Documentation Sheet
Standard Reference Black – Set 9
(SRB9 prepared according to ASTM D6915)
(Evaluated per ASTM D4483-99)
Approved by the D24.61 Subcommittee: December 9, 2019[1]
Supersedes: September 27, 2019

Introduction

The Standard Reference Blacks (SRB) are special lots of carbon black that are used to help laboratories evaluate the state of accuracy of their testing performance. The variability values of the SRBs are used to establish control chart limits for monitoring within laboratory testing performance. In some cases, the SRB mean values are used to normalize the measured test result to produce the reported final test result. Since these materials are used as testing references, an important characteristic of the SRB materials is their homogeneity across the lot. A great deal of effort is put into the development of an SRB candidate material by the producer, ASTM Committee D24 on Carbon Black members, the carbon black industry, and the distributor of the SRB to insure its homogeneity. The producer typically will increase the process control sampling and testing frequency to provide earlier detection of process deviation that could impact the homogeneity of the candidate. A selected tank may be used for isolating the product with the possibility of purging of this tank and packaging equipment to minimize the possibility of contamination from other grades produced at the location. Extra samples representing small increments of the material will be collected during packaging. These samples will be tested by the producer and the test results compared to predetermined limits to evaluate homogeneity. These test results will be reviewed by the producer and the chair of the D24.61 subcommittee and any material exceeding the limits will be removed from the candidate material. Samples from the remaining candidate material are distributed to a large number of laboratories across the carbon black industry for testing and evaluation. The data from these laboratories is reviewed by the D24.61 subcommittee members for a final determination of homogeneity (with the possible removal of additional material), the establishment of the mean and variability parameters for the test methods of interest, and approval for use as a SRB. The care and testing done during production of a SRB is much greater than that of commercially available grades of carbon black and many other reference materials, such as the Industry Reference Black used in rubber testing, which is why the SRBs have such high value.

The first SRBs were produced in the early 1960s for the purpose of normalizing the test results from the recently developed oil absorptometer (See ASTM D2414). This initial set consisted of four grades of carbon black.

Subsequent sets were numbered consecutively so this is the ninth such set. Besides the oil absorption test, these later sets have been used to normalize the test results of other test methods. The number of materials and the grades have evolved as needed to cover the range of test results for all the tests for which the SRBs are used

[1] The current version of this document is available from Balentine Enterprises, 1410 South Cedar, Suite 17, Borger, TX, 79007, www.carbonstandard.com.

The materials selected for a given SRB set are intended to span as much as possible the range of test results of the selected tests. The SRB9 set consists of seven grades of carbon black; three tread, three carcass, and one thermal. They are available for use to normalize the test results from the following carbon black ASTM test methods: D2414 – Oil Absorption Number; D3493 – Oil Absorption Number of Compressed Sample; and D6556 – Total and External Surface Area by Nitrogen Adsorption. Values have also been developed for D1510 – Iodine Number test method but these values are NOT to be used to normalize the Iodine Number results. A special set of materials (HT or INR) have been developed for this purpose and only those materials should be used to normalize the Iodine Number test results. Information on the HT and INR reference materials is available from Laboratory Standards and Technologies (See footnote 1 for contact information). When performing normalization of test results using the SRB materials, it is necessary to use at least three (3) of the appropriate materials. It is recommended that, excepting any unusual circumstances, that the materials be from the same SRB set. For example, when normalizing OAN test results for a tread grade of carbon black when there are no unusual circumstances, use the A, B, and C materials from the same SRB set. The D24 subcommittees will define any unusual circumstances and provide guidelines for normalization, as needed. See the applicable test method and D4821 for details on any exceptions and the guidelines.

The SRB-9A2 and SRB-9D materials are new production. Most of the other SRB9 materials were carried forward from the SRB8 set because they are the same carbon black grades. Those SRB8 materials were re-designated for the SRB9 set: SRB-8A2 becomes SRB-9A, SRB-8B2 becomes SRB-9C, SRB-8E2 becomes SRB-9E, SRB-8F2 becomes SRB-9F, and SRB-8G becomes SRB-9G. An available N330 grade of carbon black for which precision data is available was selected to become SRB-9B.

All of the SRB9 data has been obtained through the Laboratory Proficiency Rating System (LPRS) program of D24. The LPRS program includes a large number of laboratories (typically 60 or more) that represent the testing proficiency of the industry. The values and limits listed below are the most current as of the date of this publication. See page 7 of this Documentation Sheet for additional background on this SRB set.

While D24 attempts to produce enough of each SRB material so that they will all be depleted at about the same time and a new SRB set produced, variability in the consumption rate of each material has thwarted this goal. Rather than waste the value of the remaining materials when the first material is depleted, D24 has adopted a program of producing supplemental lots of any depleted material. The quantity of the supplemental lots is set to be depleted when the last material is depleted, thus extending the life of the set. Every effort is made to have the supplemental lots produced by the same producer location that produced the initial lot. (See ASTM D7849 for information on the nomenclature used for D24 reference materials that identifies these supplemental lots.)

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. (See ASTM D8043, Standard Guide for Carbon Black—Shelf Life for similar information on other carbon blacks.)

Properties for the SRB9 Set

The LPRS program uses ASTM D4483-99 for data analysis, outlier identification, and outlier treatment. The generated mean values become the accepted reference values (means), AR-values, for the given tests as defined below. The generated within laboratory standard deviation (Sr) and between laboratory standard deviation (SR) for each test method are used to calculate the 2 and 3 sigma limits shown in the tables. The 2 and 3 sigma limits apply to a single measurement of the listed test properties. Two times the 2 or 3 sigma limit equals the total 4 or 6 sigma range, respectively.

ASTM D4483-99 uses a one-sided k test to identify outliers having high variability. The LPRS program uses a two-sided k test to identify outliers having high and low variability. 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 same material(s).

'Accepted Reference Value' or AR-value; this is the average (mean), for the various tests and materials listed below in Tables 1 through 6, obtained in an interlaboratory test program (ITP), i.e., the LPRS program, for a large group of typical laboratories using samples taken from the various material lots. See page 7 for more details on the ITPs.

'Within Typical Laboratory' 2 and 3 sigma value; this is the within laboratory ± 2 and ± 3 standard deviation (Sr) value (for single measurements) on the SRB9 set AR-values for the various tests, as obtained from the same group of typical ITP laboratories.

'Between Typical Laboratory' 2 and 3 sigma value); this is the between laboratory ± 2 and ± 3 standard deviation (SR) value (for single measurements) on the SRB9 set AR-values for the various tests, as obtained from the same group of typical ITP laboratories.

2 sigma versus 3 sigma use considerations: Most carbon black test properties (with the exception of pellet hardness maximum) have an acceptable approximation to a normal distribution. With a normal distribution, 95.5% of all the test values are expected to fall within the limits of mean ± 2 sigma and 99.7% will fall within the limits of mean ± 3 sigma. This means that with only random variation present, approximately 1 in 20 results will fall outside the 2 sigma limits and 3 in 1000 will fall outside the 3 sigma limits. This means that when using 2 sigma limits the laboratory will be looking for a problem 1 in 20 test results when there is no problem to be found. This is a waste of valuable resources. On the other hand, when using 3 sigma limits the laboratory will be looking for a problem when there is not a problem only 3 in 1000 test results. However, if the consequences of allowing a problem to go undetected for a long time are too high, using 3 sigma limits may not give adequate warning in sufficient time to implement timely corrective action. Using 2 sigma limits will give an earlier warning of the presence of a problem. It is up to the user to balance the costs of untimely warnings versus the costs of searching for problems that do not exist.

Special consideration for bias: When no absolute reference standard exists, such as is the case with most carbon black testing, a laboratory's bias can be defined as the difference between its

results and the mean result from an ITP involving many laboratories, such as the LPRS program. Every laboratory can be expected to have some level of bias due to the unique combination of testing conditions (equipment, materials, manpower, environment, etc.) that exists within a given laboratory. The level of bias for a given laboratory may or may not be critical. A laboratory that did not participate in the ITP may find that it cannot maintain control within the control limits due to factors unique to that laboratory causing bias in its values, increased variation, or both. The laboratory should conduct an investigation to identify the presence and cause(s) of the bias and variation and eliminate them so that it is aligned with the ITP data. Participation in a multi-laboratory precision study, such as the LPRS program, may help to identify the unique sources of bias and variation. The SRB9 set can be used to assist a laboratory in determining the presence and magnitude of bias and variation using the values given in the Tables 1 to 6 below. See ASTM D4821 for specific instructions on how to use these values to evaluate a laboratory's testing proficiency (bias and variability).

Table 1 Mean (AR-value) and Limit Values for D1510, Iodine Number Methods A & B

Units	g/kg	**Within Laboratory**			**Between Laboratories**		
Material	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
SRB-9A (N326)	78.1	0.43	0.87	1.30	1.00	2.01	3.01
SRB-9A2 (N326)	83.5	0.33	0.66	0.99	0.90	1.80	2.70
SRB-9B (N330)	82.0	0.37	0.74	1.11	0.96	1.91	2.87
SRB-9B2 (N330)	80.7	0.35	0.70	1.05	1.19	2.38	3.57
SRB-9C (N134)	140.3	0.50	1.00	1.50	3.65	7.30	10.95
SRB-9D (LS Carcass)	19.5	0.30	0.60	0.89	0.89	1.77	2.66
SRB-9E (N660)	36.2	0.29	0.57	0.86	0.68	1.36	2.04
SRB-9F (N683)	36.1	0.37	0.75	1.12	0.64	1.27	1.91
SRB-9G (N990)	7.7	0.25	0.49	0.74	0.83	1.65	2.48

Table 2 Mean (AR-value) and Limit Values for D6556, NSA

Units	10^3 m^2/kg (m^2/g)	**Within Laboratory**			**Between Laboratories**		
Material	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
SRB-9A (N326)	75.9	0.31	0.63	0.94	0.70	1.39	2.09
SRB-9A2 (N326)	78.7	0.33	0.66	0.99	0.82	1.64	2.46
SRB-9B (N330)	78.2	0.27	0.54	0.80	0.77	1.54	2.31
SRB-9B2 (N330)	77.5	0.27	0.54	0.80	0.86	1.72	2.58
SRB-9C (N134)	136.2	0.39	0.78	1.17	1.92	3.84	5.76
SRB-9D (LS Carcass)	20.3	0.18	0.36	0.54	0.41	0.82	1.23
SRB-9E (N660)	34.1	0.20	0.40	0.60	0.41	0.83	1.24
SRB-9F (N683)	32.4	0.20	0.40	0.60	0.60	1.21	1.81
SRB-9G (N990)	9.1	0.13	0.26	0.39	0.42	0.85	1.27

Table 3 Mean (AR-value) and Limit Values for D6556, STSA							
Units	10^3 m^2/kg (m^2/g)	Within Laboratory			Between Laboratories		
Material	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
SRB-9A (N326)	76.0	0.47	0.93	1.40	1.24	2.48	3.71
SRB-9A2 (N326)	79.3	0.41	0.82	1.23	1.17	2.34	3.51
SRB-9B (N330)	77.2	0.41	0.81	1.22	1.22	2.45	3.67
SRB-9B2 (N330)	76.7	0.36	0.72	1.08	1.14	2.28	3.42
SRB-9C (N134)	125.7	0.46	0.92	1.38	2.63	5.26	7.89
SRB-9D (LS Carcass)	19.8	0.24	0.49	0.73	0.63	1.26	1.88
SRB-9E (N660)	33.5	0.33	0.66	0.99	0.91	1.81	2.72
SRB-9F (N683)	31.9	0.29	0.58	0.87	1.09	2.18	3.27
SRB-9G (N990)	8.2	0.21	0.41	0.62	0.60	1.21	1.81

Table 4 Mean (AR-value) and Limit Values for D2414, OAN							
Units	10^{-5} m^3/kg ($cm^3/100$ g)	Within Laboratory			Between Laboratories		
Material	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
SRB-9A (N326)	71.5	0.47	0.94	1.41	1.55	3.10	4.65
SRB-9A2 (N326)	71.4	0.34	0.68	1.02	1.18	2.36	3.54
SRB-9B (N330)	98.9	0.40	0.80	1.21	1.11	2.22	3.33
SRB-9B2 (N330)	99.3	0.40	0.80	1.20	1.34	2.68	4.02
SRB-9C (N134)	124.4	0.44	0.88	1.32	1.23	2.46	3.69
SRB-9D (LS Carcass)	34.5	0.25	0.51	0.76	0.72	1.43	2.15
SRB-9E (N660)	89.2	0.44	0.87	1.31	0.89	1.79	2.68
SRB-9F (N683)	134.5	0.53	1.07	1.60	1.59	3.18	4.78
SRB-9G (N990)	38.6	0.23	0.45	0.68	1.76	3.52	5.28

Table 5 Mean (AR-value) and Limit Values for D3493, COAN							
Units	10^{-5} m^3/kg ($cm^3/100$ g)	Within Laboratory			Between Laboratories		
Material	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
SRB-9A (N326)	67.5	0.35	0.70	1.06	1.10	2.21	3.31
SRB-9A2 (N326)	68.7	0.40	0.80	1.20	0.91	1.82	2.73
SRB-9B (N330)	90.1	0.45	0.90	1.34	1.24	2.49	3.73
SRB-9B2 (N330)	90.1	0.46	0.92	1.38	1.23	2.46	3.69
SRB-9C (N134)	102.5	0.46	0.92	1.38	1.07	2.14	3.21
SRB-9D (LS Carcass)	34.6	0.21	0.43	0.64	0.84	1.68	2.51
SRB-9E (N660)	73.2	0.43	0.86	1.29	0.91	1.82	2.73
SRB-9F (N683)	85.4	0.34	0.69	1.03	1.19	2.38	3.57
SRB-9G (N990)	38.0	0.24	0.48	0.71	1.27	2.54	3.80

Table 6 Mean (AR-value) and Limit Values for D3265, Tint Strength							
Units	Tint Strength	**Within Laboratory**			**Between Laboratories**		
Material	Mean (AR-value)	Sr	2 x Sr	3 x Sr	SR	2 x SR	3 x SR
SRB-9A (N326)	111.0	0.54	1.08	1.62	1.15	2.30	3.45
SRB-9A2 (N326)	111.8	0.46	0.92	1.38	1.28	2.56	3.84
SRB-9B (N330)	105.8	0.43	0.85	1.28	1.33	2.66	3.98
SRB-9B2 (N330)	105.1	0.50	1.00	1.50	1.42	2.84	4.26
SRB-9C (N134)	130.9	0.59	1.18	1.77	2.59	5.18	7.77
SRB-9D (LS Carcass)	40.8	0.30	0.59	0.89	0.91	1.83	2.74
SRB-9E (N660)	57.7	0.41	0.83	1.24	1.73	3.46	5.20
SRB-9F (N683)	47.8	0.33	0.66	0.99	1.31	2.62	3.93
SRB-9G (N990)	21.5	0.26	0.52	0.79	2.58	5.16	7.74

Background and Interlaboratory Test Program Details:
SRB9 Set

Background - Standard Reference Blacks (SRBs), used for a number of test methods under the jurisdiction of ASTM Committee D24, are prepared according to D6915, "Evaluation of Standard Reference Blacks" with statistical analysis per D4483-99, "Standard Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries". The objective of D24 is to select reference materials that will have values across the range of possible test results for any given test. Even better would be to select materials whose values are evenly spaced across the test range. Unfortunately, due to the realities of carbon black production and the interdependence of some properties, it is not possible to select materials that cover the test range for all tests, much less be evenly spaced across that range. The materials selected for the SRB9 set represents D24's best attempt to satisfy these objectives.

Evaluation of the SRB9 Set – The production of the various SRB9 materials is shared among the various carbon black producers. See Table 7 for a list of the producers of the various SRB9 materials. Each lot is evaluated for uniformity by the producer. That uniformity data is reviewed with the chairman of subcommittee D24.61 and the final material selected to give the best uniformity possible for all the tests of interest as listed in Tables 1 to 6.

The values listed in Tables 1 to 6 were obtained through D24's LPRS program. In this program a single blind sample is distributed to the participating laboratories. Two samples of different materials are tested each year about six months apart. (Materials other than those in the SRB9 set are also tested in the LPRS program.) Each laboratory selects two technicians to perform the testing (the same two technicians may not have performed all the tests, depending on how the laboratory is staffed and organized) and each technician performs the testing once on two different days for a total of four test results.

In addition to the test results, the LPRS program also collects information on the test conditions when the testing was performed for each sample. A questionnaire is distributed along with the data form asking about the equipment, materials, methods, and testing conditions used when testing each sample. This information is used to help identify sources of variation and bias between laboratories to help improve testing proficiency in the industry. A testing instruction sheet that specifies the testing conditions to be used for a given sample has been included with the data file because it has been determined that some laboratories were not using the correct conditions when performing the LPRS testing. With this knowledge, D24 logically concluded that only data from those laboratories reporting that they performed the testing per the conditions specified for each test method as given in the included testing conditions instructions would be used to determine the mean (AR-value) and limit values for a given material.

Interlaboratory Test Program (ITP) – See Table 7 for a list of when the various SRB9 materials were tested. Table 7 also shows how many laboratories participated in the testing for each test and how many were removed as outliers for mean (M), high variation (H), or low variation (L). 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 same material(s). Mandel's h and k statistics were used to identify outliers. Replacement values were calculated and substituted for outlier values.

Table 7 SRB9 Information

				Number of Laboratories (M/H/L)[1]					
SRB9 Material	Grade	Producer	Test Period	D1510	D6556 NSA	D6556 STSA	D2414	D3493	D3265
SRB-9A	N326	Continental	March 2013	76(1/1/2)	71(1/2/0)	64(1/2/0)	77(0/1/1)	70(0/1/0)	68(1/1/2)
SRB-9A2	N326	Sid Richardson	August 2018	75(1/2/1)	72(1/1/0)	72(2/2/0)	76(0/2/0)	69(2/1/0)	71(0/3/2)
SRB-9B	N330	Orion	March 2016	85(1/2/1)	79(1/2/1)	74(1/1/0)	87(0/2/0)	75(0/2/0)	75(1/3/0)
SRB-9B2	N330	Orion	March 2019	75(0/2/1)	70(0/2/0)	70(0/2/0)	76(0/1/0)	68(0/2/0)	69(1/3/2)
SRB-9C	N134	Cabot	August 2019[2]	77(1/2/0)	50(1/2/0)	60(1/3/0)	79(1/2/0)	68(1/2/0)	52(0/1/1)
SRB-9D	LS Carcass	Cabot	March 2018	73(0/1/1)	70(1/2/4)	69(1/3/0)	75(2/2/1)	67(1/1/0)	70(1/3/2)
SRB-9E	N660	Sid Richardson	August 2016	79(2/3/1)	74(1/3/2)	68(1/3/1)	81(1/3/0)	71(0/3/1)	72(1/2/1)
SRB-9F	N683	Orion	March 2015[3]	73(1/2/2)	71(1/2/0)	68(1/2/0)	74(1/0/0)	67(1/1/0)	58(0/2/1)
SRB-9G[4]	N990	Cancarb	August 2017	71(1/3/0)	66(1/3/2)	66(1/4/1)	74(0/2/1)	64(1/2/1)	65(1/2/2)

[1]M = number of outliers for Mean; H = number of outliers for High variation; L = number of outliers for Low variation.

[2]Tint was retested in March 2019

[3]Tint was retested in March 2019

[4]SRB-9G was produced and approved in the last half of 1996 as SRB-5G. It has been re-designated for inclusion in each SRB set since that time.

Using the SRB9 Set – For the test methods listed in Tables 1 to 6 it is strongly recommended that laboratories determine if they are operating in an "in control" manner, by the use of the ± 2 or ± 3 sigma within-laboratory limits as the laboratory may choose to use. Despite rigorous analysis of the ITP data for the AR-value(s) and associated standard deviation(s), the group of laboratories in this (and any) ITP do not represent a typical "in statistical control system" to which the usual 6 sigma limits are applied. All the assignable causes of variation that are typically eliminated to attain 'statistical control' have not and cannot be, eliminated for the AR testing.

When performing normalization of test results using the SRB9 materials, it is necessary to use at least three (3) of the appropriate materials from the SRB9 set. For example, when normalizing OAN test results for a tread grade of carbon black, use the 9A, 9B, and 9C materials.

See ASTM D4821 for detailed instructions on using the SRB9 set values to monitor a given laboratory's testing proficiency (bias and variability) for the test methods listed in Tables 1 to 6. D4821 also includes instructions on evaluating testing proficiency (bias and variability) between laboratories.

To report corrections or request changes to this document, contact Balentine Enterprises or the chairman of ASTM subcommittee D24.61.