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Ti-Pure®

TITANIUM DIOXIDE

DETERMINATION OF CARBON BLACK UNDERTONE (CBU)

METHOD: T4400.315.06.WP

TITANIUM DIOXIDE  
(Ti-Pure®)

Determination of Carbon Black Undertone  
(TP-405.6)

I. Principle

The undertone of a paste of titanium dioxide pigment and carbon black is affected by the size of the particles of titanium dioxide. In the pigmentary particle size range, the blue/amber (Z/X) ratio of the reflectance of such a paste increases significantly as the particle size of the titanium dioxide decreases. This is the basis of the carbon black undertone (CBU) test.

II. Applicability

The CBU test is used to estimate the relative particle size of titanium dioxide pigment.

III. Limitations

The value of CBU is influenced by the presence of grit and other particles. It is also influenced by the finishing process.

IV. Sensitivity, Precision and Accuracy

A. Sensitivity

Not applicable.

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
CBU	12.18	0.0834	± 0.175

The above data were calculated from 20 replicate analyses of one sample of TiO<sub>2</sub>, performed by one technician over a period of a few 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
CBU	12.94	0.18	± 0.35

The above data were calculated from 32 replicate analyses of one sample, performed by multiple technicians over a period of several days.

## C. Accuracy

No study has been made; however, results have been satisfactory based upon experience.

## V. Special Apparatus (Equivalent apparatus may be substituted)

1. Muller, a grinding apparatus with two ground glass plates, one rotating at 100 rpm, with counter to stop at 50 revolutions, weights to give 100 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).

Recommended supplier/Model:

Hoover Automatic Muller, Model M5, from Hoover Color Corp., PO Box 218, State Highway 693, Hiwassee, VA 24347. NOTE: JEL a German firm also makes a muller.

2. White lacquered paper for drawdowns, 5-1/2 x 3 or 4 inch, 11-point thickness. Order from Leneta Co., PO Box 86, Ho-Ho Kus, NJ 07423, Phone No. 201-825-7855.
3. Bird Film applicator, 0.006 inch clearance, 3 1/2 inch path width to drawdown, 0.003 inch wet film. Order from Pacific Scientific, Instrument Division, 1100 East-West Hwy., Silver Spring, MD 20910. Phone No. 301-589-4747.
4. 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 CIE XYZ and 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 700 nm, 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. Qualification standard is ability to pass ILC.

5. Variable volume repeatable preset pipetter, set to dispense 1.55 mL of silicone oil/carbon black mixture.  
  
Supplier/Model: Local lab supply firm. Fisher "Varipet" or Luer syringe, 2-mL capacity, from VWR.
6. Heavyweight 1 gallon large-mouth Nalgene jug with lid, Nalgene, Fisher or VWR.
7. Heavyweight 1 gallon small-mouth Nalgene jug with lid, same as above.

8. 1/2 Inch high-density ceramic or porcelain balls, approximately 5000 g. Available from Paul O. Abbe, 152 Center Ave., Little Falls, NJ 07424 and others.
9. Lid for wide-mouth jug with a series of 3/8 inch holes drilled in it (made on plant).
10. Lab jar roll mill for 1 gallon jugs. Two or three rollers (1 drive, 1 or 2 free spinning), rollers 3 to 6 inches dia., minimum 2' long, roll speed about 250 rpm, Typically a 1/4 hp motor (Paul O. Abbe, Little Falls, NJ.)
11. Analytical balance 50 to 100 gram capacity, good to 1 mg (0.001 g).  
Supplier/Model: Mettler Model AE 100.
12. Balance pan or scoop, aluminum or polypropylene, 20 to 30 mL capacity.
13. Surface thermometer, Recommended Model 314C from Pacific Transducer Corp., 2301 Federal Ave., Los Angeles, Ca 90064-1482, (310) 478-1134.

## VI. Reagents

1. Silicone 200 fluid, 500 centistokes viscosity at 25°C, Dow Corning.
2. Continex N-550 Carbon Black.

## VII. Special Safety Considerations

### A. Product Hazards

There are no unusual product hazards. 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, consult MSDS #2816CR.

### B. Procedure Hazards

1. Use caution putting Nalgene jar on and off the roll-mill.
2. Safety glasses must be worn when running this test as spatulas have been known to break.

3. Spatulas used in this test get very sharp over a period of time and can be a cutting hazard.
4. Wear gloves and use care when changing Hoover Muller glass plates. Use care when handling the relatively heavy Bird film applicator over the glass-covered counter top.
6. See Material Safety Data Sheets for information on Silicone Fluid and Carbon Black.

## VIII. Procedure

### A. Operating Conditions

1. Refer to the manufacturer's operating manuals for details concerning the operation of the spectrophotometer and the muller.

### B. Calibration

The spectrophotometer will be standardized each shift when used.

### C. Sampling

1. Dry TiO<sub>2</sub> Samples: Take a representative sample of the dry TiO<sub>2</sub> and proceed to Step D.2.b. If the sample is neutralized RPS, follow steps in Step 2 below.
2. TiO<sub>2</sub> slurry sample preparation.
  - a. Finished product slurry, including RPS Vantage®, can be dried as is.
  - b. Weigh 6-8 grams of slurry into an aluminum pan.
  - c. Dry the slurry by setting the aluminum pan on a hot plate or in an oven. For RPS, the slurry must be dried on a hot plate using the following temperature and time conditions that ensure complete sample drying:
    1. 310° ± 10°C hot plate surface temperature, as measured by a surface thermometer. See Part V.13 for recommended thermometer.
    2. Dry for at least 20 minutes.

- d. Make certain the cake is dry before proceeding. The hot, dry pigment in the aluminum pan after drying should appear yellow in color.
- e. Remove the aluminum pan from the hot plate and let the sample cool to room temperature. Crush the pigment to a fine powder by grinding in a mortar and pestle.

#### D. Sample Analysis

##### 1. Preparation of Masterbatch of Silicone Fluid/Carbon Black

- a. For the initial charge with a clean heavyweight, large-mouth Nalgene jug, add  $5000 \pm 10$  g of 1/2 inch ceramic balls,  $1725 \pm 10$  g Silicone Fluid and  $120 \pm 1.0$  g Carbon Black.
- b. For all subsequent charges (using the partially filled jug from a.) add  $1150 \pm 10$  g Silicone Fluid and  $80 \pm 0.5$  g Carbon Black.
- c. Grind for 16-18 hours on roll mill.
- d. Strain as much as possible of the pre-mix produced into the small-mouth jug by putting the lid with holes onto the large-mouth jug and inverting into the funnel in the small-mouth jug. If more convenient, use smaller containers such as 4-ounce jars.
- e. Keep the small-mouth jug with the pre-mix on the roll mill to prevent settling.
- f. Put the lid back on the large-mouth make-up jug and save for next pre-mix grind. Clean the "screening lid" and funnel.

##### 2. Sample Preparation

- a. The two approved standard pigments of known value and a reference standard are carried through the procedure with the first group of samples tested each shift, every time a new masterbatch of carbon black/silicone fluid is used or a change in technicians or operators is made.

NOTE: The high CBU pigment standard should be kept in an oven at 105 - 110°C, or in a desiccator or air tight container when not in use to help prevent moisture absorption.

- b. Weigh out  $2.000 \pm 0.001$  g of the sample (or standard pigment) on an analytical balance.
- c. With a Luer syringe, (or a repeatable pipette) transfer  $1.55 \pm 0.05$  mL of the premixed carbon black/silicone fluid masterbatch to the pigment on the lower plate of the muller.
- d. Transfer sample to the bottom plate of the muller.
- e. With a 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.
- f. Bring the muller plates together and lock them.
- g. Adjust the automatic counter on the machine to get 50 revolutions of the plate and adjust the weight according to the manufacture's manual to get a nominal 100 lbs pressure between the plates.
- h. Start the muller and mull the paste for 50 revolutions.
- i. 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.
- j. Repeat the above Steps f through i to get a total of 100 revolutions.
- k. Gather the paste on a spatula blade and transfer it to a lacquered panel in position for a drawdown.
- l. Draw the paste down with a 0.006 inch clearance Bird film applicator to give a wet film of approximately 0.003 inch thickness.
- m. Determine the X and Z tristimulus values of the drawdown by means of the spectrophotometer, being careful not to smear paste when putting it on the spectrophotometer. Use the #4 port and aperture (the largest) with the wet film adapter.

n. Record X and Z of all samples and standards.

#### E. Calculations

1. Carbon Black Undertone, CBU, of samples can be obtained by linear regression using the values of Z/X and the assigned values of CBU of the high and low standards as follows:
  - a. For each standard or sample under test, calculate the Z/X ratio from the values measured on the spectrophotometer and record the ratio for each paste.
  - b. Using a calculator or computer which will do linear regression, input the Z/X ratios of the standards as the "x" values and the CBU as the "y" values.
  - c. Input the Z/X ratio of a sample as the "x" and read the "y" value as CBU.
  - d. Record the calculated value of CBU to the nearest 0.1 point.
2. If a calculator or computer is unavailable, CBU can be obtained from the following formula:

A = Assigned value of low standard  
B = Assigned value of high standard  
a = Z/X ratio of the low standard paste  
B = Z/X ratio of the high standard paste  
C = Z/X ratio of the sample paste

Then:

$$\text{CBU} = A + \frac{[(C - a) \times (B - A)]}{(B - a)}$$

(If the Z/X ratio of the sample is less than that of the low Standard, then the second term becomes negative and the CBU is Lower than the low standard.)

#### IX. Quality Control

Three standards are run on each shift. The high and low standards are Used to establish the regression line. The value of the reference Standard is determined and is used for statistical process control.

X. Comments

None

XI. References

A. General

1. MSDS No. 2816CR.

XII. Appendix

None

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