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Ti-Pure®

TITANIUM DIOXIDE

DETERMINATION OF NUJOL YELLOWING

METHOD: T4400.315.09.WP

TITANIUM DIOXIDE
(Ti-Pure®)

NUJOL YELLOWING, ANALYSIS
(CI-126)

I. Principle

Titanium dioxide is mixed with a mineral oil based vehicle and exposed to UV light to determine product yellowing performance.

II. Applicability

The yellowing of titanium dioxide can be measured by this procedure.

III. Limitations

This procedure applies only to dry finished product TiO₂.

IV. Sensitivity, Precision and Accuracy

A. Sensitivity

No data is available.

B. Precision

1. Single Operator

The average analysis (\bar{X}) and standard deviation (s) established for the single operator precision of the method are as follows:

	\bar{X}	s	95% CL
Nujol Yellowing	1.1	0.4	± 0.8

2. Multiple Operator

The average analysis (\bar{X}) and standard deviation (s) established for the multiple operator precision of the method are as follows:

	\bar{X}	s	95% CL
Nujol Yellowing	1.1	0.5	± 1.0

C. Accuracy

No data is available; however, the method has proved to be satisfactory.

V. Special Apparatus (Equivalent apparatus may be substituted)

1. UV Lightbox (manufactured locally) size approximate - Length 27½" x Width 27½" x 35½". One shelf approximately 22" below light source. Fan for air circulation only. Front doors for sample placement. (See Johnsonville's operating model for information.)

Note: (The fan does not have a direct link to a temperature probe, it is there to keep the temperature from building up inside the box and more importantly, it keeps air (with O₂) moving over the samples. The temperature should be monitored but is not critical to the test. The internal standard should correct for slight temperature variations).

2. Three Spectroline Lamp housings to be mounted inside top of UV lightbox. Available from Fisher Scientific, Cat. No. 11-982-120.
3. Six Black-Ray UV lamps, 15 watts each, 2 per housing. Available from Fisher Scientific or Fairmont Supply.
4. Muller, a grinding apparatus with two ground glass plates, one rotating at 100 rpm, with counter to stop at 20 revolutions, weights to give 50 lbs pressure on plates. Minimum plate diameter = 7.5 inches (19 cm). The grinding plates must be in good condition (free of grooves and worn spots). Glass grinding plates ordered separately.
Available from Hoover Color Corp. Hiwassee, VA 24347. Model M5.
5. Weighing paper. Available from Fisher Scientific Co., Cat. No. 09-898-12A.
6. Spatula. Available from Dexter Russell Cutlery Co., Model 2494.

7. Microscope slides (glass). Plain glass microslide, clear, 75mm X 38mm X 0.97 to 1.1 mm thick. Available from Fisher Scientific Co. Cat. No. 12-553-5A
8. Microscope slides cardboard tray. Available from Fisher Scientific Co., Cat. No. 12-587-10.
9. Bird Film applicator, 0.010 inch clearance, 3½ inch path width to drawdown, 0.005 inch wet film. Available from Pacific Scientific, Instrument Division, 1100 East-West Hwy., Silver Spring, MD 20910.
10. Microscope Slide Holder, (manufactured locally), consisting of a glass plate approximately 5" X 12" X 3/16" on which microscope slides have been glued, with Super Glue or a similar type, in the shape of a "U".
The opening of the "U" should be large enough to hold the slide on which the drawdown will be made.
(The microscope slides must be the same thickness as the slides on which the drawdowns will be made).
11. Variable Volume repeatable preset pipette 4.0 mL size. Available from Fisher Scientific Co., Cat. No. 13-689-133B.
12. Analytical Balance with the capacity of weighing 0.01g. Such as Mettler H35AR or AT 200. Available from Fisher Scientific Co. or VWR Scientific Co.
13. Spectrocolorimeter using 0/45 degree geometry (typically 0 degree incident, 45 degree viewing) to exclude specular reflection, with light source filtered to approximate CIE illuminant D65. Prefer a circumferential ring of optical sensors to eliminate effect of sample orientation in measurement. Sample port size variable from 10 to 50 mm. Instrument must be capable of generating L* a* b* color measurements calculated relative to illuminant D65 and 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 700nm, with tristimulus integration based upon 31 point spectral reflectance data with an effective bandpass of 10 nm. Preferred supplier/model: Labscan Spectrocolorimeter, Model LS-5100 or LS-6000 available from Hunter Associates Laboratory, Inc., 11495 Sunset Hills Road, Reston, VA 22090. Alternate instruments must be

qualified by passing an ILC.

14. Convection oven at 110 ± 5 °C

VI. Reagents

1. Mineral Oil. Reagent grade. Available from Aldrich Chemical Co., Milwaukee, Wis. 53233, Cat. No. 16,140-3. (1 liter size).
2. BHT. (2,6-di-t-butyl-4-methylphenol). Reagent grade. Available from Aldrich Chemical Co., Milwaukee, Wis. 53233, Cat. No. D4,740-4. (Somewhat air sensitive and will degrade with time. Should be replaced with a fresh supply every year).
3. Tinuvin® 770. Available from Ciba-Geigy Corp., Madison Heights, MI 48071, ph. 800-431-1900. (Somewhat air sensitive and will degrade with time. Should be replaced with a fresh supply every year).
4. Pure White Petroleum Jelly
Available from MS Medical Supply
260 W Main St.
Hendersonville, TN 37075
Ph: 615-824-4416
5. Molecular Sieves, 4A, 1/16" beads, 8 - 12 mesh, #20,860-4.
Available from Aldrich Chemical Co., Milwaukee, WI
800-558-9160.

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. For more information, refer to MSDS #2816CR.

B. Procedure Hazards

1. Side shield safety glasses must be worn when running this test as spatulas have been know to break.

2. Wear leather gloves and use care when changing Hoover Muller glass plates.
3. Use care when handling the relatively heavy Bird film applicator with the Microscope glass slides.
4. Use extreme care when handling the Microscope glass slides. Discard any slides that are chipped or broken.
5. Do not look into the UV lightbox when black lights are on.
6. See DuPont Material Safety Data Sheets for information on Mineral Oil #0557083, BHT #05570335, Tinuvin® 770 #34410366, and Petrolatum #965.

VIII. Procedure

A. Operating Conditions

Read the manufacturer's operating manual for details on the operation of both the Spectrocolorimeter and the muller.

B. Calibration

1. The spectrocolorimeter will be standardized each shift when used.
2. Analytical balance will be checked for calibration on a frequency to be determined by each site.

C. Sampling

Samples are generally supplied by manufacturing and must be placed in a closed, sealed, container (eg. ½ pint can(s) with lid(s), when received in or by the Laboratory to prevent moisture condensation while awaiting analysis.

D. Sample Analysis

Note: Pigment (TiO₂) samples and (Standards), must be dried for at least 2 hours in a convection oven at 110 ± 5 °C for results to be meaningful. Normal procedure is to remove the

lid(s) from the ½ pint can(s) containing the sample(s), place can(s) containing the sample(s) into the convection oven at the prescribed temperature, for the prescribed time, remove can(s) and sample(s) and replace lid(s) on cans immediately to prevent moisture from getting to the sample(s) before analysis.

1. If not already on, turn on the UV lightbox for approximately 1 - 2 hours before use. The lamps should be changed monthly. Record UVA/UVB intensities measured at three spots under each bank of lights before and after lamp changeout.
2. Record sample identification numbers in a bench logbook and mark glass slides with corresponding information.
3. Adjust the automatic counter on the Hoover Muller to get 20 revolutions of the plate and adjust the weight according to the manufacture's manual to get a nominal 50 lbs. pressure between the plates.
4. With the repeatable pipette transfer 1.20 mL + .05 mL of the premixed Nujol Solution onto the lower plate of the Hoover Muller (See Below for Nujol premixed solution make-up).
5. Weigh 0.64 + 0.01 grams of dried sample pigment on weighing paper. Add pigment directly to the Nujol solution onto the Muller.
6. With an ink spatula, mix the ingredients on the Muller plate into a paste. Place the paste slightly off the center of the lower plate and remove the balance of the paste from the spatula by rubbing it on the upper muller plate.
7. Bring the Muller plates together and lock them.
8. Start the muller and mull the paste for 20 revolutions.
9. Separate the muller plates, scrape the paste from the bottom and top plates and return it to a point slightly off center on the bottom plate.
10. Repeat steps 6 to 9 to get a total of 40 revolutions.
11. Gather the paste on the spatula blade and transfer it to a glass slide.

12. Place slide and paste onto the microscope slide holder in the center of the "U".
13. Draw down the paste, in the long direction of the slide, with a 0.010 inch clearance Bird film applicator to give a wet film of approximately 0.005 inch thickness. (The Bird film applicator should ride on the "U" portion of the microscope slide holder while making the drawdown).
14. The drawdown should be made so that no paste comes in contact with the port of the spectrophotometer when making the readings. (With practice this can be easily accomplished).
15. Place glass slide with sample in the slide cardboard tray.
16. Clean the plates of the muller and film applicator with a dry towel. Repeat steps 4-16 for any additional samples.
17. Standardize the spectrophotometer according to equipment procedure or manual.
18. Use the spectrophotometer (Labscan) to check the initial b^* for each sample.
 - (a) Use the # 4, 50mm port, and the # 2, 13mm aperture.
 - (b) Remove the sample from the cardboard tray.
 - (c) Place the sample onto the instrument port. (Use care to keep paste from getting onto the port).
 - (d) Press "F3" or click on read sample icon.
 - (e) Screen will prompt to sample "ID" icon.
 - (f) Enter sample lot and tray, or "ID" number, and press enter.
 - (g) Record the b^* reading for the initial reading.
 - (h) Remove the sample from the instrument port and return to the slide cardboard tray.

- (i) Repeat steps b thru g for additional samples.
 - (j) Repeat steps b thru g for final b* readings.
19. Remove all the samples from the slide cardboard tray and place in the UV lightbox. UV intensity can vary considerably from place to place in the box. To minimize this, place the samples closely together in the center of the box.
 20. Expose the samples to the UV light for 24 hours +/- 5 minutes.
 21. Remove the samples from the UV lightbox and return to the slide cardboard tray.
 22. Repeat step 18 for all the samples.

E. Calculations

1. Calculate the raw delta b* values for all the samples.

$$\begin{aligned} \text{delta } b^* \text{ (raw)} \quad (A - B) &= C \\ (D - E) &= F \end{aligned}$$

where: A = Measured reading b* standard value final.
 B = Measured reading b* standard value initial.
 C = Difference between A and B value of b* standard.
 D = Measured reading b* sample value final.
 E = Measured reading b* sample value initial.
 F = Difference between D and E value of b* sample.

2. Use the raw delta b* values in the following formula to calculate the corrected delta b* values:

$$\begin{aligned} \text{delta } b^* \text{ (corrected)} &= (ASV - C) = CFS \\ (CFS + F) &= N \end{aligned}$$

where: ASV = Assigned Standard Value.
 CFS = Corrected Factor of Standard.
 N = Corrected delta b* of the sample.

3. Record the corrected delta b* of the sample in the logbook. Report the results.

IX. Quality Control

A reference standard is run with each series. The value of the reference standard is determined and used for Statistical Process Control.

X. Comments

1. None.

XI. References

1. Iler Research Technical Report dated August 26, 1991

XII. Appendix

Appendix 1. Preparation of Nujol Solution

The information set forth herein is furnished free of charge and is based on technical data that DuPont believes to be reliable. It is intended for use by persons having technical skill and at their own discretion and risk. Since conditions of use are outside our control, we make no warranties, express or implied, and assume no liability in connection with any use of this information. Nothing herein is to be taken as a license to operate under or a recommendation to infringe any patents.

Appendix 1

Preparation of Nujol Solution

It is extremely important to dry the Mineral Oil for 24 hours before using it in the preparation of the NUJOL Solution. Molecular Sieves (4 Angstrom) may be used for this purpose. See below for details.

1. Add 100.00 ± 0.25 grams of dry, (moisture free), Mineral Oil to a clean dry 450 ml beaker.
2. Place a large magnetic stirring bar into the mineral oil in the beaker.
3. Place the beaker on a magnetic stirrer and begin stirring at medium speed.
4. Add 2.00 ± 0.01 grams of BHT to the Mineral Oil. (The BHT dissolves best when crushed or pulverized).
5. Add 2.00 ± 0.01 grams of Tinuvin® 770 to the BHT/Mineral Oil mixture.
6. Solution should stir for a period of 8 hours minimum, at ambient temperature, to allow for proper dissolution of the reagents.
7. Add 10.0 ± 0.1 grams of Petrolatum (petroleum jelly) to the mixture. Stir until the Petrolatum is completely dissolved. (2 hours minimum).
8. Store the Nujol Solution in a sealed polyethylene jar, in the dark, until needed. It is best to prepare this solution a day in advance. The solution should be marked with date, time and maker's name. The solution can be used in the test for up to 2 months after preparation.

Note: It is extremely important to dry the mineral oil (remove any moisture) before using, and especially if stored for more than one day before use. 4A (4 Angstrom), Molecular Sieve material may be used for this purpose. An adequate portion of mineral oil, approximately 1 liter, may be transferred to a suitable sized closed container or the original container may be used, and an appropriate amount, approximately 50 grams, of dry molecular sieve material added to the container. The Mineral Oil/Molecular Sieve Mixture, approximately 50 grams/liter, is mixed by hand shaking for 1-2 minutes and allowed to set for 24 hours to allow time for the moisture to be removed from the mineral oil and the sieve material to settle out. This dry Mineral Oil should be dry enough for use until the container is empty. The dry Mineral Oil may be decanted off when ready to use. (If the Molecular/Sieve material does not readily settle out, a larger mesh eg. 1/8" Sieve material or pellets may be tried). The Analyst should be careful of inadvertently adding Mol. Sieves to the Nujol Solution. Large particles are easy to see but dust may be a problem. An appropriate size screen should be used to separate the Mol. Sieve dust from the Mol. Sieves before they are added to the Mineral Oil. Attrition of the Mol. Sieves inside the bottle of Mineral Oil should be minimal. The Molecular Sieve material should be dried in a $110 \pm 10^{\circ}\text{C}$ oven for at least 4 hours before use.