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# Standard Test Methods for Apparent Free Phenols in Synthetic Phenolic Resins or Solutions Used for Coating Purposes[1]

This standard is issued under the fixed designation D 1312; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 These test methods cover the determination of the amount of apparent free phenol in synthetic phenolic resins or solutions used for coating purposes. The test method for isolation of the free phenol applies to all the commonly used resins except those containing *p*-phenyl-phenol. Test Method A applies to the simpler phenols up to and including the xylenols; Test Method B applies to the common alkylated phenols.

1.2 *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.*

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

## 3. Purity of Reagents

3.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] 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.

3.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type III of Specification D 1193.

## ISOLATION OF FREE PHENOLS

## 4. Apparatus

4.1 *Steam Generator*.

4.2 *Distillation Flask*—A 500-mL Kjeldahl flask.

4.3 *Condenser*.

## 5. Reagents

5.1 *Sodium Hydroxide Solution* (*100 g NaOH/L*)—Dissolve 100 g of NaOH [Caution] in water and dilute to 1 L.

## 6. Procedure

6.1 Transfer 1 to 2 g of the sample, weighed to the nearest 0.01 g, to a 500-mL Kjeldahl flask. Add 50 mL of water. Lead steam from a steam generator through a T-trap and then through a tube extending to the bottom of the flask. Take off the distillate through a second bent tube that extends just through the stopper of the flask and is attached to the top of an inclined long condenser. Using a 1000-mL volumetric flask as a receiver, collect 900 mL of the distillate. A small flame may be applied to the bottom of the Kjeldahl flask during distillation to maintain the volume of water constant. If the distillate is clear, dilute to 1000 mL; if not, add several millilitres of NaOH solution to dissolve the insoluble phenols. Determine the apparent free phenol in accordance with Method *A* or *B*, as required.

NOTE 1—*p*-Phenylphenol is not completely isolated by this procedure.

## TEST METHOD A—SIMPLER PHENOLS

## 7. Summary of Test Method

7.1 Free phenols are isolated by steam distillation, reacted with a measured excess of bromine, and the excess back-titrated with standard sodium thiosulfate solution.

## 8. Apparatus

8.1 *Iodine Flasks*, 500-mL, glass-stoppered.

## 9. Reagents

9.1 *Bromide-Bromate Solution*—Dissolve 2.784 g of $KBrO_3$ and 10 g of KBr in 1 L of water.

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[1] 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 D01.33 on Polymers and Resins.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *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 Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

9.2 *Potassium Iodide Solution* (*100 g KI/L*)—Dissolve 100 g of KI in water and dilute to 1 L.

9.3 *Sodium Thiosulfate, Standard Solution* (0.1 *N*)— Dissolve 25 g of $Na_2S_2O_3 \cdot 5H_2O$ in 1 L of water. Standardize against iodine.

9.4 *Starch Indicator Solution*—Dissolve 1 g of soluble starch in 100 mL of boiling water and cool.

## 10. Procedure

10.1 Pipet a 25-mL (or larger) aliquot of the distillate into a 500-mL iodine flask. Add 25 mL of KBr - $KBrO_3$ solution, shake, and add 10 mL of HCl (sp gr 1.19). Stopper quickly, shake to mix thoroughly, and fill the gutter with water. Let stand 15 min. (If the bromine color disappears during the shaking, take a fresh aliquot, add double the amount of bromate solution, and proceed as described.) Raise the stopper carefully and add 10 mL of the KI solution. Shake, and wash down the stopper and walls of the flask. Titrate with 0.1 *N* $Na_2S_2O_3$, solution using 1 mL of starch indicator at the end.

10.2 *Blank*—Run a blank in exactly the same manner, except to omit the test material.

## 11. Calculation

11.1 Calculate the percentage of apparent free phenols (Note 2), as follows:

$$\text{Phenols, \%} = [(T_1 - T)\, N \times 1.567]/\, W \quad (1)$$

where:

$T_1$ = $Na_2S_2O_3$ solution required for titration of the blank, mL,
$T$ = $Na_2S_2O_3$ solution required for titration of the sample, mL,
$N$ = normality of the $Na_2S_2O_3$ solution, and
$W$ = sample represented in the aliquot used, g.

NOTE 2—The cresols ($CH_3C_6H_4OH$) and xylenols ($(CH_3)_2C_6H_3OH$ have one or two reactive positions on the ring, depending on the isomer, but their tendency to add more bromine as an addition product that is not later removed by KI renders the exact extent of reaction uncertain. Since those materials are ordinarily used as mixtures in a resin-forming reaction, it is convenient and sufficiently informative to express the amount found as primary phenol.

## 12. Precision

12.1 The individual test results should not differ from the mean by more than ±0.5 %.

## TEST METHOD B—COMMON ALKYLATED PHENOLS

## 13. Summary of Test Method

13.1 Free phenols are isolated by steam distillation, reacted with a measured excess of iodine, and the excess back-titrated with standard sodium thiosulfate solution.

## 14. Apparatus

14.1 *Iodine Flasks*, 500-mL, glass stoppered.

## 15. Reagents

15.1 *Iodine Solution*—Dissolve 4.2 g of iodine in 15 g of a saturated aqueous KI solution and dilute to 1 L.

15.2 *Sodium Bicarbonate Solution* (84 g $NaHCO_3$/L)—Dissolve 84 g of $NaHCO_3$ in water and dilute to 1 L.

15.3 *Sodium Hydroxide Solution* (*100 g NaOH/L*)—Dissolve 100 g of NaOH in water and dilute to 1 L.

15.4 *Sodium Thiosulfate, Standard Solution* (0.1 N)—See 7.3.

15.5 *Starch Indicator Solution*—See 9.4.

15.6 *Sulfuric Acid* (*1+19*)—Add slowly, while stirring, 1 volume of concentrated $H_2SO_4$ [Caution] (sp gr 1.84) to 19 volumes of water.

## 16. Procedure

16.1 Add 15 mL of NaOH solution to the steam distillate and dilute to 1 L. Add 100 mL of water to a 500-mL iodine flask. Pipet a 10-mL (or larger) aliquot of distillate into the flask (Note 3) and add 30 mL of the iodine solution. Stopper and shake continuously for 5 min. Add 50 mL of $H_2SO_4$ (1 + 19) to the flask and titrate with 0.1 *N* $Na_2S_2O_3$ solution to a colorless end point, using 1 mL of starch solution as the indicator.

NOTE 3—If the sample is pure *p*-phenylphenol, add 50 mL of the $NaHCO_3$ solution to the flask before the sample is added to prevent the formation of color that interferes with the titration end point.

16.2 *Blank*—Run a blank in exactly the same manner, except omit the sample.

## 17. Calculation

17.1 Calculate the percentage of apparent free alkylphenols (Note 4) as follows:

$$\text{Phenols, \%} = [(B - V)\, N \times F]/\, S \quad (2)$$

where:

$B$ = $Na_2S_2O_3$ solution required for titration of the blank, mL,
$V$ = $Na_2S_2O_3$ solution required for titration of the sample, mL,
$N$ = normality of the $Na_2S_2O_3$ solution,
$F$ = conversion factor
= 3.755 for *p*-tertiary-butyl phenol
= 4.106 for *p*-tertiary-amyl phenol
= 4.255 for *p*-phenyl phenol, and
$S$ = sample represented in the aliquot used, g.

NOTE 4—The alkyl phenols form normal di-iodo compounds.

## 18. Precision and Bias

18.1 The individual test results should not differ from the mean by more than ±0.5 %.

18.2 *Bias*—No bias can be determined since no standard phenolic resin is available.

## 19. Keywords

19.1 free phenol; iodine solution; phenolic resin