Designation: D 6802 – 02

Test Method for Determination of the Relative Content Of Dissolved Decay Products in Mineral Insulating Oils by Spectrophotometry[1]

This standard is issued under the fixed designation D 6802; 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 characterizes by spectrophotometry the relative level of dissolved decay products in mineral insulating oils of petroleum origin. While new oil is almost transparent to a monochromatic beam of light in the visible spectrum, the increasing concentration of dissolved decay products shift the absorbance curve to longer wavelengths.

1.2 This test method is applicable to compare the extent of dissolved decay products for oils in service. It can assess the effectiveness of used or stored oil purification during the reclamation process, as well.

1.3 The values stated in SI units are to be regarded as standard. The values stated in parentheses are provided for information only.

1.4 *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 to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 923 Practices for Sampling Electrical Insulating Liquids[2]

D 1524 Test Method for Visual Examination of Used Electrical Insulating Oils of Petroleum Origin in the Field[2]

D 3487 Specification for Mineral Insulating Oil Used in Electrical Apparatus[2]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *aged oil, n*—an oil that no longer complies with the standard specifications for mineral insulating oils used in electrical apparatus according to D 3487.

4. Summary of Test Method

4.1 A test specimen of mineral insulating oil is placed in a 10-mm path length glass cuvette, which is installed in an UV-VIS scanning spectrophotometer. The instrument is first zeroed with spectral grade heptane. The absorbance curve of oil is then recorded from 360 to 600 nm. Integration of the area under this curve indicates the numeric value of the dissolved decay products in the oil sample. Because of the high sensitivity of spectral analysis, the deterioration of oil purity can be assessed in the early stages of the decay process.

5. Significance and Use

5.1 The content of dissolved decay products in insulating oils is made up of a variety of compounds, such as peroxides, aldehydes, ketones, and organic acids. Each of them is partially adsorbed on the large surface of paper insulation leading to the premature aging of power transformers. The relative assessment of byproduct formation, therefore, can be used as an indicator of the aging of the mineral oil.

6. Interferences

6.1 The condition of the oil specimen should be clear according to the requirement of Test Method D 1524.

6.2 The oil specimen, therefore, should be filtered through 50-µm filter paper.

7. Apparatus

7.1 *Recording UV-Visible Automated Spectrophotometer*, capable of scanning the range between 360 and 600 nm is required. The software should permit the calculation of area under the absorbance curve of the oil specimen.

8. Reagents and Materials

8.1 *Absorption Cuvettes*—To determine the absorbance curve of a mineral insulating oil, two matched glass cuvettes having a path length of 1-cm ± 0.01-cm should be used.

8.2 *Cuvette Filling Device*—A disposable plastic dropper of 2-mL capacity is recommended; however, any other suitable pipette may be used.

8.3 *Petroleum Spirits*, of 60–80°C boiling range.

8.4 *Heptane*, spectral grade.

9. Sampling

9.1 Obtain the oil sample in accordance with Practice D 923.

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[1] This test method is under the jurisdiction of Committee D27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.03 on Analytical Tests.

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[2] *Annual Book of ASTM Standards*, Vol 10.03.

10. Preparation of Apparatus

10.1 Clean the cuvettes thoroughly with petroleum spirits.

10.2 Adjust the automated spectrophotometer in accordance with manufacturer's recommendation.

10.3 Carry out the testing procedure at room temperature (25 ± 5°C).

11. Procedure

11.1 Fill one glass cuvette with heptane; place it in the sample holder and zero the instrument by adjusting it to read zero absorbance.

11.2 Move the heptane-filled cuvette by placing it to the reference position.

11.3 Fill the second glass cuvette with the oil specimen and place it into the sample holder.

11.4 Set the instrument to scan the region from 360 to 600 nm and begin scanning the specimen.

11.5 Display the absorbance curve and set the instrument to calculate the area under the curve.

12. Interpretation of Results

12.1 A relationship exists between the area under the absorbance curve and the total amount of dissolved decay products in mineral insulating oils. New oils usually have a relative area under the curve of less than 25 Abs. × nm.

12.2 The shift of the absorbance curve to longer wavelengths indicates an increased content of dissolved decay products in the oil.

12.3 The shift of the absorbance curve to shorter wavelengths after reclaiming a used or stored oil indicates the selective removal of dissolved decay products.

13. Report

13.1 Identification of oil sample.

13.2 The value of the calculated area under the absorbance curve for the oil specimen from 360 to 600 nm.

13.3 Comparison of this area to the area of typical new oil, which is usually less than 25 Abs. × nm, represents the relative content of dissolved decay products.

14. Precision and Bias

14.1 *Precision*—The precision of this test method has not been investigated through an interlaboratory test program.

14.1.1 *Repeatability*—Repeatability measurements made in one laboratory on three samples resulted in a coefficient of variation of 2.8 %. At the 95 % confidence level, duplicate determinations should agree within 7.8 % of the average of the two results (see Table 1).

14.1.2 *Reproducibility*—No data are available on which to base an estimate of the reproducibility of this test method. An interlaboratory test program will be conducted to develop this data.

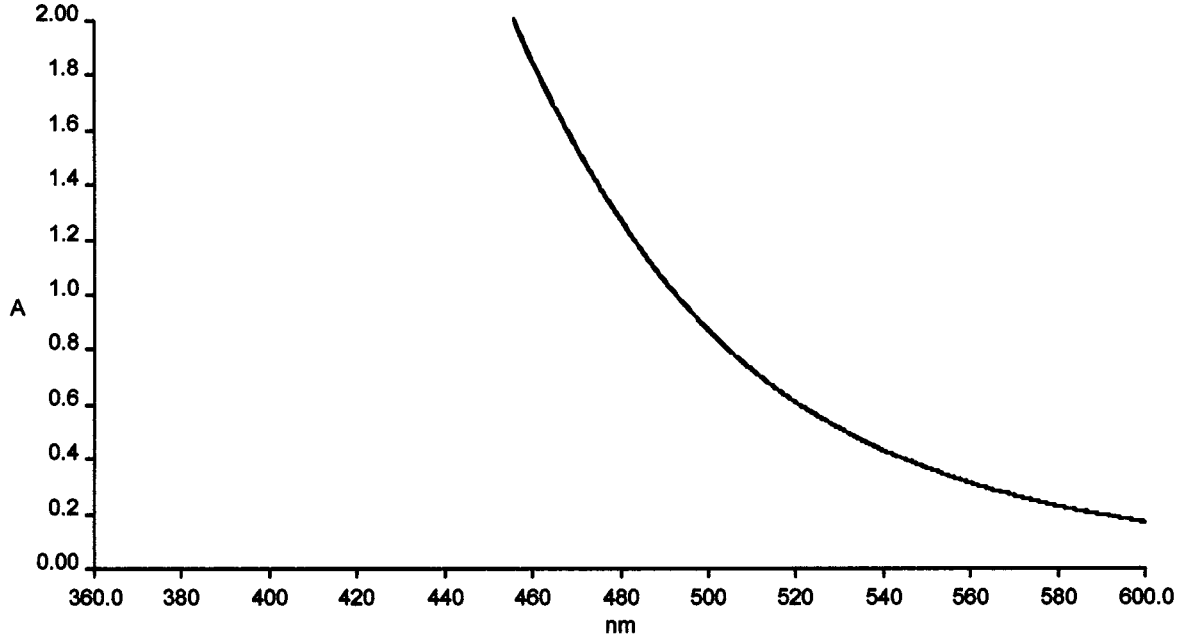
14.1.3 *Bias*—No information can be presented on the bias of the procedure for measuring the area under the absorbance curve in this test method, because no materials having an accepted reference value are available.

15. Keywords

15.1 chemical stability; dissolved decay products; insulating oil; oxidation decay; visible spectrum

TABLE 1 Data Used to Develop Precision and Bias Statements for Dissolved Decay Product Area

	Absorbance Area Under the Curve		
Sample	Aged Oil South America 1	New Oil 2	Aged Oil North America 3
Test 1	450.42	18.55	359.74
Test 2	455.54	18.39	361.03
Test 3	450.05	18.85	382.55
Test 4	443.08	18.85	387.25
Test 5	451.46	18.80	378.36
Average of tests (area)	450.11	18.69	373.79
Variance, $\sigma^2_{(n-1)}$	20.21	0.04	159.75
Standard deviation $\sigma_{(n-1)}$	4.50	0.21	12.64
Coeff. variation, σ/average, %	1.0	1.11	3.38
Number of determinations (n)	5	5	5
Number of DE (n-1)	4	4	4
Grand average, Area	280.86		
Pooled variance, σ^2	60.00		
Pooled standard dev, σ	7.75	Total FE=12	
Pooled coeff var, σ/average, %	2.76		
Repeatability std dev, σ	7.75		
ASTM repeatability 2.83 σ, area	21.92		
Coeff variation, σ/average, %	2.76		
ASTM repeat 2.83 (σ/average), %	7.81		

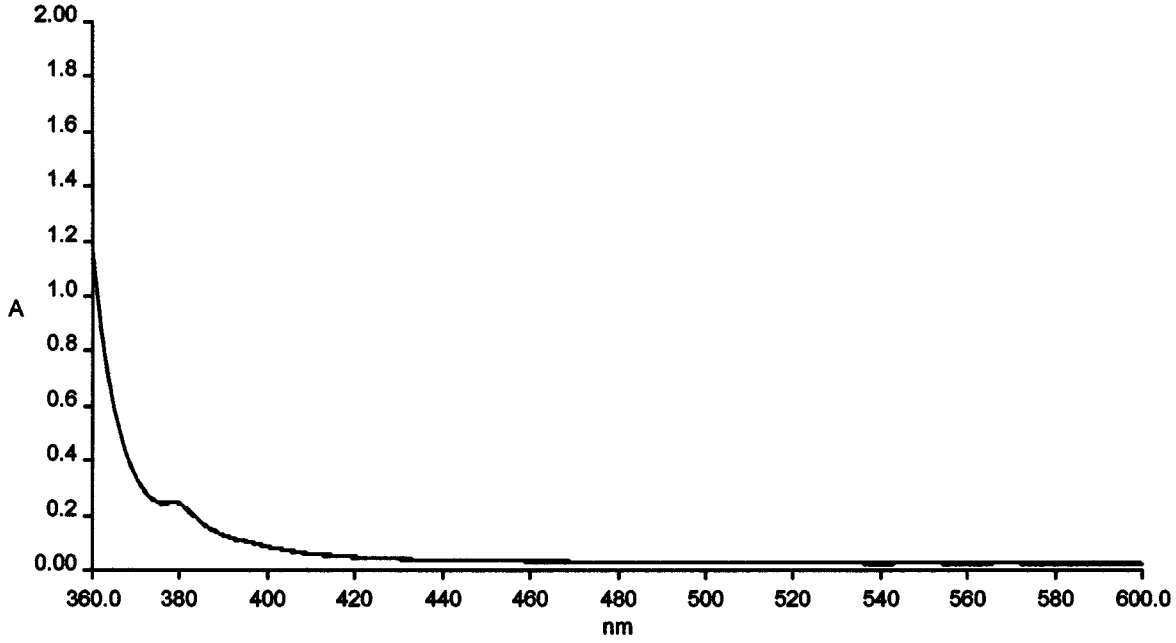


1	1S90101 - 5/11/99 - AGED OIL/SOUTH AMERICA RUN #1	A=450.42
2	2S90101 - 5/11/99 - AGED OIL/SOUTH AMERICA RUN #2	A=455.54
3	3S90101 - 5/11/99 - AGED OIL/SOUTH AMERICA RUN #3	A=450.05
4	4S90101 - 5/11/99 - AGED OIL/SOUTH AMERICA RUN #4	A=443.08
5	5S90101 - 5/11/99 - AGED OIL/SOUTH AMERICA RUN #5	A=451.46

1S90101		2S90101		3S90101		4S90101		5S90101	
WaveL.	Abs.	WaveL.	Abs.	WaveL.	Abs.	WaveL.	Abs.	WaveL.	Abs.
360.00	4.9395	360.00	6.0000	360.00	6.0000	360.00	3.8711	360.00	6.0000
380.00	3.8525	380.00	6.0000	380.00	4.3095	380.00	3.9806	380.00	3.8501
400.00	3.3844	400.00	3.4008	400.00	3.4044	400.00	3.4123	400.00	3.4070
420.00	3.3601	420.00	3.4049	420.00	3.4015	420.00	3.3607	420.00	3.3936
440.00	2.7185	440.00	2.7218	440.00	2.7185	440.00	2.6970	440.00	2.7020
460.00	1.8562	460.00	1.8476	460.00	1.8474	460.00	1.8455	460.00	1.8465
480.00	1.2799	480.00	1.2740	480.00	1.2743	480.00	1.2729	480.00	1.2722
500.00	0.8756	500.00	0.8713	500.00	0.8721	500.00	0.8709	500.00	0.8701
520.00	0.6095	520.00	0.6067	520.00	0.6075	520.00	0.6064	520.00	0.6054
540.00	0.4335	540.00	0.4314	540.00	0.4324	540.00	0.4314	540.00	0.4306
560.00	0.3126	560.00	0.3110	560.00	0.3119	560.00	0.3112	560.00	0.3103
580.00	0.2282	580.00	0.2268	580.00	0.2278	580.00	0.2273	580.00	0.2265
600.00	0.1705	600.00	0.1692	600.00	0.1701	600.00	0.1699	600.00	0.1689

A= area under the curve from(360-600)nm. Date: 12/2/99 Time: 2:21:26 PM

FIG. 1 Absorbance in the Visible Range of Spectrum

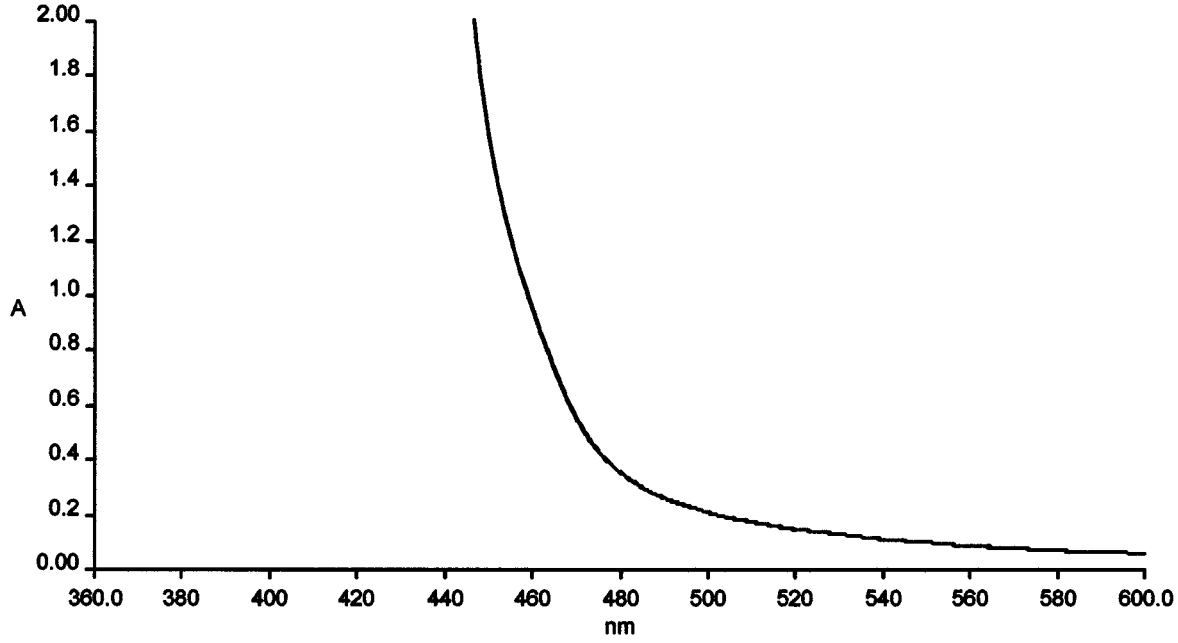


1 —— 1S80525.SP - 5/11/99 - NEW OIL/U.S. MANUFACTURER RUN #1 A= 18.55
2 —— 2S80525.SP - 5/11/99 - NEW OIL/U.S. MANUFACTURER RUN #2 A= 18.39
3 —— 3S80525.SP - 5/11/99 - NEW OIL/U.S. MANUFACTURER RUN #3 A= 18.85
4 —— 4S80525.SP - 5/11/99 - NEW OIL/U.S. MANUFACTURER RUN #4 A= 18.85
5 —— 5S80525.SP - 5/11/99 - NEW OIL/U.S. MANUFACTURER RUN #5 A= 18.80

1S80525		2S80525		3S80525		4S80525		5S80525	
WaveL.	Abs.	WaveL.	Abs.	WaveL.	Abs.	WaveL.	Abs.	WaveL.	Abs.
360.00	1.1580	360.00	1.1571	360.00	1.1610	360.00	1.1596	360.00	1.1560
380.00	0.2442	380.00	0.2431	380.00	0.2455	380.00	0.2454	380.00	0.2449
400.00	0.0860	400.00	0.0853	400.00	0.0872	400.00	0.0870	400.00	0.0871
420.00	0.0470	420.00	0.0464	420.00	0.0482	420.00	0.0482	420.00	0.0481
440.00	0.0385	440.00	0.0379	440.00	0.0397	440.00	0.0395	440.00	0.0396
460.00	0.0332	460.00	0.0328	460.00	0.0345	460.00	0.0346	460.00	0.0344
480.00	0.0309	480.00	0.0302	480.00	0.0321	480.00	0.0320	480.00	0.0319
500.00	0.0281	500.00	0.0277	500.00	0.0295	500.00	0.0295	500.00	0.0294
520.00	0.0264	520.00	0.0258	520.00	0.0277	520.00	0.0277	520.00	0.0276
540.00	0.0257	540.00	0.0248	540.00	0.0269	540.00	0.0268	540.00	0.0267
560.00	0.0248	560.00	0.0242	560.00	0.0261	560.00	0.0261	560.00	0.0260
580.00	0.0242	580.00	0.0239	580.00	0.0257	580.00	0.0258	580.00	0.0257
600.00	0.0238	600.00	0.0235	600.00	0.0255	600.00	0.0255	600.00	0.0252

A= area under the curve from(360-600)nm. Date: 12/2/99 Time: 2:26:32 PM

FIG. 2 Absorbance in the Visible Range of Spectrum



1 ——— 1S90206.SP - 5/11/99 - AGED OIL/NORTH AMERICA MANUFACTURER RUN #1A= 359.74
2 ——— 2S90206.SP - 5/11/99 - AGED OIL/NORTH AMERICA MANUFACTURER RUN #2A= 361.03
3 ——— 3S90206.SP - 5/11/99 - AGED OIL/NORTH AMERICA MANUFACTURER RUN #3A= 382.55
4 ——— 4S90206.SP - 5/11/99 - AGED OIL/NORTH AMERICA MANUFACTURER RUN #4A= 387.25
5 ——— 5S90206.SP - 5/11/99 - AGED OIL/NORTH AMERICA MANUFACTURER RUN #5A= 378.36

1S90206		2S90206		3S90206		4S90206		5S90206	
WaveL.	Abs.	WaveL.	Abs.	WaveL.	Abs.	WaveL.	Abs.	WaveL.	Abs.
360.00	6.0000	360.00	6.0000	360.00	6.0000	360.00	6.0000	360.00	6.0000
380.00	6.0000	380.00	3.9193	380.00	6.0000	380.00	6.0000	380.00	6.0000
400.00	3.1019	400.00	3.1175	400.00	3.1109	400.00	3.1790	400.00	3.1294
420.00	3.2457	420.00	3.2254	420.00	3.2505	420.00	3.2711	420.00	3.2471
440.00	3.1013	440.00	3.1441	440.00	3.1243	440.00	3.1900	440.00	3.1481
460.00	0.9533	460.00	0.9483	460.00	0.9473	460.00	0.9466	460.00	0.9458
480.00	0.3581	480.00	0.3566	480.00	0.3558	480.00	0.3557	480.00	0.3555
500.00	0.2108	500.00	0.2102	500.00	0.2097	500.00	0.2095	500.00	0.2096
520.00	0.1488	520.00	0.1484	520.00	0.1482	520.00	0.1481	520.00	0.1481
540.00	0.1124	540.00	0.1122	540.00	0.1121	540.00	0.1119	540.00	0.1119
560.00	0.0873	560.00	0.0871	560.00	0.0870	560.00	0.0870	560.00	0.0868
580.00	0.0707	580.00	0.0706	580.00	0.0705	580.00	0.0705	580.00	0.0704
600.00	0.0593	600.00	0.0591	600.00	0.0591	600.00	0.0590	600.00	0.0590

A= area under the curve from(360-600)nm. Date: 12/2/99 Time: 2:34:35 PM

FIG. 3 Absorbance in the Visible Range of Spectrum