3 in distilled water, and making to one liter in a 1000-ml volumetric flask.
- (e) Ammonium thiocyanate.--Approximately 0.1 N solution. Purchase from a reliable supply house or prepare by dissolving 7.61 grams of reagent grade $\text{NH}_4 \text{SCN}$ in distilled water and making to 1000 ml in a volumetric flask. This solution must be standardized against the 0.1 N AgNO_3 . Standardize the $\text{NH}_4 \text{SCN}$ as follows: Add 15 ml of 0.1 N AgNO_3 from a 25 ml burette to a clean 400 ml beaker. Dilute about 150 ml, add 5 ml of HNO_3 and 5 ml of Volhard indicator. Titrate to the same end point used in an actual chloride determination.
- Factor to 0.1 N $\text{NH}_4 \text{SCN}$ = $\frac{\text{ml } 0.1 \text{ N } \text{AgNO}_3}{\text{ml } \text{NH}_4 \text{SCN}}$
- (f) Ferric ammonium sulfate (Volhard) indicator.--Dissolve 10 grams of $\text{FeNH}_4 (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (reagent grade) and 10 ml of concentrated HNO_3 in distilled water, and make to 100 ml.
- (g) Calcium hydroxide-potassium nitrate mixture.--Intimately mix 9 parts of Ca(OH)_2 and 1 part of KNO_3 powder.

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4.3.1.3 Procedure.--

- (a) Place 10 gm $\text{Ca}(\text{OH})_2$ - KNO_3 mixture in a 100 ml crucible, gently tapping the crucible on a table top to settle the contents. From a weighed dropping bottle, add sufficient sample to give approximately 0.25 gm of pentachlorophenol, (for a 40% solution this would generally be about 0.6 to 0.7 gm of solution) dropping the sample on the $\text{Ca}(\text{OH})_2$ - KNO_3 in the crucible in such a manner as to give even distribution. Reweigh the bottle and obtain the exact weight to one milligram by difference. Continue as in step (b).
- (b) Over the sample in the crucible, place 20 gm of the $\text{Ca}(\text{OH})_2$ - KNO_3 and gently tap on a table top to settle and level the mixture. Heat the mixture over a burner at a low temperature for about 10 minutes (this should be done by shutting off most of the air and allowing the flame to creep up the side of the crucible almost to the top.) If heating is properly done, no black fumes or burning at the surface should occur. The crucible should not be more than 1/2 inch above burner. At the end of 10 minutes, gradually increase the amount of air to the burner so that full heat is obtained in about 5 minutes, and finally heat at full heat for 15 minutes. Experience may indicate a longer time to be necessary on some types of oils. Samples should be free of unburned carbon. However, unless a large amount is present, no errors should be introduced.
- (c) Cool until the crucible can be handled and empty the contents of the crucible into a clean 400 ml beaker by gently tapping the crucible. Place a watch glass on the beaker and cautiously dilute with distilled water to about 70 ml. Scrub the crucible with distilled water, and a stirring rod equipped with a rubber policeman to loosen any remaining residue, and add it to the beaker containing the bulk of the sample. The volume at this point should not be much more than 100 ml. Place the beaker in an ice bath and neutralize the $\text{Ca}(\text{OH})_2$ with concentrated HNO_3 added in small increments (30 gm $\text{Ca}(\text{OH})_2$ requires about 51 ml conc. HNO_3). The solution should be checked periodically with a suitable indicator paper (for example, Congo Red paper) as the equivalence point is approached to insure against too great an excess of HNO_3 . Not more than 2 or 3 ml excess should be present. If desired, a 2% HNO_3 solution may be used to wash out the crucibles. However, this is generally not necessary.
- (d) From a burette, add 45 - 50 ml of standard 0.1 N AgNO_3 solution. Cover and boil gently for several minutes to coagulate the precipitated AgCl . Cool and filter through a rapid paper into a clean 400-ml beaker, and wash several times with distilled water. Test a few drops of the wash

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4.3.1.3 Procedure.--

(d) Continued

water with NH_4SCN ; no turbidity indicates that all excess silver has been washed out. Where a vacuum line, pump, or aspirator is available, it may be found desirable to replace the gravity filtration with suction filtration using a 500-ml suction flask and a 2" Buechner funnel. In either case the volume should not exceed 200-250 ml after washing. Add 5 ml of Volhard indicator and back-titrate excess AgNO_3 with standard 0.1 N NH_4SCN from a 25-ml burette to a pink end point that lasts at least 5 min. Run a blank on all reagents and untreated oil, if possible, unless oil is known to be free of chlorides.

4.3.1.4 Calculations.--Using the following formula, apply the appropriate temperature and normality corrections to convert the silver nitrate and ammonium thiocyanate volumes to those of 0.1 N solutions:

$$\text{Percent pentachlorophenol} = \frac{(A - B) \times 0.5327}{C}$$

where A = ml 0.1 N AgNO_3
B = ml 0.1 N NH_4SCN
C = weight of sample in grams.

4.3.1.5 Note.--No appreciable loss of chlorine has been noted with this method due to cracking of the $\text{Ca}(\text{OH})_2$ bed, if initial heating is not too rapid and if KNO_3 concentration does not exceed 1 gram per 9 grams $\text{Ca}(\text{OH})_2$ (10%). Definite losses were noted, however, (up to 50%) in cases where rapid combustion takes place as with 20% KNO_3 - 80% $\text{Ca}(\text{OH})_2$.

4.3.1.6 Reference.--R. H. Kimball and L. E. Tufts, Ind. Eng. Chem., Anal. Ed. 10, 530-1 (1938).

4.3.2 Method II.--This method is specific for chlorophenols. It is unaffected by other organic chlorides in the concentrate, which may be reported as pentachlorophenol when concentrates are analyzed by methods based on total chlorine content. It provides a qualitative identification as well as a quantitative estimation of the amount of technical pentachlorophenol in 10:1 concentrates.

By this method the chlorophenols are extracted from the concentrate as sodium salts, precipitated by acidification with HCl and redissolved in benzene. They are then converted into highly colored chloroquinones with HNO_2 and the optical density determined with a photoelectric colorimeter and light filter. The optical density is compared with a curve of optical densities plotted against known concentrations of technical pentachlorophenol.

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4.3.2.1 Apparatus.---

- 1 weighing bottle (5ml) with dropper and ground glass joint.
- 1 pipette, 10-ml
- 1 pipette, 20-ml
- 3 separatory funnels, short stemmed, 125-ml
- 1 graduated cylinder, 50-ml
- 1 volumetric flask, 50-ml
- 1 volumetric flask, 100-ml
- 1 volumetric flask, 250-ml
- 4 Erlenmeyer flasks, 125-ml
- 1 photoelectric colorimeter
- 1 light filter giving maximum transmission at 450 millimicrons.

4.3.2.2 Reagents.---

Benzene, nitration grade
Sodium hydroxide, 1% solution
Hydrochloric acid, concentrated
Hydrochloric acid, 10%
Nitric acid, 2:1 (2 vols, conc. HNO_3 to 1 vol. H_2O)
Anhydrous sodium sulfate
Technical pentachlorophenol (for calibration of optical density curve.)

4.3.2.3 Procedure.---

Weight accurately (± 0.001 gram) from a dropper weighing bottle a quantity of sample which will contain about 250 mg of pentachlorophenol into a 250-ml volumetric flask. The sample weight will be 0.6-0.7 gram for a 10:1 concentrate. Make up to volume with benzene.

Pipette 10 ml of this benzene solution into a 125-ml separatory funnel (funnel A). Add 15 ml of benzene and 25 ml of 1% sodium hydroxide solution. Shake for one minute and allow the layers to separate cleanly. If an emulsion forms, it can be broken by centrifuging. Draw off the lower (aqueous) layer into another 125-ml separatory funnel (funnel B), rinsing the stem of funnel A with distilled water.

Add an additional 25 ml of 1% sodium hydroxide to the benzene solution in funnel A, shake, separate, and draw off the lower (aqueous) layer into funnel B as above. Add 5 ml of water to the benzene in funnel A, shake, separate, and run the lower (aqueous) layer into funnel B. Discard the benzene solution in funnel A and clean.

Acidify the solution in funnel B to Congo red with 10% hydrochloric acid (5.5. to 6.0 ml should suffice). Add 30 ml of benzene and shake for one minute. Drain the lower (aqueous) layer

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into funnel A and the upper (benzene) layer into a 125-ml Erlenmeyer flask. Wash the aqueous portion in funnel A by shaking with 5 ml of benzene. Discard the aqueous layer and run the benzene into funnel B, using it to wash the sides of this funnel. Drain into the Erlenmeyer flask and rinse funnel B with an additional 5 ml of benzene. Add 10 ml of 2:1 nitric acid and a drop of concentrated hydrochloric acid to the benzene solution in the flask. Place on a steam bath for twelve minutes. Quench immediately with 60 ml of distilled water. Cool to room temperature. An intense yellowish-red color of chloroquinones is a qualitative indication of the presence of chlorophenols in the concentrate. Pour the entire contents of the flask into a clean 125-ml separatory funnel, rinsing the flask twice with 5 ml of benzene. Shake the funnel for thirty seconds and allow the layers to separate. Discard the lower (aqueous) layer and wash the benzene with an additional 25 ml of water. Allow the layers to break and discard the lower (aqueous) layer.

Drain the benzene solution from the funnel into a 100-ml volumetric flask which contains 2.0 grams of anhydrous sulfate. Rinse the funnel twice with 5 ml portions of benzene, draining these into the volumetric flask. Make up to volume with benzene, and shake until the benzene appears dry (clear). Read the optical density of the benzene solution with a photoelectric colorimeter, using the same filter as is used in preparing the calibration curve. If the color is too intense for a reading, the solution may be diluted quantitatively with benzene to the proper color range. A benzene blank should be used for the reference cell, or, alternatively, the optical density of a benzene blank may be subtracted from the optical density of the test solution measured against fresh benzene.

4.3.2.4 Calibration curve.—Prepare a benzene solution containing one milligram of technical pentachlorophenol per milliliter. Pipette 2.0, 5.0, 10.0 and 15.0 ml portions of this solution to 125-ml Erlenmeyer flasks. Add sufficient benzene to each to make the total volume 40 ml. Add 10 ml of 2:1 nitric acid solution and a drop of concentrated hydrochloric acid to each and develop the color as described under "Procedure" above. Plot the optical densities of the final diluted benzene solutions against the weight of pentachlorophenol in milligrams in the aliquots originally taken, correcting for the benzene blank as indicated above.

A blue filter having a transmission maximum at 450 millimicrons is recommended. If a combination of Corning Glass filters Signal Purple A No. 5551, Noviol Shade No. 3389, and Dark Shade Blue Green No. 4303 is used, the optical density - concentration curve will be a straight line through the origin.

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4.3.2.5 Discussion.—The double extraction technique used in this method effectively eliminates interference from the solvents, auxiliary solvents, antiblooming agents, and water repellents employed in commercial pentachlorophenol concentrates and treating solutions. In developing the method, a zero blank was obtained on the "solvent" portion of five proprietary concentrates, including such ingredients as diacetone alcohol, aromatic oils, pine oil, Aroclor 5460 (chlorinated terphenyls), cobalt naphthenate, paraffin, fish oil, and other water repellents and antiblooming agents.

4.4 Cold stability test.—

4.4.1 Method I.—Place 200 ml of the concentrate in a clean, dry 250-ml Erlenmeyer flask, stopper securely and place in a cold box at 0° F for 24 hours. Remove stopper after 24 hours, add a small crystal or two of pentachlorophenol and restopper. Perform this operation in a short period of time to prevent condensation of moisture inside the flask. If no crystallization occurs, replace the flask in the cold box and hold 72 more hours. Examine again for crystal deposition. If no crystallization has occurred, the concentrate is acceptable. If crystals are observed at either time of observation, allow the temperature of the chilled concentrate to rise to 32° F with stirring. If the crystals redissolve at that temperature the concentrate is acceptable.

4.4.2 Method II.—As mentioned in paragraph 3.5 footnote, containers of 10:1 concentrate often show some sedimentation under storage conditions. Since the concentration of pentachlorophenol in the solution can be determined by Method I or Method II, par. 4.3, what one really wants to learn from the cold stability test is whether pentachlorophenol will come out of solution at 32° F. The true solution point can be determined by the solution point method.

Using solution decanted from a 10:1 concentrate, weigh 30 gms into a 1.3 x 8 inch (33 x 203 mm) Pyrex tube. This is not a commercial test tube size but can easily be made from 33 mm Pyrex tubing. A stirrer assembly consisting of a thermometer surrounded by a close-fitting Pyrex tube carrying stirring paddles (Figure 1) is inserted in the tube containing the sample. A thermometer of the alcohol type covering the range of -58° F to 122° F (-50° C to +50° C) is recommended.

Using rapid agitation the concentrate sample is chilled to -20° F (or lower if necessary) to get crystal formation. A dry ice - alcohol or dry ice-acetone bath can be made easily. A small Dewar flask (3" diameter, 7" deep) is a convenient receptacle for the bath. Once crystals start to form, the solution is stirred for 15 minutes to assure complete crystallization of the pentachlorophenol. Where crystallization does not start readily, it may be necessary to seed the solution or scrape the surface of the tube to start crystal formation.

After complete crystallization, the temperature is raised to 15° F and then slowly (approximately 5° F per hour) with stirring. The stirrer is stopped periodically and the solution examined by transmitted light to see when all crystals are dissolved and the solution is clear. On very dark solutions where the crystals cannot be seen by transmitted light, the solution can be left at a

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given temperature without stirring for 5 minutes. If crystals are present they will usually appear in the bottom of the tube. The temperature at which all crystals dissolve is the solution point of the concentrate and indicates the storage temperature above which the pentachlorophenol will not drop out of solution.

4.5 Color.—Dilute a sample of concentrate in the ratio of one part of concentrate to 10 parts kerosene. Place two drops of the diluted concentrate on a clean piece of white pine or basswood, and two drops of the kerosene on the wood at a distance of approximately two inches from the diluted concentrate. After five minutes, compare the staining produced by the kerosene and the diluted concentrate. There shall be no appreciable difference.

5. LABELING

5.1 The manufacturer's instructions for dilution shall be given on the container label, or accompanying literature. The label shall also state, in legible type, under what conditions wood treated with the preservative is paintable.

5.2 In order that the purchaser may be assured that the product complies with this commercial standard, it is recommended that the following statement be included on labels 3/, contracts, sales literature, invoices, etc:

This concentrated pentachlorophenol solution complies with all requirements of Commercial Standard CS194-53, as developed by the trade under the procedure of the Commodity Standards Division, and issued by the U. S. Department of Commerce.

3/ This labeling is in addition to, and not in lieu of, that required under the Federal Insecticide, Fungicide and Rodenticide Act. Before shipment in interstate commerce, such products must be registered with the Insecticide Division, Livestock Branch, Production and Marketing Administration, U. S. Department of Agriculture, Washington 25, D. C.

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U. S. DEPARTMENT OF COMMERCE
Office of Technical Services
Commodity Standards Division

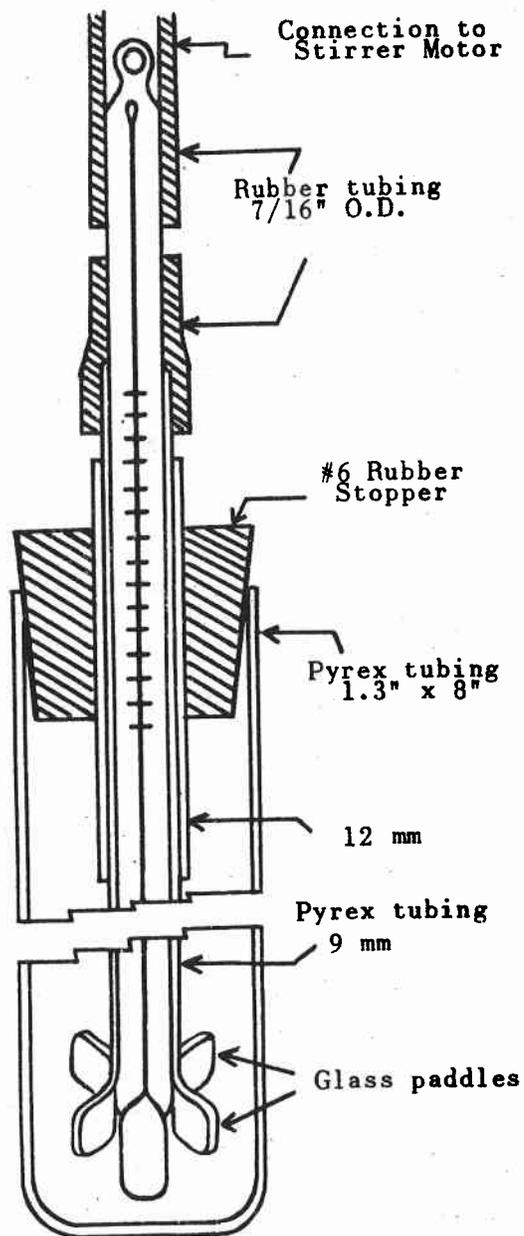


FIG. 1

Cold Stability Tester

federal register

**National Bureau of Standards
COMMERCIAL STANDARDS****Action on Proposed Withdrawals**

In accordance with § 10.12 of the Department's "Procedures for the Development of Voluntary Product Standards" (15 CFR Part 10, as revised; 35 FR 8349 dated May 28, 1970), notice is hereby given of the withdrawal of Commercial Standards CS 72-54, "Household Insecticide (Liquid Space Spray Type for Flying Insects)," CS 69-38, "Pine Oil Disinfectant," and CS 194-53, "Pentachlorophenol Concentrate for Wood Preservation and Soil Poisoning."

This action is taken in furtherance of the Department's announced intentions as set forth in the public notices appearing in the FEDERAL REGISTER of July 24, 1973 (38 FR 19850), to withdraw these standards.

The effective date for the withdrawal of these standards will be 60 days after the publication of this notice. This withdrawal action terminates the authority to refer to these standards as voluntary standards developed under the Department of Commerce Procedures.

Dated: November 13, 1973.

RICHARD W. ROBERTS,
Director.

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