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TITANIUM DIOXIDE

DETERMINATION OF COLOR L*a*b* BY SPECTROCOLORIMETER

METHOD: T4400.315.01.WP

TITANIUM DIOXIDE
(Ti-Pure®)

Determination of Color by Spectrocolorimeter
(TP-512.1)

I. Principle

Color can be described and quantified in a number of different ways. The system used in this method is based on the CIE 1976 L*a*b* color scale. These color scales give measurements of color in units of approximate visual uniformity throughout the color solid. Where L* measures lightness approximately as the eye would evaluate it, and varies from 100 for perfect white to zero for black; and where a* measures redness when positive, gray when zero and greenness when negative; and b* measures yellowness when positive, gray when zero and blueness when negative.

II. Applicability

A. General

This procedure can be used to measure the "color" of titanium dioxide (TiO₂) pigment.

B. Specific

This procedure applies to the determination of "color" of in process and finished titanium dioxide samples for process control and finished product specification. It also can be used in characterizing competitive samples. L* of plastic grades normally runs from 97 to 99.5; all other grades run from 97.5 to 99.7. TiO₂ samples will read close to the top of the scale and on occasions, readings of 100+ are possible.

III. Limitations

None

IV. Sensitivity, Precision and Accuracy

A. Sensitivity

No data is available.

B. Precision

1. Single Operator

The average analysis (\bar{X}), standard deviation (s) and 95% confidence limits (95% CL) established for the single operator precision of the method were as follows:

	\bar{X}	s	95% CL
L*		99.32	0.035 ± 0.083
a*	-0.81	0.012	± 0.028
b*		3.06	0.023 ± 0.054

The above data were calculated from eight replicate analyses of one sample performed by one technician over a period of two days.

2. Multiple Operator

The average analysis (\bar{X}), standard deviation (s) and 95% confidence limits (95% CL) established for the multiple operator precision of the method were as follows:

	\bar{X}	s	95% CL
L*		99.35	0.045 ± 0.092
a*	-0.79	0.026	± 0.053
b*		2.96	0.071 ± 0.145

The above data were calculated from thirty-two replicate analyses of one sample performed by eight technicians over a period of several days.

C. Accuracy

No study has been made; however, the method has proved to be satisfactory based on experience.

V. Special Apparatus

1. Spectrocolorimeter using 0/45 degree geometry (typically 0 degree incident, 45 degree viewing) to exclude specular reflection, with light source filtered to approximate CIE illumination D65. Prefer a circumferential ring of optical sensors or illumination to eliminate effect of sample orientation in measurement. Sample port size variable from 10 to 50 mm.

Instrument must be capable of generating CIE XYZ and CIE L*a*b* color measurements calculated relative to illuminant D65 and the CIE 1964 10 degree standard observer. Preferred operator interface is PC control/cathode ray tube with keyboard input.

Preferred optical processors should be capable of full spectrum scanning from 400 to 700 nm, with tristimulus integration based up to 31 point spectral reflectance data with an effective bandpass of 10 nm.

Preferred Supplier/Model:

Labscan spectrocolorimeter Model LS-5100, available from Hunter Associates Laboratory, Inc., 11495 Sunset Hills Road, Reston, VA 22090.

Alternate instruments must be qualified. Qualification standard is ability to pass ILC.

2. Aluminum or brass rings, ~1-1/16 inch (27 mm) ID or larger, ~1-1/4 inch (32 mm) OD, 3/8" (9-10 mm) high, with square and parallel ends (important). Supplier: Fabricated locally from aluminum pipe (See Appendix 1).
3. Sample ring jig, fabricate locally; sketch attached in Appendix 1.
4. Hydraulic lab press, minimum 3 ton capacity, platen size 4 to 6 inches, stroke range 2 to 6 inches. Two column design, with pressure gauge.

Press modified with steel or brass ram, 3 to 4 inches long, 1" diameter (fits cleanly inside sample rings) screwed into top stationary portion of press. (See attached sketch) Steel ram to be fabricated from 1" OD rod.

Supplier/Model:

Carver Catalog No. 3889 15-ton auto "C" press (preferred) OR Fisher Scientific 13-872/Carver 12-ton mini "C" press or standard "C" press. From Carver, Inc., 1569 Morris Street, P.O. Box 544, Wabash, Indiana 46992-0544, www.carverpress.com. Modified as purchased locally.

5. Filter paper, Whatman #50, 5.5 cm or equivalent.
6. Hand ram, constructed of brass stock or Delrin, about 3 to 4" long, 1" dia., fits cleanly inside sample rings. (See Appendix 1)

VI. Reagents

None

VII. Special Safety Considerations

A. Product Hazards

No product hazards have been identified. However, titanium dioxide is regulated as an air contaminant and care should be exercised to minimize product dusting. Wipe up all spills with a damp paper towel. See MSDS #2816CR for more information on Titanium Dioxide.

B. Procedure Hazards

None

VIII. Procedure

A. Operating Conditions

1. When pressing exhibits of titanium dioxide using the automatic hydraulic press, the Dwell Time should be set at 2 seconds and the Pressure at 2000 psig. When pressing using the manual hydraulic press (Section VIII-D), apply approximately 2000 ± 5 psig for 2 ± 1 seconds.
2. Read the manufacturer's operating manual for both the spectrophotometer and the hydraulic press carefully. Also read the procedure T4400.042.01.WP (Calibration and Use of the Spectrophotometer).

B. Calibration

Calibrate the Labscan at the beginning of every shift and whenever the software is restarted. A complete calibration consists of calibrating the Labscan to the black and white tiles, hitching to the alternate 'hitch' standard, and checking the calibration by running the reference standard. All three of these steps should be taken each time the instrument is calibrated.

Press new reference and alternate hitch standards at the beginning of each shift prior to calibrating the instrument. Refer to Standard Sample Management, T4400.010.09.WP for current sample and values. The standard is prepared the same as the samples in Sample Analysis D. 1-6.

Use D-65 illuminant and 10 degree observer according to the procedure described in T4400.042.01.WP, Calibration and Use of the Labscan (5000 & 5100) Spectrocolorimeter or equivalent procedure for another instrument.

C. Sampling

Samples are normally supplied by manufacturing in a paper bag but any clean dry container is satisfactory. No mixing is required.

D. Sample Analysis

1. Clean all parts of the jig and sample ring before using with a clean dry paper towel.
2. Place a *new* piece of the filter paper on the milled flat surface of the base of the jig. Do not reuse filter paper sides in pressing pellets. Assure that the base of the jig is smooth and free of indentations.
3. Place a sample ring in the top section of the jig; place it over the bottom section. And tighten so that the sample ring is lying flat. The top section can be secured so that the ring lies flat by tightening the thumb screws of opposite corners simultaneously.
4. Fill sample ring with sample or standard and compress using the hand ram. Add sample and compress again so that the sample ring is almost full.
5. Transfer the jig to hydraulic press and compact by applying 2000 ± 5 psig pressure for 2 ± 1 seconds. L^* , a^* , and b^* are sensitive to pressure differences. If using a manual press, take precautions to ensure that the same amount of pressure is applied by all analysts and by the same analyst each time a color pellet is pressed.

6. Remove the jig from the press, remove the sample ring and examine the exhibit. There should be no pigment on the ring or visible flaws such as voids or cracks on the bottom face of the exhibit. Any imperfect samples should be removed from the ring and preparation repeated.
7. Assure that Labscan port is free of contamination inside and outside and that pellet is level on base before placing sample pellet on reflectance port. If necessary, wipe the port with a clean dry paper towel or cloth.
8. Read L*, a*, and b* values of the samples according to T4400.042.01.WP "Calibration and Use of Labscan (5000 & 5100) Spectrocolorimeter" or equivalent. The values are displayed digitally and should be read and recorded to the nearest 0.01 unit.

E. Calculations

L*, a*, and b* values are reported directly as measured as described above.

Color differences can be calculated from analysis of samples and a standard following the procedure outlined above. When a comparison against a color standard is required, ΔL^* , Δa^* , and Δb^* , and ΔE (ΔE is the total color difference) are calculated by the following four equations respectively:

$$\Delta L^* = L_{sample}^* - L_{standard}^*$$

$$\Delta a^* = a_{sample}^* - a_{standard}^*$$

$$\Delta b^* = b_{sample}^* - b_{standard}^*$$

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

IX. Quality Control

A. General

1. Measure color (L*a*b*) on the current color reference standard each shift or as required by individual sites.
2. Plot the values obtained from this analysis using statistical process control Techniques

If the results of the reference standard are off aim, refer to the troubleshooting guide in Section IX, B.

B. Troubleshooting Guide

Most color analysis problems are related to improper instrument calibration, Alternate Standard/Reference Standard pellet condition, or incorrect pellet press pressure.

- Always press a new alternate standard and reference standard at the beginning of each shift and insure that all pellets are pressed to 2000 pounds!

Problem:

The Reference Standard is out-of-CUSUM tolerance

Action:

- *Remove and clean the port and lens with lens cleaning solution and kimwipes. Replace the port. Close and restart UNIVERSAL software. Refer to site SJP for operation of the Labscan. Standardize the Labscan with the Black and White tiles. Press a new Alternate Standard pellet and hitch the instrument. Read the Alternate Standard (Hitch Standard) as an unknown sample. The Alternate Standard should read very close to its Hitch value. Press a new Reference Standard pellet and analyze. If the Reference Standard values are still out-of-tolerance, proceed to the step below.*
- *Verify that the instrument is properly configured. The color scale should be CIELAB, illuminant should be D65, and observer should be 10°. If the Reference Standard values are still out-of-tolerance, proceed to the step below.*
- *Verify that the Alternate Standard and Reference Standard is the correct material by pressing new Standards from different containers. If the Reference Standard values are still out-of-tolerance, proceed to the step below.*
- *Set up and operate a backup Labscan.*

Problem:

Low color on in-process/packed TiO₂ samples or if a delta of consecutive sample results is +/-0.3 L, +/- 0.3 a*, or +/- 0.8 b*.*

Action:

- *Verify instrument calibration by analyzing the Reference Standard. If the Reference Standard is out-of-tolerance, follow the steps in the above problem “The Reference Standard is out-of-tolerance”. Record the Reference Standard analysis result in the logbook and enter into CQMS.*
- *Insure that the sample is prepared correctly (if slurry) and proper pellet pressure is applied (2000 pounds). See the procedure T4400.315.06WP for TiO₂ slurry preparation and T4400.315.01WP for color analysis.*

- *Recheck the TiO₂ samples that are low in color.*

Remember that proper instrument operation can be verified by pressing and analyzing the color reference standard. If the reference standard analysis result is typical, the instrument is functioning correctly.

X. Comments

A. General

None

B. Specific

None

XI. References

A. General

1. Instruction Manual for the Hunterlab Spectrocolorimeter.
2. ASTM D-1535 Specifying Color by the Munsell system.
3. ASTM D-1729 Visual Evaluation of Color Differences of Opaque Materials.
4. ASTM D-2244 Instrumental Evaluation of Color Differences of Opaque Materials.
5. ASTM E-308 Recommended Practice for Spectrophotometry and Description of Color in CIE 1931 System.
6. MSDS No. 2816CR.

B. Specific

1. TP-512.1 (3/7/1975) "Instrumental Color Determination Using Du-Color Color Difference Meter" the first dry TiO₂ method.

2. T4400.042.01.WP "Calibration and Use of Labscan (5000 & 5100) Spectrocolorimeter."
3. T4400.010.09.WP "Standard Sample Management."
4. It was decided by the TiO₂ Test Committee, at the meeting held April 28 and 29, 1993, at Delisle, that a pigment standard would be used in the determination of Color L*a*b* rather than a standard tile.

See Standard Sample Management, T4400.010.09.WP, for current sample identification and values.

XII. Appendix

1. Jig for Pressing TiO₂ Samples for Optical Measurement
2. Revision Sheet

XIII. Approval/Certification

Origin: Johnsonville Plant, March 10, 1975

Prepared by: JV R&D

Approved by: TiO₂ Test Committee

Supersedes: T4400.315.01.WP, dated October 22, 2001

APPENDIX 1

JIG FOR PRESSING TiO₂ SAMPLES FOR OPTICAL MEASUREMENTS

(Contact Methods Manager for hard copy)