Designation: D1832 – 04 (Reapproved 2009)

TAPPI Method T 659 wd-85

Standard Test Method for Peroxide Number of Petroleum Wax[1]

This standard is issued under the fixed designation D1832; 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 This test method covers the determination of the peroxide number of petroleum wax.

1.2 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are mathematical conversions to SI units that are provided for information only and are not considered standard.

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.*

2. Terminology

2.1 *Definitions:*

2.1.1 *peroxide number*—the milliequivalents of constituents per 1000 g of wax that will oxidize potassium iodide.

3. Summary of Test Method

3.1 A quantity of sample is dissolved in xylenes and acidified with acetic acid solution. A solution of potassium iodide is added and, after a reaction period, the solution is titrated with sodium thiosulfate solution to the end point indicated by the color change of added starch solution.

4. Significance and Use

4.1 The magnitude of the peroxide number is an indication of the quantity of oxidizing constituents present. Deterioration of petroleum wax results in the formation of peroxides and other oxygen-carrying compounds. The peroxide number measures those compounds that will oxidize potassium iodide.

5. Apparatus

5.1 *Iodine Flask*, borosilicate glass, 250-mL capacity, glass-stoppered.

6. Reagents and Materials

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 Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[2] 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 distilled water or water of equal purity.

6.3 *Acetic Acid Solution*—Mix 4 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) with 996 mL of ACS special reagent grade glacial acetic acid (CH_3CO_2H). The acetic acid must pass the ½-h test for substances reducing $K_2Cr_2O_7$.

6.4 *Xylenes*, (**Warning—**Flammable liquid. Vapor harmful.) Treated to remove oxidizing impurities. One way to do this is to pass the xylenes through an activated alumina column shortly prior to use.

6.5 *Potassium Dichromate, Standard Solution (0.1 N)*—Recrystallize potassium dichromate ($K_2Cr_2O_7$) twice from an aqueous solution and dry at about 325°F (164°C) to constant weight. Dissolve 2.452 g of the purified $K_2Cr_2O_7$ in water and dilute to 500 mL in a volumetric flask.

6.6 *Potassium Dichromate, Standard Solution (0.01 N)*—Dilute 100 mL of 0.1 *N* $K_2Cr_2O_7$ solution with water to 1000 mL in a volumetric flask.

6.7 *Potassium Iodide Solution*—Dissolve 120 g of potassium iodide (KI) in 100 mL of water. Discharge any color from this solution as follows: put 1 mL of KI solution, 50 mL of water, and 5 mL of starch solution in a 300-mL flask and blanket with nitrogen or carbon dioxide. If a blue color develops, add 0.005 *N* $Na_2S_2O_3$ solution from a microburet

[1] This test method is under the jurisdiction of the ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.10.0A on Physical/Chemical Properties.

Current edition approved Oct. 1, 2009. Published November 2009. Originally approved in 1961. Last previous edition approved in 2004 as D1832–04. DOI: 10.1520/D1832-04R09.

[2] *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 *Annual 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.

until color just disappears. Calculate and add sufficient $Na_2S_2O_3$ solution to the main KI solution to convert all free iodine to iodide. When starch solution is added to 1 mL of KI solution a blue color should not develop, but upon the addition of 1 drop of 0.01 *N* $K_2Cr_2O_7$ solution and 2 drops of concentrated hydrochloric acid (HCl, sp gr 1.19), a blue color should develop. Store this solution under chloroform by adding a few millilitres to the surface of the liquid.

6.8 *Sodium Thiosulfate, Standard Solution (0.1 N)*—Dissolve 12.5 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) and 0.1 g of sodium carbonate (Na_2CO_3) in 500 mL of water. Let stand a week or more before using. Standardize against 0.1 *N* $K_2Cr_2O_7$ solution. Restandardize at intervals frequent enough to detect changes of 0.0005 in normality.

6.9 *Sodium Thiosulfate, Standard Solution (0.005 N)*—Dilute 100 mL of 0.1 *N* $Na_2S_2O_3$ solution with water to 2000 mL in a volumetric flask. Standardize against 0.01 *N* $K_2Cr_2O_7$ solution.

6.10 *Starch Solution*—Dissolve 1 g of soluble starch plus a few milligrams of mercuric iodide (HgI_2) in 100 mL of boiling water.

7. Procedure

7.1 Melt a representative portion of wax sample on a water bath or in an oven. Do not heat above 150°F (65.6°C) or more than 20°F (11°C) above the congealing point as excessive heating may change the peroxide content.

7.2 Weigh, to the nearest 1 mg, 1 ± 0.2 g of the wax into a weighed iodine flask. To the flask, add 25 mL of xylenes (treated to remove oxidizing impurities) and quickly dissolve the sample, in an atmosphere of carbon dioxide (CO_2) on a steam bath. (**Warning**—A hood is advised.) Do not heat above 150°F (65.5°C) unless necessary to dissolve the sample. With the flask still on the steam bath, bubble a vigorous flow of CO_2 through the solution for 1 min. Reduce the flow of CO_2 so that the rate is 1 bubble per second, and add 20 mL of acetic acid solution that has been warmed sufficiently to prevent precipitation of the wax. Remove the flask from the steam bath, still continuing the flow of CO_2. Add 2 mL of KI solution and swirl vigorously for exactly 30 s. With the CO_2 bubbling through the mixture, set the flask aside and let stand for 5 min ± 3 s. Stop the flow of gas, add 100 mL of water, and mix thoroughly for 1 min. Titrate with 0.005 *N* $Na_2S_2O_3$ solution to a light yellow color. Add 5 mL of starch solution and continue the titration until 1 drop of the thiosulfate solution causes the blue color to disappear and not reappear for at least 30 s.

7.3 Make a blank determination on the reagents. Proceed as directed in 7.1 and 7.2 except to omit the sample.

8. Calculation

8.1 Calculate the peroxide number as milliequivalents per 1000 g of sample, as follows:

$$\text{Peroxide number} = [(A - B)N \times 1000]/S \quad (1)$$

where:

A = millilitres of $Na_2S_2O_3$ solution required for titration of the sample,
B = millilitres of $Na_2S_2O_3$ solution required for titration of the blank,
N = normality of the $Na_2S_2O_3$ solution, and
S = grams of sample used.

9. Precision and Bias

9.1 The following criteria should be used for judging the acceptability of results (95 % confidence):

9.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Range	Repeatability
0 to 15 peroxide number	1.5

9.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Range	Reproducibility
0 to 15 peroxide number	3.3

NOTE 1—Precision limits have not been established for values above 15 peroxide number.

NOTE 2—While the subcommittee's solvent replacement study found treated xylenes to be essentially a direct replacement for carbon tetrachloride in this test method, it should be noted that the precision limits in 9.1.1 and 9.1.2 were determined using carbon tetrachloride rather than xylenes.

9.2 *Bias*—The procedure in this test method has no bias because the value of peroxide number can be defined only in terms of a test method.

10. Keywords

10.1 peroxide number; petroleum wax; wax