Documentation Sheet
Industry Tint Reference Black (ITRB)
Standard Oils for Use in the Tint Test
Standard Zinc Oxides for Use in the Tint Test
For Use with ASTM D3265, Carbon Black—Tint Strength
(Evaluated per ASTM D4483-99)
Approved by D24.61: June 26, 2018[1]
Supersedes: None

Introduction

There are three primary materials used in the tint strength test: carbon black, a white powder (zinc oxide), and a liquid vehicle (soybean oil epoxide). When mixed together per the instructions of D3265, these three materials form a black or gray paste. The paste is spread to produce a surface suitable for measuring the reflectance of the mixture by means of a photo-electric reflectance meter. (See D3265 for details on the spreading and measuring processes.) The reflectance of the tested carbon black is compared to the reflectance of a reference carbon black material prepared in the same manner. The tint strength of the tested carbon black is expressed as units of the reflectance of the reference carbon black material divided by the reflectance of the tested carbon black and multiplied by 100. (See D3265 for details of the calculation of tint strength.)

Industry Tint Reference Blacks:

D3265 was originally approved in 1973. The reference carbon black material selected for defining tint strength was Industry Reference Black Number 3 (IRB3). IRB3 is an N330 type carbon black produced by Ashland Carbon Black and accepted for use by D24 in June 1969. (See D4122 for a history of the IRB materials.) A quantity of IRB3 was set aside as a designated lot for use as the reference carbon black material for tint strength testing. This lot of material was designated as Industry Tint Reference Black (ITRB). The ITRB was assigned a tint strength of 100. There are no existing records of the initial quantity of ITRB or on what testing program was performed to arrive at the assigned value of 100.

It was reported at the June 2010 D24 meetings that the inventory of ITRB was expected to be depleted within 24 months and that a replacement material was needed. At its December 2010 meetings, D24 decided to set aside 5000 pounds of IRB8 for use as the new tint reference material, to be known as ITRB2. With annual sales of 200 to 300 pounds, the ITRB2 lot was expected to last at least 16 years. Samples of ITRB2 were distributed as part of the March 2011 LPRS program. The test results were evaluated and reported at the June 2011 D24 meetings. The data was analyzed per D4483-99 with the exception that a two-sided test was used to identify outlier laboratories with variation that is statistically too high or too low when compared to the variation within the ITP data set. This approach is thought to better represent expected variability in real-world testing and helps to offset memory-bias from an individual's repeated testing of the

[1] The current version of this document is available from Laboratory Standards and Technologies, Inc., 227 Somerset Street, Borger, TX, 79007, www.carbonstandard.com.

same material(s). Mandel's h and k statistics were used to identify outliers. Replacement values were calculated and substituted for outlier values. The ITRB2 material was approved for use at the June 2011 D24 meeting.

The ITP results showed that ITRB2 had a tint value of 101.34 when tested using ITRB as the carbon black reference material and the lots in use at that time of zinc oxide and soybean oil epoxide. A correction factor of 101.34 was introduced into the tint calculations for those laboratories using ITRB2 to normalize the tint values back to those obtained using ITRB to maintain compatibility with previous processes and materials.

Industry Tint Zinc Oxide:

Horsehead, through its subsidiary The New Jersey Zinc Company, started producing zinc oxide in 1848 and in the 1970's was the largest zinc producer in the United States. In the 1970's, many chemical companies used Horsehead's zinc oxide as the benchmark for developing global zinc chemical products. In 1987 Horsehead acquired the zinc assets of St. Joe Minerals, forming a subsidiary Zinc Corporation of America (ZCA) for selling its zinc products, and became the largest zinc oxide producer in the world.

The zinc oxide originally selected in the 1970's to be the Industry Tint Zinc Oxide was produced by Horsehead Corporation. Why this particular material was selected, its specifications, or if other materials were considered is not known. The material was distributed by Forcoven Products, Inc. As each lot approached depletion, Forcoven would contact Horsehead to produce another lot to the same specifications, with each lot being consecutively numbered.

Zinc oxide Lot 8 was the current lot in use when ITRB2 was approved for use in June 2011. Lot 8 was produced by Horsehead at its Monaca, Pennsylvania plant. It is not known if Lots 1 to 7 were produced at the Monaca plant. Some, none, or all of Lots 1 to 7 may have been produced at Horsehead's Palmerton, Pennsylvania plant, which was in operation in the 1970s.

Horsehead acquired Zochem, located in Brampton, Ontario, Canada in 2012. This facility produced zinc oxide Lots 9 and 10. The Monaca, PA plant was closed in 2014.

By the June 2014 D24 meetings, several users were reporting getting differences in tint values using Lot 9. A task group was formed to investigate the problem. After several years of investigation of Lots 9 and 10 with occurrences of inadequate performance, different properties of these two lots and other zinc oxide materials, and performance evaluation of zinc oxides from other sources, a material was found that performs satisfactorily in the tint test. This material has been designated as Lot 11. Lots 9 and 10 are suspect and not recommended for use in tint testing.

Lot 11 was produced by Zinc Oxide LLC in Dickson, Tennessee. Zinc Oxide LLC acquired Zochem from Horsehead in 2017, becoming the largest zinc oxide producer in North America. Since Zochem has broad name recognition having been a zinc oxide manufacturer since 1933 and Zinc Oxide LLC was a new company, Zinc Oxide LLC renamed itself to be Zochem.

Balentine Enterprises, Inc., dba as Laboratory Standards and Technologies (and hereafter shown as Balentine Enterprises) purchased all of Lot 11 from Zinc Oxide LLC in October 2015 and is the sole distributor of Lot 11.

The Dickson, TN plant is new with state-of-the-art reactor features which allowed it to set the manufacturing conditions to emulate those used for the production of Lot 8 when it was producing Lot 11. Future zinc oxide lots for D3265 will only be produced at the Dickson plant.

The most common process around the world for making zinc oxide from purified zinc is the Indirect or French Process. All the zinc oxide lots for the tint test have been produced by the French Process. The French Process feedstock is either primary zinc ingots direct from smelters or secondary zinc for recycling from galvanizers or zinc die casters.

Zinc vapor enters the reactor either from a refining column or a muffle furnace. The reactor design influences the zinc oxide's properties. The two basic reactor designs are "downdraft" or "updraft". The downdraft design holds the reaction heat longer, resulting in increased grain growth and sintering. Increased sintering is evidenced by increased crystal corner rounding and increased aggregate bond strength. Sharp angle crystals (versus slightly rounded crystal corners) changes the way the light is reflected in the tint test. In a process that is not fully understood, the increased aggregates may impact the way the carbon black coats the zinc oxide and thus changing the light reflection.

The French Process produces zinc oxide crystals that are hexagonal or nodular in shape. Other processes produce zinc oxide crystals that are star or needle shaped.

In spite of much effort, it was not possible to develop a specification to define the properties for zinc oxide that performs well in the tint test. However, SEM microscopic pictures showed that larger and regular particles of zinc oxide having a lower nitrogen surface area of approximately 3 m^2/g seem to provide acceptable results and are preferred to irregular zinc oxide particles with higher surface areas.

The investigation of the zinc oxide problem has brought a lot of information regarding the differences in zinc oxide to the members of D24. It is now obvious that not all zinc oxides are created equal.

Soybean Oil Epoxide:

The initial liquid vehicle selected for the tint test was a soybean oil epoxide with the trade name of Paraplex G-62, available from C.P. Hall Company. Nothing is known about why this material was selected as the liquid vehicle or if other materials were investigated. The manufacturer assigned lot numbers to the material but these were not tracked by D24 as all lots were considered to be equivalent. Balentine Enterprises purchased Paraplex G-62 from C.P. Hall in 55-gallon barrels and repackaged it in smaller quantities for the convenience of customers starting in February 2006.

At the same June 2014 D24 meetings where problems with the zinc oxide were reported, several users also reported problems with their lots of Paraplex G-62. The task group formed to investigate the zinc oxide problem was also charged with investigating the Paraplex problems. The task group learned that later lots of Paraplex-62 oil showed the presence of aromatic compounds, which were not present in the previous oils and made it unsuitable for the tint test. It is believed that the producer of Paraplex G-62 had changed the catalyst in their process. The mechanism of how these aromatic compounds affect the tint test is unknown. Efforts to develop

a specification for oils with acceptable performance were not successful. During the investigation it was noticed that Paraplex lots that have a "1" as the first digit of the lot number do not contain aromatic impurities while those that have "4" or "5" as the first digit have aromatic impurities that interfere with the test result. Paraplex G-62 lots with "4" or "5" as the first digit are suspect and not recommended by D24 for use in the tint test.

The task group investigated soybean oil epoxide available from other producers for suitability for use in the tint test. An oil from GreenChem with lot number 7170 (Designated as Greenflex 7170) was found to perform satisfactorily. Balentine Enterprises purchased this lot so it would be available for D24's use. To avoid future issues with the oil, GreenChem agreed not to sell this oil directly to users and will only sell to Balentine Enterprises.

Using the ITRB2, Zinc Oxide Lot 11, and Greenflex 7170 Soybean Oil Epoxide Materials:

The introduction of ITRB2 and the problems with the zinc oxide and Paraplex G-62 raised a number of concerns with the D24 members, not the least of which was backward compatibility and the impact on the historical tint values. An ITP was organized to investigate the impact of these materials on the tint values. The results of the ITP determined that those laboratories using ITRB2, zinc oxide lot 11, and the Greenflex 7170 oil got the same tint values as when using ITRB, zinc oxide lot 8, and Paraplex G-62 with a lot number with "1" as the first digit. There is no need to apply a correction factor to maintain backwards compatibility.

Recommendation:

The knowledge gained by members of D24 while investigating the zinc oxide and Paraplex problems makes it clear that there are many characteristics of zinc oxide and soybean oil epoxide that can be measured but are not predictive of successful use in the tint test. There may be unknown, and perhaps unmeasurable characteristics, which are critical to the successful performance of these materials in the tint test. Thus, the lack of success in establishing specifications for these materials. Therefore, to help remove these materials as factors in the testing variability between laboratories, D24 strongly urges that testing laboratories use lots of zinc oxide and soybean oil epoxide for the tint test that have been evaluated by D24 members and found to give acceptable performance. Zinc oxides and soybean oil epoxides from other sources may not give acceptable and equivalent performance. These materials from other sources may appear to give acceptable results with certain grades of carbon black but there is no guarantee that they will work with all grades of carbon black.

Shelf Life

Per ASTM D6915, Standard Practice for Carbon Black—Evaluation of Standard Reference Blacks, the shelf life of the Standard Reference Black (SRB) carbon blacks is indefinite when properly stored in a manner that protects it from exposure to sources of moisture, such as precipitation, other sources of liquid water, or high humidity environments. Since ITRB2 is a sublot of IRB8, which is also included in the SRB materials, it can be safely inferred that the shelf life of ITRB2 is also indefinite. Information from the manufacturers and accelerated life testing has shown that the shelf life of the zinc oxide and Greenflex 7170 oils is longer than the expect depletion time of the current lots.

To report corrections or request changes to this document, contact Laboratory Standards and Technologies (Balentine Enterprises), the chairman of ASTM subcommittee D24.61, or the chairman of ASTM subcommittee D24.21.