Ti-Pure®

# TITANIUM DIOXIDE

## DETERMINATION OF VINYL TINT STRENGTH & UNDERTONE

METHOD: T4400.010.04.WP

TITANIUM DIOXIDE
(Ti-Pure®)

Determination of Vinyl Tint Strength and Undertone
(TP490.2)

## I. Principle

The titanium dioxide to be evaluated in optical properties is dispersed in black vinyl compound on a Two-Roll Mill. The tristimulus values of the vinyl sheet are measured using a Spectrocolorimeter and tinting strength and undertone are calculated versus standards prepared at the same time. L*, a* and b* can be read directly on the spectrocolorimeter if needed.

## II. Applicability

This method can be used to determine the tinting strength and undertone of titanium dioxide.

## III. Limitations

None

## 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 |
|---|---|---|---|
| Tinting Strength | 104.5 | 1.05 | ± 2.20 |
| Undertone | 0.0040 | 0.0012 | ± 0.0024 |

The above data were calculated from 20 replicate analyses of one sample of R-101 performed by one technician over a period of several days.

2. Multiple Operators

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 |
|---|---|---|---|
| Tinting Strength | 110.3 | 0.80 | ± 1.57 |
| Undertone | 0.005 | 0.00116 | ± 0.0023 |

The above data were calculated from 32 replicate analyses of one sample of R-101 performed by 8 technicians over a period of several days repeated in four different laboratories.

C. Accuracy

No study has been done, but the method has been satisfactory.

V. Special Apparatus (Equivalent apparatus may be substituted)

1. Two-roll mill, 6 X 13 inch, high pressure steam heated or oil heated, variable roll speed. Model # OX, Kobelco Stewart Bolling, Inc., 1600 Terex Road, Hudson OH 44236.

2. Digital thermometer, Model 872, 200-1400°F range, Cambridge Instrument Company, or equivalent.

3. Micrometer.

4. Spectrocolorimeter using 0/45° geometry (typically 0° incident, 45° 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 CIE L*a*b* color measurements calculated relative to illuminant D65 and the CIE 1964 10° 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/instrument: Labscan spectrocolorimeter, Model LS-5100, available from Hunter Associates Laboratory, Inc., 11495 Sunset Hills Rd., Reston, VA 22090. Alternate instruments must be qualified. Qualification standard is ability to pass ILC.

5. Gra-Lab 15 minute timer, Model 172, Dimco-Gray Company, Dayton, OH, or equivalent.

6. Leather gloves which are easy to remove. Smooth leather "Truckers" gloves, cut off at the cuff leaving only the palm and fingers are an example, obtain locally.

7. Mettler balance, PE300 or PM3600 or equivalent.

## VI. Reagents

1. Medium-hard vinyl masterbatch (P-1-B). Chestnut Run (Plastics Group) will order the ingredients and oversee the compounding and shipment of the vinyl masterbatch by an approved supplier. The supplier will compound and package the masterbatch and ship to the Control Labs according to expected consumption.

NOTE: A new supply of (P-1-B) masterbatch must be qualified before use by using the method of Periodic, Mini or Continuous ILC and comparing the data from the new masterbatch vs. data from the old.

## VII. Special Safety Considerations

### A. Product Hazards

1. 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 No. 2816CR.

2. Masterbatch will give off Carbon Monoxide above 400°F. Refer to MSDS No. 34410653 for P-1-B Masterbatch information.

3. Masterbatch contains DOP (dioctyl phthalate), which is listed on MSDS No. DU000885 as a carcinogen. Refer to the MSDS for this and other chemicals with which you are unfamiliar.

### B. Procedure Hazards

1. The use of a Two-Roll Mill involves hazards not ordinarily encountered. Therefore, under no circumstances is the mill to be operated by anyone not specially trained in its operation and familiar with the safety rules which apply to its operation. In addition to the normal precautions which apply to any procedure, the following rules apply to the operation of the mill.

2. No one shall attempt to operate the Two-Roll Mill without instruction and supervised training. Remember at all times that this is a dangerous machine. Never operate the mill unless someone is nearby to render assistance if it becomes necessary.

3. Eye protection must be worn when operating the mill.

4. Operators must wear approved leather gloves which are easily removed. Short-wristed gloves are preferred.

5. Neckties or other loose clothing must not be worn while

operating the mill. Shirt sleeves must be short or rolled up above the elbow. No jewelry is to be worn on the fingers or wrists. Nothing should be carried in shirt pockets.

6. If mill is left running and unattended, access to the area must be restricted to approved operators. Local site safety rules must be followed and may require a sign stating, RESTRICTED ACCESS AREA - AUTHORIZED PERSONNEL ONLY.

7. It is the duty of the operator to check all safety switches before commencing work. Faulty operation of the stop switches must be corrected before the mill is operated.

8. Do not carry on a conversation while operating the mill. To work safely, you need to concentrate 100% of the time on the operation.

9. When adding ingredients, use extreme caution. Keep your fingers tucked into your palm. Watch what you are doing. If the container is dropped onto the bank (into the nip of the mill) do not grab it. Stop the mill. Hold containers of ingredients only as near to the bank as required to keep the material from flying around.

10. Keep the hands away from the nip of the rolls and together as much as practicable below the front center of the rolls.

11. Stocks shall be cut on or below the front center of the roll and the hands shall not go above this point during this part of the operation.

12. When removing stock from the mill, do not grab. You can't buy new fingers. Cut a small section from one side of the roll and start pulling the sheet from the roll with the other hand. Proceed to cut the width of the roll. If the cut is missed, try again.

13. Do not allow stock to twist around or fold over any part of the hand or arm during milling. Beware of stock twisting around knife.

14. Never work over or under one roll on the other roll, attempt any operation across the nip or pass the knife across the rolls to anyone on the other side.

15. When the pigment, grease or masterbatch sticks to the rolls, then the rolls need to be cleaned as follows:

    Using specially-folded towels (all edges folded in), dry or wet with mineral spirits, the operator may clean the rolls by hand while the rolls are in motion. However the hand must be palms up and kept well below front center of the rolls. If necessary the operator may clean the roll with 153 grams of DPE6611 mixed with 2 or 3 teaspoons of sand.

16. No smoking is allowed in the mill lab.

17. In the event that anyone is caught in the mill, proceed as follows:

    a. Stop the rolls.

    b. Open the rolls by turning the ratchet adjustment cranks counterclockwise.

    c. Extract the hand carefully.

    d. Summon medical help at once.

    e. Administer first aid as require

    f. Chemical cold packs or equivalent must be available for use on burns.

VIII. Procedure

A. Operating Conditions

Refer to the manufacturer's operating manual for detail of the operation of the Two-Roll Mill and the spectrocolorimeter, and T4400.042.01.EM: Calibration and Use of the Labscan.

B. Calibration

The roll clearance is adjusted by turning the adjusting screws in or out. The clearance is measured by passing a piece of solid core solder (~1/8 inch diam.) through the rolls and measuring the thickness of the solder with a micrometer. (A new piece of solder should be used each and every time the roll clearance is checked). Adjust the roll clearance from 0.022 to 0.025 of an inch, with a

± 0.001 inch tolerance, from one end of the rolls to the other. On a properly adjusted mill, the `bank' or roll of vinyl material of the fluxed masterbatch, will be approximately 1/4 to 3/8 of an inch in diameter.

NOTE: At the present time the department has vinyl mills that range in age from ~1 to ~40 years. Each location with a mill or mills will have to determine the proper settings and roll clearance for their individual pieces of equipment. The size of the bank is very important and the mill settings should be established to obtain the proper size bank as described above. Roll settings will be determined and established by the use of Statistical Process Control (CUSUM) of the Reference Standard or the ability of the location to pass Inter Laboratory Cross Checks.

Roll Speed can be measured by marking the shaft of each roll (for instance with a brush pen) and determine the time required for 10 revolutions.

Roll circumference (in feet) x 10 Speed in Ft./Min. (FPM) = Time in minutes

If the speed is different than the setting, a series of points might be required to determine the correct setting for the test.

C. Sampling

Samples are usually provided by manufacturing.

D. Sample Analysis

1. Clean mill thoroughly as described in Section VII-15 above.

2. Heat mill rolls to surface temperature of 300°F ± 5° as measured with the surface pyrometer.

3. Weigh 153 ± 0.5 g of P-1-B masterbatch in a suitable container for each sample and standard.

4. Weigh 5.00 ± 0.01 g of each sample of titanium dioxide in an aluminum dish.

5. Place two clean sheets of wrapping paper on the surface below the mill rolls.

6. Turn on the mill and set roll speed to:

   Front 35 feet per minute (FPM)
   Rear 45 feet per minute (FPM)

   (Front roll is that roll closest to the operator).

7. Slowly add the weighed masterbatch to the nip of the revolving rolls. The masterbatch will plasticize in about 30 seconds. Be sure that it bands on the front roll. Return any material which drops through the rolls to the nip.

8. Two minutes after banding the vinyl masterbatch, add sample evenly across the nip and brush any TiO2 remaining in the aluminum dish into the nip with a clean camel hair brush. Give 5 cuts in 2-3 minutes. Return any material which drops through the rolls to the nip. Cut alternately from left and right sides; cutting diagonally toward the other side to make a strip about 4 inches wide. Do not cut closer than 2 inches from the other side. Return the strip to the nip.

9. Cut stock from the mill and let it cool for one minute on the paper sheet below the rolls.

10. Reband stock on the front roll. Do not add anymore material which drops through the rolls to the nip after this point.

11. Make 15 more cuts in the next 3-3/4 minutes (10 to 15 seconds interval between cuts).

12. Continue to band for one minute.

13. Carefully remove plastic from the roll and place on clean wrapping paper to cool, machine side up.

14. Repeat Steps 3 through 14 for each sample and standard.

15. When all samples are finished, clean mill and shut down the mill according to shutdown procedure appropriate to the mill.

16. Allow vinyl sheets to cool for a minimum of 15 minutes before reading.

17. Make three reading on each sheet and average the results. Make readings on the side of the sheet that was next to the roll.

E. Calculations

1. The tristimulus values, X, Y and Z of the tinting strength sheets are measured on the spectrocolorimeter. L*, a* and b* can be measured if required.

2. Tinting Strength (TS)

K/S values are derived from the Y tristimulus value using the Kubelka-Munk ratios in the Appendix. TS is calculated from the following equation:

$$TS = \frac{K/S\ (standard) \times TS\ (standard)}{K/S\ (sample)}$$

3. Undertone (UT)

Undertone is defined as the difference between Z/X ratio of the standard and the sample as follows:

UT = Z/X (sample) - Z/X (standard) + UT (standard)

If the UT of the standard is 0.000, then the equation reduces to:

UT = Z/X (sample) - Z/X (standard)

If the value of the standard is less than 0.000, the UT (standard) becomes negative and is subtracted. The UT (standard) is the actual value of undertone of the standard and is included in the appendix of the "Standard Sample Management" procedure (T4400.010.09.EM) along with the Tinting Strength value.

NOTE: The following are examples of the TS/UT calculations.

TINTING STRENGTH

$$TS = \frac{K/S\ STANDARD \times ASSIGNED\ STANDARD\ VALUE}{K/S\ SAMPLE}$$

EXAMPLE

| | STANDARD | SAMPLE |
|---|---|---|
| Green (Y) reflectance | 41.28 | 41.17 |
| K/S (from attached table) | .4172 | .4196 |
| TS | 108.7(assign) | 108 (calc) |

$$\frac{.4172 \times 108.7}{.4196} = 108$$

UNDERTONE

$$UT = \frac{BLUE\ (sample)}{RED\ (sample)} - \frac{BLUE\ (standard)}{RED\ (standard)} + UT\ value\ of\ standard$$

EXAMPLE

| | RED (X) | BLUE (Z) | RATIO |
|---|---|---|---|
| STANDARD | 38.98 | 44.26 | 1.1355 |
| SAMPLE | 38.87 | 44.35 | 1.1461 |

$$UT = \frac{44.35}{38.87} - \frac{44.26}{38.98} + .00493 \text{ OR}$$

UT = 1.1410 - 1.1355 + .00493 = .010

If the assigned standard UT value is negative, it will be subtracted.

IX. Quality Control

1. A reference standard is run once each shift and the results are used for statistical process control.

X. Comments

None

XI. References

1. ASTM D 1925-70.

2. MSDS No. DU000885 (dioctyl phthalate).

3. MSDS No. 2816CR (titanium dioxide).

4. MSDS No. 34410653 (P-1-B Masterbatch).

XII. Appendix

K/S Table



APPENDIX

K/S TABLE

| Y | K/S | Y | K/S | Y | K/S | Y | K/S |
|---|---|---|---|---|---|---|---|
| 30.0 | .8167 | 34.0 | .6406 | 38.0 | .5058 | 42.0 | .4005 |
| 30.1 | .8116 | 34.1 | .6368 | 38.1 | .5028 | 42.1 | .3982 |
| 30.2 | .8066 | 34.2 | .6330 | 38.2 | .4999 | 42.2 | .3958 |
| 30.3 | .8017 | 34.3 | .6292 | 38.3 | .4970 | 42.3 | .3935 |
| 30.4 | .7967 | 34.4 | .6255 | 38.4 | .4941 | 42.4 | .3912 |
| 30.5 | .7918 | 34.5 | .6218 | 38.5 | .4912 | 42.5 | .3890 |
| 30.6 | .7870 | 34.6 | .6181 | 38.6 | .4883 | 42.6 | .3867 |
| 30.7 | .7822 | 34.7 | .6144 | 38.7 | .4855 | 42.7 | .3845 |
| 30.8 | .7774 | 34.8 | .6108 | 38.8 | .4827 | 42.8 | .3822 |
| 30.9 | .7726 | 34.9 | .6072 | 38.9 | .4798 | 42.9 | .3800 |
| 31.0 | .7679 | 35.0 | .6036 | 39.0 | .4770 | 43.0 | .3778 |
| 31.1 | .7632 | 35.1 | .6000 | 39.1 | .4743 | 43.1 | .3756 |
| 31.2 | .7586 | 35.2 | .5964 | 39.2 | .4715 | 43.2 | .3734 |
| 31.3 | .7539 | 35.3 | .5929 | 39.3 | .4688 | 43.3 | .3712 |
| 31.4 | .7494 | 35.4 | .5894 | 39.4 | .4660 | 43.4 | .3691 |
| 31.5 | .7448 | 35.5 | .5860 | 39.5 | .4633 | 43.5 | .3669 |
| 31.6 | .7408 | 35.6 | .5825 | 39.6 | .4606 | 43.6 | .3648 |
| 31.7 | .7358 | 35.7 | .5791 | 39.7 | .4580 | 43.7 | .3627 |
| 31.8 | .7313 | 35.8 | .5756 | 39.8 | .4553 | 43.8 | .3606 |
| 31.9 | .7269 | 35.9 | .5723 | 39.9 | .4526 | 43.9 | .3584 |
| 32.0 | .7225 | 36.0 | .5689 | 40.0 | .4500 | 44.0 | .3564 |
| 32.1 | .7181 | 36.1 | .5655 | 40.1 | .4474 | 44.1 | .3543 |
| 32.2 | .7138 | 36.2 | .5622 | 40.2 | .4448 | 44.2 | .3522 |
| 32.3 | .7095 | 36.3 | .5589 | 40.3 | .4422 | 44.3 | .3502 |
| 32.4 | .7052 | 36.4 | .5556 | 40.4 | .4396 | 44.4 | .3480 |
| 32.5 | .7010 | 36.5 | .5524 | 40.5 | .4371 | 44.5 | .3461 |
| 32.6 | .6967 | 36.6 | .5491 | 40.6 | .4345 | 44.6 | .3441 |
| 32.7 | .6926 | 36.7 | .5459 | 40.7 | .4320 | 44.7 | .3421 |
| 32.8 | .6884 | 36.8 | .5427 | 40.8 | .4295 | 44.8 | .3401 |
| 32.9 | .6843 | 36.9 | .5395 | 40.9 | .4270 | 44.9 | .3381 |
| 33.0 | .6802 | 37.0 | .5364 | 41.0 | .4245 | 45.0 | .3361 |
| 33.1 | .6761 | 37.1 | .5332 | 41.1 | .4220 | | |
| 33.2 | .6720 | 37.2 | .5301 | 41.2 | .4196 | | |
| 33.3 | .6680 | 37.3 | .5270 | 41.3 | .4172 | | |
| 33.4 | .6640 | 37.4 | .5239 | 41.4 | .4147 | | |
| 33.5 | .6600 | 37.5 | .5208 | 41.5 | .4123 | | |
| 33.6 | .6561 | 37.6 | .5178 | 41.6 | .4099 | | |
| 33.7 | .6521 | 37.7 | .5148 | 41.7 | .4075 | | |
| 33.8 | .6483 | 37.8 | .5118 | 41.8 | .4052 | | |
| 33.9 | .6444 | 37.9 | .5088 | 41.9 | .4028 | | |