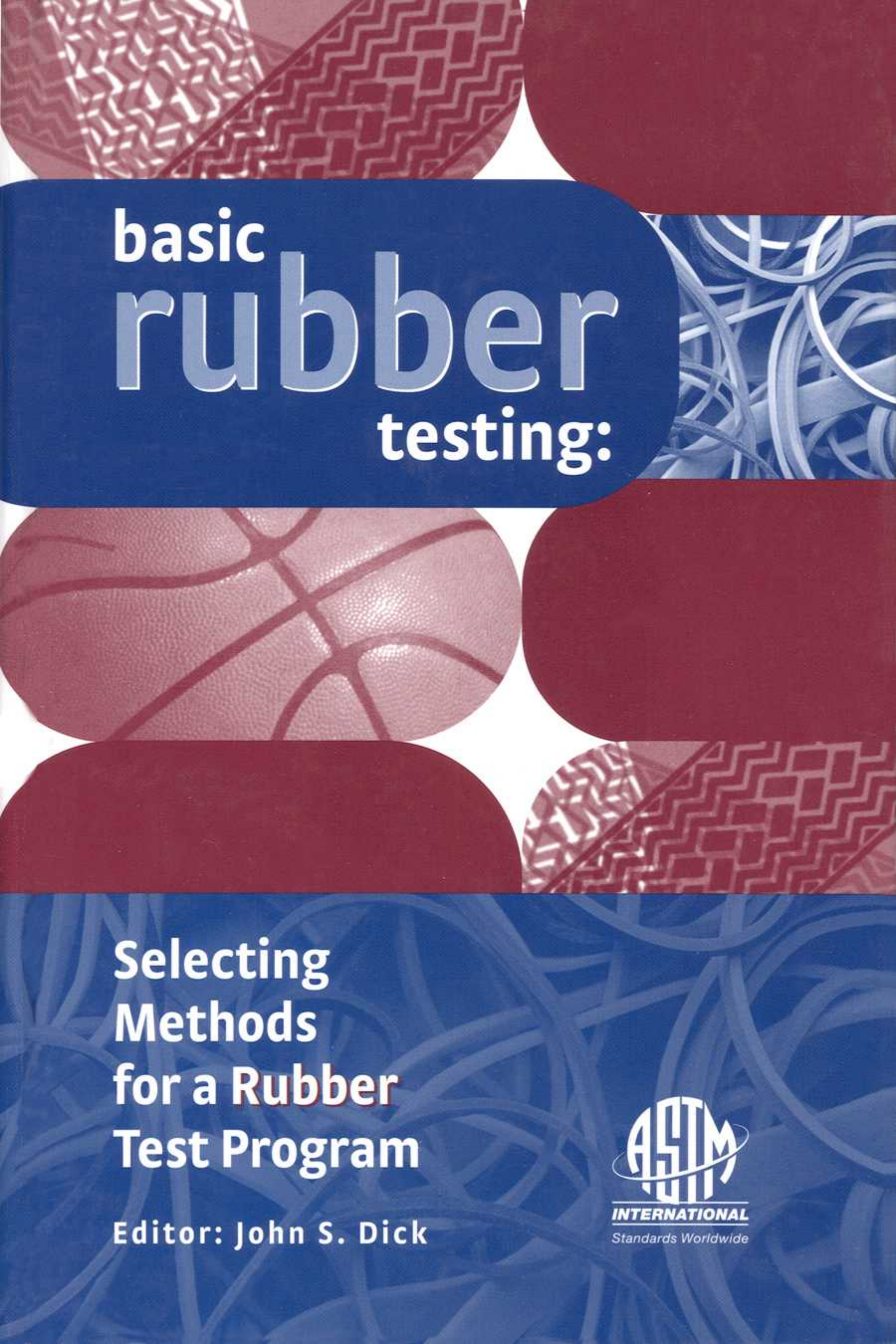

basic rubber testing:

Selecting Methods for a Rubber Test Program

Editor: John S. Dick

ASTM INTERNATIONAL
Standards Worldwide

Basic Rubber Testing: Selecting Methods for a Rubber Test Program

John S. Dick, editor

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Foreword

THIS PUBLICATION, *Basic Rubber Testing: Selecting Methods for a Rubber Test Program*, was sponsored by Committee D11 on Rubber and D24 on Carbon Black. This is Manual 39 in ASTM International's manual series.

Contents

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

CHAPTER 8

CHAPTER 9

CHAPTER 10

Preface

TODAY THERE IS A NEW initiative in the rubber industry, brought on by new quality programs such as Six Sigma, to reduce variation and eliminate quality problems significantly in the manufacture of a very wide scope of different rubber products. For example, the automotive manufacturers are beginning to design vehicles to last 150 000 miles with minimum maintenance. This severely challenges many rubber part manufacturers, perhaps more than other groups in the automotive supply base, to improve their quality and reduce variation.

One large source of product variation in the rubber industry can be nonuniformity of received raw rubber and other compounding ingredients. There are currently over 140 ASTM Standard Methods that are actively used to test these raw materials used in the rubber industry. The mixing process also is a very large source of variation in the factory. There are another 25 ASTM methods that are used to test the quality of mixed batches. This book is designed to be a practical guide to the rubber technologist in selecting the appropriate methods for use in a testing program of raw materials, compounding ingredients, or mixed stock.

This book characterizes each group of raw materials. It explains what are some of the important chemical and physical properties that should be used in making judgements on the quality of a raw material and its usability in the production plant. It gives a basic description of the test methods that are currently available. More importantly, this book compares and contrasts the advantages and disadvantages of selecting various test methods. However, this book is not a substitute for reading the actual ASTM method itself. This book will help the reader in deciding which ASTM methods should be selected for testing a given raw material or mixed stock. This information is important to assure that a rubber laboratory is running efficiently. In today's business climate where testing resources are being restricted in many cases, it is vital that the most important tests be selected and that redundant testing be eliminated. Selecting the wrong tests wastes valuable resources and money.

John S. Dick

Award of Merit Recipients *(continued)*

YEAR RECEIVED	AWARD RECIPIENTS	ACHIEVEMENTS
1981	Edwin English	Was secretary of D11 from 1975 to 1976. Was leader of the U.S. delegation to ISO TC45 for 12 years (succeeding R. Stiehler and retained this until 1992)
1982	Charles E. Tidd, Jr.	Was Chairman of D11, Rubber. Also contributed to Physical Testing (D11.10). Active with ISO TC45 as well
1984	William J. Holley	Very active with Synthetic Rubber standards (D11.23). Also active with ISO TC45
1987	Charles P. Gerstenmaier	Major contributions in the development of Carbon Black Test Methods. Also active in ISO TC45
1989	Rodney McGarry	Past Chairman of D24, Carbon Black. Major contributions in the development of Carbon Black Test Standards. Also active in ISO TC45
1989	Bobby Buffington	Major contributions in the development of Carbon Black Test Standards. Also active in ISO TC45
1990	John S. Dick	Chairman of D11.20 on Compounding Materials from 1981 to 1991. Involved in Rubber Processability Test Methods. Became the leader of the U.S. Delegation to ISO TC45 in 1992
1993	Thomas H. Spurlock	Major contributions in the development of Carbon Black Test Methods

Distinguished Service Award

YEAR RECEIVED	AWARD RECIPIENT	ACHIEVEMENTS
1998	Peter Surette	For his work in D11 Rubber, including physical testing (D11.10), time-temperature dependent properties (D11.14)
1998	Julia Zimmerman	For her contributions in D11, Rubber, including Chemical Analysis (D11.11)
1998	John Bailey	For his activities in D24, Carbon Black, including his extensive statistical contributions
1998	Charles Gillingham	For his activities in D24, Carbon Black
1999	Clair Harmon	For his participation in D11, Rubber, including his involvement with Natural Rubber (D11.22)
1999	Paul Gatza	For his contributions to D11, Rubber, including physical testing, and rubber products
1999	Jack Thompson	For his achievements in D24, Carbon Black
2000	Ricky MaGee	For his contributions in D24, Carbon Black
2001	Ivan Erwin	For his accomplishments in D11, Rubber, including his chairmanship of D11.15, Rubber Degradation Testing
2001	Denise Kotz	For her contributions to D11, Rubber, including physical testing
2001	Frank Lussier	For his contributions to D11, Rubber, and especially toward Chemical Analysis (D11.11)
2001	Jeff Melsom	For his leadership and contributions to D24, Carbon Black, and his chairmanship of D24
2001	Lee Coates	For his contributions in D24, Carbon Black
2002	Alec Vare	For his accomplishments in D11—Rubber, and especially his chairmanship of D11 and D11.22 on Natural Rubber
2002	Charles Rader	For his activities in D11, Rubber, and especially for his chairmanship of D11.08 (Nomenclature and Terminology)
2002	Tom Powell	For his contributions in D24, Carbon Black and his activities in the Executive Subcommittee

Acknowledgment

Acknowledgment of Contributors to ASTM Rubber Standards

The many ASTM standards discussed in this book were created through the excellent technical knowledge, strong commitments, and hard work of hundreds of rubber technologists who volunteered their time and effort in various task groups and subcommittees of ASTM D11 (on Rubber) and D24 (on Carbon Black). These standards truly represent a consensus of the rubber industry.

Thousands of ASTM members have contributed over the last 90 years to the development of these rubber standards and their efforts should be recognized. Therefore, it is appropriate to recognize directly those ASTM members who received the ASTM "Award of Merit" or the "Distinguished Service Award" in the last 50 years. However, it should be noted that many other ASTM members, who are not listed below, have also given countless hours of excellent work to develop ASTM standards and should be recognized as well. If it were not for all these contributors, these ASTM standards would not be at the high quality level they are today.

Award of Merit Recipients

YEAR RECEIVED	AWARD RECIPIENTS	ACHIEVEMENTS
1956	Simon Collier	Chairman of D11 for 14 years (from 1944 to 1962)
1959	Elmer G. Kimmich	Very active in D11, Rubber
1961	John J. Allen	For work in D11, Rubber. Also an honorary member of D11
1962	Harry G. Bimmerman	For work in D11, Rubber. Also an honorary member of D11
1964	Arthur Juve	Very active in Rubber Compounding Materials (now D11.20), Recipient of the Goodyear Medal from the ACS
1965	Issac Drogin	Very active in D11, Rubber
1966	Benjamin S. Garvey, Jr.	Known for his contributions in rubber processability testing as well as rubber testing in general. Known for the "Garvey Die" design
1968	Robert Stiehler	Longest continuous participation in D11 activities. Major contributions to D11. Established the Technical Advisory Group to ISO TC 45 on Rubber. Held position as Leader of USA Delegation to ISO TC 45 from the formation date of the TAG until he retired in 1980.
1969	Joseph F. Kerscher	Chairman of D11 from 1972 to 1978. Also made honorary member. Very active in the ISO TC45 TAG
1970	Gustav Maassen	Contributions include Rubber Aging and Degradation Testing
1972	Maynard Torrence	Very active in Rubber Terminology (D11.08). Also active in ISO TC45
1974	William H. King	Very active in developing Rubber Physical Testing Standards (D11.10). Also active in ISO TC45
1974	Thomas D. Bolt	Significant contributions to development of Carbon Black Standards
1975	W. Howard Bryan	Contributions include Coated Fabrics (D11.37) and Rubber Thread. Also active in ISO TC45
1976	Francis G. Mees	Chair of D24 on Carbon Black for six years. Major contributions in development of carbon black standards as well as Chemical Analysis (D11.11) and Rubber Nomenclature (D11.08). Very active in ISO TC45 activities
1977	Floyd S. Conant	Chairman of D11.14, Rubber Time and Temperature Dependent Properties. Also contributed to F9—Tires. Involved in ISO TC45 activities as well
1977	J. Frank Svetlik	Major contributions in the development of Carbon Black Test Methods. Also active in ISO TC45
1978	Alan Veith	Next to R. D. Stiehler, probably has the record for longest continuous participation in D11 activities (beginning in 1952). Major contributions to D11 on Rubber as well as F9 on Tires. Also very active in statistical standards and participates in E11 and D17. Very active in ISO TC45
1978	Francis Lyon	Major contributions in the development of Carbon Black Test Methods
1979	Clifford E. McCormick, Jr.	Very much involved in Statistical Methods for application to Carbon Black testing (D24) as well as Rubber Testing (D11). Authored several publications on Statistical Analysis of Carbon Black Testing
1981	Peter Larsen	Chaired Subcommittee on Time and Temperature Dependent Properties (D11.14) and Rubber Terminology. Very active in ISO TC45 on Rubber

1

Introduction

by John S. Dick[1]

1.1 HISTORY

THE RUBBER INDUSTRY ESSENTIALLY STARTED IN 1839 when Charles Goodyear discovered vulcanization (the curing process). Since this date, a large industry has grown that manufactures thousands of rubber products such as tires, hoses, belts, seals, gaskets, bearings, bushings, mounts, etc. In fact, rubber is essential for a modern industrialized economy [1].

While rubber is used virtually everywhere, its greatest use is in the automotive industry. Indeed, a modern passenger car will usually have over 600 rubber parts. Quality variation in these parts can lead to performance and reliability problems for automobiles. Historically, rubber has been a more variable material compared to steel or other metal alloys. Sometimes rubber parts can vary dimensionally by ±15 %, which can pose quality problems. Today the automotive manufacturers are talking about future plans to build the "150,000 mile car," which can be driven reliably with low maintenance for ten years or more. To make this vision come true, producers of rubber parts will have to improve the quality of these parts and significantly reduce dimensional variation. Effective test methods are essential in achieving this goal [2].

1.2 ASTM D11 STANDARDS

ASTM Committee D11 on Rubber is one of the oldest committees in the ASTM organization. This committee was formed in 1912, while ASTM D24 Committee on Carbon Black Used in Rubber was founded in 1956. Through literally hundreds of thousands of technical work hours, these two committees have produced over 300 active technical standards that are used daily throughout the world. This represents a huge investment by the rubber in-

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dustry in the development of these standards. However, with so many standards, most rubber technologists today have a problem finding, understanding, and selecting the appropriate ASTM methods when setting up a new rubber testing program [3]. The purpose of this book is to assist rubber technologists in their selections. However, it is not intended to substitute for reviewing the ASTM standards themselves for the needed details in implementing a testing program. Only by referencing these ASTM standards can the reader successfully perform these tests and interpret the test results.

One of the large sources of product variation in the rubber industry can be nonuniformity of received raw rubber and other raw materials. There are currently over 150 ASTM methods actively used to test these raw materials. Also, there are 15 commonly used methods for testing mixed rubber compounds for processing characteristics, and over 100 other ASTM methods for testing cured physical properties.

1.3 PURPOSE

This book is designed to be a practical guide for the rubber technologist when selecting the appropriate ASTM methods for use in a testing program of raw materials and/or compounding ingredients. Also, the book discusses which ASTM methods should be selected to test mixed rubber stocks from internal mixers and/or mills to predict downstream processability behavior.

This book characterizes each group of raw materials. It explains some of the important chemical and physical properties that should be used in making judgments on the quality of a raw material and its suitability in production. It gives a basic description of the test methods currently available and compares and contrasts the advantages and disadvantages of selecting various test methods. This book will help the reader in deciding which ASTM methods should be selected for testing a given raw material or mixed rubber compound. This information is important to assure that a rubber laboratory is running efficiently. In today's business climate, where testing resources are being restricted in many cases, it is vital that the most important tests be selected and that redundant testing be eliminated. Selecting the wrong tests wastes valuable resources and money.

1.4 ECONOMIC SAVINGS FOR USERS AND PRODUCERS THROUGH TEST METHOD RATIONALIZATION

By using ASTM standard methods, the rubber industry has achieved very substantial cost savings. Consider the situation shown in Figure 1.1 in which you are a raw material supplier with multiple customers.

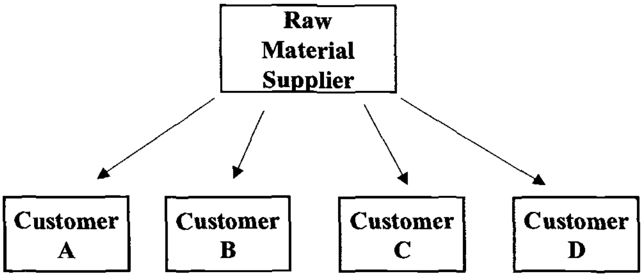


FIG. 1.1—Specification complexity of multiple customers.

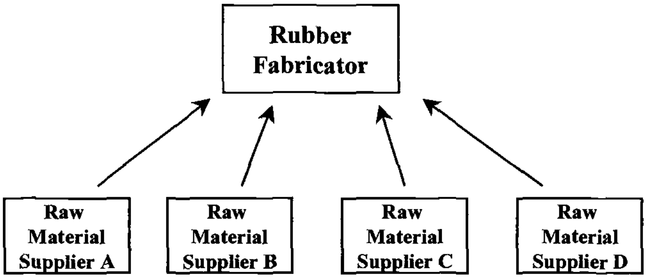


FIG. 1.2—Specification complexity of multiple raw material sources.

If each of your customers had different test methods and different specification requirements, the operating cost of your business would be significantly increased. On the other hand, if you and your customers were all using the same ASTM standards and had agreed on the same target values, or at least the same specifications, your operating costs would be greatly reduced. There would be a significant reduction in the number of different tests your laboratory would have to perform, a reduction in the frequency of testing, and the establishment of more effective target values in production [4].

In Figure 1.2, a similar situation exists, if you have multiple suppliers, providing you with the "same" raw material.

Here, if you have multiple sources for the "same" raw material, but each supplier is using a different test method, meaningful comparisons based on vendor data are nearly impossible. Many times this type of situation will force you to greatly increase your frequency of testing to ensure that you are indeed receiving consistent and uniform raw material for the quality specifications you have established for your process. On the other hand, if you and all your suppliers are using the same ASTM methods and the same target values or specification limits, the relationship you will have with these suppliers will be much simpler. You will have much higher confidence in the vendor data you receive and how these data relate to your needs. Lastly, you may develop the confidence to reduce your level of testing on incoming raw material shipments from each supplier [5].

On a macro scale, if both the producers and users in the rubber industry utilize the same ASTM methods in assuring the quality of raw rubber and rubber compounding ingredients, the following advantages will result:

- Proliferation of different test methods and laboratory equipment requirements by producers and users alike is greatly reduced or eliminated.
- The producer can more accurately control his production process to conform to the users' specification requirements.
- The user can rely more on vendor data received for the acceptance of each shipment without having to resort to a higher frequency of testing by his laboratory.

1.5 IMPORTANCE OF QUALITY

If the proper ASTM methods are selected, very important material quality defects can be identified that relate to the final rubber product performance. Examples of these defects are given in Table 1.1.

If you cannot assure or control the quality of the raw materials going into the mixing process, you will not have good quality rubber batches coming from the mixing process, as demonstrated in Table 1.1 [6].

TABLE 1.1—Examples of the Importance of Quality Testing.

RAW MATERIAL DEFECT	RESULT
"Nervy" raw rubber	Increased die swell during extrusion, poor dimensional stability
High-viscosity raw rubber	Poor mold flow, nonfills
High grit in carbon black	Surface appearance problems, lower tensile properties
Low surface area for carbon black	Poorer tire tread wear characteristics
Low-surface-area zinc oxide	Reduced modulus, poorer hysteresis
Poorly ground sulfur	Poor dispersion, poor uniformity as indicated from curemeter cure times and maximum torque
High methanol-insolubles in sulfenamide accelerators	Scorh problems
Nonuniformity of special wax blends	Inconsistent ozone protection, cracking
High unsaturation in fatty acid activator	Higher hysteresis
High sieve residues for ground coal filler	Flex cracking
Highly acidic phenolic resin tackifiers	Affects cured physicals, retards cure
Overexposure of magnesium oxide to atmopheric moisture	Lower modulus, higher compression set, scorchy stock
Nonuniformity of clay particle size distribution	Changes modulus and processing characteristics

TABLE 1.2—Examples of the Importance of Quality Testing for Compounded Mixed Rubber Stocks.

MIXED COMPOUND BATCH DEFECT	RESULTS
Poor consistency of mix (as indicated by variation in uncured G′ from ASTM D 6204)	High variation in extrusion die swell, poor dimensional control; trapped air and non-fills from injection molding
Poor dispersion of curatives (as indicated from variation in scorch, cure times, and max torque values per ASTM D 5289)	Poor control of scorch, poor-cured tensile properties
Poor consistency of mix and poor dispersion of curatives (as indicated from cured dynamic properties such as cured G′ or tan δ from ASTM D 6601)	Poor control of spring rate constants, K′, K″, K* and variation in rubber part dynamic performance

Furthermore, Table 1.2 shows examples of quality problems that can result from poorly mixed stocks that have good, uniform raw materials going into the mix.

These examples show that you can have good raw materials coming into a plant, yet still experience a great deal of nonuniformity because of variation in mixing conditions and "state of mix," which leads to downstream processability problems. There can be many assignable causes of variation in a rubber-mixing operation. Even the manner in which a batch is dumped is of great importance. These variations in state of mix and other processing steps can be monitored with ASTM test methods discussed in Chapter 2 [7].

1.6 STANDARD TARGET VALUES AND "TOLERANCE STACK-UP"

In the 1980s the automotive manufacturers became very concerned about "tolerance stack-up." Being within specification tolerances is vital to a modern industrial society; however, just being "in-spec" may not be good enough for multiple component systems such as an automobile or a rubber compound that is composed typically of 8 to 20 different compounding ingredients (raw materials). Figure 1.3 illustrates this point. This figure shows raw material properties that might affect compound scorch safety (the time before the onset of vulcanization). In this illustration, an increase in Mooney viscosity could contribute to a higher temperature during mixing that would contribute more heat history. Also, a higher structure carbon black might generate more viscous heating during mixing and also contribute more to the heat history. Thirdly, a higher concentration of MBTS as an impurity in a commonly used rubber accelerator such as CBS will make the rubber compound more scorchy. And lastly, a process oil with higher concentrations of polar compounds (heterocyclic compounds based on oxygen, nitrogen, and/or sulfur) can also shorten scorch times. Perhaps no increase in any one of these four raw material characteristics would in and of itself cause the re-

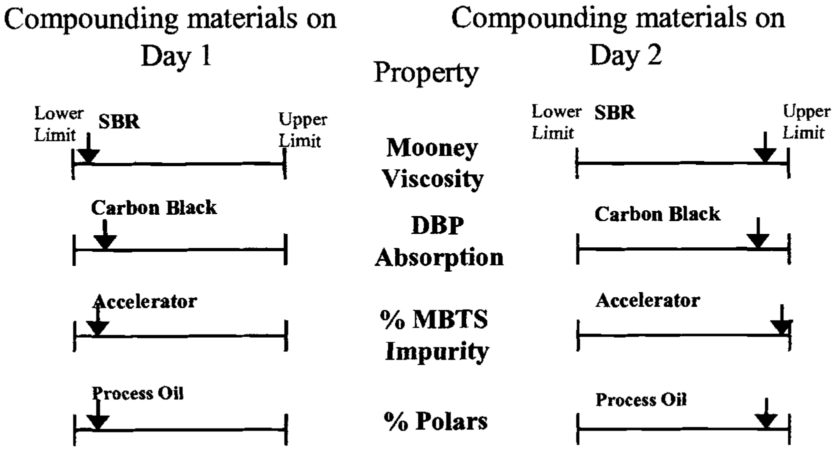


FIG. 1.3—Demonstration of "tolerance stack-up" in a rubber plant.

sulting mixed rubber compound to be "too scorchy." In fact, the specification limits established for all four of these quality characteristics are probably quite reasonable for most situations. So on Day 1, all four of these parameters are within specifications near the lower limit and a good scorch safety time is achieved. However, on another day—Day 2, all four of these parameters happen to be near the upper specification limits, but still within specification. Even though all four quality characteristics are still within specification, it should be no surprise that there is a scorch problem. The reason for this problem is that all four quality characteristics are on the high side of their respective specification limits. This is the "additive effect" or "tolerance stack-up" effect. This is why just staying within specification is no longer "good enough." This is particularly true in the automotive industry today. These "tolerance stack-up" problems can be avoided when a new emphasis is placed on *target values* (usually the midpoint of a specification). The closer the process can be kept "on target," the less likely a "tolerance stacking" problem will be encountered.

When both users and producers in an industry are using the same ASTM methods, it is beneficial for them to reach agreement on target values for the different grades of raw rubber and compounding ingredients. If a *producer* has only one target value that he must focus on for a given grade of raw material, he can increase his production output and not have to slow down or stop production to change to another target for that grade. Also from the *user's* point of view, having an agreed-upon target value for a given grade of raw material is a great advantage as well. This is because, at least in theory if not practice, there should be fewer problems when a user switches from one producer of a given standard grade of raw material to another producer. In theory, if they are both producing to the same industrially recognized target value, there should be fewer adjustments necessary when a switch is made by the user [8,9].

In ASTM D11 Committee on Rubber and ASTM D24 Committee on Carbon Black, target values have been established for some raw materials used in the rubber industry. For example, in the early 1980s, target values for iodine adsorption number and DBP absorption number were established and published in ASTM D 1765 for 45 different grades of carbon black used routinely in the rubber industry. A new standard, which was introduced in 1994 through ASTM D11 (Committee on Rubber), has helped establish new target values for some grades of SBR. This new standard is ASTM D 5605.

1.7 TESTING BIAS

Even if two laboratories are using the same ASTM test method, they may still generate different test results when they test the same material. This is because a standard test method can only give you the same results consistently if all the potential testing variables are addressed and controlled. There are obvious variables, such as time, temperature, sample size, equipment, etc., which can affect the test results greatly. However, many times variables can be more subtle. For example, Fig. 1.4 shows a significant difference between two laboratories (user and producer) for phenolic tackifying resin shipments using a standard ASTM ring and ball softening point procedure.

Even though conditions such as rate of temperature rise, equipment, and glassware were all the same, the producer consistently had a positive ten-

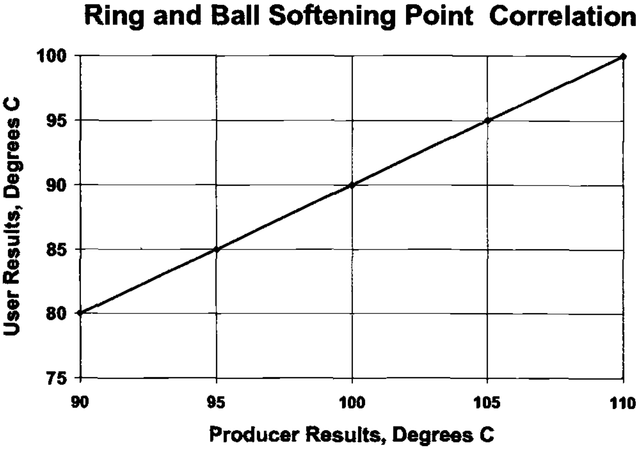


FIG. 1.4—Interlaboratory test bias (between the producer and user) for ring and ball softening point for a phenolic tackifying resin used in rubber compounding.

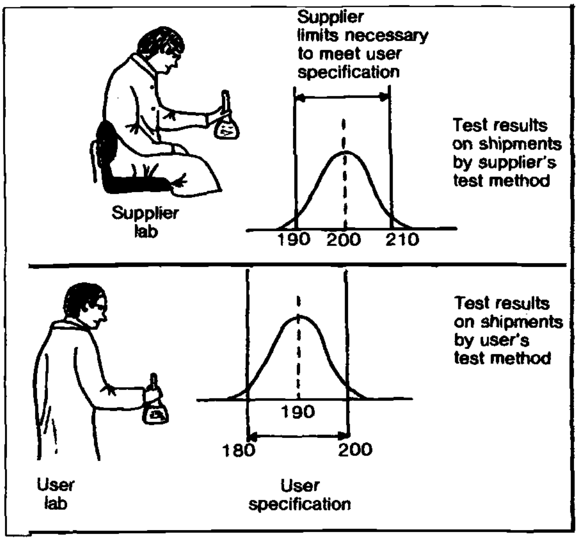


FIG. 1.5—Illustration of an interlaboratory testing bias between laboratories.

point bias versus the user. As it turns out, one laboratory was using a different heating medium, which was reacting with the subject resin being tested. When both laboratories agreed to use the same heating medium, they achieved excellent agreement. When laboratories are using the "same" ASTM methods, there still can be interlab biases, even when the procedure is well written. If these biases do exist, it is to the mutual benefit of both the user and producer to resolve these differences. Otherwise, producing to a standard specification or receiving shipments of the subject material meeting the same standard specification will be a major problem, as shown in Fig. 1.5 [10].

1.8 WHAT MAKES FOR A GOOD STANDARD TEST METHOD?

ISO 9001, Section 4.11.2, states "... identify all inspection, measuring and test equipment that can affect product quality, and calibrate and adjust them at prescribed intervals, or prior to use, against certified equipment having a known valid relationship to internationally or nationally recognized standards..." In accordance with QS-9000 Quality System Requirements, Section 4.11.1 states "... establish and maintain documented procedures to control, calibrate and maintain inspection, measuring and test equipment . . . to demonstrate the conformance of product to the specified requirements." Therefore, for a good quality control measurement system to exist, the standard test methods used should have the following attributes, especially if these methods are to be used in statistical quality control. These five desirable attributes for standard test methods are as follows [11,12].

1. Good accuracy
2. Good repeatability
3. Good reproducibility
4. Good stability
5. Good linearity

1.8.1 Accuracy

Accuracy can be very important for many standard test methods. If the test results are units that may reflect a property such as percent concentration, it might not be too difficult to relate those results to the so-called "true value." With other standard methods, such as the Mooney viscometer, which reports values in arbitrary Mooney units, it may be more difficult to get at the absolute "true" Mooney value and know just how much testing bias a given Mooney viscometer might possess. One way to try to address this is to participate in scheduled interlaboratory cross-checks that are sometimes conducted by the ASTM membership. Through such programs, at least you will know how your lab results compare to results from a large population of instruments or methods performed in other laboratories. Also, ASTM industry reference materials (IRMs) can sometimes be used. Sometimes these IRMs will have ASTM "documentation sheets" that show the statistical analysis results for the specific IRM lot from a large interlaboratory cross-check (see Chapter 10). Also, an important point is to use an IRM that is stable over time and will always give the same results when tested over time. An example of this is IRM 241, butyl rubber, which is used with Mooney viscometers and other ASTM processability tests.

1.8.2 Repeatability

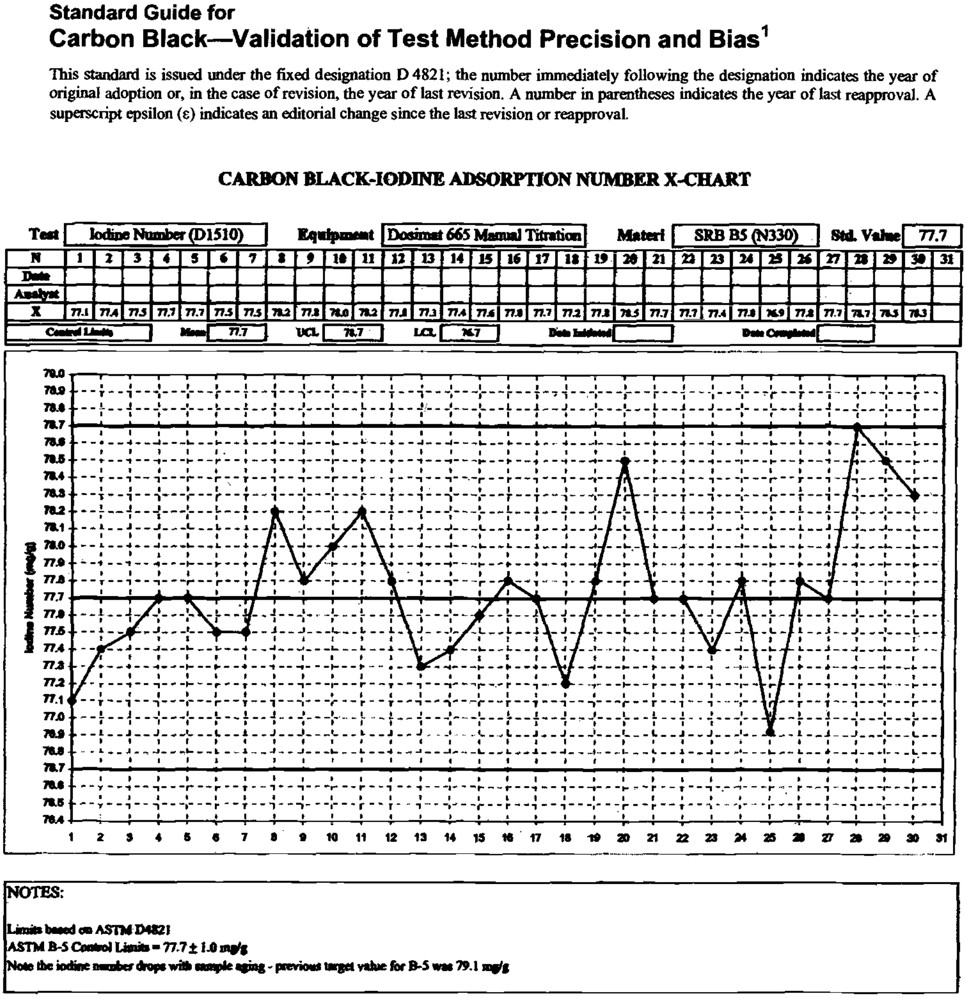
Repeatability relates to the test method variation from a single test instrument or laboratory. This is defined and discussed in more detail in Chapter 10. There is short-term repeatability (what you might experience over the course of one day) or longer-term repeatability (what you might experience from week to week—see "Stability"). Repeatability can also be checked as part of a gage R&R study (in accordance with AIAG—Automotive Industry Action Group) or by participating in an ASTM interlaboratory cross-check.

1.8.3 Reproducibility

Reproducibility has two definitions. For Gage R&R terminology from AIAG, it is the variation in measurements by different operators and is called appraiser variation (AV). Some test standards, especially those with subjective endpoints, can have high AV. In ASTM D11 terminology, however, the term *reproducibility* is defined as the ability of multiple instruments or laboratories to agree with each other. Usually this type of reproducibility can be measured through an interlaboratory cross-check with the same homogeneous reference material. It is very important that this reference material be "stable."

1.8.4 Stability

Stability for a standard test method is very important. Sometimes standard test method results may drift over time. By using a *stable* standard ref-



Standard Guide for
Carbon Black—Validation of Test Method Precision and Bias[1]

This standard is issued under the fixed designation D 4821; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

CARBON BLACK-IODINE ADSORPTION NUMBER X-CHART

Test Iodine Number (D1510) **Equipment** Dosimat 665 Manual Titration **Materi** SRB B5 (N330) **Std. Value** 77.7

N	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Date																															
Analyst																															
X	77.1	77.4	77.5	77.7	77.7	77.5	77.5	78.2	77.8	78.0	78.2	77.8	77.3	77.4	77.6	77.8	77.7	77.2	77.8	78.5	77.7	77.7	77.4	77.8	76.9	77.8	77.7	78.7	78.5	78.3	

Control Limits **Mean** 77.7 **UCL** 78.7 **LCL** 76.7 **Date Initiated** **Date Completed**

NOTES:

Limits based on ASTM D4821
ASTM B-5 Control Limits = 77.7 ± 1.0 mg/g
Note the iodine number drops with sample aging - previous target value for B-5 was 79.1 mg/g

FIG. 1.6—Chart using guide D-4821 Control Limits

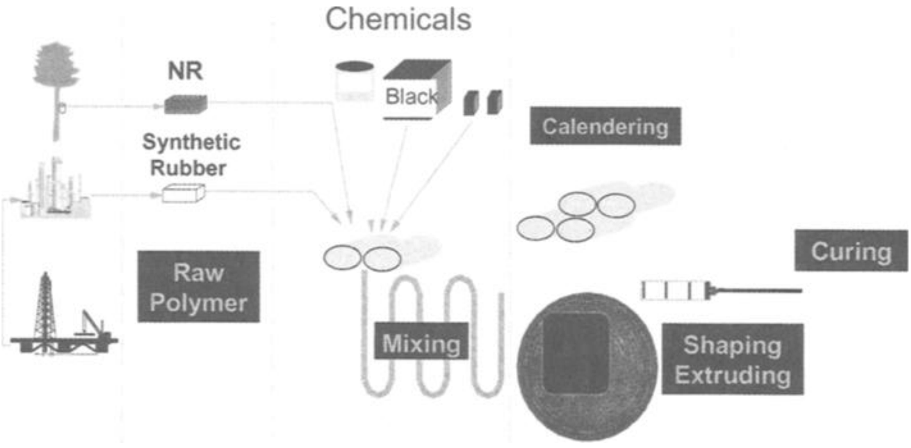


FIG. 1.7—Typical rubber process flow chart. Photograph courtesy of Alpha Technologies.

erence material periodically to check the stability of test results being generated over time, one can determine if a method is stable. Control charting these results over time is encouraged. By making periodic weekly checks and charting them with a Shewhart control chart, one can determine if the test method is in a state of statistical control over time or if there is a special cause(s) that is causing test values to drift or to suddenly shift "out of control." By using such SPC techniques with a stable standard reference material (one that does not change with the passage of time), one can look for and find any "assignable causes of variation" that might be occurring with the standard method. Usually these "special causes" of variation can be corrected. A good example of the use of a control chart to keep a standard test method in statistical control is shown in Fig. 1.6.

This figure depicts the control chart given in ASTM D 4821 to be used with standard reference blacks (SRBs) to keep ASTM carbon black tests such as DBP Absorption, Iodine Adsorption, etc. in a state of statistical control. ASTM D 4821 even directs the reader to the possible "assignable causes" of variation that might cause the specific carbon black method to go "out of control" statistically. This will be discussed more in Chapter 10.

1.8.5 Linearity

Linearity is defined as the difference in accuracy over the expected operating range of the instrument or test method. The accuracy of a test can change over a wide range of measurements. This means that calibration should be performed at more than one point. It also means that more than one standard reference material may be required because a range of *accepted reference values* (AR values) may be needed to represent the useful operating range of the standard test method (see ASTM D 4678 for more information about AR values). This is why ASTM D 3324 provides a total of six different standard reference blacks to be used over a wide range of values for iodine adsorption, DBP absorption, CTAB adsorption surface area, etc.

1.9 THE RUBBER PROCESS

The process for fabricating rubber parts can be quite varied. However, usually these processes have certain steps in common.

Most rubber processes have systems for receiving, storing, and distributing raw rubber, fillers, and compounding ingredients. This may be a very simple system or a very elaborate system with automatic weighing and auto injection into a mixer. At some point in this process, samples of raw materials may be taken for quality testing using standard ASTM raw material tests, which will be discussed in this book. Chapter 3 will discuss natural rubber testing. Chapter 4 will discuss synthetic rubber testing. Chapter 5 reviews carbon black testing, while Chapter 6 discusses silica. Chapter 7 discusses mineral fillers, while Chapter 8 reviews standard methods and practices for oils, plasticizers, and rubber chemicals, followed by Chapter 9, which reviews the latest standards for testing recycled rubber. Also, information in these chapters can be used to help in the interpretation of vendor data or to conduct vendor quality audits and technical meetings.

Usually rubber processors have a system of mixing where the raw rubber, carbon black, oil, curatives, etc. are all mixed together. This mixing will generally occur either in an internal mixer (such as a Banbury®) or on an open two-roll mill. If an internal mixer is used, it usually dumps onto a two-roll mill and is then slabbed off as sheets. Also, these dump mills are often configured to produce continuous sheet. Mixing operations may involve one pass through the internal mixer, two passes, or even three or more passes through the internal mixer (depending on how difficult it is to achieve good dispersion). Samples may be taken after any of these passes. Chapter 2 will discuss some of the general ASTM standard methods that are used to measure these test samples. For rapid tests to predict state of mix and downstream processing behavior, such tests as the new ASTM D 6204 for the Rotorless Shear Rhometer (commonly referred to as the rubber process analyzer or RPA) and the older ASTM D 1646 for the Mooney viscometer may be used. For predicting curing behavior for "final" batches (batches with curatives) further downstream, the newer ASTM D 5289 for the rotorless curemeter and older ASTM D 2084 for the oscillating disk rheometer can be used. For predicting after-cure dynamic properties, ASTM D 6601, using the rotorless shear rheometer with forced air cooling, can also be used.

Three-roll and four-roll calendars are used to convert mixed rubber stocks into uncured sheeting or to calender the rubber stock onto a fabric.

Shaping processes from extrusion operations are commonly performed. The preforms from such operations are sometimes press molded and cured at preselected elevated temperature into a final product. On the other hand, some extrudates are cured in autoclaves. Also some rubber parts are products of injection molding, for greater productivity. Figure 1.7 demonstrates some of these processes.

1.10 RAW RUBBER AND COMPOUNDING INGREDIENTS

ASTM D 5899 gives a detailed classification system for most of the raw materials used in a rubber mixing process. This classification system is shown in Table 1.3.

The following chapters will discuss these materials in more detail and the ASTM tests that can be used to test these materials.

1.11 THE RECIPE

The rubber recipe (or formulation) is the heart of rubber technology. The composition of a given rubber compound is based on a specified recipe. It is accepted convention in the rubber industry to base all part levels as "parts per hundred rubber" or "phr." This means that the total parts of one, two, three, or more different rubbers called for in a specific recipe must be defined as 100. Thus, all the other nonrubber ingredients are ratioed against this "100 parts" (that represents all the rubber hydrocarbon).

Table 1.4 shows a typical rubber recipe for a radial passenger tire tread [13,14].

In the rubber industry, there are literally tens of thousands of different recipes used in commerce every day. Each one is unique in that it may be based on very different rubbers, filler/oil systems, cure systems, antioxidant systems, etc. In general, many of these very different compounding ingredients are mentioned in Table 1.3. As can be seen, rubber compounding can become very complex requiring many hours of technical development and testing to obtain the desired properties for a new customer application, possess the needed processing characteristics, and be competitively priced.

Table 1.3—Classification System.

- *Accelerators*
    - Dithiocarbamates
    - Guanidines
    - Maleimides
    - Sulfenamides and sulfenimides
    - Thiazoles
    - Thioureas
    - Thiurams
    - Other
- *Adhesion Promoters*
    - Methylene donors
    - Resorcinol donors
    - Cobalt salts/compounds
    - Other
- *Antidegradants*
    - Alkyl aryl phenylene diamines
    - Bis phenols
    - Dialkyl phenylene diamines
    - Diaryl phenylene diamines
    - Quinolines
    - Substituted amines
    - Substituted phenols
    - Waxes
    - Other
- *Antistatic Agents*
- *Blowing Agents*
    - Azodicarbonamide
    - Carbonates
    - Other
- *Colorants*
    - Iron oxide
    - Titanium dioxide
    - Other inorganic colorants
    - Other organic colorants
- *Fillers, Extenders, and Reinforcing Agents*
    - Calcium carbonates
    - Carbon Blacks, Hard
        - N100 series
        - N200
        - N300
        - Other
    - Carbon Blacks, Soft (larger particle size than N300 type)
        - N400 series
        - N500 series
        - N600 series
        - N700 series
        - N800 series
        - N900 series
        - Conductive Carbon blacks (other than given above)
        - Other carbon blacks
    - Clays
    - Ground Coal
    - Flocs
    - Reinforcing Resins (reactive)
    - Silicas
        - Precipitated
        - Pyrogene
        - Mineral
    - Silicates
    - Other
- *Flame Retardants*
    - Halogen Donors
    - Metallic Oxides
    - Hydrates
    - Others
- *Fungicides*
    - Organic
    - Other
- *Masterbatches*
    - Internal (Rework)
    - External
- *Odorants*
    - Essential Oils
    - Other
- *Processing Materials*
    - Ester Plasticizers, Phthalates
    - Ester Plasticizers, Other
    - Hydrocarbon Resins and mixtures
    - Peptizers, (chemical plasticizers)
    - Petroleum Oil, Aromatic
    - Petroleum oil, Naphthenic
    - Petroleum oil, Paraffinic
    - Soaps and mixtures
    - Polyethylenes
    - Titanates
    - Other
- *Promotors and Coupling Agents for Fillers and Reinforcing Agents*
    - Amines
    - Silanes
    - Titanates
    - Other
- *Rubbers*
    - Acrylonitrile Butadiene Rubber (NBR/HNBR/XNBR)
        - NBR, ACN<22.9%
        - NBR; 23%<ACN<29.9%
        - NBR; 30<ACN<37.9
        - NBR; 38<ACN<44.9%
        - NBR; ACN>45%
        - Hydrogenated NBR (HNBR)
        - Other
    - Acrylonitrile Butadiene Rubber / Polyvinyl Chloride (NBR/PVC)
    - Acrylic Rubber

(continues)

Table 1.3—*(Continued)*

- Butyl and Halobutyl Rubber (IIR, BIIR, CIIR)
  - IIR
  - BIIR
  - CIIR
  - Other
- Chlorosulfonated Polyethylene
- Epichlorohydrin Rubber
- Ethylene/Acrylric Rubber
- Ethylene Propylene Rubber (EPR, EPM, EPDM)
  - EPM
  - EPDM; ML(1+4)125°C<45
  - EPDM; 45.1<ML(1+4)125°C<59.9
  - EPDM; ML (1+4)>60
  - Other
- Fluoroelastomer
- Natural Rubber and Synthetic Polyisoprene (NR and IR)
  - NR
  - IR
  - Other
- Polybutadiene Rubber
  - BR; High-cis; >97
  - BR; Low-cis; <96.9
  - Other
- Polychloroprene (CR)
  - M-grade
  - S-grade
  - XL-grade
  - Other
- Polynorbornene
- Polysulfide
- Silicone Rubber (VMQ)
- Styrene Butadiene Rubber (SBR)
  - SBR 1000; Hot emulsion
  - SBR 1500; Cold emulsion
  - SBR 1600; Cold emulsion, Black extended masterbatch
  - SBR 1700; Cold emulsion, Oil extended masterbatch
  - SBR 1800; Cold emulsion, Black & oil extended masterbatch
  - High Styrene SBR (HSBR)
  - Solution SBR

Retarders and Inhibitors
- Organic Acids
- Phthalic Anhydride
- Phthalamides
- Other

Tackifiers
- Hydrocarbon resins
- Phenolic Resins
- Rosins and Rosin Derivatives
- Other

Thermoplastics
- Polyethylene
- Polypropylene
- Polystyrene
- Styrene Butadiene Styrene Elastomer
- Thermoplastic Elastomer
- Other

Vulcanizing Agents and Activators
- Alkyl Phenol Disulfide
- Amine Activators
- Coagents for Peroxide Cures
- Dithiodimorpholine
- Fatty Acid Activators
  - Stearic acid
  - Other
- Glycol Activators
- Lead Compounds
- Magnesium Compounds
- Peroxides
  - Dialkyl peroxides
  - Diacyl peroxides
  - Perketal peroxides
  - Other peroxides
- Phenolic Curing Resins
- Sulfur
- Sulfur Donors
- Zinc Compounds
  - Zinc oxide
  - Other zinc salts
- Other

TABLE 1.4—A Typical Rubber Recipe.

INGREDIENT ID	PARTS PER HUNDRED RUBBER
SBR 1502 (synthetic rubber)	80.0
SIR 20 (natural rubber)	20.0
N299 carbon black	65.0
Naphthenic oil	10.0
TMQ (antioxidant)	1.0
6PPD (phenylene diamine antiozonant)	3.0
Wax blend	2.0
Zinc oxide	5.0
Stearic acid	1.0
TBBS (sulfenamide accelerator)	1.2
Sulfur (Vulcanizing Agent)	2.5
TOTAL	190.7

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2

General Test Methods

by John S. Dick[1]

2.1 INTRODUCTION TO THE RUBBER TEST LABORATORY

THE TYPICAL RUBBER TEST LABORATORY can be relatively small or large, depending on the mission. However, most have certain equipment items in common that we will discuss in this chapter.

Note: There are multiple suppliers for most of the items of laboratory equipment discussed in this chapter. Current ASTM rules state that an equipment supplier can be listed in an ASTM standard only if one supplier is available. Otherwise, for more information on available suppliers for equipment, parts, and apparatus cited in current ASTM standards, call (610) 832-9585 and ask to speak to the ASTM Staff Manager for Rubber. He may be able to help provide you with a list of suppliers for needed equipment.

2.1.1 Compounding Ingredient Storage System

Rubber laboratories in general will mix raw rubber and various compounding ingredients on a rubber laboratory mill or in an internal mixer into a rubber compound. A typical ASTM rubber recipe may contain five to seven ingredients (some commercial recipes may contain as many as 23 different ingredients). Obviously, to mix a variety of different rubber recipes will require the acquisition of a large number of different polymers, fillers, and rubber chemicals. Some of these compounding ingredients for ASTM recipes may be Industry Reference Materials (IRMs), which are listed on the ASTM web site (www.astm.org). (IRMs will be discussed extensively in Chapter 10.) Other compounding ingredients may not be available as IRMs. One must endeavor to find the best match for the compounding ingredient specified that is available in the marketplace. Sometimes references such as the *Blue Book* by *Rubber World Magazine* are very useful [1]. Once these compounding ingredi-

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ents are received, they must be properly handled, logged in, cataloged, and stored in accordance with the manufacturer's instructions. (Some peroxides, for example, may have to be stored under refrigeration.) Relevant material safety data sheets (MSDSs) must be properly organized and made available to all workers in accordance with local, state, and federal laws. All local, state, and federal safety and health regulations and laws must be followed. There are new computer laboratory information management systems (LIMS) available today to help track the inventories of these different compounding ingredients and their use in the mixing of various compound formulations.

2.1.2 Weighing Systems

All compounding ingredients must be weighed within specific tolerances. For preparation of ASTM test recipes, these tolerance limits are given in Section 5 (Weighing of Materials) in ASTM D 3182. Usually more than one weighing scale is used because of different precision and accuracy requirements for high-part loadings of ingredients versus low-part loading requirements for a specific test recipe. Many times the precision of weighing smaller loadings of ingredients can be very critical. Sometimes the ingredients used

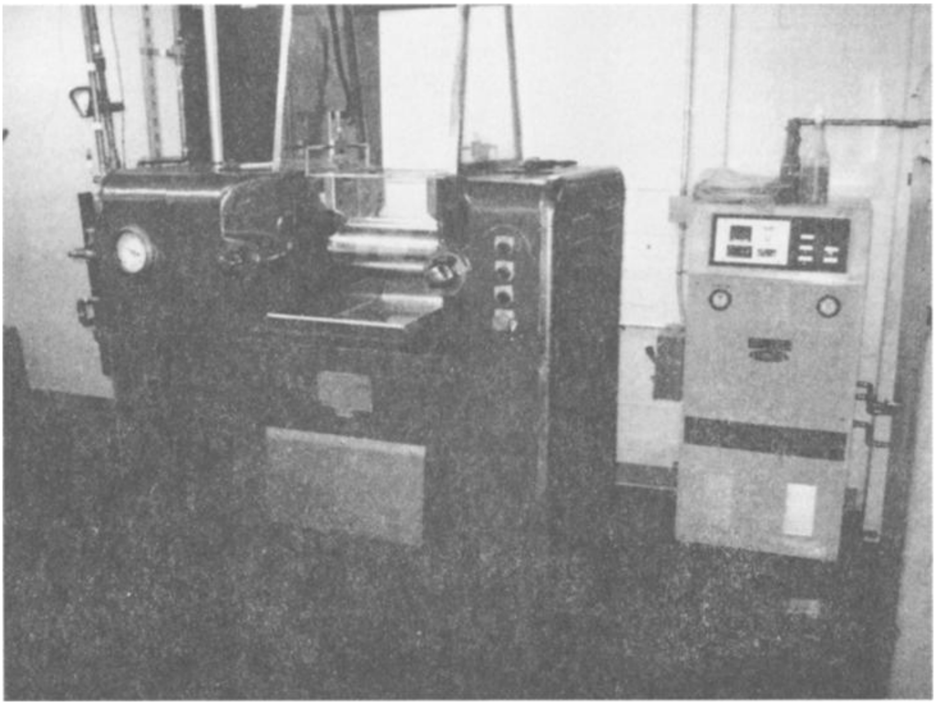


FIG. 2.1—A laboratory mill. (*Photo courtesy of Smithers Scientific, Akron, Ohio.*)

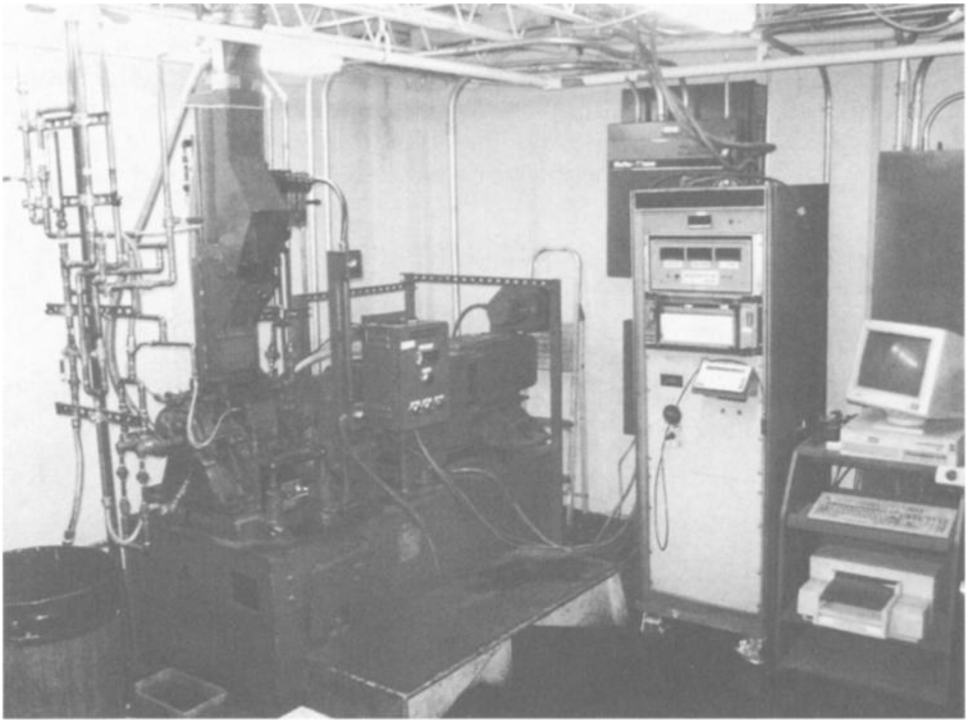


FIG. 2.2—A laboratory internal mixer. (*Photo courtesy of Smithers Scientific, Akron, Ohio.*)

at lower loadings will be poured into tared containers such as aluminum trays, for example.

2.1.3 Mixer Systems

To prepare and test standard ASTM recipes requires the use of a rubber mixer. There are three basic types of rubber mixers that can be used in a rubber laboratory: (1) two roll mills, (2) internal mixers, and (3) miniature internal mixers (MIMs). Each of these methods of mixing is discussed in ASTM D 3182. A two-roll laboratory mill is the most common method used for preparing standard ASTM test formulations. Laboratory internal mixers, such as the Banbury®, are used to speed up the mixing process and provide larger batches of mixed stock. Miniature internal mixers can be used when only small quantities of materials are available for testing. Figures 2.1 and 2.2 show a laboratory mill and a laboratory internal mixer, respectively.

Appropriate safety procedures should be followed for all rubber mixing and testing procedures.

Once the test recipe is mixed, a wide variety of common industry tests can be applied. Some of these tests include: (1) the Mooney viscometer, (2) the rotorless shear rheometer, (3) the oscillating disc curemeter, (4) the rotorless curemeter, and (5) stress-strain tensile testing. These methods are the most commonly performed tests in the rubber industry. They have general applicability to a wide variety of situations as evidenced throughout this book.

2.1.4 Curing Procedure

After a rubber compound is mixed, it may be molded in a press and cured as a suitable specimen (usually as a standard sheet) for further testing such as stress-strain tensile tests. ASTM D 3182 describes in detail how these mixed stocks can be cured into standard-sized ASTM sheets. Dumbbell specimens can be die cut directly from these cured sheets for stress-strain testing. Other standard ASTM tests can also be performed by cutting the appropriate specimens from the ASTM sheets.

2.2 GENERAL METHODS

2.2.1 Mooney Viscometer ASTM D 1646

The Mooney viscosity test is a well-established test dating back to the 1930s when Dr. Melvin Mooney of U.S. Rubber Company first developed this method, which is one of the most common procedures performed in the rubber industry today. It is used extensively to measure the viscosity of raw rubbers, as well as mixed batches of rubber compound. Also, it is commonly used to measure the time to scorch (time to the formation of incipient crosslinks in a rubber compound). The Mooney test is so widely used that most rubber compounders tend to think in terms of Mooney units when judging the quality of a raw rubber or mixed compound.

The Mooney viscometer consists of rotating a serrated rotor imbedded in a rubber specimen, contained within a sealed, pressurized cavity. Figure 2.3 shows a diagram of this sealed cavity used to test a rubber sample in accordance with ASTM D 1646.

Figure 2.4 shows a photograph of this rotor while the cavity is open.

The temperature of the cavity can be adjusted to a standard in accordance with ASTM D 1646. The rotor turns at 2 revolutions per minute (rpm), again in accordance with this ASTM standard (any faster speed may cause viscous heating to result). As can be seen from Figs. 2.3 and 2.4, the rotor is serrated in accordance with this ASTM standard in order to prevent or minimize slippage between the rotor and the rubber. Any slippage will introduce error and reduce the sensitivity of this method to real rubber property changes. From this constant speed, the rotor experiences a given resistance to

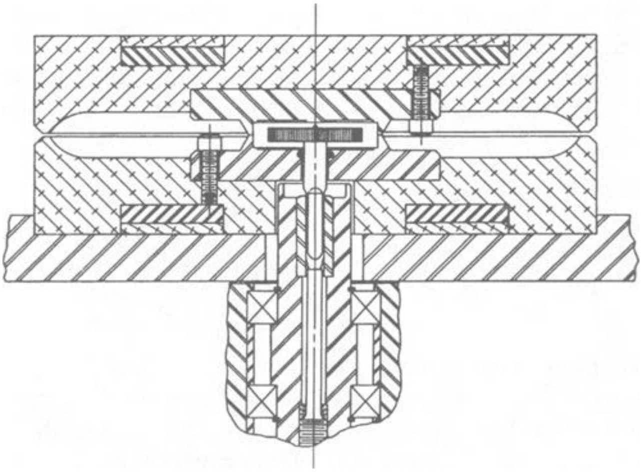


FIG. 2.3—Cross section of a typical shearing disk viscometer.

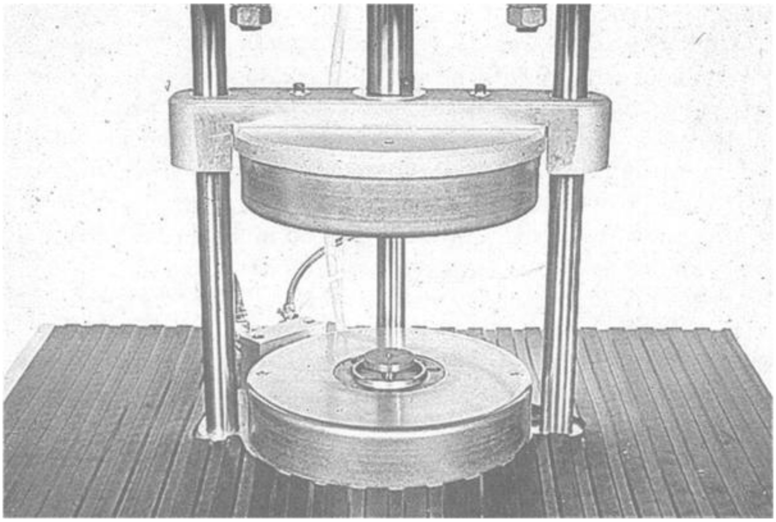


FIG. 2.4—Photograph of rotor while the cavity is open.

rotation that is recorded as torque in N-m. ASTM D 1646 describes the algorithm used to convert this torque into arbitrary Mooney Units (MU) [2].

There are three ways which the Mooney viscometer can be used as outlined in ASTM D 1646:

Part A—Measuring the Mooney viscosity.
Part B—Measuring the Mooney stress relaxation.
Part C—Measuring the pre-vulcanization characteristics.

2.2.1.1 Mooney viscosity This property is commonly used to characterize and monitor the quality of both natural and synthetic rubber. It measures the resistance to flow of the rubber at a relatively low shear rate of about 1.3 S^{-1}. When designating a Mooney test, one must specify the following conditions:

1. Massed or unmassed.
2. Test temperature.
3. Preheat time.
4. Test running time.
5. Size of rotor.

Raw polymers can be massed (milled) or unmassed before running a Mooney viscosity test. It is very important that one condition or the other is specified because massing almost always affects the results. Previous ASTM Committee D11 work has shown that testing raw polymers unmassed gives a significant improvement in test repeatability. This should improve test sensitivity to real changes in a given natural or synthetic rubber. This improvement in Mooney test repeatability by not massing versus massing is shown in Table 2.1.

As can be seen from Table 2.1, the repeatability for the massed (milled) rubber samples is significantly worse than what is noted for the unmassed samples. Sometimes the repeatability from the massed samples is almost twice as bad as from the unmassed rubber samples. However, sometimes it may still be appropriate to mass (mill) a Mooney sample if you must expel air from the sample, consolidate particles of rubber, etc. If results are from an unmassed specimen, then a "U" should be placed in front of the "ML" in order to distinguish this test result from a massed Mooney.

When performing a Mooney viscosity test, it is important that a standard test temperature be specified. Mooney viscosity decreases with a rise in test temperature. Table 2.2 gives the standard ASTM temperatures that are allowed in accordance with ASTM D 1646.

As can be seen, usually the standard test temperature for the Mooney is 100°C; however, EPM or EPDM might contain small concentrations of crystallites that should be melted before the final Mooney viscosity values are recorded. Therefore ASTM D 1646 requires that EPM/EPDM polymers must be tested at 125°C.

Preheat time and running time must also be specified. As indicated in Table 2.2, usually a ML (1 + 4) Mooney viscosity—1 min preheat without rotation of the rotor and 4 min running time with rotation—is the most common test condition used. However, the table above also shows that an ML (1 + 8) is cited for butyl rubber (IIR) and halobutyl rubber (BIIR and CIIR).

Figure 2.5 shows the thixotropic effect from standard Mooney testing. This figure shows the Mooney viscosity dropping versus time as the rotor turns. The actual Mooney viscosity to be reported is defined by ASTM D 1646

TABLE 2.1—Typical Precision for Unmassed vs. Massed Rubber Samples (ASTM D 1646).

Details on Rubbers and Compounds for Precision Testing Programs

Rubber or Material	Description	Test Temperature, °C	Other Details
	Programs 1 and 2—Rubbers for Mooney Viscosity Precision Testing		
1	IIR (Butyl), IRM 241bn	100	ML-1 + 8
2	TSR-20, Technically Specified Natural Rubber	100	ML-1 +4
3	BR 220, Butadiene Rubber	100	ML-1 +4
4	NBR-CLT, Acrylonitrile-Butadiene Rubber	100	ML-1 +4
5	SBR 1712, Oil-extended SBR	100	ML-1 +4
6	CR-S3, Chloroprene rubber	100	ML-1 +4
7	EPDM 538, EPDM Terpolymer	125	ML-1 +4
8	EPDM 6505, EPDM Terpolymer	125	ML-1 +4
9	SBR 1848, Black and Oil-extended SBR	100	ML-1 +4
10	SBR 1815, Black and Oil-extended SBR	100	ML-1 +4
	Program 3—Rubbers for Mooney Stress Relaxation Precision Testing		
Rubber or Material	Description	Test Temperature, °C	Other Details
1	IIR (Butyl), IRM 241a	100	ML-1 + 8, 2m SR
2	SMR L, Natural Rubber	100	ML-1 + 4, 2m SR
3	SBR 1500, SRM 386j	100	ML-1 + 4, 2m SR
4	EPDM 7006, EPDM Terpolymer	125	ML-1 + 4, 2m SR
5	EPDM 70A, EPDM Terpolymer	125	ML-1 + 4, 2m SR
	Program 4—Rubber Compounds for Mooney Pre-Vulcanization Characteristics Precision Testing		
Rubber or Material	Description	Test Temperature, °C	Rotor Size
1	SBR 1505, D 3185 Formulation, Mill Mixed	150	Small
2	SBR 1500, D 3185 Formulation, Mill Mixed	150	Small
3	SBR 1849, D 3186 Formulation, Mill Mixed	150	Large
4	SBR 3651, D 3186 Formulation, Mill Mixed	150	Large

(continues)

TABLE 2.1—*(Continued)*

Type 1 Mooney Viscosity Precision for Clear Rubbers

Part A—Samples Prepared Without Mill Massing[A]

		Within Laboratories[B]			Between Laboratories[B]		
Material	Mean Level	S_r	r	(r)	S_R	R	(R)
BR-220	41.0	0.244	0.691	1.69	0.785	2.222	5.42
SBR 1712	44.8	0.731	2.067	4.61	1.043	2.950	6.58
CR-S3[A]	54.3	0.664	1.880	3.46	1.045	2.958	5.45
EPDM 6505	53.0	0.358	1.012	1.91	1.449	4.100	7.73
NBR-CLT	66.6	0.618	1.748	2.62	1.362	3.854	5.78
EPDM 538[A]	71.3	0.838	2.370	3.31	1.447	4.096	5.73
TSR-20 (NR)	96.0	0.769	2.176	2.27	1.136	3.214	3.35
Pooled (Average) Values	61.0	0.637	1.802	2.95	1.448	4.098	6.72
IIR (IRM 241b), ML-1 +8@125°C	49.8	0.546	1.545	3.10	0.921	2.606	5.23
IIR (IRM 241b), ML-1 +8@100°C	72.5	0.637	1.803	2.49	1.493	4.225	5.83

Part B—Samples Prepared With Mill Massing

		Within Laboratories[B]			Between Laboratories[B]		
Material	Mean Level	S_r	r	(r)	S_R	R	(R)
BR-220	40.3	0.338	0.955	2.37	0.701	1.983	4.92
SBR 1712	47.4	1.135	3.212	6.77	1.925	5.447	11.49
CR-S3	48.8	1.377	3.897	7.97	2.257	6.387	13.06
EPDM 6505	51.4	0.611	1.729	3.37	1.647	4.662	9.07
NBR-CLT	67.0	0.768	2.174	3.26	1.853	5.244	7.87
EPDM-538	70.9	1.493	4.224	6.15	2.275	6.437	9.37
TSR-20 (NR)	91.3	1.193	3.375	3.79	1.909	5.403	6.07
Pooled (Average) Values	59.6	1.063	3.009	5.05	1.862	5.268	8.84

[A] The unmilled CR (Chloroprene) rubber test sample was formed by layering pieces of rubber above and below the rotor.
The unmilled EPDM 538 (a friable crumb rubber) test sample was formed by compacting the rubber in a press heated to 100°C for 5 minutes before cutting.

[B] S_r = repeatability standard deviation.
r = repeatability = 2.83 × (Square root of the repeatability variance)
(r) = repeatability (as percentage of material average)
S_R = reproducibility standard deviation.
R = reproducibility = 2.83 × (Square root of the reproducibility variance)
(R) = reproducibility (as percentage of material average)

TABLE 2.2—Standard Viscosity Test Conditions.

Type Rubber[A]	Sample Preparation, See Section	Test Temperature, °C[B]	Running Time, min[C]
IRM 241	7.1 and 7.3	100 ± 0.5 or 125± 0.5	8.0
Unmassed sample	7.1 and 7.3	Use conditions listed below for type rubber being tested.	
NR	7.1 and 7.2.1	100 ± 0.5	4.0
BR CR IR NBR SBR	7.1 and 7.2.2	100 ± 0.5	4.0
BIIR CIIR IIR	7.1 and 7.2.2	100 ± 0.5 or 125 ± 0.5[E]	8.0
EPDM EPM	7.1 and 7.2.2	125 ± 0.5	4.0
Synthetic rubber black masterbatch	7.1 and 7.2.3	100 ± 0.5	4.0
Compounded stock reclaimed material	7.1 and 7.3	100 ± 0.5	4.0
Miscellaneous	If similar to any group above, test accordingly. If not, establish a procedure.		

[A] See Practice D 1418.

[B] Test temperatures are 100 ± 0.5°C (212± 1°F) or 125± 0.5°C (257 ± 1°F).

[C] Time after the standard 1.0-min warm-up period at which the viscosity measurement is made.

[D] If no air bubbles are visible in the sample, 7.2.2 may be omitted.

[E] Use a temperature of 125 ± 0.5°C (257± 1°F) whenever specimen has a viscosity higher than 60-ML 1 + 8(100°C).

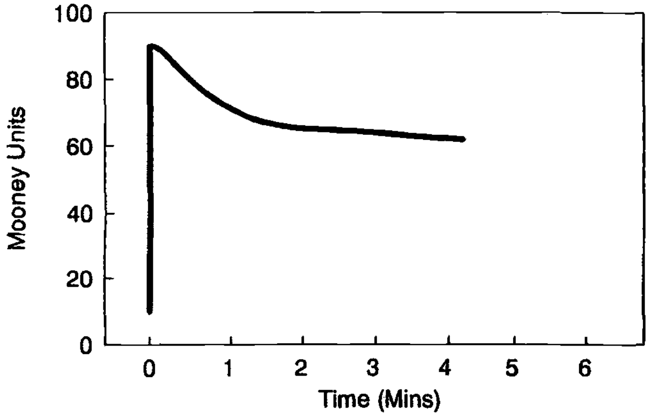


FIG. 2.5—Typical Mooney viscosity curve. (*Photo courtesy of Alpha Technologies, Akron, Ohio.*)

as follows: "Take as the viscosity the minimum value to the nearest whole Mooney Unit during the last 30-s interval preceding the specified time of reading." This has to be defined because of the *thixotropic* nature of rubber (where the measured viscosity decreases with time).

The standard also allows either a large rotor (ML) or a small rotor (MS) to be used for measuring the Mooney viscosity. It is much more common to use a large rotor for Mooney viscosity testing; however, sometimes a smaller rotor might be selected if the rubber specimen is very tough (high in viscosity). The rotor size selected has a definite effect on the Mooney values measured and must always be reported.

2.2.1.2 Mooney Stress Relaxation Test Part B of ASTM D 1646 describes the procedure for using a Mooney viscometer to measure the stress relaxation of rubber. To perform this method well, the Mooney viscometer *must* be able to stop the rotation of its rotor very quickly (within 0.1 s) after completion of the viscosity test (discussed earlier). With this procedure, Mooney torque values are automatically recorded 1 s after stopping the rotation of the disk. Of course, these values drop very rapidly at first but then slow their rate of decrease as shown in Fig. 2.6.

This shows what is called a "power law" drop. The stress relaxation of rubber can usually be described through this power law model, which is given in Eq 2.1 below.

$$M = k(t)^a \tag{2.1}$$

where:

M = Mooney units (torque) from the Mooney stress relaxation test,

k = a constant equal to torque in Mooney units 1 s after the rotor has stopped, and
a = an exponent that measures the rate of stress relaxation.

Now, with a power law decay, if we convert Eq 2.1 into a log-log expression, we convert it into a new equation shown in Eq 2.2 below.

$$\text{Log } M = a(\log t) + \log k \tag{2.2}$$

So if we place the data in Fig. 2.6 into a log-log plot, and if this rubber is complying with the power law model, the stress relaxation becomes a straight line as shown in Fig. 2.7.

Mooney viscosity relates crudely to the average molecular weight of an elastomer. However, it is quite possible to have two rubber samples with the same Mooney viscosity but processing quite differently. Sometimes this is because one polymer has more uncured elasticity than the other polymer. An example of this is shown in Fig. 2.8, where two raw EPDM polymers were tested with a Mooney viscometer. Both of these elastomers had the same final Mooney viscosity value but quite different elasticity values as indicated from the different stress relaxation slopes.

Higher elasticity can definitely affect how a rubber mixes, extrudes, calenders, and molds. The slope a in Eq 2.2 is one method of quantifying this property. The steeper the slope, the faster the rate of decay of the Mooney torque when the rotor is suddenly stopped. A steep slope indicates the rubber has less uncured elasticity and therefore less *nerve*. Less elasticity can mean better processing in that there may be faster filler incorporation during

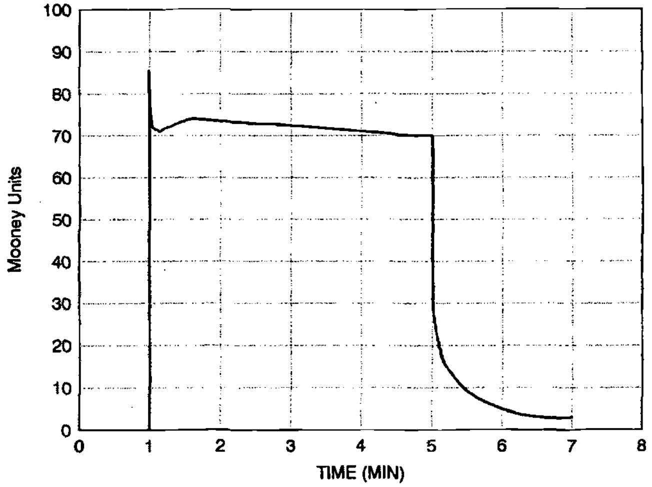


FIG. 2.6—Torque curve from a Mooney viscosity test with a stress relaxation test.

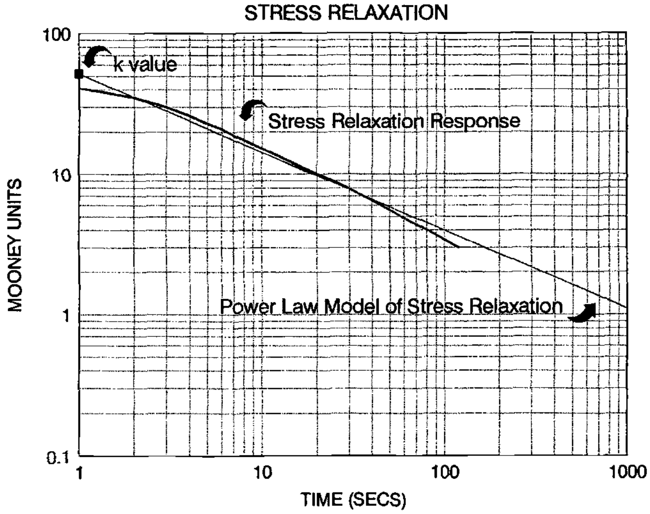


FIG. 2.7—Log-log plot of Mooney units versus time from a stress relaxation test.

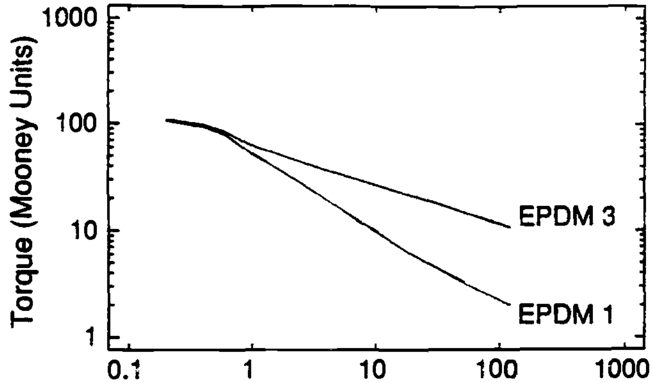


FIG. 2.8—Two raw EPDM polymers tested with a Mooney viscometer for stress relaxation. (*Photo courtesy of Alpha Technologies, Akron, Ohio.*)

mixing and sometimes less die swell during extrusion of mixed compounds with better dimensional stability. On the other hand, if the decay slope *a* is relatively flat, the rubber may require more time to break down in the mixer and the resulting compound may be more nervy, not behave as well on the mill, and perhaps have greater die swell during extrusions. Therefore Part B of ASTM D 1646 can provide additional quality information which Part A (Mooney viscosity test) cannot provide.

Table 2.3 shows the repeatability of the Mooney Stress Relaxation Test.

TABLE 2.3—Type 1 Mooney Stress Relaxation Precision.

		Within Laboratories[A]			Between Laboratories[A]		
Material	Mean Level	S_r	r	(r)	S_R	R	(R)
		Part A—Stress Relaxation Slope, (Mooney Units/minute)					
SMR L (NR)	-0.1810	0.0059	0.0168	9.28	0.0114	0.032	17.79
SBR 1500 (SRM 386j)	-0.3582	0.0042	0.0120	3.35	0.0143	0.041	11.36
IIR (IRM 241a Butyl)	-0.5081	0.0067	0.0189	3.72	0.0178	0.050	9.92
EPDM 70A	-0.5385	0.0098	0.0280	5.29	0.0370	0.105	19.52
EPDM 7006	-0.9561	0.0680	0.1940	20.29	0.2060	0.584	61.00
		Part B—Stress Relaxation Intercept, (Mooney Units)					
SMR L (NR)	69.97	0.749	2.120	3.03	2.849	8.060	11.53
SBR 1500 (SRM 386j)	31.70	1.192	3.370	10.63	1.630	4.620	14.55
IIR (IRM 241a Butyl)	56.02	0.855	2.240	4.32	1.608	4.560	8.12
EPDM 70A	29.21	0.758	2.150	7.36	1.410	3.980	13.66
EPDM 7006	18.36	1.640	4.630	25.22	3.326	9.410	51.23

[A] S_r = repeatability standard deviation.
r = repeatability = 2.83 × (Square root of the repeatability variance)
(r) = repeatability (as percentage of material average)
S_R = reproducibility standard deviation.
R = reproducibility = 2.83 × (Square root of the reproducibility variance)
(R) = reproducibility (as percentage of material average)

As noted above, polymers that experience a very rapid rate of decay usually display poor repeatability and reproducibility of Mooney stress relaxation values [3].

2.2.1.3 Measuring Pre-Vulcanization Characteristics Part C of ASTM D 1646 describes how the Mooney viscometer can be used to measure the time to scorch for a rubber compound containing curatives. The time to scorch is the time at a preselected temperature required for a given rubber compound containing curatives to form incipient crosslinks (the onset of vulcanization), after which the rubber compound cannot be processed further. According to ASTM D 1646 Part C, suggested temperatures (in accordance with ASTM D 1349) are 70, 85, 100, 125, 135, or 150°C. However, any temperature may be chosen according to ASTM D 1646 Part C for scorch measurements. The temperature chosen is somewhat dependent on the rate of cure for the subject rubber compound being tested. It is best to standardize on a temperature that will allow enough time to see the scorch event with good test repeatability and sensitivity while not causing the scorch test to be excessively long. (The higher the standard test temperature, the faster the cure reaction and the shorter the scorch safety time.)

Mooney scorch with a large rotor (ML) is a measure of the time required for the Mooney viscosity to rise 5 Mooney units (MU) above the minimum at a preset temperature as shown in Fig. 2.9.

When Mooney scorch is measured with a small rotor (MS), the time to rise 3 MU is used instead of 5 MU.

Also a *cure index* can also be measured with the Mooney viscometer in accordance with Part C as shown below.

$$\Delta t_s = t_{18} - t_3 \tag{2.3}$$

$$\Delta t_L = t_{35} - t_5 \tag{2.4}$$

Obviously, the lower the Δt_S (for small rotor) or Δt_L (for large rotor) means the faster the cure rate. The repeatability and reproducibility values for the Mooney scorch test (Part C) are shown in Table 2.4.

As can be seen from the precision statements given in Tables 2.2 (Part A, Mooney Viscosity), Table 2.3 (Part B, Mooney Stress Relaxation), and Table 2.4 (Part C, Mooney Scorch), the precision for Part A and Part C is fairly good. However, the precision for Part B may be only fair, depending on the nature of the polymer tested.

2.2.2 *Oscillating Disk Curemeter*

ASTM D 2084—This test instrument is commonly referred to as the oscillating disk rheometer or ODR. It was developed in the 1960s and gives an advantage over the Mooney viscometer because it cannot only measure scorch time and cure rate of a given rubber compound, but can also measure

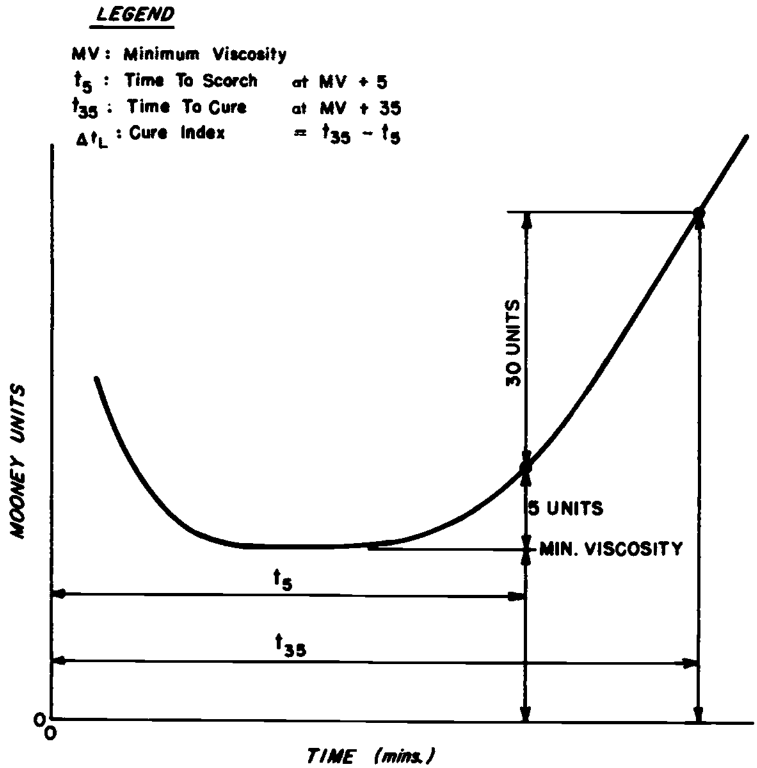


FIG. 2.9—Typical scorch curve using a large rotor.

state of cure. This is because the ODR oscillates a biconical disk as shown in Fig. 2.10.

This special disk is embedded in a rubber specimen when the dies are closed at a preset cure temperature as shown in Fig. 2.11.

This disk sinusoidally oscillates back and forth in either a ±1 or ±3 degree arc. This is quite different from the Mooney viscometer, which continuously rotates at a constant speed only in one direction and never oscillates. This means that as the uncured rubber compound reaches scorch, it becomes less fluid and more solid (as crosslinking occurs through the vulcanization process). By oscillating through a preset arc, the ODR is quite effective at relating to the density of these crosslinks and the rising hardness. On the other hand, the Mooney viscometer disk starts to slip and tear during the vulcanization process because it is rotating in a material that is becoming more of a solid. Figure 2.12 illustrates this.

TABLE 2.4—Type 1 Mooney Pre-Vulcanization Characteristics Precision.

Material	Test	Features	Mean Level	Within Laboratories[A]			Between Laboratories[A]		
				S_r	r	(r)	S_R	R	(R)
		Part A—Minimum Viscosity, (Mooney units)							
SBR 1505		small rotor	21.6	0.346	0.979	4.53	0.931	2.635	12.20
SBR 1500		small rotor	25.2	0.282	0.798	3.17	0.934	2.643	10.49
SBR 1849		large rotor	27.1	0.460	1.302	4.80	0.803	2.725	10.06
SBR 3651		large rotor	37.7	0.547	1.548	4.11	1.065	3.014	7.99
Pooled (Average)	Values		27.9	0.421	1.192	4.27	0.938	2.654	9.51
			Part B—Scorch Time, (minutes)						
SBR 1505		small rotor, t_3	8.1	0.177	0.501	6.18	0.821	2.323	28.68
SBR 1500		small rotor, t_3	8.2	0.221	0.625	7.63	0.983	2.782	33.93
SBR 3651		large rotor, t_5	8.2	0.289	0.818	9.97	0.967	2.737	33.37
SBR 1849		large rotor, t_5	9.2	0.220	0.623	6.77	0.898	2.540	27.62
Pooled (Average)	Values		8.43	0.230	0.652	7.73	0.920	2.602	30.87
		Part	C—Cure Index,		(minutes)				
SBR 1505		small rotor, t_{18}-t_3	1.98	0.088	0.249	12.58	0.145	0.410	20.72
SBR 3651		large rotor, t_{35}-t_5	2.29	0.073	0.206	8.97	0.207	0.586	25.58
SBR 1849		large rotor, t_{35}-t_5	2.56	0.190	0.538	21.02	0.364	1.030	40.24
SBR 1500		small rotor, t_{18}-t_3	2.63	0.122	0.345	13.13	0.249	0:705	26.79
Pooled (Average)	Values		2.37	0.127	0.359	15.16	0.254	0.719	30.35

[A] S_r = repeatability standard deviation.
r = repeatability = 2.83 × (Square root of the repeatability variance)
(r) = repeatability (as percentage of material average)
S_R = reproducibility standard deviation.
R = reproducibility = 2.83 × (Square root of the reproducibility variance)
(R) = reproducibility (as percentage of material average)

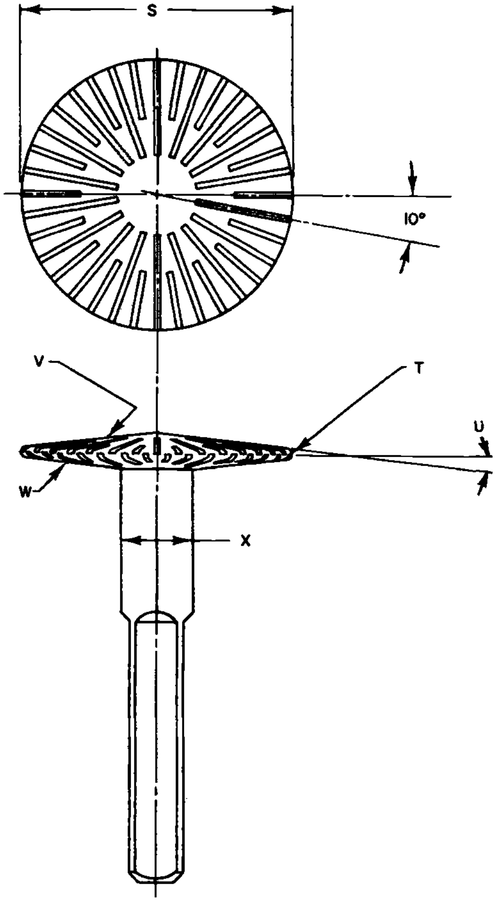


FIG. 2.10—Biconical disk.

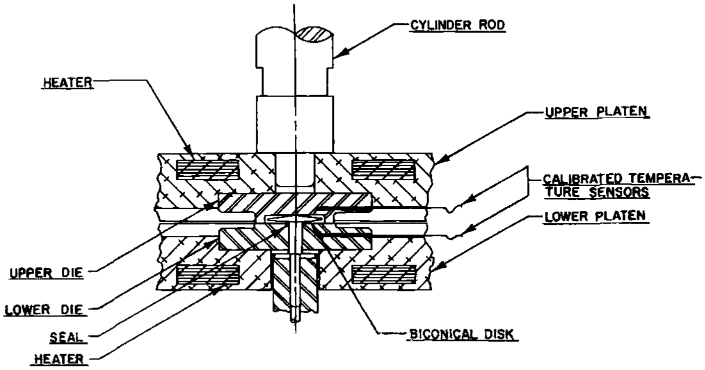


FIG. 2.11—Special disk embedded in rubber specimen.

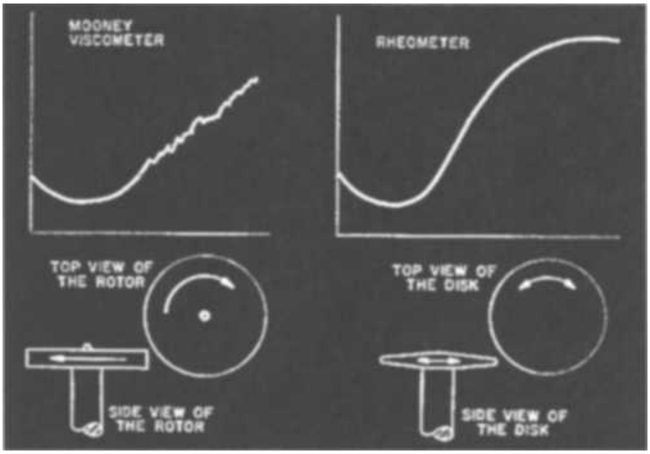


FIG. 2.12—Views of rotor and disk. (*Photo courtesy of Alpha Technologies, Akron, Ohio.*)

2.2.2.1 ODR Cure Test Parameters There are several important standard test characteristics described in ASTM D 2084 which relate to the ODR cure curve. They are described below.

- M_L *minimum torque*—Relates crudely to processability of the rubber compound.
- M_H *maximum torque*—Relates to the ultimate crosslink density that results from the vulcanization process.
- t_s1 *scorch*—Time till one torque unit rise above the minimum, which measures scorch safety time, i.e., the time to reach the onset of vulcanization or the first signs of incipient crosslinking.
- t_s2 *scorch*—Time till two torque unit rise above the minimum, which measures scorch safety time. By using two unit rise instead of one (for t_s1), you achieve a more positive indicator of true scorch; however, it is a little more delayed in time compared to t_s1.
- $t'10$ *cure time*—This is the time required for the compound to reach 10 % of the total state of cure. This parameter (or t' 5) can be used as another method of measuring scorch safety (discussed above). This parameter may be better for comparing the scorch time of rubber compounds with greatly different cured hardness values.
- $t'50$ *cure time*—This is the time required for the compound to reach 50 % of the total state of cure. This property relates to the cure rate. Some compounds can have similar scorch safety but significantly different cure rates as indicated by t' 50.
- $t'90$ *cure time*—This is the time required for the compound to reach 90 % of the total state of cure. This is another method for measuring cure rate.

Figure 2.13 shows how M_L and M_H are determined as well as Δ torque. While ASTM D 2084 does not address Δ torque (delta torque), it is commonly used in the rubber industry. Some feel that Δ torque relates more to the pure chemical crosslinking, while M_L relates to the uncured physical "crosslinking" (or chain entanglements).

Figure 2.14 shows how t_s 2 scorch is determined. This is a common method for measuring the scorch safety of a rubber compound containing curatives under isothermal conditions at a preselected temperature.

As discussed earlier, cure times ($t'x$) are determined from the time required to reach the torque value expressed in Eq 2.3 below.

$$t'x = \text{time in minutes to reach } (M_L + x\,(M_H - M_L)/100) \qquad (2.3)$$

where:

$t'x$ = time to x % state of cure,
x = percent state of cure,

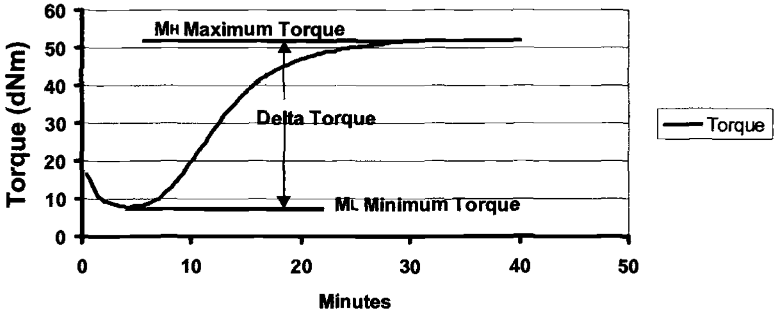


FIG. 2.13—ODR cure curve.

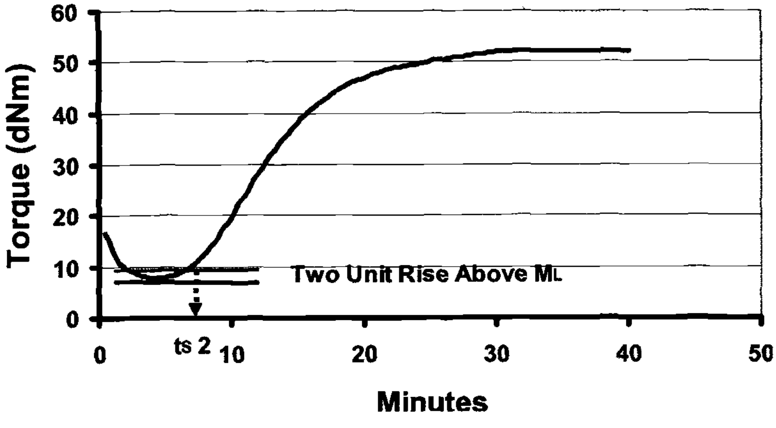


FIG. 2.14—ODR cure curve.

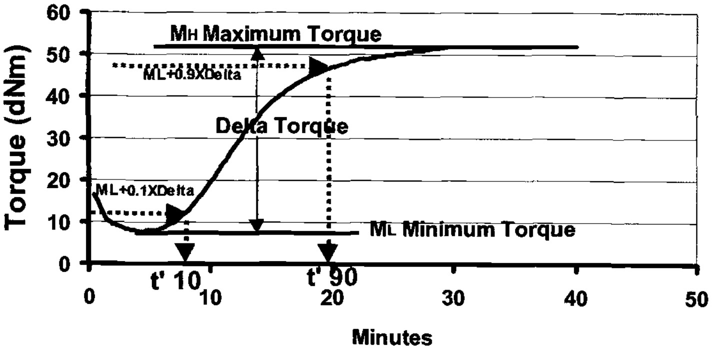


FIG. 2.15—ODR cure curve.

M_L = minimum torque, and
M_H = maximum torque.

Figure 2.15 illustrates the calculation of both *t*′ 10 and *t*′ 90 cure times. The *t*′ 10 can be used in some situations as a substitute for t_s1 or t_s2 scorch points (discussed earlier). *t*′ 90 is a common parameter which can relate to cure times under certain circumstances.

ASTM D 2084 also describes what is called the *cure rate index* (CRI), which is calculated from the scorch point and *t*′ 90 as shown in Eq 2.4 below.

$$CRI = 100/(t'\,90 - t_s1) \tag{2.4}$$

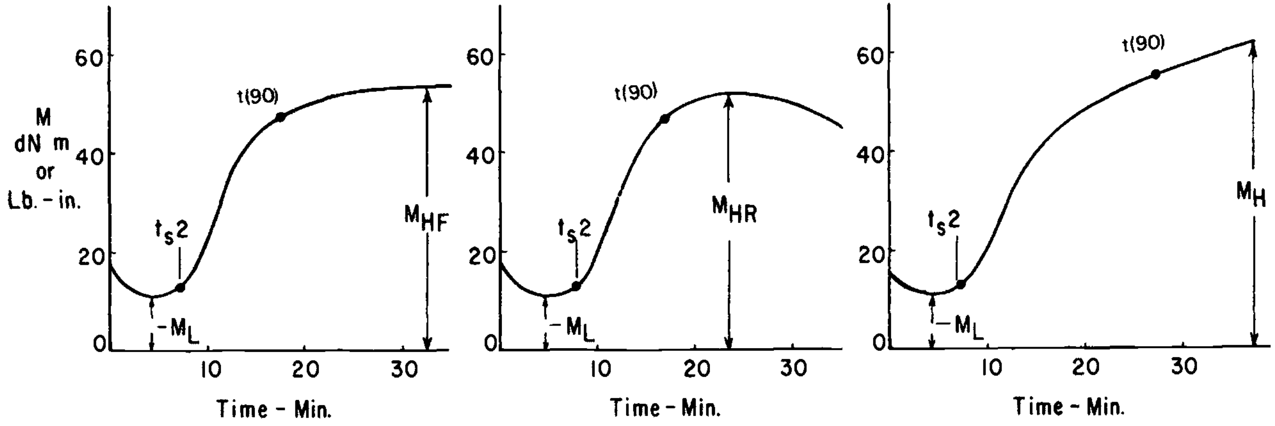
If the compound is faster curing, then the difference between *t*′ 90 and t_s1 will be less and the calculated CRI will be higher. If the compound is slower curing (has a slower average cure rate), the opposite will be true.

One last comment about the ODR test is the shape of the cure curves. Figure 2.16 shows the difference between a cure curve that plateaus, one that reverts, and one that marches.

The curve on the left represents a cure that forms a perfect plateau. Rubber compounds in this category reach the ultimate state of cure (ultimate crosslink density) without any additional chemical crosslinking reactions occurring.

The curve in the middle shows an example of reversion. Natural rubber formulations are one example of compounds that will revert if the cure temperature is high enough. Many times there is a competing reaction that is also occurring during the vulcanization reaction. Usually if the cure test is performed at a lower temperature, there will be less reversion but the test will take longer.

Lastly, to the right is a cure curve that "marches" or has "marching modulus." It continuously increases in hardness and never does fully plateau. Some EPDM compounds will give this type of cure profile. At some point in the cure test you have to decide to stop because it will never truly plateau.



Cure to Equilibrium Torque

Cure to Max. Torque with Reversion

Cure to no equilibrium in Max Torque

FIG. 2.16—Difference between a cure curve that plateaus, one that reverts, and one that marches.

2.2.3 Rotorless Curemeter

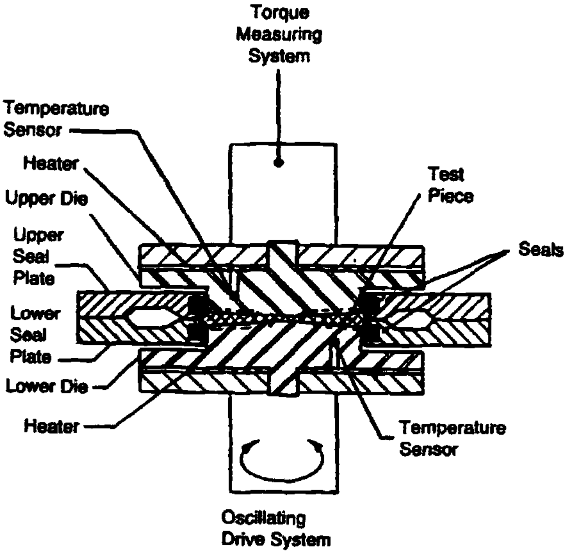
ASTM D 5289—In the 1960s, the oscillating disk curemeter was developed and introduced to the rubber industry. However, there were several problems with the use of a rotor in the original curemeter described in ASTM D 2084 (described earlier). These problems caused by the presence of this rotor are as follows [4].

- The presence of the unheated metal rotor embedded in the rubber during the test acts as a "heat sink" that takes up heat from the dies and platens and delays the "temperature recovery" of the rubber sample while performing the ODR test. Sometimes the temperature recovery time (the time required for the temperature of the sample to reach the set temperature of the instrument) can be 4 to 5 min. This means that the ODR cures are not truly isothermal in nature.
- The torque signal for the ODR must be measured through the shaft of the rotor. Because of the inherent friction associated with the movement of this rotor, the signal-to-noise ratio is not very good, which hurts test sensitivity.
- Because of this same mechanical friction, it is very difficult to measure true dynamic properties.
- After the ODR test is complete, the cured rubber sample must be "pried" off the rotor, which may be difficult at times.
- Because the rotor has a shaft, it is not practical to use film to keep the dies from fouling.
- Automating the ODR test is very difficult because of the presence of the rotor.

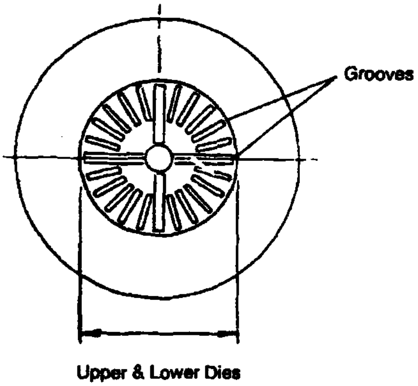
To overcome many of these problems, the rotorless curemeters were developed in the 1980s. ASTM D 5289 gives the standard methods for their utilization. There are four different die designs allowed, all giving different test results. The most commonly used die design is shown in Figure 2.17 below.

Only cure meters with this die design were used in determining the precision of the ASTM D 5289 data given below in Table 2.5 [5].

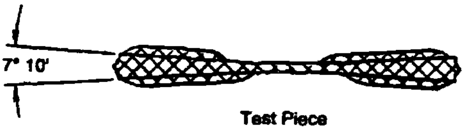
In the absence of a rotor, the temperature recovery time for rubber samples being tested (i.e., the time required before the temperature of the specimen reaches the set temperature of the dies after the dies are closed) is significantly less than the temperature recovery times seen for ODRs (ASTM D 2084). This means that the scorch times and the cure times measured with a rotorless curemeter will be shorter. For example, the typical temperature recovery for the ODR design may be about 4 to 5 min, while the temperature recovery of the rotorless curemeter is perhaps only 30 s. Moreover, all things being equal (i.e., strain, frequency, temperature), the ODR will give higher torque values for M_H and M_L than those measured with the rotorless curemeter (because of surface area differences). On the other hand, the rotorless



A) Measuring Principle



B) Reaction Dies



Test Piece

FIG. 2.17—Typical sealed, torsional-shearing rotorless curemeter die design.

TABLE 2.5—Precision of Rotorless Curemeters, D5289.

NOTE 1—*SR* = within laboratory standard deviation,

r = repeatability (in measurement units),

(r) = repeatability (in percent),

SR = between laboratory standard deviation,

R = reproducibility (in measurement units), and

(R) = reproducibility (in percent).

Test Parameter	Mean Value	Within Laboratory			Between Laboratory		
		Sr	r	*(r)*	*SR*	R	*(R)*
Compound A:							
M_L (dN m)	1.35	0.007	0.02	1.4	0.071	0.20	14.8
M_N (dN m)	13.60	0.025	0.07	0.5	0.608	1.72	12.7
t_s1 (min)	1.55	0.009	0.02	1.6	0.065	0.18	11.8
t '50 (min)	3.10	0.007	0.03	0.8	0.061	0.17	5.6
t '90 (min)	4.93	0.015	0.04	0.9	0.147	0.42	8.5
Compound B:							
M_L (dN m)	1.00	0.008	0.02	2.2	0.048	0.14	13.6
M_N (dN m)	10.17	0.024	0.07	0.7	0.478	1.35	13.3
t_s1 (min)	2.22	0.008	0.02	1.0	0.076	0.21	9.6
t '50 (min)	3.55	0.007	0.02	0.6	0.098	0.28	7.8
t '90 (min)	5.74	0.023	0.06	1.1	0.156	0.44	7.7
Compound C:							
M_L (dN m)	1.50	0.011	0.03	2.1	0.076	0.22	14.3
M_N (dN m)	12.30	0.045	0.13	1.0	0.571	1.62	13.1
t_s1 (min)	1.80	0.011	0.03	1.7	0.063	0.18	9.9
t '50 (min)	3.34	0.009	0.03	0.8	0.098	0.28	8.3
t '90 (min)	5.73	0.018	0.05	0.9	0.156	0.44	7.7

These values are Type I precision values, obtained from fully prepared test specimens (compounds mixed in one laboratory) which were circulated to all participating laboratories.

curemeters are more productive in a manufacturing environment because they can provide the same cure information as the ODR in significantly less time. Also, it has been reported that some of the rotorless curemeter designs have greater statistical test sensitivity (better signal-to-noise ratio) than the ODR design, probably due to the elimination of the mechanical friction associated with the rotor [6,7].

2.2.4 *Rotorless Shear Rheometer (RPA)*

ASTM D 6204—In the 1990s, the rotorless shear rheometer was introduced to the rubber industry. This instrument is more commonly known as the rubber process analyzer or RPA. In some ways this test instrument was an evolution from the rotorless curemeter just discussed. In fact, this rubber process analyzer uses the exact same die design that was shown in Fig. 2.17. What makes the RPA mechanically different from the rotorless curemeter is an advanced, special, robotic motor with direct drive that can be programmed to vary the frequency and strain in a sinusoidal oscillation of the lower die to achieve significantly better sensitivity to actual changes in processability characteristics for both raw rubbers and their compounds [8].

Figure 2.18 shows a specimen of raw EPDM being removed from the lower die after the completion of a test with the RPA instrument.

Figure 2.19 shows the sinusoidal movement of the lower die and the complex torque response (S^*), which is measured from the reaction torque transducer that is attached to the upper die.

The reader should note that the complex torque response does not peak at the same point in time as the applied strain. This complex torque response that is measured through the torque transducer is out of phase by the phase angle δ. The reason that the response is out of phase with the sinusoidal strain

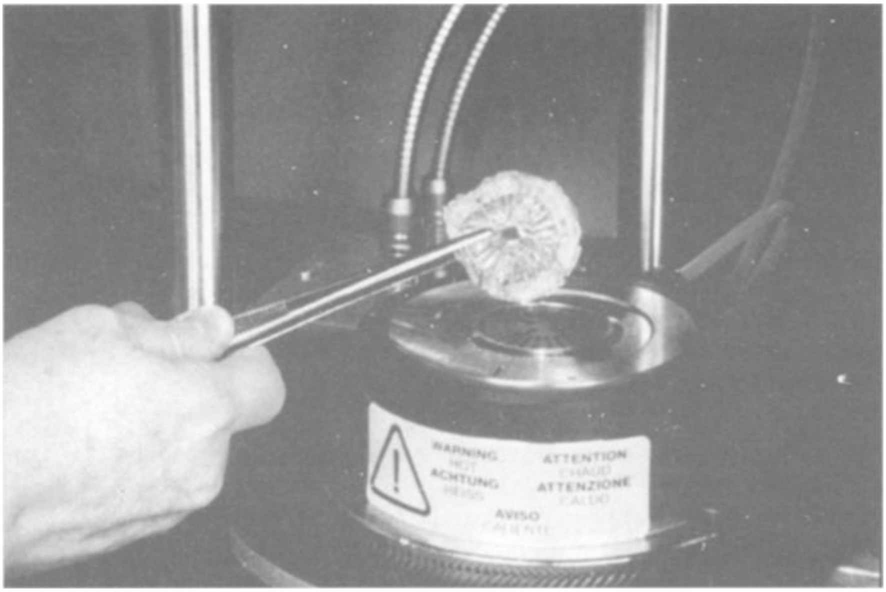


FIG. 2.18—Specimen of raw EPDM being removed from the lower die.

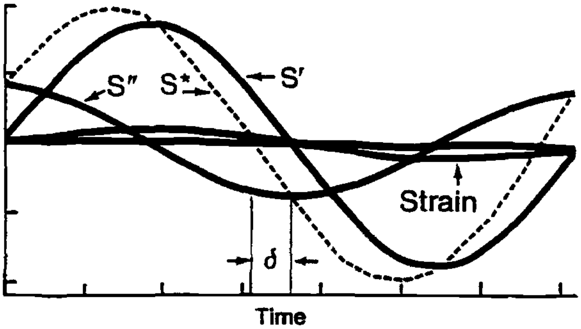
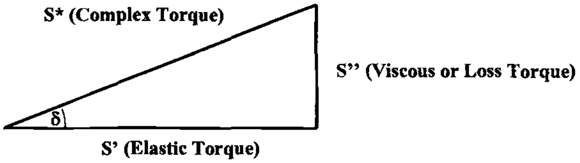


FIG. 2.19—Application of sinusoidal deformation is an effective method to separate S* torque into viscous and elastic components.



$$\text{Tan } \delta = S'' / S'$$

$$S^* = [(S')^2 + (S'')^2]^{1/2}$$

FIG. 2.20—Phase angle δ.

is due to the viscoelastic properties of rubber. Rubber, whether it is uncured or cured, is neither perfectly elastic nor perfectly viscous. In other words, rubber is both viscous and elastic. A large phase angle δ indicates high viscous quality and low elastic quality. Conversely, the smaller the phase angle δ means the rubber has higher elasticity. In the uncured state, higher elasticity can mean that a raw rubber or mixed stock could have problems in processing such as excessive die swell in extrusions, nerviness, dimensional stability problems, and molding problems.

Through a computer program, the pure elastic torque *S'* and viscous torque *S''* can be calculated. The vector analysis above illustrates how this can be done.

As can be seen from Fig. 2.20, the elastic torque *S'* and the viscous torque *S''* can be calculated from trigonometry functions. A parameter called tangent delta, tan delta, or loss tangent is simply calculated as the ratio of the viscous torque divided by the elastic torque.

2.2.4.1 Elastic Torque (S') This relates to the pure elastic quality of the rubber. This is the torque response which is precisely in-phase with the applied strain. This is the same quality which a spring displays. S' relates to the following rubber characteristics.

- Increasing chain entanglements and gel cause *S'* to rise for uncured rubber.
- The formation of crosslinks from the vulcanization process causes *S'* to rise.

This quality can relate to "nerviness" in uncured rubber processing

2.2.4.2 Viscous Torque (S'') This relates to the pure viscous quality of the rubber. This is the torque response that is responding to the rate of change of the applied strain. It is precisely 90° out-of-phase with the applied strain. This is the same quality that a dash pot displays. *S''* is commonly used to calculate real dynamic viscosity (discussed later). S'' relates to the following rubber characteristics.

- S'' relates to the pure flow characteristics of the rubber.
- S'' usually (but not always) decreases with a lower frequency or higher temperature.

However, as stated before, rubber has both elastic and viscous qualities, whether it is uncured or cured.

2.2.4.3 Tangent δ *(Delta)* This is simply the ratio of the viscous quality divided by the elastic quality. It is also referred to as tan δ or V/E ratio. Since it is a ratio, it is a dimensionless parameter. Tan δ relates to the following rubber characteristics.

- This V/E ratio for a rubber compound is always relatively high in the uncured state and low in the cured state.
- This ratio relates to the processability of rubber in the uncured state.
- This ratio relates to heat buildup (hysteresis) and inversely relates to rebound (resiliency) for rubber in the cured state.

2.2.4.4 Storage (Elastic) Modulus (G′) This is the elastic peak amplitude shear stress divided by peak amplitude shear strain for the torque component in-phase with the sinusoidally applied strain (see Eq 2.5).

$$G' = [(S'/\text{Area})/\text{Peak Strain}] \tag{2.5}$$

2.2.4.5 Loss (Viscous) Modulus (G″) This is the viscous peak amplitude shear stress divided by peak amplitude shear strain for the torque component 90° out-of-phase with a sinusoidally applied strain (see Eq 2.6).

$$G'' = [(S''/\text{Area})/\text{Peak Strain}] \tag{2.6}$$

If G' and G'' do not decrease with an increase in applied strain, this testing is said to be in the linear viscoelastic region for the subject material. However, if the G' and G'' start to drop with an increase in applied strain, the testing is in the nonlinear viscoelastic region.

2.2.4.6 Dynamic Viscosity η′ η″ η* These values can all be calculated from dynamic moduli G' and G'' as shown below.

$$\text{Real Dynamic Viscosity } \eta' = G''/\omega \tag{2.7}$$

$$\text{"Imaginary" Dynamic Viscosity } \eta'' = G'/\omega \tag{2.8}$$

$$\text{Complex Dynamic Viscosity } \eta^* = [(\eta')^2 + (\eta'')^2]^{1/2} \tag{2.9}$$

where

ω = frequency of sinusoidal oscillation in radians/second.

Increasing the frequency is equivalent to increasing the applied shear rate to a rubber specimen. Rubber compounds are basically non-Newtonian materials, meaning that their viscosity decreases with a rise in applied shear rate. This is commonly referred to as "shear thinning" behavior. Different rubber compounds may experience a decrease in viscosity at different rates. Therefore it is possible for rubber Compound A to have a lower viscosity than Compound B at low shear rates; however, Compound A could actually have a higher viscosity than Compound B at higher shear rates. This is very important because different factory rubber processes have greatly different shear rates. The Mooney viscometer only measures viscosity at low shear rates of 1.3 s^{-1}, while many rubber processes are much higher. The RPA can measure viscosity at very low and relatively high shear rates. Figure 2.21 shows how two rubber compounds can actually cross over in their ordinal comparison for viscosity [9].

Here rubber Compound A has a higher viscosity than Compound C at the low shear rate; but Compound A has a lower viscosity than Compound C at the higher shear rate. In other words, these two compounds "shear thin" differently. This could be especially important in an injection molding or extrusion process. The Mooney viscometer can only compare compounds at the low shear rates, not the higher shear rates, which many times are more relevant to processing.

ASTM D 6204 calls for a three-point frequency sweep to be performed on either a raw rubber or a mixed rubber compound. The exact conditions for this RPA test are given in Table 2.6.

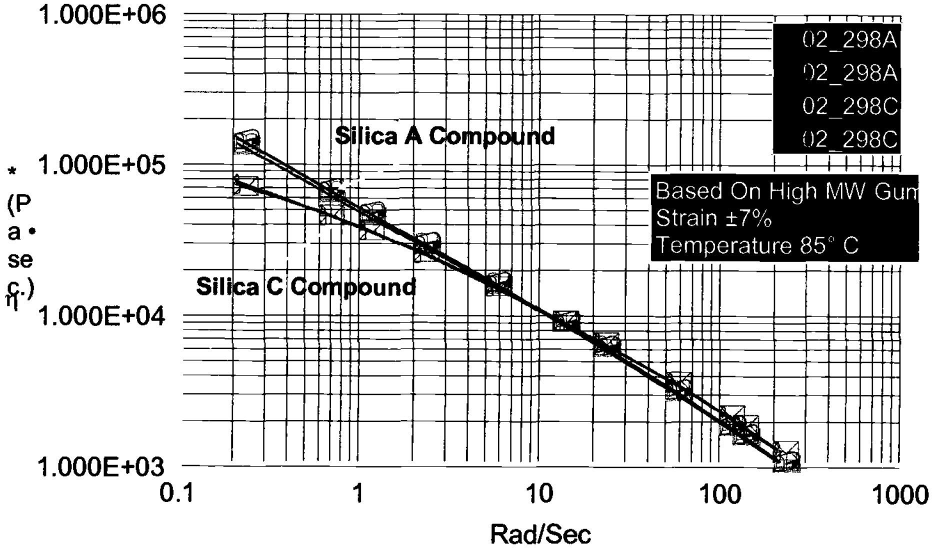


FIG. 2.21—Shear thinning from RPA frequency sweep. (*Photo courtesy of Alpha Technologies, Akron, Ohio.*)

TABLE 2.6—Standard Test Conditions for Oscillating Shear Rheometer with Closed Die Cavity.

Type Rubber	Condition Temp. (°C)	Condition Strain ± %	Condition Freq. (Hz)	Condition Time (Minutes)	Freq. Sweep Temp. (°C)	Freq. Sweep Strain (± %)	First Freq. of Sweep (Hz)	Second Freq. of Sweep (Hz)	Third Freq. of Sweep (Hz)
IRM 241	100 ± 0.3 or 125 ± 0.3	2.8	0.5	5.0	100 ± 0.3 or 125 ± 0.3	7	0.1	2.0	20
Unmassed Sample									
NR	100 ± 0.3	2.8	0.5	8.0	100 ± 0.3	7	0.1	2.0	20
BR	100 ± 0.3	2.8	0.5	5.0	100 ± 0.3	7	0.1	2.0	20
CR	100 ± 0.3	2.8	0.5	5.0	100 ± 0.3	7	0.1	2.0	20
IR	100 ± 0.3	2.8	0.5	5.0	100 ± 0.3	7	0.1	2.0	20
NBR	100 ± 0.3	2.8	0.5	5.0	100 ± 0.3	7	0.1	2.0	20
SBR	100 ± 0.3	2.8	0.5	4.0	100 ± 0.3	7	0.1	2.0	20
BIIR	100 ± 0.3 or 125 ± 0.3	2.8	0.5	5.0	100 ± 0.3 or 125 ± 0.3	7	0.1	2.0	20
CIIR	100 ± 0.3 or 125 ± 0.3	2.8	0.5	5.0	100 ± 0.3 or 125 ± 0.3	7	0.1	2.0	20
IIR	100 ± 0.3 or 125 ± 0.3	2.8	0.5	5.0	100 ± 0.3 or 125 ± 0.3	7	0.1	2.0	20
EPDM	125 ± 0.3	2.8	0.5	5.0	125 ± 0.3	7	0.1	2.0	20
EPM	125 ± 0.3	2.8	0.5	5.0	125 ± 0.3	7	0.1	2.0	20
Synthetic rubber black masterbatch	100 ± 0.3	2.8	0.5	4.0	100 ± 0.3	7	0.1	2.0	20
Compounded Stock reclaimed material	100 ± 0.3	2.8	0.5	2.0	100 ± 0.3	7	0.1	2.0	20
Miscellaneous									

The RPA is programmed with the appropriate test configuration for specific raw elastomers and rubber compounds as described. As Table 2.6 indicates, the time of the conditioning step varies depending on the specific rubber. For example, raw natural rubber requires a longer conditioning time than some of the other synthetic rubbers because it typically has more elasticity (nerviness). Also, temperature conditions vary depending on the elastomer being tested. RPA and Mooney testing of EPDM is specified at 125°C. However, the most frequently specified temperature is 100°C.

The RPA is a more advanced test than the Mooney viscometer [10]. There are many examples where two sources or lots of the same natural or synthetic rubber will have the same Mooney viscosity value but process very differently. This difference could be in the way or speed in which the polymer takes up filler during mixing. It could also be in the resulting quality of mix and how these batches extrude, calender, or mold. Figure 2.22 shows this situation where two different sources of SBR 1006 have almost exactly the same Mooney but significantly different viscoelastic profiles from the RPA data shown below.

Also the RPA is commonly used to determine the state of mix from an internal mixer as shown in Fig. 2.23.

Frequently the elastic response (either S' or G'), or the tan δ, is used to monitor the quality of mix being dumped from an internal mixer. Generally, the more work history a given rubber compound has seen means the resulting uncured elasticity (G') will be lower and usually the resulting uncured tan δ will be higher. Generally if a rubber compound has seen more work his-

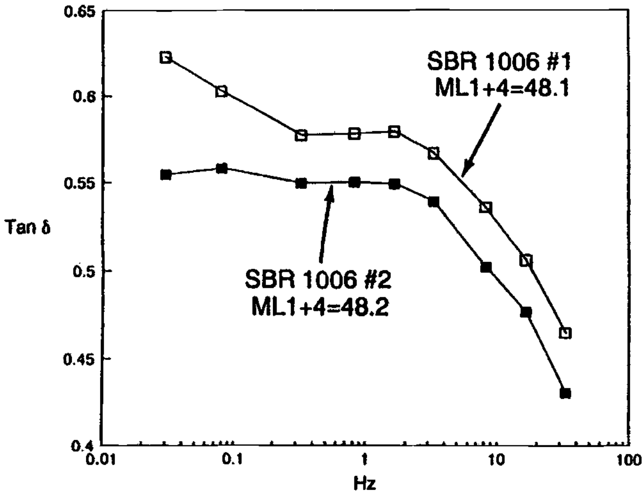


FIG. 2.22—Two sources of SBR 1006 with different viscoelastic profiles. (*Photo courtesy of Alpha Technologies, Akron, Ohio.*)

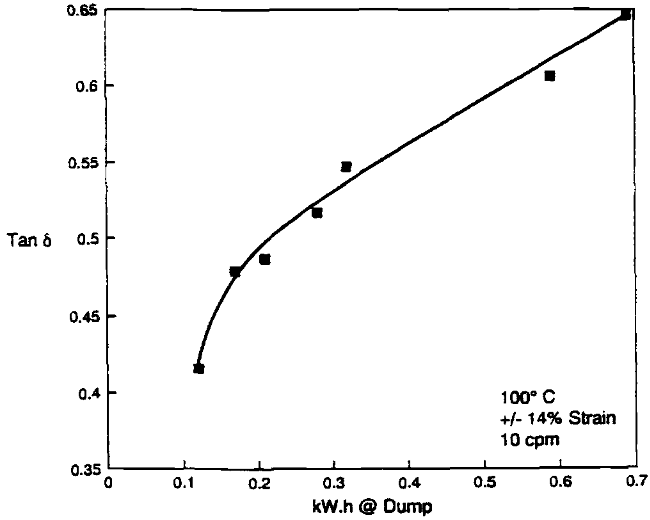


FIG. 2.23—RPA determined state of mix. (*Photo courtesy of Alpha Technologies, Akron, Ohio.*)

tory, the resulting filler dispersion will probably be higher with a better mixing quality [11].

The greater sensitivity of this type of testing has led to its greater use as a better processability test for quality assurance of raw elastomers as well as mixed batches.

In 2002 a new *Part B* to ASTM D 6204 was accepted to include a second two-point frequency sweep (0.1 and 1 Hz) at 100 % applied strain. It is believed that this higher strain condition will give even better sensitivity to subtle quality differences among mixed rubber stocks and still allow the use of protective film.

2.2.5 Tensile Properties

ASTM D 412—Before RPA testing in the 1990s, before ODR testing in the 1960s, and before Mooney viscosity testing in the 1930s, there was tensile testing of rubber. Tensile testing can be used to relate to the ultimate state of cure as well as crudely relating to the cure rate (by measuring tensile properties of some undercured sheets). This method simply consists of cutting out dumbbells from standard cured ASTM sheets, using a cutting die, and pulling them apart with a tensile tester at a standard rate of 500 mm/min to a distance of at least 750 mm using special mechanical grips at each end of the dumbbell. Figure 2.24 shows the dimensions of the die used to cut the dumbbells from standard cured sheets.

Tensile properties have traditionally been the most commonly cited physical properties for a cured rubber compound. From the separation of a

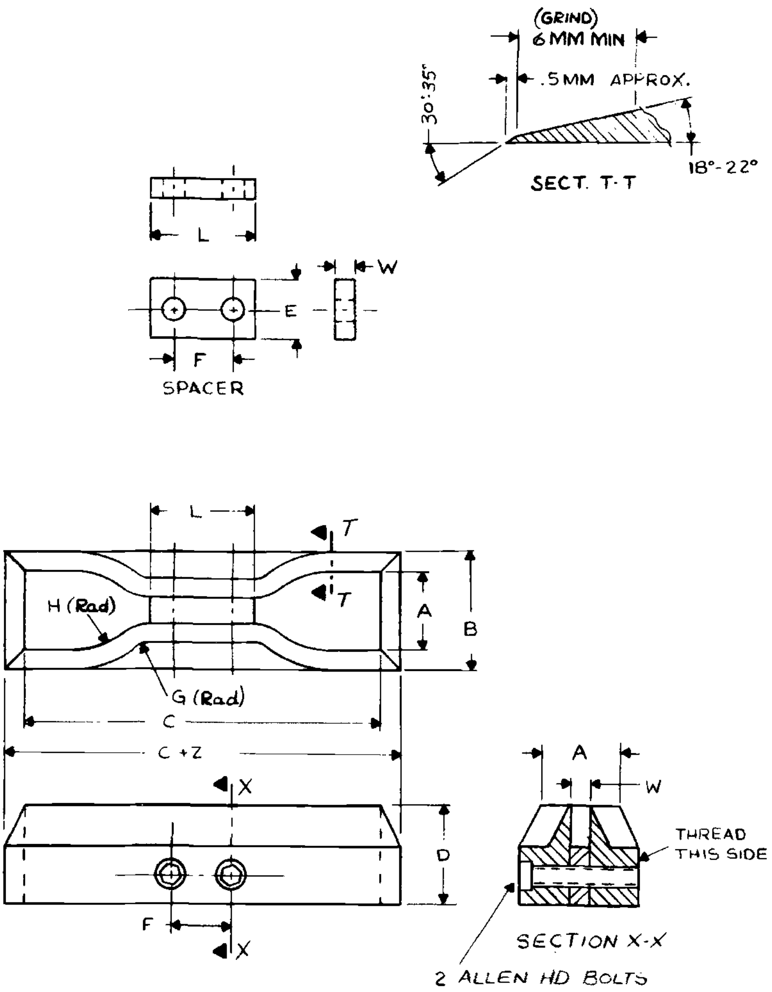


FIG. 2.24—Standard dies for cutting dumbbell specimens.

cured dumbbell rubber specimen, tensile properties such as ultimate tensile strength, ultimate elongation, and stress at 100 and 300 % elongation are measured.

Ultimate tensile strength and ultimate elongation result from pulling the dumbbell specimen to rupture (failure). This is a destructive test, which relates to the intrinsic strength of the rubber compound. This strength is usually related to such properties as the quality of the base rubber that was selected, the type of filler/oil system used in the compound, and the ultimate crosslink density and type of crosslinks resulting from the selected cure system. As a rubber compound development tool, this test is very useful. However, it sometimes has limited use in routine quality testing because of limited relevancy to the end product's application (many rubber products never see a deformation greater than 75 %), its less than perfect repeatability, and the excessive time required to perform this test. The other tests already discussed in this chapter are faster and sometimes more sensitive to rubber compound quality variations. However, variation in tensile properties can indicate quality problems such as mis-compounding, etc. Variations in ultimate tensile strength can be an early indicator of problems with carbon black dispersion during mixing. To help overcome problems with the test length, method B of ASTM D 412 was added for tensile testing with cut ring specimens.

The reader is cautioned that many variables can affect tensile repeatability including the manner in which the specimen was prepared, any "nicks" in the cutting dies, variation in the rate of separation of the specimen, temperature, humidity, etc. [12].

2.2.6 *After-Cure Dynamic Properties for Quality Assurance and Development*

ASTM D 6601—This new method uses a rotorless shear rheometer, which is commonly referred to as a rubber process analyzer (RPA) as discussed in ASTM D 6204, to measure after cure dynamic properties of a final rubber batch containing curatives. This method calls for the RPA to cure the rubber specimen at either a static condition or at a low strain of 2.8 % in order to minimize these oscillating strain effects on the after-cure dynamic properties. This standard calls for a cure temperature of 140, 160, or 180°C. The 140°C is performed on compounds that are sensitive to reversion (such as compounds based on natural rubber). The 160°C is the more common temperature for curing compounds based on general purpose elastomers other than natural rubber, while 180°C is chosen when a shorter test period is required. The reader should realize that the selection of a cure temperature in many cases determines the type of crosslinks which may be produced. This could affect the values of the dynamic properties.

After curing a compound under one of the conditions described above, forced air cooling is used to drop the temperature of the specimen down to either 100 or 60°C. The 100°C condition is commonly used in non-tire applications. This temperature can be reached in less time, and there may be less chance of mechanical slippage when making the dynamic property measurements. On the other hand, the 60°C test temperature is more commonly used in tire applications because it is closer to the actual operating temperature of a passenger tire. Dynamic property measurements made at this temperature relate better to tire performance characteristics such as rolling resistance.

Once the instrument has reduced the temperature of the rubber test piece to either 100° or 60°C, a strain sweep at either 1 or 10 Hz is performed.

According to this standard, a sweep of 1, 2, 5, 10, and 20 % strain can be applied. Because of the "break in effect" from the first strain sweep, often two back-to-back strain sweeps are automatically performed to quantify what is referred to as *strain-induced softening* effects. Compounds that contain high loading of fully reinforcing carbon blacks can possess high strain-induced softening effects [13].

The cured dynamic properties report in ASTM D 6601 using the RPA are mathematically the same as those properties discussed earlier for ASTM D 6204. However, in the cured state, rubber has a much higher elastic G' (storage modulus) in comparison to the G'' (loss modulus). This means that the calculated tan δ is much lower for rubber in the cured state versus the uncured tan δ. Moreover, the cured tan δ can relate to just how energy absorbing (hysteretic) a given vulcanizate is at a specified applied strain. A very low tan δ indicates that the cured rubber should display good rebound (resiliency), while a relatively high cured tan δ shows that the vulcanizate absorbs and dissipates much of the applied energy as "heat buildup." Compounds with a higher cured tan δ at a relevant applied strain display a greater damping effect.

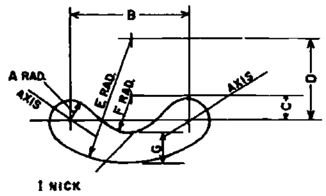
ASTM D 6601, using the RPA, is the only method to date that can quickly provide cured dynamic properties because it calls for the specimen to be cured in-place, followed by a drop in temperature for rapid dynamic property measurements. This method is practical for quality assurance as well as R&D [14].

2.2.7 Other Cured Physical Property Measurements

There are some important physical properties of cured rubber compounds that are commonly reported. Examples of these common vulcanizate properties are as follows:

- Tear resistance
- Air aging
- Heat buildup
- Flex fatigue
- Fluid immersion properties
- Compression set
- Durometer hardness
- Abrasion resistance
- Low temperature properties
- Ozone resistance

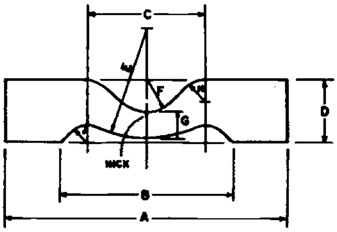
2.2.7.1 Tear Resistance ASTM D 624 is very important in many rubber applications. Usually tear properties are reported as the force required to pull a rubber test piece apart using a tensile testing instrument under con-



DIE A

Dimension	Millimetres		Inches	
	Value	Tolerance	Value	Tolerance
A	7.6	±0.05	0.3	±0.002
B	42	±0.50	1.65	±0.02
C	8.6	±0.05	0.34	±0.002
D	29	±0.05	1.14	±0.002
E	43.2	±0.05	1.7	±0.002
F	12.7	±0.05	0.5	±0.002
G	10.2	±0.05	0.4	±0.002
Nick^A	0.50	±0.05	0.02	±0.002

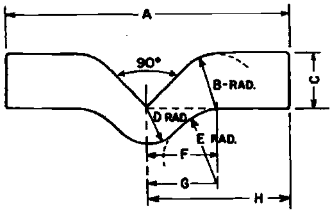
^A Nick to be cut in specimen with a razor.



DIE B (ISO/ 34 CONFIGURATION)

Dimension	Millimetres		Inches	
	Value	Tolerance	Value	Tolerance
A	110	±0.50	4.3	±0.02
B	68	±0.50	2.7	±0.02
C	45	±0.05	1.8	±0.002
D	25	±0.05	1	±0.002
E	43	±0.05	1.7	±0.002
F	12.5	±0.05	0.5	±0.002
G	10.2	±0.05	0.4	±0.002
H	9	±0.05	0.375	±0.002
J	7.5	±0.05	0.3	±0.002
Nick^A	0.5	±0.05	0.02	±0.002

^A Nick to be cut in specimen with a razor.



DIE C

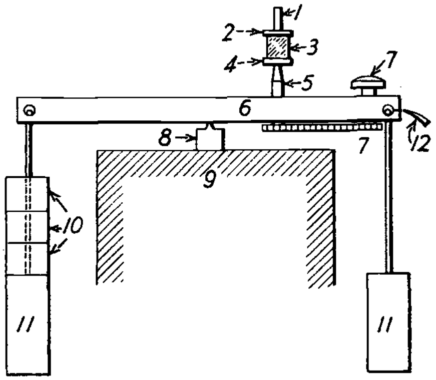
Dimension	Millimetres		Inches	
	Value	Tolerance	Value	Tolerance
A	102	±0.50	4.0	±0.02
B	19	±0.05	0.75	±0.002
C	19	±0.05	0.75	±0.002
D	12.7	±0.05	0.5	±0.002
E	25	±0.05	1.0	±0.002
F	27	±0.05	1.061	±0.002
G	28	±0.05	1.118	±0.002
H	51	±0.25	2.0	±0.01

FIG. 2.25—Types A, B, and C tear test specimen cutting dies.

trolled conditions given in ASTM D 624. Sometimes a special cut is applied to the specimen. Examples of the tear specimen (die A, B, and C) are given in Fig. 2.25.

2.2.7.2 Air Oven Aging ASTM D 573 is an important test that relates to the longevity of a rubber compound. It is not normally used for quality assurance, but rather as a screening test for compound development. Multiple dumbbell specimens are exposed to air oven aging and the change in tensile properties at different time intervals is recorded. Also, ASTM D 865, aging in a test tube enclosure, is sometimes used when the cross migration of compounding ingredients (such as phenylene diamine AOs, discussed in Chapter 8) is to be avoided. Test tube aging sometimes is not as severe as regular hot air aging.

2.2.7.3 Goodrich Flexometer Heat Buildup ASTM D 623 is an empirical method for comparing cured rubber compounds in terms of their hysteretic behavior. As discussed in Section 2.2.6 for measuring dynamic properties, a cured rubber specimen is not totally elastic. Vulcanizates, no matter how tightly cured, still possess a small amount of viscous quality (which is measured as the cured *G*″ loss modulus by ASTM D 6601) that generates a given amount of heat from an applied deformation. The Goodrich flexometer is an instrument introduced over 50 years ago to quantify this heat buildup. This instrument applies a cyclical deformation to a standard cylindrically shaped rubber specimen under standard conditions of frequency and temperature. A thermocouple mounted at the base of the rubber cylinder records the temperature rise. One problem with this method is that the heat buildup is affected not only by the hysteresis of the compound, but also by the thermal conductivity of the compound. By measuring hysteresis with the tan δ parameter from modern dynamic mechanical testers (such as the RPA in ASTM D 6601), there is little effect from changes in the thermal conductivity of a rubber compound. Figure 2.26 shows the Goodrich Flexometer as described in ASTM D 623.



1—Connection to eccentric which drives top anvil.
2—Top anvil.
3—Test specimen.
4—Lower anvil.
5—Support for lower anvil.
6—Lever through which load is applied.
7—Calibrated micrometer device.
8—Knife-edge.
9—Supporting base.
10—Test load.
11—Inertia mass of 24 kg (53 lb).
12—Pointer and reference mark for leveling of lever.

FIG. 2.26—Goodrich flexometer.

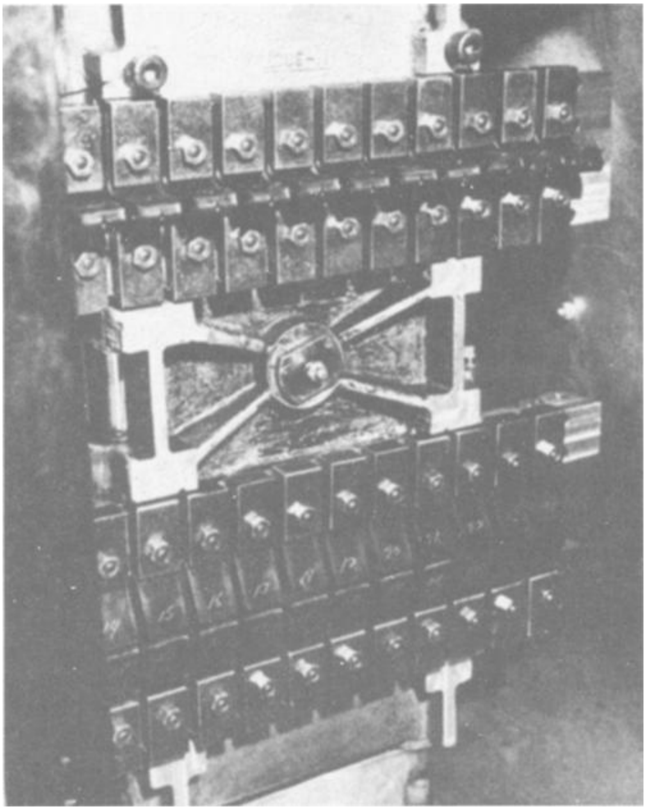


FIG. 2.27—De Mattia tester with time switch for starting or stopping, arranged with specimens for flex-cracking test.

2.2.7.4 Flex Cracking Resistance ASTM D 430 measures the propensity for a cured rubber compound to form cracks from repeatedly being flexed under standard conditions. Flex cracking resistance cannot be predicted very well from dynamic property measurements. ASTM D 430 is just one of several methods of measuring this property. There are several other methods which can also be used. These different flex cracking tests all give different results. Figure 2.27 shows the De Mattia Flex fatigue tester. ASTM D 4482, Fatigue to Failure, is another commonly used test.

2.2.7.5 Liquid Immersion Properties ASTM D 471—Liquid immersion properties are very important when developing a new rubber compound that may have contact with various liquids while in service. For example, rubber products, such as seals, may be exposed to an oil environment if used in an automotive engine. The ability of a cured rubber specimen to withstand certain liquids without swelling or deteriorating is highly relevant to the rubber product's service life.

ASTM D 471 calls for a cured rubber specimen to be immersed in a specified liquid at a specified temperature for a specified time. The deterioration of the specimen may be measured by changes in physical properties such as hardness, stress-strain tensile properties, and changes in weight, volume, and/or dimension. There are several standard immersion liquids. Some examples of these are industry reference materials such as IRM 902 or IRM 903 oils. Figure 2.28 below shows an example of an apparatus which is used to immerse rubber samples.

2.2.7.6 Compression Set ASTM D 395—A cured rubber piece is measured for its tendency to take a set from either a constant force (Method A) or constant strain (Method B) under preselected standard conditions of temperature, time, percent deflection (for Method B) and recovery time. Normally Method B is the most commonly used procedure, while only very hard vulcanizates may be tested by Method A. Compression set is used by seal manufacturers to ascertain how well a rubber compound resists taking a set. Figure 2.29 shows the apparatus used to condition rubber specimens for compression set measurements by applying a constant strain.

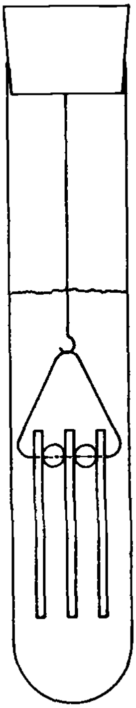


FIG. 2.28—Method of separation in immersion (D 471).

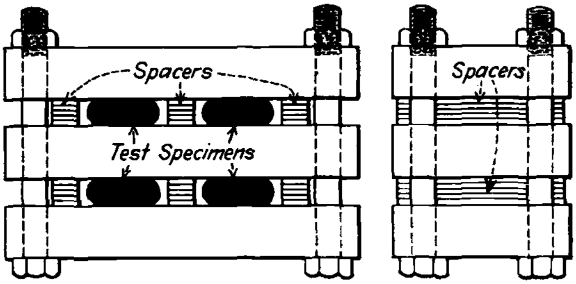


FIG. 2.29—Device for compression set test under constant deflection, Test Method B.

2.2.7.7 Rubber Hardness ASTM D 2240—A so-called durometer measures the hardness of a cured rubber specimen quickly from the penetration of a special indentor. This durometer may be mounted or hand held. This is a quick, but perhaps crude way to determine if a rubber specimen has achieved a given crosslink density from the curing process. This method is quick but precision is not as good as some other methods we have discussed. The repeatability of the durometer is usually poorer than the maximum torque measurements from a rotorless curemeter (ASTM D 5289). However a durometer hardness measurement is more rapid.

A mounted durometer is shown in Fig. 2.30.

2.2.7.8 Abrasion Resistance ASTM D 2228—While this property is important, it is very difficult to predict a rubber product's wear resistance while in service from results of a standardized abrasion test. This is because service conditions for rubber products such as tire treads, shoe soles, belts, etc. see a very wide variety of service conditions that can affect a cured product quite differently from those conditions imparted to it by a standardized abrasion tester. However, it is still useful as a standard for screening new rubber compounds.

The Pico Abrader measures the abrasion resistance of a cured rubber test piece to a pair of rotating tungsten carbide knives under standard conditions noted in ASTM D 2228. Mass loss from a standard rubber test piece is compared to the abrasion resistance of the subject compound. Figure 2.31 shows the Pico Abrasion Test apparatus.

2.2.7.9 Low Temperature Properties ASTM D 1053—These properties are important considerations in selecting compounds for use in commerce. ASTM D 1053 is the Gehman test. Here, a special apparatus, shown in Fig. 2.32, is used to measure the relative low-temperature stiffening of a rubber specimen after an exposure time at specified sub-ambient temperatures.

Also, Fig. 2.33 shows a typical plot of twist versus temperature for a Hevea gum stock. The lower the angle of rubber specimen twist means the higher the modulus of the compound at the measured temperature. With a lowering of the temperature, the rubber becomes stiffer and higher in modulus.

How well a rubber compound performs under specific sub-ambient conditions is extremely important in automotive, aerospace, military, and other applications.

Another test which is commonly used to measure low temperature properties of rubber is ASTM D 2137 for Brittleness point.

2.2.7.10 Ozone Resistance ASTM D 1171 Ozone resistance is very important to perform when developing new rubber compounds. This method calls for the preparation of triangular cross-sectional cured-rubber specimens

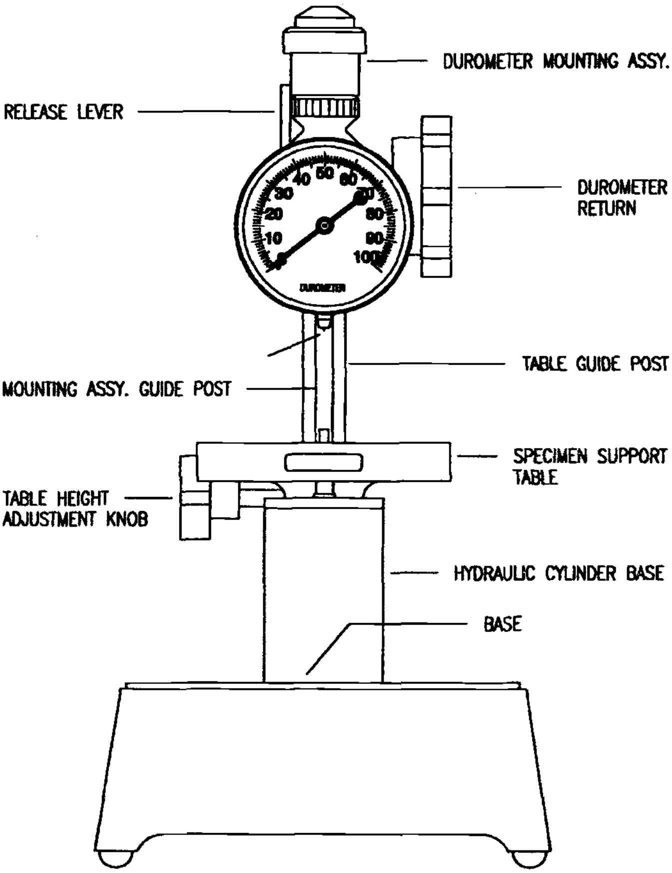


FIG. 2.30—A mounted durometer.

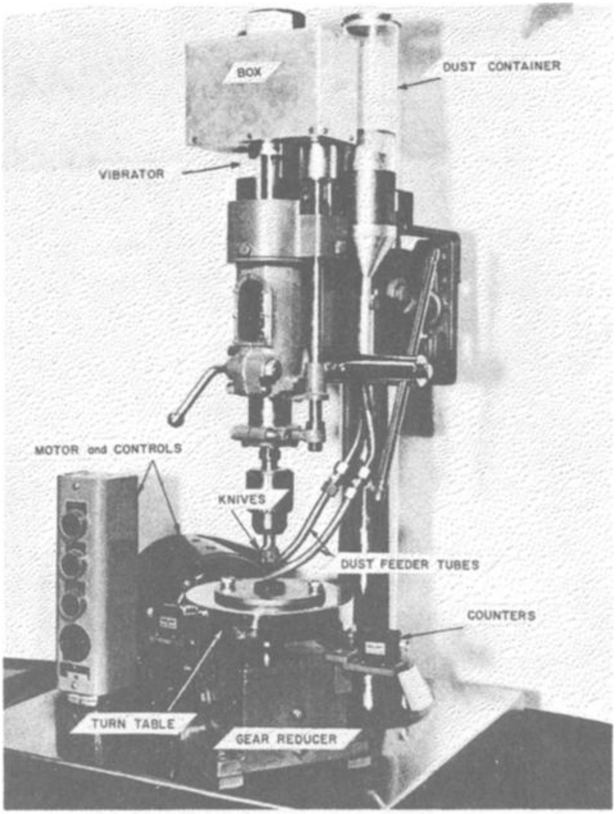
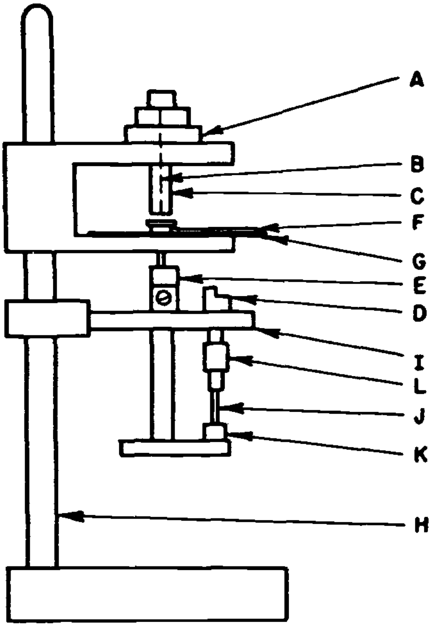


FIG. 2.31—Typical pico tester.

that are mounted and strained around a standard wooden mandral and placed in a laboratory ozone chamber for predesignated time periods of exposure. The reference standard used to rate the degree of cracking of these ring specimens after exposure in the ozone chamber is shown below in Fig. 2.34.

2.2.8 The Standard Classification System for Rubber Products used in Automotive Applications

ASTM D 2000—This is the internationally recognized classification system which resulted from a collaboration between Society of Automotive Engineers (SAE) and ASTM. Rubber products can be arranged into "characteristic material designations." These "designations" are determined by "types" that are based on *resistance to heat aging,* as well as by "classes" that are based



A Torsion head
B Torsion wire
C Sieve
D Clamp stud
E Screw connector
F Pointer

G Movable protractor
H Supporting stand
I Specimen rack
J Test specimen
K Bottom clamp
L Top clamp

FIG. 2.32—Drawing of apparatus for low-temperature stiffness test.

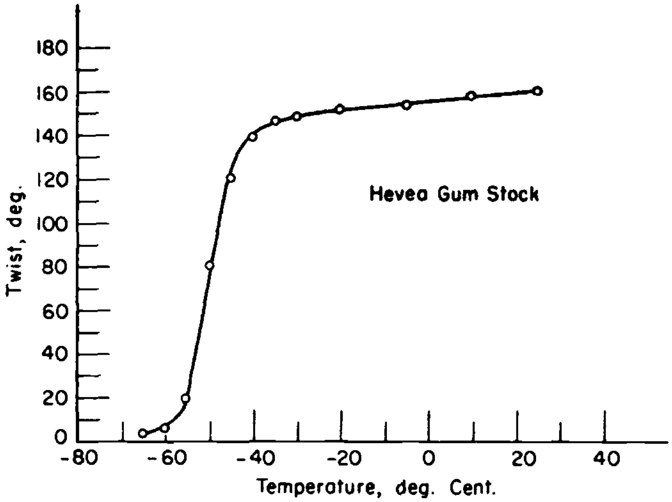


FIG. 2.33—Illustration chart of twist versus temperature.

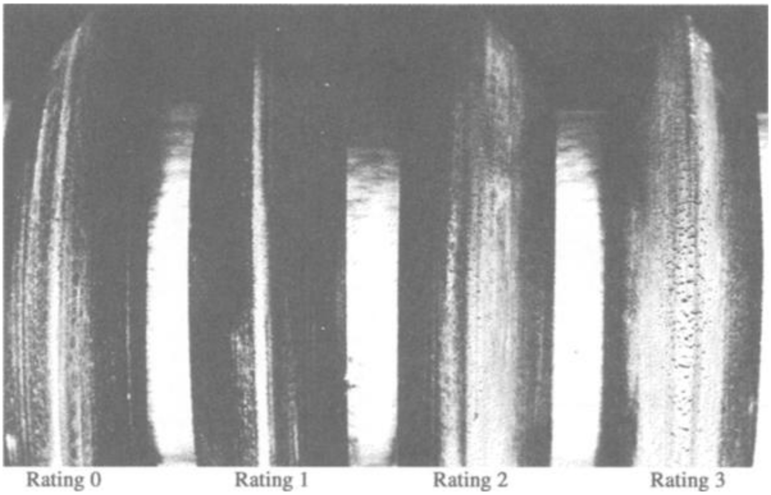


FIG. 2.34—Ratings for weathering tests of rubber compounds (specimens mounted on mandrel). (ASTM D 1171.)

on measured *resistance to swelling* in specified oils and other fluids. This standard provides some guidance for the engineer in selecting commercially available rubber materials, and specifying such materials by a simple "line call-out" designation.

In working out this classification system, the following ASTM tests may be used.

- D 412 Rubber properties in tension
- D 2240 Durometer hardness
- D 573 Air oven aging
- D 865 Test tube aging
- D 395 Compression set
- D 1171 Surface ozone cracking outdoors or chamber (triangular specimen)
- D 575 Rubber properties in compression
- D 471 Testing the effects of liquids
- D 1053 Stiffening at low temperatures
- D 2137 Low temperature properties, brittleness point
- D 1329 Retraction at lower temperatures (TR Test)
- D 624 Tear resistance
- D 430 Dynamic fatigue
- D 429 Adhesion to rigid substrates
- D 925 Staining of surfaces (contact, migration, and diffusion)
- D 945 Mechanical oscillograph

Many of these test methods were discussed earlier.

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3

Testing Natural Rubber

by Alek Vare[1]

3.1 INTRODUCTION AND HISTORY

As is well known, natural rubber was the only polymer from which rubber products could be made until the first synthetic rubber, Neoprene, was invented and became commercialized in the 1930s. Natural rubber was the only polymer used in large ticket items such as tires until the Second World War. When the natural rubber supply was cut off in the early 1940s, the mainstay synthetic, SBR (Styrene Butadiene Rubber) was developed and commercialized.

Natural rubber is an agricultural product. Tests to determine the so called "quality" of natural rubber parallel the increased sophistication and growth of the rubber industry. Tests were developed to distinguish good from bad. These tests, however, were mostly used internally by large companies to assist in product development. In other words, they were the tools that compounders used and had little commercial impact because natural rubber was bought and sold only against visual standards. The introduction of the technically specified rubber (TSR) concept by Malaysia in the late 1960s changed the commercial aspect of natural rubber. ASTM tests became important, and were referenced in commercial purchase contracts. Referee laboratories were established on most continents. Also up to the 1970s there were 22 official grades of natural rubber, mostly differentiated by different production and packing methods. All of them were visually inspected to determine conformance to requirements. Table 3.1 describes some of the more commonly used grades. All the ribbed smoked sheets are visually graded today and the purchase contracts stipulate accordingly.

As mentioned earlier, the Ribbed Smoked Sheets, with the exception of RSS6, are still valid and sold today. There were four grades of thick pale crepe. The first two, the lightest, are still sold today. The "Ambers" are no longer sold in the United States but are still used in other parts of the world.

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TABLE 3.1—Historic Natural Rubber Quality Grades (Used in Visual Inspection).

GRADE	QUALITY DESCRIPTION
Ribbed Smoked Sheets #1 (RSS #1)	Coagulated field latex. Strained for impurities and smoked to a light honey color brown, no resin or other blemishes are allowed, no holes from cut outs are allowed (cuts to remove impurities).
Ribbed Smoked Sheets #2 (RSS #2)	Same as above, except very fine pieces of leaf or bark allowed.
Ribbed Smoke Sheets #3 (RSS #3)	Same as above, slightly larger impurities allowed, cut outs allowed, uneven smoking allowed.
Ribbed Smoked Sheets #4 (RSS #4)	Also from coagulated field latex, but latex not strained. These sheets can be fairly dark and unevenly smoked, have pieces of leaf or bark in sheets, and have cut outs, slight resin is also allowed.
Ribbed Smoked Sheets #5 (RSS #5)	Same as above but more impurities. And very uneven smoking, some sheets so dark it is difficult to inspect by looking through the sheet.
Ribbed Smoked Sheets #6 (RSS #6)	This grade is no longer traded, but it was worse than RSS#5 in that burnt sheets were allowed. These sheets were overheated in the smoke houses.
Pale crepe 1X These can be thin or thick milling	Coagulated field latex treated with a "bleaching agent," extremely clean and almost paper white, usually packaged in poly bags inside paper bags or cardboard cartons.
Pale crepe #1	Same as above but not bleached, light yellow color.
Pale crepe #2	Same as above but the color is dark yellow.
Thin brown Crepes #2, #3, and #4	These grades, as the ambers, were made from cup lump and coagulated sheets. This rubber was thin milled with grade depending on the highness of color.
Smoked Blanket	This grade is no longer used in N. America, but it was made from Ribbed Smoked sheet cuttings which were then washed in wash mills and dried. The blankets were expected to have a smoked odor.
1 and 2 Amber	These grades were made of clean cup lump or unsmoked clean sheets. The grade depended on the color. The high light brown color was 1 amber.
3 and 4 Amber	These grades were made from cup lump which was washed, hanged to dry and then the sheets stacked and baled. Grade depended on the color, cleanliness of the rubber and softness or state of degradation.
Flat bark	This grade was the lowest natural rubber grade and was basically a dirt masterbatch with a sand content of 2 to 3 %. Starting materials were ground scrap, tree lace, and floor sweepings of natural rubber. This rubber was usually very soft and degraded with black liquidized rubber present.

There were four grades of ambers. The "Thin Browns" and the "Smoked Blankets" are no longer internationally sold or traded, but are produced and used internally in some countries in Asia. The lowest priced grade was "Flat Bark" which was produced from tree lace and ground scrap and then milled "to death" to remove the impurities. Flat bark bales often were black and sticky from degraded and oxidized rubber.

All these rubber grades were sold against visual standards, or "Type Samples." The last time the international type samples were renewed was in

1968. At that time the major producing and consuming countries received master type samples and in the case of the United States, they are stored under refrigeration by the North American Rubber Trade Organization in the New York area.

In the 1960s the major tire companies were starting quantitative testing programs for rubber internally to supplement the visual standards. Much earlier, it was already agreed and accepted by most, if not all manufacturers, that sand in rubber was bad. Sand or dirt lowered tensile strength, and in tire applications, could initiate tread separation. Because sand has almost the same reflective index as natural rubber, visual detection of sand was very difficult. Thus the dirt test was one of the earliest developed methods to classify natural rubber grades internally for use in critical compounds such as the ply compounds in bias tires, and later radial tire belt compounds. Ribbed Smoked Sheets were, and are today, the lowest impurity grades along with the technically specified rubber (TSR) five grades. ASTM tests were developed, usually from internal tests from large tire companies and later from methods developed by instrument makers who recognized a need to define a given property critical to the use of natural rubber.

Another very significant test area is the testing of the rubber molecule by sophisticated test equipment where the low and high frequency strains are applied and the test data predicts how raw rubber will process, vulcanize and what are the finished product performance results.

In this chapter these tests are discussed, including the reason for their development and the perceived benefit gained from this information.

3.2 SAMPLING AND SAMPLE PREPARATION BY ASTM D 1485

This standard deals with sampling and sample preparation of rubber from natural sources. It may be used when there is cause to arbitrate quality issues, or whenever contractual problems arise when deciding how to sample natural rubber. In reality, however, this standard has not been used in North American quality disputes in the last 30 years. The reason for this is that the standard is very complex and not easily applied at a moment's notice. The users would have to look up information before the sampling is started. Disputes are normally settled under the guide of the *Green Book*. The *Green Book* addresses quality issues between sellers and buyers, and sampling usually is agreed upon by both parties on what percent of bales to open. Customarily, 5 or 10 % of bales in a given lot are opened for inspection. This aspect is easily understood and accepted by sellers in Asia, and buyers in North America, but may not be accepted in other parts of the world.

The ASTM D 1485 sampling scheme allows taking or accepting a percentage of defectives. In natural rubber, however, the degree and nature of defectives is much more important than the percentage. For instance, if it is decided to open 20 bales (33 kg each) for sampling or inspection of TSR20 (technically specified rubber with dirt less than 0.2 %), and one bale of the 20 bales is found contaminated with metal shavings or plastics shavings, this lot will no doubt be rejected by most factories. However, 6 % defectives would theoretically be allowed under the ASTM D 1485 sampling program.

On the other hand, let's assume that the 20 bales are opened and 5 of the 20 bales show "slight mould," or very small pieces of tree bark, this lot may be accepted, possibly with an allowance off the sale price. In the first instance, where metal shavings were present, no amount of allowance of price reduction would be acceptable to a tire maker. In the second example a large number of minor defects might be accepted.

The standard also specifies how this rubber is to be sampled and the samples handled. This is also usually agreed between the seller and a buyer. This standard is a good guide for sample handling if other instructions are absent.

In North America, customary percent opening for a lot is 5 to 10 %, because labor in the U.S. ports is extremely expensive. To open up one shrink-wrapped unit of rubber weighing 1.2 tons costs approximately $80. From each shrink-wrapped unit, normally four bales are cut and sampled. A 100 ton lot may have 86 shrink-wrapped units and a 10 % "opening" means that eight units are opened. From each unit four bales are sampled. In essence, 32 specimens are taken, which is comparable to what ASTM D 1485 proposes. It roughly agrees with a sampling plan in Table 1 of this standard. However, as discussed earlier, the issue arises on allowable percent defectives.

3.3 TECHNICAL GRADES AND BASIS FOR CLASSIFICATION BY ASTM D 2227

This standard covers the technical grades of natural rubber. It should be understood that defined grades referenced in this standard are all "block" rubbers shipped in shrink-wrapped units or wooden crates, 36 bales per unit or 30 bales per unit. Visually graded rubbers, such as ribbed smoked sheets or pale crepes are not covered by this standard. Table 3.2 shows this classification. The five grades are technically specified rubber TSR L, TSR CV (constant viscosity) regular 5 grade, regular 10 grade, and TSR 20.

The grades differ by percent dirt content, plasticity retention index and Mooney viscosity. The designation of 5, 10 or 20 is based on a percent dirt allowed in each grade. The TSR five is < 0.05 % dirt, TSR10 can have < 0.10 % dirt and TSR 20 is < 0.20 % dirt.

The most common grade used in the United States today is the TSR 20. The TSR 20 could be SIR 20, SMR 20, STR20, SVR20, SPR20 or SAR20 (which stand for standard Indonesian, Malaysian, Thai, Vietnamese, Phillipine or African rubber). In reality, if one measures the dirt from a typical lot received

TABLE 3.2—Technical Grades and Basis for Classification.

	RUBBER GRADE[A]				
PROPERTY	GRADE L	GRADE CV[B]	GRADE 5	GRADE 10	GRADE 20
Dirt, retained on 45 μm sieve, % max	0.050	0.050	0.050	0.100	0.200
Ash, % max	0.60	0.60	0.60	0.75	1.00
Volatile matter, % max	0.80	0.80	0.80	0.80	0.80
Nitrogen, % max	0.60	0.60	0.60	0.60	0.60
Initial plasticity, min	30	...	30	30	30
Plasticity retention index, min	60	60	60	50	40
Color index, max	6.0	...	...	...	...
Mooney viscosity	...	60 ± 5	...	...	...

[A] Skim rubber is not permitted in any grade, and Grades L, CV, and 5 must be produced from intentionally coagulated latex.

[B] Other Mooney ranges of Grade CV are available, CV − 50 ± 5 and CV − 70 ± 5. CV without suffix is the 60 ± 5 as shown in the table.

in the United States, the dirt content is < 0.1 %. By the *Green Book*, standards, these grades and all CV and "CV five" should be "latex grades." It means that the starting material is from controlled coagulated latex, which in practice means that the latex collected from the trees (field) is coagulated by adding proper amounts of formic or acetic acid to form a processable coagulum. Recently there has been a move under way from the producing countries to allow regular clean cup as the starting material for the TSR five. Producers claim that there is no difference whether the rubber is produced from cup lump or latex, as long as the dirt requirements are met. This debate is still ongoing at ISO, where the consuming countries try to maintain the original standard where all TSR five grades are produced from latex. This debate will no doubt be continued at the future International Standards Organization (ISO) meetings.

The 5CV 60 is a latex grade rubber where the viscosity is controlled to 60 ± 5 Mooney units. This control is achieved by adding small amounts of antibranching agents into liquid latex before coagulation. These agents are neutral sulfates, where the most common in use is hydroxyl amine neutral sulfate. In addition to the 5CV 60, there are also viscosity controlled customers for such grades as 5CV 70 and 5CV50.

The table is self explanatory and summarizes well this standard which is also a specification.

3.4 METHODS FOR CHEMICAL ANALYSIS OF NATURAL RUBBER BY ASTM D 1278

ASTM D 1278 deals with the analytical chemical test methods used in classifying natural rubber.

3.4.1 Percent Dirt

Probably the most important test for determining the usability of natural rubber is the "dirt test" or % retains on the 325 mesh screen. In the last 30 years, many papers have been written and published dealing with the percent dirt, which is mostly sand in natural rubber. The general conclusion from these studies is that impurities in natural rubber have a degrading effect if the rubber is a performance expected polymer. This is especially important for tire applications where small particles of dirt in critical places can cause tread separation.

The dirt test itself is very simple. The NR test specimen is dissolved in a rubber solvent, usually with the aid of a small amount of a peptizer, and the rubber solution is filtered through a 325 mesh screen. Anything remaining on the screen is dried and weighed to the second decimal. ASTM D 1278, sections 9 through 13 cover this thoroughly.

Here are some useful hints on how to conduct this test. The fine mesh screens have to be inspected often to make sure that there are no holes in the screens. This has to be done with a low magnifying microscope or a powerful magnifying hand lens. It is also important that the rubber specimen be thoroughly dissolved in the solvent. If for some reason the rubber specimen is not thoroughly dissolved, some gel (slightly crosslinked, more difficult to dissolve nodules) may remain on a screen giving high erroneous results. It is also advisable to visually inspect the retains on the screen. As mentioned earlier, most of the weight is probably sand. Other common impurities include leaf and bark, woodchips and insects, but these do not contribute as much to the weight as dirt. Generally speaking, the non-sand impurities are less harmful as they break down in mixing cycles and are easier to disperse.

3.4.2 Volatile Matter

The next most important test is volatile matter. For natural rubber, this is usually water although with synthetic polymers, volatile matter can be both water and residual rubber hydrocarbons. In the last ten years there have been significant advances in drying technology in most of the producing countries. It is now rare that poorly dried rubber is detected in the consuming plants. Also moisture or water is easily detected by visual inspection. In any case, great care must be taken in selecting and handling the test specimen before it is analyzed in the laboratory. ASTM D 1278 sections 6 through 8 cover this procedure well.

3.4.3 Copper Content

Another procedure, not currently conducted very often, is the copper test. Copper is a strong degradant (a pro-oxidant) in natural rubber, even at very low concentrations. The copper test can be an indication of how this raw material was handled. If the copper results are high, it may be an indication that the rubber came in contact with the earth (soil). Also elevated percentages of copper may be very detrimental to performance of the finished product. In reality, elevated copper levels are rare in current deliveries to consumers. It is suggested that ASTM D 4004 Method D, for copper determination may be performed to determine the presence of this element.

3.4.4 *Manganese*

Like the copper test, the manganese test is also not commonly performed. It is also recommended that ASTM D 4004 Method E be used. Manganese like copper, is a strong degradant in natural rubber, but in recent years elevated manganese levels have not been a problem.

3.4.5 *% Ash*

This is still a very important test if the presence of impurities, such as fine mineral fillers, calcium carbonate, talc, aluminum silicate, and clay are suspected as contaminants. These may be inadvertently introduced into the rubber by reworking off-spec baled rubber or GSA/DLA RSS bales into TSR grades. Sometimes partitioning agents are used to keep the unsmoked sheets from adhering to each other by dusting them with minerals. The particle size of these minerals is so small that the dirt test may not detect the additional impurities, but an ash test will. Also it is possible to examine the ash with analytical tools, as well as optical or electron microscopy to determine the ash composition. As far as the usability of the rubber is concerned, the user will have to decide if a given amount of ash content is acceptable in a given product.

3.4.6 *Iron Content*

The iron content test is again seldom used because for many years iron concentration has not been a problem or an issue. Historically, the test was an indication of how the rubber was handled before packaging. Many rubber producing regions are in iron rich soil. In Liberia for instance, iron ore mines were "neighbors" with rubber plantations. If the rubber came into contact with the soil, elevated iron levels would result. Low concentrations of iron are not always a strong degradant in rubber.

3.4.7 *Acetone Extract*

This test is very important as it determines the non-rubber ingredients in the given grade. In many rubber latex producing factories, the whole field latex is centrifuged to a given rubber hydrocarbon concentration. The serum, or effluent from this operation still contains rubber hydrocarbons and a process known as secondary coagulation is used to capture the last remaining rubber molecules. This material is commonly known as skim latex. When dried, it has a high non-rubber content. Natural rubber has a non-rubber content of 7 %, meaning that the rubber is 93 % rubber hydrocarbon; the skim latex could be 80 % rubber hydrocarbon and 20 % acetone soluble non-rubber ingredients. These non-rubber ingredients have a dramatic effect on processability, curing and end product performance. In processing, the rubber may be stiff or boardy; it may be difficult to mix or process. With elevated non-rubber ingredients present, it is usually very scorchy, and with a reduced rubber hydrocarbon content, it will have lower physicals such as tensile strength. When performing this test, it is advisable to run acetone extract on known samples, and compare the known with the suspected samples. A "stand alone" value may not give the information one needs when running the acetone extraction test. If skim latex is suspected, it would also be highly recommended to conduct the percent nitrogen test described in 3.4.8 below.

3.4.8 Nitrogen

This test is another measure of non-rubber components (usually proteinacious) in a given rubber lot or shipment. Going back to the acetone extract test, a large portion of the extractables would be compounds usually high in nitrogen. Percent nitrogen determinations are commonly done using the Kjeldahl method ASTM D 3533, or other analytical methods less cumbersome.

3.5 PLASTICITY RETENTION INDEX, ASTM D 3194-99

This test is better known as the Wallace Plasticity Test. It is the most widely used test for natural rubber in the world. It is also known as the PRI test. PRI stands for plasticity retention index. All the producing countries have Wallace Plasticity test equipment in their laboratories. Many large companies in the Western world, United States, and Europe are also equipped to run the Wallace Test. Ten years ago, three slightly different test methods existed. They were the ISO method, the Rubber Research Institute of Malaysia (RRIM) method, and the ASTM method. In the 1991 Stockholm ISO TC 45 meeting, all ISO delegates agreed to adopt the RRIM version. After several debates, agreement was reached and all three tests are now almost identical. This test is very operator and equipment sensitive. In the laboratories of producing countries, there are hundreds of samples tested daily with good testing repeatability achieved. In the United States today, the Wallace test is seldom run, as test results from producing countries are generally accepted. The most common value used today is the P_o. The P_o test is a measure of the original plasticity (before aging). It correlates with the processability of natural rubber in the factory. As mentioned above, this test is very operator and equipment sensitive. Variability in test results is due to the following factors: differences in milling the specimen, the cigarette paper used in wrapping the specimen as it is inserted into the test cavity, and calibration of the instrument.

If PRI is determined, then another set of variables is introduced. These are: design of the heating oven, air circulation in the oven and temperature control of the oven. Small variations in these operations can have a significant impact on the PRI values.

It is generally agreed that a higher P_o means it may be harder to process the rubber in the factory, but also that the rubber molecule is more intact, meaning less chain scission. Any lot where the P_o is testing less than 30 is generally considered rejectable by the international purchase agreements. It may be also significant to state, that many factories prefer to have SIR or SMR or SVR rubber testing 34 or 35 ± 2 on P_o because of easier processability. To accomplish this, the rubber processing factories in the producing countries control the dryer temperature and residence time in the dryers. Higher dryer temperatures lower the P_o. Also longer residence in the dryers lowers the P_o. This is a "tight rope" many producers walk to satisfy the customer, yet stay above the standard to do business.

3.6 COLOR INDEX ASTM D 3157

This test was designed to measure the color of rubber in applications where it is important. An example would be fashion items such as shoe soles made of thick pale crepe or light rubber such as TSR L or CV going into white sidewall tire compounds. A darker rubber may require additional amounts of TiO_2 to meet a brightness standard. In this test, sample selection is important as a given lot of rubber may have significant color variation depending on which bales the samples were obtained. This is also a test where decisions are made on visual examination of comparative sample disks in the commonly used apparatus: the Lovibond Colorimeter. An observation here is that the sample preparation is important and should be conducted exactly as the standard dictates.

3.7 STANDARD TEST METHOD FOR EVALUATION OF NATURAL RUBBER ASTM D 3184

This standard with its three test recipes is the main evaluation tool to determine the rubber's conformance to requirements. Again it is important

TABLE 3.3—Standard Test Recipes for Evaluating Natural Rubber.

	QUANTITY, PARTS BY MASS, AND FORMULA NO.			
MATERIAL	NIST SRM NO.	1A GUM	2A BLACK FILLED	3A[A] GUM
Natural rubber	...	100.00	100.00	100.00
Zinc oxide	370	6.00	5.00	6.00
Sulfur	371	3.50	2.25	3.50
Stearic acid	372	0.50	2.00	0.50
Oil furnace black[B]	378	...	35.00	...
Mercaptobenzothiazole	383	0.50	...	...
TBBS[C]	384	...	0.70	0.70
Total		110.50	144.95	110.70

to run known samples with this test method. Generally speaking the pure gum recipe (the one without carbon black) is the more precise measure of a given lot of rubber when tensile, modulus, and elongation values are critical. Carbon black has a leveling effect and small differences in the physicals will be masked by the addition of the given Standard Reference Black (IRB).

The three standard test recipes for evaluating natural rubber are given in Table 3.3 shown above.

Over the years much discussion has taken place concerning the merits of each test recipe, pure gum versus black loaded. Compounders will often claim that their compounds contain carbon black anyway, so if the test can't discriminate, then his compound can't either. There is appreciable data on how different grades of natural rubber should test using ASTM D 3184.

3.8 NEW STANDARD TEST METHOD FOR CHARACTERIZING NATURAL RUBBER GRADES—ASTM D 6204, PART B

As discussed earlier in Chapter 2 (Section 2.2.4), the rotorless shear rheometer (RSR) technology (commonly known as the rubber process analyzer or RPA) was introduced in the 1990s for characterizing and controlling the quality of raw rubber and mixed stocks. In 1995, ASTM D 11.22 Task Group on Definitive Testing discovered that high strain testing with the RPA was much more sensitive to subtle quality differences among different lots of natural rubber than traditional rheological methods such as Wallace Plasticity P_0 and Mooney viscosity. Figure 3.1 demonstrates this improved sensitivity to differences in elastic quality between different sources of TC10 natural rubber that have the same Mooney viscosity.

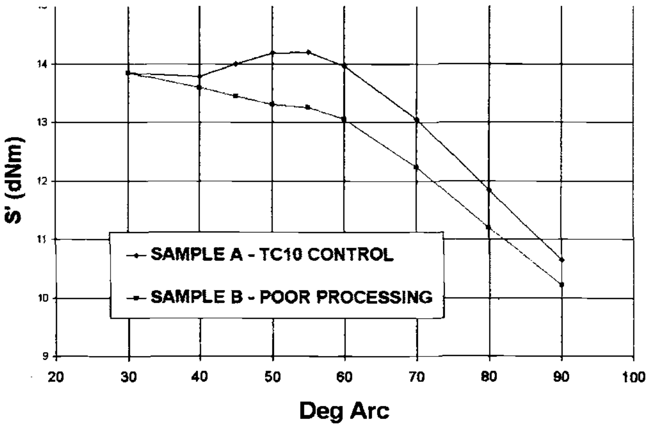

FIG. 3.1—Comparison of Elastic Torque S′ response for two different natural rubber "TSR 10 sources" with the same Mooney Viscosity values vs. increasing applied strain by the Rotorless Shear Rheometer.

Because conditions of higher strain with RPA testing were found to be more sensitive to actual factory performance differences among natural rubber lots, it was decided to add a "Part B" to the established ASTM D 6204 RSR standard to accommodate high strain testing. Part B allows RPA testing at 100 % strain. This Part B of ASTM D 6204 will not only provide more sensitive testing for raw natural rubber lots, but will also be used to test more effectively mixed batches of factory compounds.

4

Testing Synthetic Rubber

by Julia B. Zimmerman[1]

4.1 SYNTHETIC RUBBER HISTORY AND NOMENCLATURE

SYNTHETIC "RUBBERS" WERE DEVELOPED during the 1940s as alternatives to natural rubber. Much of the early development of these products in the United States was done in federal government-owned plants, hence an old system of nomenclature that included GR-A, GR-I, GR-M, GR-S, and GR-T (standing for "government rubber" with acrylonitrile, isobutylene, monochlorobutadiene, styrene, and thiosulfide respectively).

ASTM Standard Practice for Rubber and Rubber Latices—Nomenclature (D 1418) is the authoritative reference for a more modern nomenclature that has replaced the old "GR" nomenclature. Table 4.1 shows how ASTM D 1418 has assigned a letter to designate various general classes of polymers.

The "classification" letter from Table 4.1 is preceded by other letters which describe modifications of the basic polymer type to give polymer abbreviations like those in Table 4.2. These are the common usage abbreviations for the various polymers currently in commercial production.

Examination of Tables 4.1 and 4.2 will allow the reader to understand quickly the chemical constituents of a polymer simply by examining the abbreviation. For instance, SBR is a rubber with unsaturation in the chain and which is composed of styrene and butadiene monomers.

Synthetic rubbers are now widely used in both tire and non-tire applications, partly as a replacement for natural rubber whose supply is not sufficient to meet all demands, but also because the properties of various synthetic rubbers can be tailored to meet the specific needs of a certain compound. For instance, nitrile rubbers (NBR) and especially hydrogenated nitrile rubbers (HNBR) are chemically resistant; isoprene-

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[1] Bridgestone/Firestone, Inc., Chemical Laboratory, 1200 Firestone Parkway, Akron, OH 44317.

TABLE 4.1—The Classification Foundation for ASTM Rubber Nomenclature (Taken from ASTM D 1418).

LAST LETTER IN ASTM ABBREVIATION FOR RUBBER	MEANING
M	Rubbers having a saturated chain of the polymethylene type
N	Rubbers having nitrogen, but not oxygen or phosphorus
O	Rubbers having oxygen in the polymer chain
R	Rubbers having an unsaturated carbon chain, for example, natural and synthetic rubbers derived at least partly from diolefins
Q	Rubbers having silicon and oxygen in the polymer chain
T	Rubbers having sulfur in the polymer chain
U	Rubbers having carbon, oxygen, and nitrogen in the polymer chain
Z	Rubbers having phosphorus and nitrogen in the polymer chain

isobutylene rubber (IIR, commonly referred to as "butyl rubber") is air-impermeable; rubbers made from ethylene-propylene-diene monomers (EPDM) are used in weather-resistant roofing material. This chapter will not attempt to recommend specific synthetic rubbers (also simply called polymers); that subject is best left to compounding texts. This chapter reviews the various ASTM test methodologies that might be of use in specifying the grade of polymer needed by a consumer so that both consumer and producer can agree on test methods resulting in satisfactory product quality.

4.2 CONSUMER-PRODUCER AGREEMENT

The agreement of consumer and producer is necessary any time a commercial sale is being made. ASTM Standard Practice for Styrene-Butadiene Rubber (SBR)—Establishing Raw Mooney Viscosity Target Values (D 5605), nominally a practice for establishing raw Mooney viscosity target values for SBR, contains within its language several helpful hints for coming to such an agreement:

1. Standardization of specifications to increments (in this case, 5 Mooney units) allows the producer to produce more consistent material to fewer target values
2. The more consistent material leads to reduced sorting at the producer plant and more consistency at the consumer plant
3. The customer can determine the property range within which the product can be used and specify that as the acceptable range
4. Consumer and producer must agree not only on the values for parameters, but also on the test methods to be used. ASTM standards are an invaluable aid in getting test method agreement

TABLE 4.2—Standard Abbreviations for Commercially Available Synthetic Elastomers Based on ASTM D 1418.

STANDARD ASTM ABBREVIATIONS	RUBBER CHEMICAL IDENTIFICATION
ACM	Copolymers of ethyl or other acrylate and a small amount of monomer which facilitates vulcanization
CM	Chloro-polyethylene
CFM	Polychloro-trifluoro-ethylene
CSM	Chloro-sulfonyl-polyethylene
EOM	Copolymers of ethylene and an octene
EPDM	Terpolymer of ethylene, propylene, and a diene with the residual unsaturated portion of the diene in the side chain
EPM	Copolymers of ethylene and propylene
EVM	Copolymers of ethylene and vinyl acetate
FEPM	A fluoro rubber of the polymethylene type only containing one or more of the monomeric alkyl, perfluoroalkyl, and/or perfluoroalkoxy groups, with or without a cure site monomer (having a reactive pendant group)
FFKM	Perfluorinated rubbers of the polymethylene type having all fluoro, perfluoroalkyl, or perfluoroalkoxy substituent groups on the polymer chain; a small fraction of these groups may contain functionality to facilitate vulcanization
FKM	Fluoro rubber of the polymethylene type that utilizes vinylidene fluoride as a comonomer and has substituent fluoro, alkyl, perfluoroalkyl or perfluoroalkoxy groups on the polymer chain, with or without a cure site monomer (having a reactive pendant group)
CO	Polychloromethyl oxirane (epichlorohydrin polymer)
ECO	Ethylene oxide (oxirane) and chloromethyl oxirane (epichlorohydrin copolymer)
GECO	Epichlorohydrin-ethylene oxide-allylglycidylether terpolymer
GPO	Polypropylene oxide and allyl glycidyl ether
BIIR	Bromo-isobutene-isoprene rubber
CIIR	Chloro-isobutene-isoprene rubber
CR	Chloroprene rubber
ENR	Epoxidized natural rubber
HNBR	Hydrogenated acrylonitrile-butadiene rubber
IIR	Isobutene-isoprene rubber
IR	Isoprene, synthetic rubber
NBR	Acrylonitrile-butadiene rubber
NR	Natural rubber
SBR	Styrene-butadiene rubber
SIR	Styrene-isoprene rubber
XNBR	Carboxylic-acrylonitrile-butadiene rubber
FVMQ	Silicone rubber having fluorine, vinyl, and methyl substitute groups on the polymer chain
PMQ	Silicone rubbers having both methyl and phenyl substituent groups on the polymer chain
PVMQ	Silicone rubbers having methyl, phenyl, and vinyl substitutent groups on the polymer chain
MQ	Silicone rubber having only methyl substituent groups on the polymer chain, such as dimethyl polysiloxane
VMQ	Silicone rubber having both methyl and vinyl substituent groups on the polymer chain
AU	Polyester urethane rubber
EU	Polyether urethane rubber
OT	A rubber having either a —CH_2-CH_2-O-CH_2-O-CH_2-CH_2 group or occasionally an —R- group, where R is an aliphatic hydrocarbon between the polysulfide linkages in the polymer chain
EOT	A rubber having a —CH_2-CH_2-O-CH_2-O-CH_2-CH_2 group and R groups that are usually —CH_2-CH_2 but occasionally other aliphatic groups between the polysulfide linkages in the polymer chain

4.3 PHYSICAL TESTS FOR SYNTHETIC RUBBER

ASTM Standard Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer) (D 1646) contains directions for performing the Mooney viscosity test for raw polymers and compounded stocks. It also includes tests for stress-relaxation and pre-vulcanization characteristics. In addition to these directions, ASTM D 1646 contains a table of the standard viscosity test conditions that have been agreed upon by a consensus of suppliers and consumers of these materials. Table 4.3 gives those test conditions.

Another characteristic which can be the subject of consumer-producer agreement is some measurement of the unvulcanized rheological properties of the polymer. ASTM Standard Test Method for Rubber—Measurement of Unvulcanized Rheological Properties Using Rotorless Shear Rheometers (D 6204) treats this subject and includes a table of standard test conditions for testing these dynamic properties on uncured polymers and compounded stocks. Table 4.4, taken from ASTM D 6204, illustrates these conditions.

Table 4.3—Standard Viscosity Test Conditions.

TYPE RUBBER[A]	SAMPLE PREPARATION, SEE SECTION	TEST TEMPERATURE, °C[B]	RUNNING TIME, MIN[C]
IRM 241	7.1 and 7.3	100 ± 0.5 or 125 ± 0.5	8.0
Unmassed sample	7.1 and 7.3	Use conditions listed below for type rubber being tested	
NR	7.1 and 7.2.1	100 ± 0.5	4.0
BR	7.1 and 7.2.2	100 ± 0.5	4.0
CR			
IR			
NBR			
SBR			
BIIR	7.1 and 7.2.2[D]	100 ± 0.5 or 125 ± 0.5[E]	8.0
CIIR			
IIR			
EPDM	7.1 and 7.2.2	125 ± 0.5	4.0
EPM			
Synthetic rubber black masterbatch	7.1 and 7.2.3	100 ± 0.5	4.0
Compounded stock reclaimed material	7.1 and 7.3	100 ± 0.5	4.0
Miscellaneous	If similar to any group above, test accordingly. If not, establish a procedure		

[A] See Practice D 1418.

[B] Test temperatures are 100 ± 0.5°C (212 ± 1°F) or 125 ± 0.5°C (257 ± 1°F).

[C] Time after the standard 1.0-min warm-up period at which the viscosity measurement is made.

[D] If no air bubbles are visible in the sample, 7.2.2 may be omitted.

[E] Use a temperature of 125 ± 0.5°C (257 ± 1°F) whenever specimen has a viscosity higher than 60-ML 1 + 8 (100°C).

TABLE 4.4—Standard Test Conditions for Oscillating Rheometer with Closed Die Cavity.

TYPE RUBBER	CONDITION TEMP. (°C)	CONDITION STRAIN ± %	CONDITION FREQ. (Hz)	CONDITION TIME (MINUTES)	FREQ. SWEEP TEMP. (°C)	FREQ. SWEEP STRAIN (± %)	FIRST FREQ. OF SWEEP (Hz)	SECOND FREQ. OF SWEEP (Hz)	THIRD FREQ. OF SWEEP (Hz)
IRM 241	100 ± 0.3 or 125 ± 0.3	2.8	0.5	5.0	100 ± 0.3 or 125 ± 0.3	7	0.1	2.0	20
Unmassed Sample									
NR	100 ± 0.3	2.8	0.5	8.0	100 ± 0.3	7	0.1	2.0	20
BR	100 ± 0.3	2.8	0.5	5.0	100 ± 0.3	7	0.1	2.0	20
CR	100 ± 0.3	2.8	0.5	5.0	100 ± 0.3	7	0.1	2.0	20
IR	100 ± 0.3	2.8	0.5	5.0	100 ± 0.3	7	0.1	2.0	20
NBR	100 ± 0.3	2.8	0.5	5.0	100 ± 0.3	7	0.1	2.0	20
SBR	100 ± 0.3	2.8	0.5	4.0	100 ± 0.3	7	0.1	2.0	20
BIIR	100 ± 0.3 or 125 ± 0.3	2.8	0.5	5.0	100 ± 0.3 or 125 ± 0.3	7	0.1	2.0	20
CIIR	100 ± 0.3 or 125 ± 0.3	2.8	0.5	5.0	100 ± 0.3 or 125 ± 0.3	7	0.1	2.0	20
IIR	100 ± 0.3 or 125 ± 0.3	2.8	0.5	5.0	100 ± 0.3 or 125 ± 0.3	7	0.1	2.0	20
EPDM	125 ± 0.3	2.8	0.5	5.0	125 ± 0.3	7	0.1	2.0	20
EPM	125 ± 0.3	2.8	0.5	5.0	125 ± 0.3	7	0.1	2.0	20
Synthetic Rubber Black Masterbatch	100 ± 0.3	2.8	0.5	4.0	100 ± 0.3	7	0.1	2.0	20
Compounded Stock reclaimed material	100 ± 0.3	2.8	0.5	2.0	100 ± 0.3	7	0.1	2.0	20
Miscellaneous									

4.4 STANDARD TEST RECIPES AND TEST PROCEDURES

Polymers in their raw, uncompounded state differ a great deal from compounded rubbers. Sometimes polymer performance differences can only be detected when tested in a compound test recipe. Because lot-to-lot differences within one polymer grade can be the subject of specifications, ASTM has published standard formulas (recipes) for the evaluation of different types of polymers. Generally these compounds are simple recipes to be mixed on a mill or a miniature internal mixer (MIM) using standard compounding ingredients, usually specified as Industry Reference Materials (IRMs). Testing of these simple recipes may reveal differences in curing or cured behavior that the customer may wish to know before accepting. Table 4.5 lists the locations of the various ASTM test recipes for synthetic rubber.

The formulas themselves are simple. Generally some carbon black and a simple curative package will be added to the raw polymer to allow testing of various cured rubber properties. Two things are important to note about the formulas:

(1) Wherever possible, it is in the interest of both the producer and the consumer of the polymer to use standardized raw materials for the compounding work. These include the latest Industry Reference carbon Black (IRB) and Industry Reference Materials (IRMs). Since each material added to a batch can affect its cure and other characteristics, the only way to obtain agreement is to use standard "other materials" when testing a new lot of polymer.

(2) Following the compounding convention generally used in the United States, the amount of polymer is set to 100 parts. Other materials are added to this polymer at specified phr concentrations (referred to as parts per hundred of rubber). Simplistically, one can think of 100 g (or kg, or lb) of polymer, and the same mass unit of the other materials. When these recipes are mixed in a miniature-internal-mixer (MIM), on a mill, or in a standard laboratory internal mixer, it will be necessary

TABLE 4.5—Location of Test Recipes for Synthetic Rubbers.

SYNTHETIC RUBBER BEING TESTED	ASTM TEST METHOD
SBR with or without oil	D 3185
SBR oil and black masterbatch	D 3196
Polybutadiene	D 3189
Oil extended polybutadiene	D 3484
EPDM with or without oil	D 3568
IIR (butyl)	D 3188
BIIR and CIIR	D 3958
IR (synthetic polyisoprene)	D 3403
NBR	D 3187
NBR mixed with carbon black (masterbatch)	D 3848
CR	D 3190

to adjust proportionately the total amount of materials used to obtain good mixing. See comments in the individual test methods.

Tables 4.6 through 4.13 show the test recipes found in the above-mentioned ASTM standards, which may be examined with reference to the above comments.

TABLE 4.6—SBR Test Recipe from ASTM D 3185.

INGREDIENTS	PARTS PER HUNDRED RUBBER (PHR)
Subject SBR	100.00
Zinc oxide	3.00
Sulfur	1.75
Stearic acid	1.00
Standard reference black (IRB)	50.00
TBBS accelerator	1.00
Total	156.75

TABLE 4.7—NBR Test Recipe from ASTM D 3187.

INGREDIENTS	PARTS PER HUNDRED RUBBER (PHR)
Subject NBR	100.00
Zinc oxide	3.00
Sulfur, specially coated	1.50
Stearic acid	1.00
Standard reference black (SRB-B4)	40.00
TBBS Accelerator	0.70
Total	146.20

TABLE 4.8—IIR Test Recipe from ASTM D 3188.

INGREDIENTS	PARTS PER HUNDRED RUBBER (PHR)
Subject IIR	100.00
Zinc oxide	3.00
Sulfur	1.75
Stearic acid	1.00
Industry reference black (IRB)	50.00
TMTD	1.00
Total	156.75

TABLE 4.9—BR Test Recipe from ASTM D 3189.

INGREDIENTS	PARTS PER HUNDRED RUBBER (PHR)
Subject BR	100.00
Zinc oxide	3.00
Sulfur	1.50
Stearic acid	2.00
Industry reference black (IRB)	60.00
TBBS Accelerator	0.90
ASTM 103 type petroleum oil	15.00
Total	182.40

TABLE 4.10—CR Test Recipes from ASTM D 3190.

INGREDIENTS	1	2	3	4
Subject CR, sulfur modified	100.00	100.00	...	...
Subject CR, mercaptan modified	...	...	100.00	100.00
Stearic acid (SRM 372)	0.50	0.50	...	...
Magnesium oxide (use IRM)	4.00	4.00	4.00	4.00
Industry reference black (IRB)	...	25.00	...	25.00
Zinc oxide IRM 91	5.00	5.00	5.00	5.00
3-methyl thiazolidine thione-2-80% in polymeric binder (curative)	...	...	0.45	0.45
Total	109.50	134.50	109.45	134.45

TABLE 4.11—IR Test Recipe from ASTM D 3403.

INGREDIENTS	PARTS PER HUNDRED RUBBER (PHR)
Subject isoprene rubber	100.00
Zinc oxide	5.00
Sulfur (SRM 371)	2.25
Stearic acid (use available from NIST)	2.00
Industry reference black (IRB)	35.00
TBBS accelerator (RM 8384)	0.70
Total	144.95

TABLE 4.12—EPDM Test Recipe from ASTM D 3568.

INGREDIENTS	PARTS PER HUNDRED RUBBER (PHR)
Subject EPDM	100.00
Zinc oxide (IRM 91)	5.00
Sulfur (SRM 371)	1.50
Stearic acid (SRM 372)	1.00
Standard reference black SRB B4	80.00
ASTM type 103 petroleum oil	50.00
TMTD accelerator	1.00
MBT accelerator	0.50
Total	239.00

TABLE 4.13—BIIR and CIIR Test Recipe from ASTM D 3958.

INGREDIENTS	PARTS PER HUNDRED RUBBER (PHR)
Subject BIIR or CIIR	100.00
Zinc oxide	5.00
Stearic acid	1.00
Indusry reference black (IRB)	40.00
Total	146.00

4.5 PROCESSABILITY OF SBR WITH THE MOONEY VISCOMETER

ASTM Standard Test Methods for Rubber Property—Processability of SBR (Styrene-Butadiene Rubber) with the Mooney Viscometer (D 3346), is a special test that is frequently used in specifications for emulsion polymerized SBR. This test is commonly referred to as the "Delta Mooney" test. Although

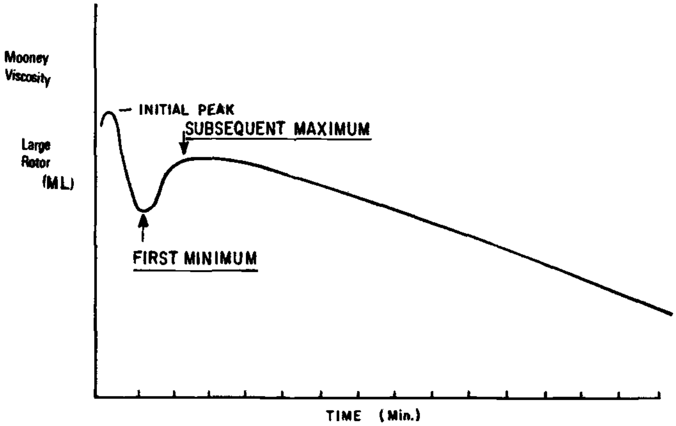

FIG. 4.1—Mooney versus time curve for processability test of select emulsion SBR.

this test is of limited application, it gives important information to the purchasers of these types of rubber. The difference between the minimum and the subsequent maximum viscosity can often be related to the processability of the polymer in a factory setting. Figure 4.1 shows a typical Mooney viscosity curve made by testing such a polymer.

4.6 CHEMICAL TESTS FOR SYNTHETIC RUBBERS

4.6.1 Organic Acids, Soap, Oil, Total Extractables

The non-polymer (or non-rubber hydrocarbon) portion of commercial polymers can play an important role in the functioning of compounded rubber stocks. ASTM Standard Test Methods for Rubber from Synthetic Sources—Chemical Analysis of Extractables (D 5774) is explicitly written for emulsion polymerized SBR, but parts of the standard may find application to other types of polymers of commercial interest. Each section of the standard will be explained separately below

4.6.1.1 Total Extractables In order to measure any of the other constituents cited above, it is necessary to first extract the polymer to separate the rubber from the additives. This is generally accomplished through thinly sheeting out the polymer (either on a mill or by pressing into a screen), and boiling or otherwise refluxing in solvent. The two solvents listed, ETA (Ethanol-Toluene Azeotrope) and H-ITM (Hydrous Isopropanol-Toluene Mixture), may be used interchangeably for this procedure if emulsion SBR is being tested. *Note: Solution SBR, Polyisoprene, and other types of polymers may require different solvents or special drying conditions to remove residual solvent, but* *these changes should be the subject of agreement between the producer and consumer.* The calculated total extractable will also allow a rubber compounder to determine the amount of non-rubber hydrocarbon material in the polymer, and adjust the cure package accordingly.

4.6.1.2 Organic Acid and Soap In the emulsion polymerization process, organic acid is used in forming the emulsion. In the course of finishing, some of the acid will be neutralized to soap. Residual organic acid will change the cure rate of a compound. Uncontrolled variation in the organic acid can be a hidden cause of lot-to-lot variation. Soap, generally present at a small level, must be measured as part of the determination of the constituents of the total extractables. Both soap and organic acid are determined by testing the extracted material from the polymer in question. The free acid is determined by titrating one aliquot with standardized base, while the soap is determined by titrating another aliquot with standardized acid. In both parts of this test, the calculation of weight percentage requires that the analyst know the identity of both the type of acid used and the cation in the soap. While these identities may vary from producer to producer, they should be readily obtainable from the producers' literature.

4.6.1.3 Oil Oil is added to many polymers, not only emulsion SBR, to reduce the viscosity of long chain polymers and allow them to process in typical factory equipment. The oil is added generally before the drying process so that it is thoroughly incorporated into the dry polymer block. The test method is a fairly simple extraction of a thinly sheeted piece of polymer. These methods (there are two presented) are widely applicable to oil-extended polymers of all types, but the analyst should note that it may be necessary to vary the solvent so that the polymer itself does not also dissolve with the oil.

4.6.2 Volatile Matter

A bale of dried polymer will often contain a low level of volatile matter. This volatile matter will often be residual solvent, water (if emulsion polymer), or perhaps even residual monomer or low molecular weight polymer. ASTM Standard Test Methods for Rubber from Synthetic Sources—Volatile Matter (D 5668) presents four ways of performing this test depending on the equipment available in the laboratory. The traditional test method, A, calls for weighing the polymer, then passing it through a heated laboratory mill to constant mass. Method A is not practical for polymers that become sticky or from which pieces of polymer are lost during the milling.

Methods B and C call for milling an amount of rubber on a cold mill, then placing the milled sheet into an oven to devolatilize. These methods are not suitable for polymers that do not mill well on a cold mill.

Method D calls for the use of a laboratory press with heated platens that will flatten the polymer and drive off the volatiles.

The results obtained by these methods may not be exactly comparable, but the choice is often dependent on the type of polymer at hand.

4.6.3 Total and Water Soluble Ash

Total and water soluble ash content of a rubber can affect the properties of compounded, vulcanized rubber such as water absorption, swell, electrical properties, etc. ASTM Standard Test Method for Rubber from Synthetic Sources—Total and Water Soluble Ash (D 5667) presents common analytical tests requiring the use of a muffle furnace. As the significance section notes, these tests will chiefly be used for referee purposes as commercial polymers commonly have quite low levels of ash.

4.6.4 Determination of Carbon Black in Masterbatch

These carbon black/polymer masterbatches are a special type of (primarily) emulsion SBR into which carbon black has been intimately mixed during the finishing process of the polymer. They allow a compounder to obtain excellent carbon black dispersion by only mixing in the other ingredients. ASTM Standard Test Methods for Rubber from Synthetic Sources—Carbon Black in Masterbatches (D 5805) presents three different but related methods. All require that a known quantity of masterbatch by pyrolized, leaving behind the carbon black and the ash. Ash is determined and subtracted to leave the amount of carbon black.

The first method requires that the sample be heated to a high temperature (approximately 550°C) under carbon dioxide (CO_2) for the pyrolysis; then the sample is cooled under CO_2 and weighed. The carbon black is combusted in oxygen or air to determine the ash.

The second method requires a similar pyrolysis step under reduced pressure (vacuum), and a subsequent combustion. Figure 4.2 shows a diagram of the apparatus used for this reduced pressure pyrolysis.

The third method in ASTM D 5805 uses a commercial Thermogravimetric Analyzer (TGA) for the same determination.

The production and use of a "determinate black masterbatch" (see footnote 3 in ASTM D 5805) is suggested for all procedures as a check of the validity of the method employed.

4.6.5 Percent Gel, Swelling Index, and Dilute Solution Viscosity

ASTM Standard Test Method for Rubber, Raw—Determination of Gel, Swelling Index, and Dilute Solution Viscosity (D 3616) states that its methods are applicable to non-oil extended and non-pigmented SBR and NBR. Other rubbers can be tested by these methods, although solvents may need to be changed depending on the exact rubber. The determination of gel content

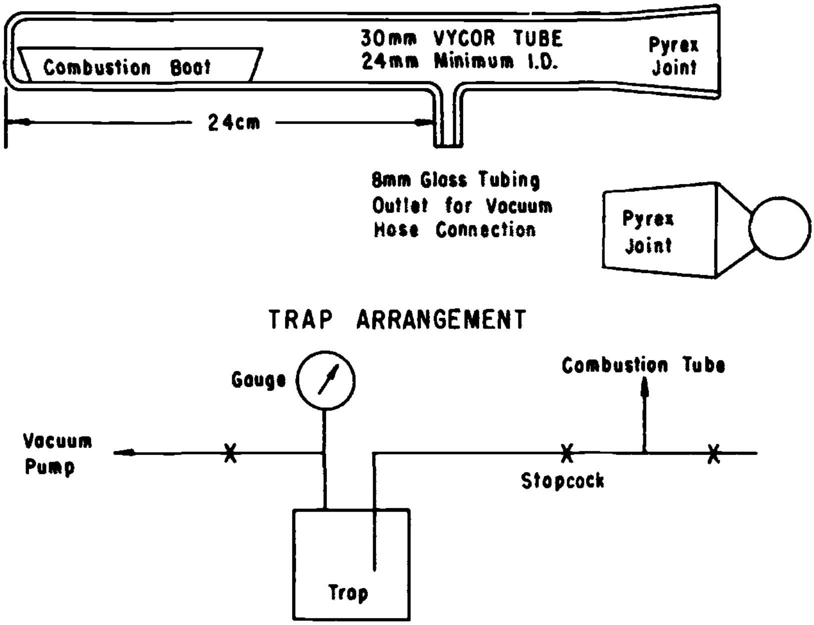

FIG. 4.2—Vacuum combustion tube and trap arrangement.

and the classification of the gel type are done by means of a specified collection of screens as shown in Fig. 4.3. This apparatus, while apparently simple, is quite ingenious in allowing the separation of the soluble and non-soluble material in one fairly simple test.

Gel is normally thought to be partially cross-linked or badly entangled chains within the rubber. Percent gel measures the insoluble material found in a polymer. This number is usually fixed by the polymerization process used. Changes may indicate that the process has been altered. Total gel is determined by allowing the polymer to dissolve in a special screen apparatus, then determining the amount that dissolved.

The swelling index measurement allows the determination of the type of gel. "Hard gel" (low swelling index) will be difficult to break down on a mill, and may not accept carbon black during mixing. "Loose gel" (high swelling index) can be broken down easily. The determination of whether polymer with a given swelling index can be used in a process will need to be determined from experience.

The dilute solution viscosity is a direct indication of the molecular weight of the polymer. It must be noted that solution viscosity is determined after the gel has been removed. The presence of gel often leads to factory mixing behavior that would not be predicted by the solution viscosity.

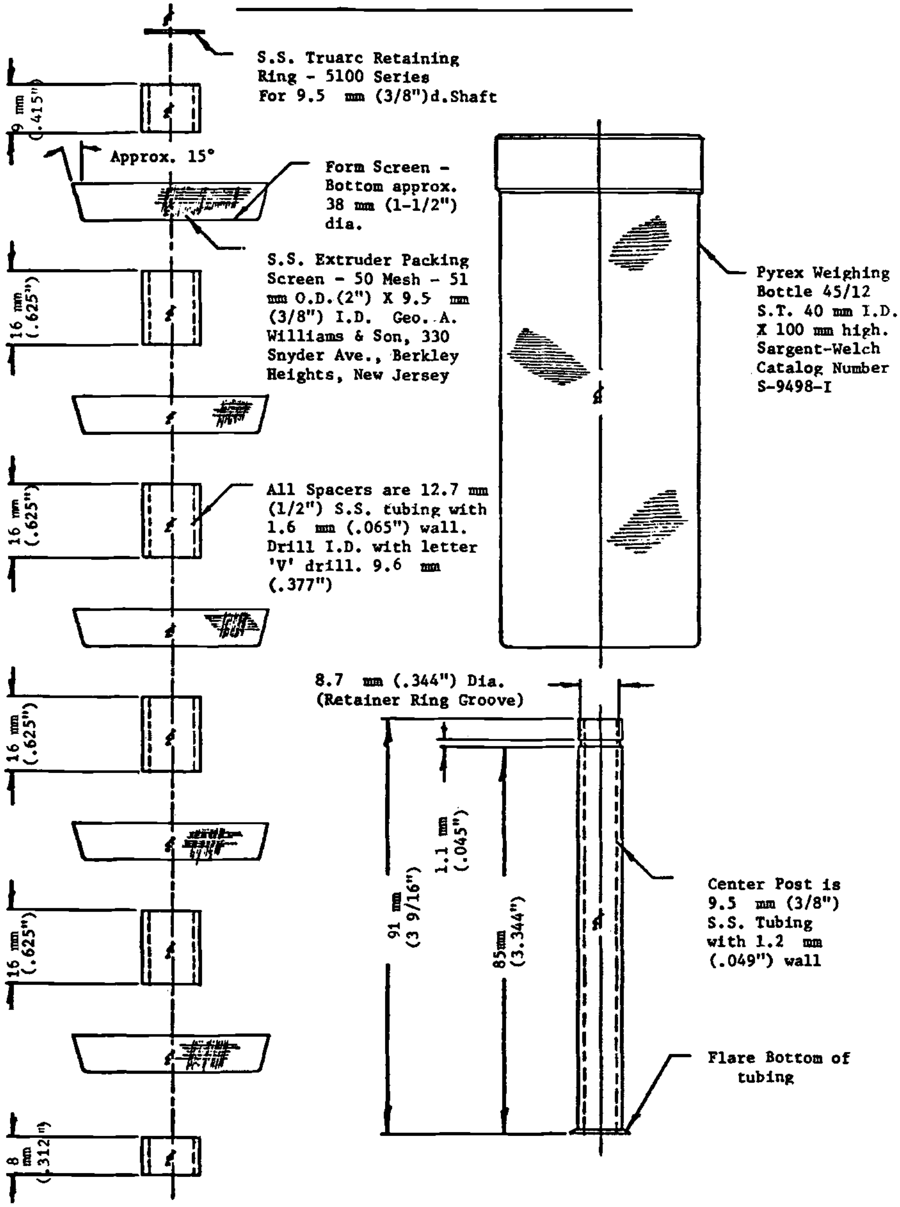

FIG. 4.3—Gel test apparatus.

4.6.6 Nitrogen Content of NBR (or HNBR)

ASTM Standard Test Method for Rubber—Nitrogen Content (D 3533) is known to be applicable both to natural rubber and synthetic rubbers. The only commonly used synthetic polymer that contains nitrogen is acrylonitrile-butadiene rubber, commonly known as nitrile rubber or NBR. This rubber also is sold in a hydrogenated form, known as HNBR. ASTM D 3533 describes both the macro and semimicro methods for Kjeldahl nitrogen determination. Note that in the scope of this method there is the cautionary statement that the amount of (or purity of) NBR or HNBR may be estimated, provided that there are no other nitrogen-containing species in the sample. These would include antioxidants as well as any natural rubber.

4.6.7 Test Methods for HNBR

4.6.7.1 Unsaturation of HNBR by Iodine Value The amount of unsaturation found in HNBR will determine its resistance to heat, ozone, and chemicals. That resistance is the chief reason that compounders use HNBR. However, a very saturated polymer is difficult to sulfur cure, requiring peroxide or radiation cure instead. A somewhat less saturated polymer can be cured more conventionally using sulfur. The balance, then, between resistance and ease of sulfur curing makes knowledge of the saturation level crucial. ASTM Standard Test Method for Rubber—Determination of Residual Unsaturation in Hydrogenated Nitrile Rubber (HNBR) by Iodine Value (D 5902), describes the use of Wijs solution for the determination of the unsaturation of the polymer. The test is a fairly straightforward titration method. The solution preparation and ratio of the components is critical to the success of this test. Directions for the preparation of the iodine solution are found in ASTM Test Method for Iodine Value of Drying Oils and Fatty Acids (D 1959) and the cautions noted there must be followed.

4.6.7.2 Unsaturation of HNBR by Infrared Spectrophotometry ASTM Standard Test Method for Rubber—Determination of Residual Unsaturation in Hydrogenated Nitrile Rubber (HNBR) by Infrared Spectrophotometry (D 5670) presents an alternative method for the determination of unsaturation, using infrared spectroscopy (IR) rather than a titration. While the method is straightforward, it requires some skill in IR, and as pointed out in Section 8, if certain bands are not balanced in their absorption, the results will be skewed toward too large unsaturation. It would be prudent, therefore, to determine samples in the range of interest by both ASTM D 5902 and ASTM D 5670 and compare the results with manufacturer's results before relying solely on ASTM D 5670 for this determination. Spectra in Fig. 4.4, taken from ASTM D 5670, illustrate the kinds of bands seen and the calculations necessary for this method.

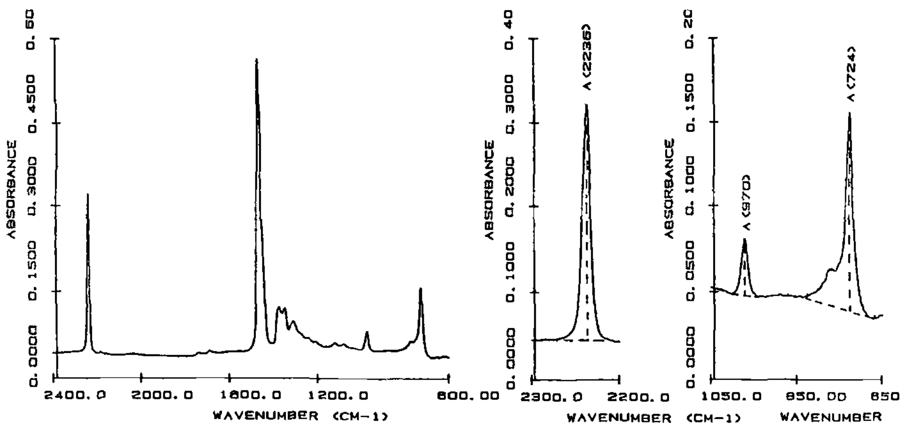

FIG. 4.4—Absorbance spectrum HNBR, medium ACN, partially unsaturated.

4.6.8 EPDM Tests

4.6.8.1 Percent ENB or DCPD in EPDM Terpolymers EPDM is the standard abbreviation (see ASTM D 1418) for a polymer consisting of ethylene, propylene, and a third diene monomer. Since this third monomer is unsaturated, its exact concentration determines the curing characteristics of the polymer as well as its cured physical properties. ASTM Standard Test Methods for Rubber, Raw—Determination of 5-Ethylidenenorbornene (ENB) or Dicyclopentadiene (DCPD) in Ethylene-Propylene-Diene (EPDM) Terpolymers (D 6047) is an infrared spectroscopy method for determining the amount of the third monomer as well as its identity (if unknown). The method states that previously this determination was done by refractive index, a method that is still valid if FTIR is unavailable or impractical. ASTM D 6047 also relies on the analyst having a series of known EPDM samples for calibration of the FTIR. Having those well-characterized samples depends on a relationship with a supplier of EPDM capable of making and analyzing such standards, preferably by nuclear magnetic resonance spectroscopy (NMR). ASTM D 6047 does, however, list in footnote 5 one source of calibration standards for ENB-containing polymer and one for DCPD-containing polymer.

4.6.9 SBR Tests

4.6.9.1 Bound Styrene in SBR The quantity of bound styrene in SBR polymer determines the processing properties not only of the raw polymer, but also has an impact on the physical properties of the compounded rubber, most notably because the styrene content directly affects the glass transition (Tg) of the polymer. ASTM Standard Test Method for Rubber from Synthetic Sources—Bound Styrene in SBR (D 5775) offers one method for determining the styrene content, using the relationship that has been established between the styrene content and the refractive index of the polymer. Note that there are two assumptions made in this method. The first is that the polymers of interest have only one microstructure in the polybutadiene portion. (Varying vinyl content, especially, will drastically change the refractive index even if styrene content is held constant.) In fact, the table in ASTM D 5775 was developed for the butadiene microstructure that is obtained from emulsion polymerized SBR. While the methodology is transferable to solution SBR of different microstructure, the refractive index table is not. A new table must be constructed for each differing microstructure.

The second assumption in ASTM D 5775 is that it is possible to extract completely all non-polymer contents from the polymer before determining the refractive index. Oil, soap, fatty acid, and any other non-polymer additives will change the refractive index of the mixture. When the polymer shrinks during extraction, trapping some of those non-polymer chemicals within the mass, the refractive index may be dramatically altered, thus leading to erroneous values for the bound styrene.

Alternative methods of determining the styrene content of SBR include infrared spectroscopy and NMR. Infrared spectroscopy would require standards of known microstructure to calibrate the instrument. NMR is a primary method.

4.6.10 Tests for CIIR or BIIR

4.6.10.1 Determination of Bromine in the Presence of Chlorine by Oxygen Combustion The halogenation introduced into an isobutene-isoprene rubber allows for some measure of compatibility with other types of elastomers. It is seldom necessary to determine the amount of bromine or chlorine in the presence of the other unless one is attempting to determine which one was used for the halogenation. On the other hand, ASTM Standard Practice for Rubber—Determination of Bromine in the Presence of Chlorine by Oxygen Combustion (D 3566) gives an outline of a straightforward method for the determination of the halogen that is known to be present. The sample is burned in a special oxygen combustion flask, the hydrohalic acid so formed is absorbed into liquid at the bottom of the flask and titrated with silver nitrate. Although other (instrumental) methods of determination of chlorine or bromine are available, this method is relatively quick, and has the advantage of low cost for infrequent users.

4.6.11 General Comment on Determination of Metals in Polymers

ASTM Standard Test Methods for Rubber—Determination of Metal Content by Flame Atomic Absorption (AAS) Analysis (D 4004) is sometimes quoted as the test method that was used to determine small amounts of metal impurities in synthetic rubbers. This is generally a misapplication of the test method. ASTM D 4004 is a determination by Atomic Absorption Spectroscopy (AAS) of metals that have been compounded into the rubber (for instance, zinc oxide used in a curative system), or which are found there in large quantities. The metals found in synthetic polymers are generally catalyst residues which will be found in much lower levels. The techniques found in ASTM D 4004 are not generally applicable to the determination of catalyst residues.

5

Testing Carbon Black

by Jeffery A. Melsom[1]

5.1 INTRODUCTION

CARBON BLACK IS A PRODUCT resulting from the partial combustion or thermal decomposition of hydrocarbons manufactured under controlled conditions. For partial combustion only one process is used today and that is via the carbon black "furnace" method, primarily using oil as the feedstock. Carbon black from the thermal decomposition process has limited use. It is produced in an air-free environment.

5.1.1 How is Carbon Black Used?

Carbon black has numerous uses within the rubber industry and accounts for the consumption of approximately 90% of all production. It is used primarily as a reinforcing filler. Within the tire industry, modulus, hysteresis, and wear and tear resistance can be controlled by careful selection of the carbon black. Additionally, the rubber industry can control abrasion and failure properties by choosing an appropriate black for items such as seals, hoses, and other consumer products.

5.1.2 What are Surface Area, Structures, and Surface Activity—Why are they important?

Surface area is that area of the carbon aggregate that can be measured indirectly by the adsorption of specific molecules. Three primary methods are used: Iodine Adsorption (ASTM D 1510); Total and External Surface Area by Nitrogen Adsorption (ASTM D 6556); and CTAB (Cetyltrimethyl Ammonium Bromide) Surface Area (ASTM D 3765). Porosity, residual hydrocarbons and the chemical nature of the carbon black surface may affect the mea-

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surement. Therefore, when interpreting test results, these factors must be taken into consideration.

Structure refers to the way carbon black is constructed. Structure is further explained by dividing carbon black into its fundamental parts: particles, aggregates, and agglomerates. The smallest nondiscrete carbon black component is the particle. Carbon black particles are spheroidally shaped and paracrystalline [1]. Particles make up the larger aggregates and are separated only by fracturing. Aggregates are the smallest discrete carbon black component and are made from the random construction of particles. The largest structures are agglomerates that are collections of aggregates, loosely bound but not fused together. The formation of agglomerates makes it much easier to disperse a carbon black in a rubber matrix where the agglomerates are broken down into aggregates. The difference between the three structures can be seen in the micrograph (Fig. 5.1) [2].

A high-structure carbon black is characterized by primary aggregates that contain many particles and considerable branching. Conversely, a low-structure carbon black consists of relatively few particles and is more compact (Fig. 5.2).

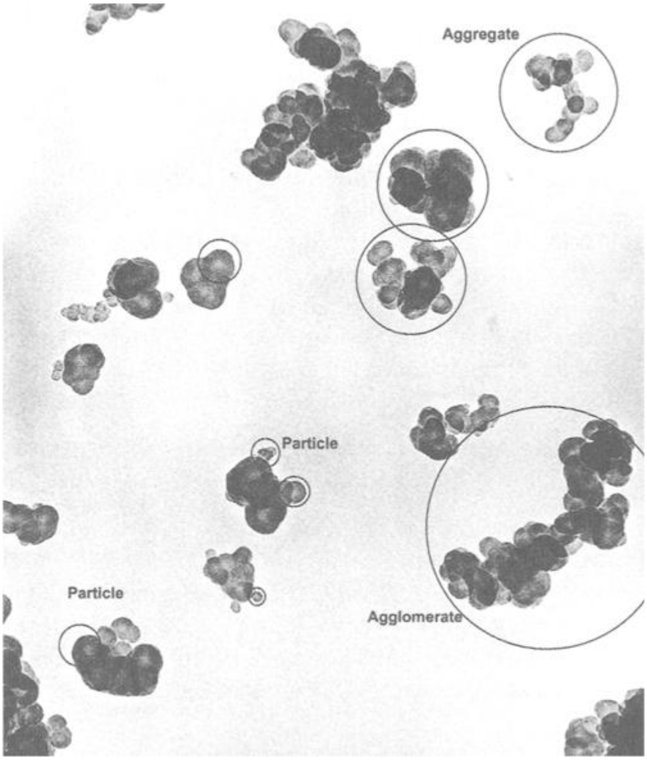
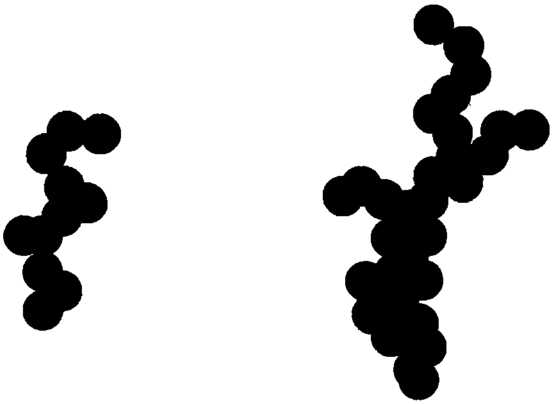


FIG. 5.1—Electron micrograph of carbon black particles, aggregates, and agglomerates.



Low Structure High Structure

FIG. 5.2—Comparison of low- and high-structure carbon black.

The area between and around primary aggregates is referred to as void space. A high-structure carbon black has more void space. Low-structure carbon blacks are more tightly packed and have higher interaggregate attractive forces, making them more difficult to disperse [3].

Surface activity is an elusive area to define and measure. No acceptable definition has been developed, although attempts have been made at creating such a definition. Several tests have been developed that are purported to be related to surface activity, but as yet there is no consensus [4].

5.2 CLASSIFICATION

5.2.1 Basis for Classification (D 1765)

Rubber grade carbon blacks are classified using a four-character designation. The first character can be either an "N" or an "S." The assigned letter designates the effect on the cure rate of a typical rubber compound containing the black. The cure rate may be normal–"N" or slow–"S." The vast majority of all carbon blacks assigned an ASTM designation are "N" type, typical of furnace technology. The "S" designation is used to define channel blacks or modified furnace blacks where the cure rate has been reduced. (Currently, there are only two "S" grades designated in ASTM D 1765: S212 and S315.) The second character is a single digit that defines the average surface area as measured by nitrogen surface area (ASTM D 4820). Ten groups have been defined to characterize the range of the surface areas. The groups are defined in Table 5.1.

The third and fourth characters are arbitrarily assigned by the chairman of Subcommittee D24.41, if the requestor has not asked for a specific designation.

Inherent in the assigning of an ASTM number is the definition of the target and typical values, normally provided by the requestor at the same time

TABLE 5.1—Carbon Black Classification (based on ASTM D 6556).

GROUP NO.	AVERAGE NITROGEN SURFACE AREA, m^2/g
0	>150
1	121 to 150
2	100 to 120
3	70 to 99
4	50 to 69
5	40 to 49
6	33 to 39
7	21 to 32
8	11 to 20
9	0 to 10

TABLE 5.2—Target Values of ASTM Designated Carbon Blacks.

PROPERTY	TEST PROCEDURE
Iodine Number	D 1510
Oil Absorption Number	D 2414

TABLE 5.3—Typical Values of ASTM Designated Carbon Blacks.

PROPERTY	TEST PROCEDURE
Total and External Surface Area by Nitrogen Adsorption	D 6556
Compressed Oil Absorption Number	D 3493
Tint Strength	D 3265
Pour Density	D 1513
Stress at 300 % Elongation, 30 min.	D 3192

an ASTM number is requested. The target and typical properties that define a particular carbon are shown in Tables 5.2 and 5.3.

The target values are agreed-upon values on which producers center their process and consumers center their specifications. Once an ASTM number is assigned, the target values are not changed.

Typical values further define a given carbon black and are dependent on the target values, but often vary between producers because of differences in equipment and process conditions. Rarely are all typical properties matched for a given grade between any two producers. Table 5.4 lists the ASTM grades with their target and typical properties.

5.3 STANDARD REFERENCE BLACKS

ASTM's Technical Committee on Carbon Black (D24) has developed a set of seven standard reference blacks (SRBs A-G)[2] that are to be used to monitor the precision of those carbon black test methods for which standard values

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[2] Standard reference blacks (SRBs) are available only from Laboratory Standards and Technologies, 227 Somerset Street, Borger, TX 79007. Website: www.carbonstandard.com.

TABLE 5.4—Carbon Black Properties.

NOTE 1—The iodine adsorption number and DBP number values represent target values. A target value is defined as an agreed upon value on which producers center their production process and users center their specifications. All other properties shown are averages of typical values supplied by several manufacturers. Typical properties are dependent upon the target values and may vary from producer to producer at the same iodine adsorption and DBP absorption numbers because of the differences in processing equipment.

NOTE 2—The cure rate of vulcanizates containing of carbon black compounded by Test Methods D 3192 may be measured by Test Method D 2804.

	TARGET VALUES^A		TYPICAL DESCRIPTIVE VALUES^A					
ASTM CLASSIFICATION	IODINE ADSORPTION NO.,^{B} D 1510 g/kg	OIL ABSORPTION NO. D 2414, 10^{-5} m^3/kg	OIL ABSORPTION NO. COMPRESSED SAMPLE, D 3493, 10^{-5} m^3/kg	NSA MULTIPOINT D 6556, 10^3 m^2/kg (m^2/g)	STSA D 6556 10^3 m^2/kg (m^2/g)	TINT STRENGTH, D 3265	POUR DENSITY, D 1513, (kg/m^3) (lb/ft^3)	Δ STRESS^C AT 300 % ELONGATION, MPA(PSI), CURED AT 145°C, D 412, D 3182, AND D 3192 30 MIN
N110	145	113	97	127	115	123	345 (21.5)	−3.2 (−470)
N115	160	113	97	137	124	123	345 (21.5)	−3.1 (−440)
N120	122	114	99	126	113	129	345 (21.5)	−0.4 (−60)
N121	121	132	111	122	114	119	320 (20.0)	−0.1 (−10)
N125	117	104	89	122	121	125	370 (23.0)	−2.6 (−380)
N134	142	127	103	143	137	131	320 (20.0)	−1.5 (−210)
N135	151	135	117	141	...	119	320 (20.0)	−0.4 (−60)
S212	...	85	82	120	107	115	415 (26.0)	−6.4 (−930)
N220	121	114	98	119	106	116	355 (22.0)	−2.0 (−280)
N231	121	92	86	111	107	120	400 (25.0)	−4.6 (−670)
N234	120	125	102	119	112	123	320 (20.0)	−0.1 (−10)
N293	145	100	88	122	111	120	380 (23.5)	−5.2 (−750)
N299	108	124	104	104	97	113	335 (21.0)	0.7 (90)
S315	...	79	77	89	86	117	425 (26.5)	−6.4 (−930)
N326	82	72	68	78	76	111	455 (28.5)	−3.6 (−530)
N330	82	102	88	78	75	104	380 (23.5)	−0.6 (−80)
N335	92	110	94	85	85	110	345 (21.5)	0.2 (30)
N339	90	120	99	91	88	111	345 (21.5)	0.9 (140)
N343	92	130	104	96	92	112	320 (20.0)	1.4 (210)

(continues)

TABLE 5.4—*(Continued)*

N347	90	124	99	85	83	105	335 (21.0)	0.5 (70)
N351	68	120	95	71	70	100	345 (21.5)	1.1 (160)
N356	92	154	112	91	87	106	...	1.4 (200)
N358	84	150	108	80	78	98	305 (19.0)	2.3 (330)
N375	90	114	96	93	91	114	345 (21.5)	0.4 (60)
N539	43	111	81	39	38	...	385 (24.0)	−1.3 (−180)
N550	43	121	85	40	39	...	360 (22.5)	−0.6 (−90)
N582	100	180	114	80	...	67		−1.8 (−260)
N630	36	78	62	32	32	...	500 (31.0)	−4.4 (−640)
N642	36	64	62	39	...	...		−5.4 (−780)
N650	36	122	84	36	35	...	370 (23.0)	−0.7 (−110)
N660	36	90	74	35	34	...	440 (27.5)	−2.3 (−330)
N683	35	133	85	36	34	...	355 (22.0)	−0.4 (−60)
N754	24	58	57	25	24	...		−6.6 (−960)
N762	27	65	59	29	28	...	515 (32.0)	−4.6 (−660)
N765	31	115	81	34	32	...	370 (23.0)	−0.3(−40)
N772	30	65	59	32	30	...	520 (32.5)	−4.7 (−690)
N774	29	72	63	30	29	...	490 (30.5)	−3.8 (−550)
N787	30	80	70	32	32	...	440 (27.5)	−4.2 (−610)
N907	...	34	...	9	9	...	640 (40.0)	−9.4 (−1360)
N908	...	34	...	9	9	...	355 (22.0)	−10.2 (−1480)
N990	...	43	37	8	8	...	640 (40.0)	−8.6 (−1250)
N991	...	35	37	8	8	...	355 (22.0)	−10.2 (−1480)

[A] See Note 1 above.

[B] In general, Test Method D 1510 can be used to estimate the surface area of furnace blacks but not channel, oxidized, and thermal blacks.

[C] Δ Stress = stress at 300 % elongation of test black minus the stress at 300 % elongation of IRB No. 7.

[D] New numbers are marked to designate that the requestor has a one-year period, starting from the number's approval date as shown in Footnote 1, to revise, by letter ballot, target and typical values.

have been established. These can also be used to help troubleshoot problems a laboratory may encounter when performing the different carbon black test methods. Two practices have been developed to assist a laboratory in validating the precision and bias of a test method and for improving their laboratory's reproducibility.

5.3.1 *Validation of Test Method Precision and Bias (ASTM D 4821)*

This practice covers the procedure for using ASTM Standard Reference Blacks (SRBs) to continuously monitor the precision of those carbon black test methods for which standard values have been established. It also offers guidelines for trouble-shooting various test methods. Within this guide, limits are established for which the statistical calibration procedure of ASTM Practice D 3324 can be applied. ASTM D 4821 also establishes the limits for an out-of-calibration condition beyond which the statistical calibration procedure of ASTM D 3324 cannot be applied. ASTM D 4821 uses statistical control charts, as discussed in *STP 15D*[3], to determine if a laboratory's test results differ significantly from the accepted values of the SRBs and provides a format for reporting test data for specified tests on the SRB blacks. These control charts are used to validate the testing precision and bias of an individual laboratory (Table 5.5).

One of the major causes of poor test precision is the lack of calibration or standardization of instruments, apparatus, reagents, and technique among laboratories. In addition to the calibration of a test method by physicochemical means, ASTM D 3324 describes a statistical method for achieving calibration of a test method.

5.3.2 *Improving Test Reproducibility Using ASTM Reference Blacks (ASTM D 3324)*

This practice provides a statistical procedure for improving test reproducibility. It is used when a laboratory cannot physically calibrate its apparatus to obtain the standard value of the ASTM reference blacks within the ranges given in the precision statement of the test method concerned. Table 5.5 defines the control chart limits when using SRB 6.

5.4 TESTS THAT RELATE TO SURFACE AREA (PARTICLE SIZE)

5.4.1 *Iodine Adsorption Number (ASTM D 1510)*

Iodine adsorption is one of the major characteristics of carbon black and one of the oldest surface area measurements used due to its simplicity. It is

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[3] Symposium on Manual on Presentation of Data and Control Chart Analysis, ASTM STP 15D, ASTM, 1976.

TABLE 5.5—SRB 6 Control Chart Limits.

TEST PROPERTY	ASTM STANDARD	SRB	TARGET VALUE	3 s VALUE	LOWER CONTROL LIMIT	UPPER CONTROL LIMIT
Iodine adsorption number,[A] g/kg	D 1510	A 6 (N134)	137.2	3.00	134.20	140.20
		B 6 (N220)	117.9	2.28	115.62	120.18
		C 6 (N326)	82.4	1.08	81.32	83.48
		D 6 (N762)	26.5	1.26	25.24	27.76
		E 6 (N660)	35.3	1.62	33.68	36.92
		F 6 (N683)	33.1	1.44	31.66	34.54
Dibutyl phthalate (DBP) absorption number, 10^{-5} m^3/kg ($cm^3/100$ g)	D 2414	A 6 (N134)	123.7	1.83	121.87	125.53
		B 6 (N220)	114.3	1.11	113.19	115.41
		C 6 (N326)	70.3	1.05	69.25	71.35
		D 6 (N762)	67.4	1.50	65.90	68.90
		E 6 (N660)	88.2	1.80	86.40	90.00
		F 6 (N683)	133.6	3.33	130.27	136.93
		G 5 (N990)	36.2	0.75	35.45	36.95
DBP absorption number of compressed sample (CDBP), 10^{-5} m^3/kg ($cm^3/100$ g)	D 3493	A 6 (N134)	101.0	2.46	98.54	103.46
		B 6 (N220)	98.5	1.80	96.70	100.30
		C 6 (N326)	68.1	1.59	66.51	69.69
		D 6 (N762)	60.2	1.59	58.61	61.79
		E 6 (N660)	76.0	2.49	73.51	78.49
		F 6 (N683)	88.6	2.58	86.02	91.18
Surface area by multipoint B.E.T nitrogen adsorption (NSA), 10^3 m^2/kg (m^2/g)	D 4820	A 6 (N134)	143.9	2.10	141.80	146.00
		B 6 (N220)	110.0	1.59	108.41	111.59
		C 6 (N326)	78.3	1.20	77.10	79.50
		D 6 (N762)	30.6	0.75	29.85	31.35
		E 6 (N660)	36.0	1.20	34.80	37.20
		F 6 (N683)	35.3	1.41	33.89	36.71
		G 5 (N990)	9.1	0.36	8.74	9.46
Tint Strength	D 3265	A 6 (N134)	129.8	4.11	125.69	133.91
		B 6 (N220)	117.8	3.36	114.44	121.16
		C 6 (N326)	113.1	1.68	111.42	114.78
		D 6 (N762)	56.8	2.01	54.79	58.81
		E 6 (N660)	60.0	1.92	58.08	61.92
		F 6 (N683)	51.7	1.47	50.23	53.17
External surface area by multipoint nitrogen adsorption (STSA), $10^3 m^2/kg$ (m^2/g)	D 5816	A 6 (N134)	135.7	4.11	131.59	139.81
		B 6 (N220)	105.4	2.88	102.52	108.28
		C 6 (N326)	79.2	2.07	77.13	81.27
		D 6 (N672)	29.6	1.35	28.25	30.95
		E 6 (N660)	35.1	2.31	32.79	37.41
		F 6 (N683)	34.1	1.83	32.27	35.93
		G 5 (N990)	8.4	0.60	7.80	9.00

one of the two major characteristics used to define the target values of a carbon black, as indicated in Table 5.2. The test itself is relatively quick, using classical "wet" chemistry, and requires only basic laboratory equipment. Because it is simple and rapid, most producers use the iodine test as one means to control their process. Residual hydrocarbons (from the feedstock), porosity, and surface oxidation can influence iodine adsorption. For low-volatile, nonporous carbon blacks, the iodine number correlates well with nitrogen surface area (NSA), Fig. 5.3. However, depression of the iodine number occurs for carbon blacks that are surface treated (oxidized), oil beaded, or con-

	Iodine	NSA
N110	145	130
N115	160	143
n120	122	126
n121	121	124
n125	117	122
n134	142	145
n135	151	141
n220	121	115
n231	121	111
n234	120	120
n293	145	130
n299	108	103
n326	82	78
n330	82	79
n335	92	85
n339	90	92
n343	92	96
n347	90	85
n351	68	71
n356	92	91
n358	81	82
n375	90	93
n539	43	40
n550	43	41
n582	100	80
n630	36	34
n642	36	39
n650	36	37
n660	36	35
n683	35	37
n754	24	25
n762	27	28
n765	31	36
n772	30	31
n774	29	29
n787	30	30

FIG. 5.3—Iodine number and NSA value correlation graph.

tain residual oil. Due to its simplicity and precision, the iodine number remains the most widely used control test for surface area.

5.4.2 Nitrogen Adsorption

Total and External Surface Area by Nitrogen Adsorption (ASTM D 6556) This test method is used to measure the total and external surface area of carbon blacks based on multipoint nitrogen adsorption. The NSA measurement is based on the Brunauer, Emmett, and Teller (B.E.T.) theory and includes the total surface area, inclusive of micropores, but excluding pore diameters less than 20 Å [5,6]. The external surface area, based on the Statistical Thickness Surface Area Method (STSA), is defined as the specific surface area that is accessible to rubber. This method is becoming the standard within the carbon black and rubber industry to define surface area. The STSA can be correlated to CTAB, thus essentially eliminating the need to perform the CTAB method.

5.4.3 CTAB (Cetyltrimethylammonium Bromide) Surface Area (ASTM D 3765)

This test method, until recently, was a primary method for measuring external surface area. It is based on the covering of the carbon black surface with a monolayer of CTAB molecules and then titrating the excess CTAB with dioctyl sodium sulfosuccinate. The amount of CTAB absorbed can be related to the surface area available for reaction with rubber. However, since this method is extremely sensitive to operator error and environmental conditions, it is not widely supported by either the carbon black or the rubber industries. Both industries are shifting to the more accurate STSA method described in ASTM D 6556.

5.4.4 Primary Aggregate Dimensions from Electron Microscope Image Analysis (ASTM D 3849)

This test method covers the morphological characterization of carbon black primary aggregates from transmission electron microscope images. The measurements are applicable to carbon blacks in the dry (as manufactured) state, extracted from unvulcanized rubber compounds and in a cellulose acetate butyrate paint chip dispersion. This method requires a substantial financial investment and a high level of expertise in electron microscopy, measurement, and interpretation of images. This type of testing is normally used in a research environment and not utilized in a typical quality control rubber laboratory.

5.5 TESTS WHICH RELATE TO STRUCTURE (AGGREGATES AND AGGLOMERATES)

5.5.1 Oil Absorption Number (ASTM D 2414)

This test method was more commonly referred to as DBP absorption. Recently the name has been changed to Oil Absorption because the method has been modified to include paraffin oil. The determination of a carbon black's oil absorption is the primary method for indirectly determining structure. The structure measured is the open areas of the aggregates where an oil, either DBP or paraffinic, can be absorbed by the carbon black. A high oil absorption value may indicate either very large structures or numerous smaller structures with accessible voids.

The test is carried out using an absorptometer that has a predefined mixing chamber volume with mixing blades set at 125 rotations/min and 250 rotations/min. Oil is titrated into the chamber using a constant-rate burette at 4 cm^3/min. As the void spaces are filled, the carbon black undergoes a transition from a free flowing powder to a semiplastic agglomerated mass, resulting in a sharp rise in viscosity and a subsequent increase in the torque. The absorptometer and burette automatically shut off at a selected torque level (normally 70 % of maximum torque), and the oil absorption value is reported as cm^3 of oil/100 g of carbon black.

The torque limit is set based on the value of a standard reference black (SRB F-6). The absorptometer is then calibrated using SRBs at various oil absorption levels. There are three possible methods available to establish the calibration of an absorptometer. The preferred procedure is to record the torque data using a chart recorder or a data acquisition system. From the curve, 70 % of the torque can be calculated. The classical procedure adjusts the torque limit switch or indicator set point in such a way that SRB F-6 falls within its defined target limits. This works well for hard (tread) blacks, but soft (carcass) blacks may still encounter a problem in cutting off. If the absorptometer doesn't cut off, then the torque limit switch or set point may be reduced. Normally a regression analysis of the measured versus the standard values is used to normalize raw results.

5.5.2 Oil Absorption Number of Compressed Sample (ASTM D 3493)

This method indirectly measures the structure after the agglomerates and aggregates have been broken down. This test simulates the typical breakdown a carbon black may encounter during mixing with rubber. The difference between oil absorption and compressed oil absorption can be an indicator of the stability of the structure. Typically the higher structure blacks (N121 and N234) show a greater reduction in oil absorption after compression than do lower structure blacks (N326 and N762). Another factor that can affect the amount of breakdown is the linearity of the carbon black structures. More linear structures typically don't breakdown as much as those exhibiting branching.

In this test the carbon black is compressed using a mechanical press that crushes a carbon black sample in a cylinder at 165 MPa (24 000 psi). The compression process is repeated four times. Each compression is broken up prior to the next compression. The oil absorption number is then measured per ASTM D 2414 using the calibration established using uncompressed SRBs.

5.5.3 Compressed Volume Index (ASTM D 6086)

The compressed volume index is defined as a normalized void volume expressed as the ratio (X 100) of the void volume measurement of a candidate carbon black to the void volume of a reference carbon black, SRB B5. Void volume is a measure of the irregularity and nonsphericity of carbon black aggregate particles. It is expressed as the difference between the compressed volume and the theoretical volume) for a mass of carbon black. The theory of the compressed volume index is widely accepted, but the method has not been adopted because of the unavailability of a reasonably priced and compact instrument.

5.6 PELLET QUALITY

5.6.1 Pour Density (ASTM D 1513)

The pour density is the measure of the mass to volume ratio of carbon black beads, typically reported in lb/ft^3. The pour density of carbon black is useful for estimating the weight-to-volume relationship for certain applications, such as automatic batch loading systems, and for estimating the mass of bulk shipments.

The test is conducted by pouring an excess of carbon black into a cylindrical container to a level approximately 50 mm (2 in.) above the rim. After the container has been filled and a cone formed, the container is leveled with a straightedge. The pour density is then calculated based on the volume of the container and the mass of carbon black in the container. The ASTM pour density test (ASTM D 1513) measures the mass, in grams, of a 624-cm^3 portion of carbon black. The grams of carbon black per 624 cm^3 is conveniently converted to lb/ft^3 by dividing by 10, see equation.

$$\frac{\times\ \text{g}}{624\ \text{cm}^3} \times \frac{2.54^3\ \text{cm}^3}{\text{in}^3} \times \frac{12^3\ \text{in}^3}{\text{ft}^3} \times \frac{\text{lb}}{453.6\ \text{g}} = 0.1\ \text{lb/ft}^3$$

5.6.2 Pellet Size Distribution (ASTM D 1511)

The pellet size distribution measures the variation in the size of the pellets. That variation may relate to the level of dispersion and to the ease of handling within a user's process. Because of many other variables that influence dispersion and handling, the user must determine the significance of the pellet size distribution within his process.

The test is conducted by stacking five sieves (Sieve Nos. 10, 18, 35, 60, and 120) on a receiving pan. A 100-g sample is placed in the top sieve, covered, and the entire assembly placed in a shaker. Care must be taken to assure the selected shaker does not impart enough energy to cause a fracturing of the pellets during the test. The carbon black is shaken for a set time, dependent on the type shaker, and the distribution calculated based on the amount retained by each sieve.

5.6.3 Pelleted Fines and Attrition (ASTM D 1508)

The fines content of carbon black is related to the bulk flowability, dustiness, and, in some instances, the level of dispersion, while attrition can be an indication of pellet stability. The initial amount of fines generated during manufacturing and the subsequent fines generated in conveying, handling, and transporting the carbon black may have a direct impact on the user's ability to transfer or disperse the material. Each user must determine the effects of fines and attrition within their process.

The test for fines is conducted by placing a 25-g sample in a Standard No. 120 sieve with a receiving pan. The sample is then shaken for 5 min. Weigh the material collected in the receiving pan. Any material passing through the sieve into the receiving pan is considered to be fines. Attrition is determined by reassembling the sieve, using the same sample, and shaking for an additional 15 min then reweighing.

5.6.4 Sieve Residue (ASTM D 1514)

The quantity of water-washed sieve residue of carbon black is important in some molded or extruded products as it may relate to the surface appearance of those products. Sieve residue, depending on the application and if sufficiently high, may be considered a contamination. The maximum residue in each application is normally determined and agreed upon between the user and the manufacturer.

A second purpose for measuring sieve residue is to determine the source of the residue. Many suppliers can analyze the residue and determine its source and then correlate it back to the condition of their equipment. Tracking the amount of sieve residue and understanding its origin can assist the manufacturer in predicting the effects on their process, determining equipment condition, and predicting unscheduled maintenance.

5.6.5 Individual Pellet Hardness

Pellet hardness is an important property for predicting the handling properties of a carbon black. Soft beads may fracture during the transportation or conveying process, resulting in the formation of fines, while hard beads may not be adequately broken down in mixing, resulting in poor dispersion. Ideally, the carbon black bead should be hard enough to withstand shipping and conveying, yet soft enough to facilitate easy dispersion.

Pellet hardness or crushing strength is the measure of force required to fracture a carbon black bead. A minimum of 20 beads in the 12 to 14 mesh size range (1.4 to 1.7 mm) is evaluated with the average, maximum, and minimum individual pellet hardness values reported. Certain grades of carbon black may not contain enough beads in the 12 to 14 mesh size range; therefore, smaller fractions are used, for example, 18 to 35 mesh (0.5 to 1.0 mm).

Within a given carbon black sample, the smaller beads are softer; therefore, when comparing samples it is imperative to use the same bead size fraction for pellet hardness measurements [8].

5.6.5.1 Individual Pellet Hardness (ASTM D 3313) Pellet hardness (or pellet crush strength) can be related to several carbon black characteristics. Among these are mass strength and attrition. The subsequent level of dispersion obtained in some mixed compounds containing the carbon black may be affected by pellet crush strength. The user and the producer must agree on acceptable pellet hardness properties.

This test is very time consuming and can be significantly influenced by the operator. Because of this and the availability of automated test equipment, ASTM Committee D24 recommends the automated procedure be used (D 5239).

5.6.5.2 Automated Individual Pellet Hardness (ASTM D 5230) This test method covers a procedure for measuring the crush strength of individual pellets of carbon black using an automated pellet hardness tester. Pellet hardness (or pellet crush strength) can be related to several carbon black characteristics. Among these are mass strength and attrition. The subsequent level of dispersion obtained in some mixed compounds containing the carbon black may be affected by pellet crush strength. The user and the producer must agree on acceptable pellet hardness properties.

5.6.5.3 Mass Strength (D 1937) This test method covers the determination of the mass strength of pelleted carbon black. Mass strength gives an indication of the flowability in bulk handling systems. Due to the vast differences in the handling systems and the influence of other variables, acceptable mass strength levels must be determined between the user and the producer.

Mass strength is determined using a piston to compress a volume of carbon black, contained in a cylinder, to a point where the carbon black will not flow when the bottom plate of the cylinder is removed. The minimum force required to impede the flow is reported as the mass strength. As a general rule, higher fines content decreases the mass strength.

5.7 RUBBER TEST RECIPES AND PROPERTIES

5.7.1 Carbon Black in Styrene-Butadiene Rubber—Recipe and Evaluation Procedure (ASTM D 3191) and Carbon Black Evaluation in Natural Rubber (ASTM D 3192)

The major portion of carbon black consumed by the rubber industry is used to improve the physical properties, life expectancy, and utility of rubber products. These two methods cover the standard materials, test formulation, mixing procedure, test methods, and directions for evaluating carbon black intended for use in synthetic elastomers and natural rubber (NR) formulations.

These test methods may be used to characterize carbon black in terms of specific properties of the standard compound. These test methods are useful for the quality assurance of carbon black production. They may also be used

TABLE 5.6—List of ASTM Carbon Black Test Methods Procedures.

ASTM DESIGNATION	ASTM TITLE
D 1506	Standard Test Methods for Carbon Black—Ash Content
D 1508	Test Method for Carbon Black, Pelleted Fines and Attrition
D 1509	Standard Test Methods for Carbon Black—Heating Loss
D 1510	Standard Test Method for Carbon Black—Iodine Adsorption Number
D 1511	Standard Test Method for Carbon Black—Pellet Size Distribution
D 1512	Standard Test Methods for Carbon Black—pH value
D 1513	Standard Test Method for Carbon Black, Pelleted—Pour Density
D 1514	Standard Test Method for Carbon Black—Sieve Residue
D 1618	Standard Test Method for Carbon Black Extractables—Transmittance of Toluene Extract
D 1619	Standard Test Methods for Carbon Black—Sulfur Content
D 1765	Standard Classification System for Carbon Blacks Used in Rubber Products
D 1799	Standard Practice for Carbon Black—Sampling Packaged Shipments
D 1900	Standard Practice for Carbon Black—Sampling Bulk Shipments
D 1937	Standard Test Method for Carbon Black, Pelleted—Mass Strength
D 2414	Standard Test Method for Carbon Black—Oil Absorption Number
D 2663	Standard Test Methods for Carbon Black—Dispersion in Rubber
D 3053	Standard Terminology Relating to Carbon Black
D 3191	Standard Test Methods for Carbon Black in SBR (Styrene-Butadiene Rubber)—Recipe and Evaluation Procedures
D 3192	Standard Test Methods for Carbon Black Evaluation in NR (Natural Rubber)
D 3265	Standard Test Method for Carbon Black—Tint Strength
D 3313	Standard Test Method for Carbon Black—Individual Pellet Hardness
D 3324	Standard Practice for Carbon Black—Improving Test Reproducibility Using ASTM Reference Blacks
D 3493	Standard Test Method for Carbon Black—Oil Absorption Number of Compressed Sample
D 3765	Standard Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area
D 3849	Standard Test Method for Carbon Black—Primary Aggregate Dimensions from Electron Microscope Image Analysis
D 4122	Standard Practice for Carbon Black—Evaluation of an Industry Reference Black
D 4527	Standard Test Method for Carbon Black—Solvent Extractables
D 4583	Standard Practice for Carbon Black—Calculation of Process Indexes from an Analysis of Process Control Data
D 4821	Standard Guide for Carbon Black—Validation of Test Method Precision and Bias
D 5230	Standard Test Method for Carbon Black—Automated Individual Pellet Hardness
D 5817	Standard Practice for Carbon Black, Pelleted—Reduction and Blending of Gross Samples
D 6086	Standard Test Methods for Carbon Black—Compressed Volume Index
D 6556	Standard Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption
D 6602	Standard Practice for Sampling and Testing of Possible Carbon Black Fugitive Emissions or Other Environmental Particulate, or Both

for the preparation of reference compounds to confirm the day-to-day reliability of testing operations used in the rubber industry for the evaluation of experimental compounds and quality control of production compounds.

ASTM Committee D24 has 34 active standards applicable to carbon black. Table 5.6 lists the active carbon black standards.

REFERENCES

Note: Many of the significant uses and test descriptions are direct quotations from ASTM's *Annual Book of ASTM Standards, Section Nine, Rubber, Vol. 09.01. 2000.*

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[4] Magee, R. W., Columbian Chemicals Co., Marietta, GA.
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[6] Brunaer, Emmet, and Teller, *Journal of American Chemical Society,* Vol. 60, 1938, p. 309.
[7] Magee, R. W., *Rubber Chemistry and Technology,* Vol. 68, No. 4, 1995, p. 590.
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6

Testing Silica and Organosilanes

by Jeffery A. Melsom[1]

6.1 INTRODUCTION

Silica (Silicon Dioxide—SiO_2) is an ever-increasing raw material used in rubber compounds. In recent years silica usage has increased in the rubber industry, especially in the tire industry. As a non-black filler, silica provides improvements in adhesion, abrasion resistance, age resistance, and tear strength. Because of these property improvements, silica is used as a reinforcing filler replacing carbon black, but more often used in conjunction with carbon black. In many applications, silica is used with an organosilane coupling agent. Because they are so closely linked, the two are discussed together in this section.

Silica properties are in many instances characterized using the same techniques used to describe carbon black. In fact, many of the silica tests were derived directly from tests developed in ASTM's Technical Committee D24 on Carbon Black.

6.2 SILICA TYPES

Silica is classified into two general types: fumed (pyrogenic or anhydrous) silica and precipitated hydrated silica. Their names are derived from the way they are manufactured. Fumed silica is produced by reacting silicon tetrachloride with water at a high temperature in a hydrogen-oxygen furnace.

$$(SiCl_4 + 2\,H_2O \rightarrow SiO_2 + 4\,HCl)$$

Immediately after exiting the furnace, the product is quenched, washed, and then dried. The resulting silica is highly active, very pure (> 99 %), very

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[1] Michelin Tyre Research & Development Centre (Shanghai) Co., Ltd., 2915 Jian Chuan Road, Ming Hang Development Zone, Shanghai, 201111 P. R. China.

fine (7–15 nm) and with less than 1 % water. Because of high reactivity, difficulties in compounding and higher cost, fumed silicas are not normally used in most general-purpose rubber applications. They are used mainly in silicone rubber applications. Fumed silicas are very stable at high temperatures, have good electrical properties, and good transparency, which are important properties for silicone rubber products.

Precipitated hydrated silica is produced using a two-step process. In the first step, melted sand is reacted with sodium carbonate (Na_2CO_3). The resulting sodium silicate is dissolved in water, producing a solution of "water glass." In the second step, the sodium silicate solution is neutralized with an acid (normally H_2SO_4), thus precipitating the silica. It is in this precipitating stage that the morphology, and chemical characteristics are determined. The resulting salts are washed out and the precipitated silica is filtered and dried. Once dried, the silica may be further processed, resulting in a better physical form for compounding and handling. Precipitated silica has a particle size between 7–100 nm. It is much easier to compound and significantly less expensive than fumed silicas. Therefore, precipitated hydrated silica is the most common type of silica used in the general rubber industry.

6.2.1 Silica Applications versus Carbon Black

Silica has numerous uses within the rubber industry (primarily as precipitated hydrated silica), and is used mainly as a reinforcing filler. Within the rubber industry, modulus, hystersis, wear and tear resistance can be improved by the careful selection and formulation of silica. In most cases it is also necessary to use a coupling agent (organosilane) to obtain the improved properties.

6.2.2 Classification

ASTM Technical Committee D11.20 on Rubber Compounds has not developed a classification system for silicas used in the rubber industry. This is an item under discussion and will be addressed in future technical committee meetings. Before any discussions can progress in this area, good test methods must be available with precision and bias statements. Within the last two years, four new methods were developed and approved to characterize precipitated silica. Thus Committee D11.20 is continuing their work in developing the precision and bias statements for these new methods.

ISO Technical Committee 45 has developed a basic classification system for silicas in general. They have classified silicas into six different categories: A–F based on the single point nitrogen surface area procedure (ISO 5794-1:1994(E)—Annex D). In ISO 5794-1 (Annex E) the following categories have been defined in Table 6.1.

ISO has defined "Typical Values of Physical and Chemical Properties" for precipitated hydrated silicas. They only reference general values that are

TABLE 6.1—A Basic Classification System for Silicas.

GRADE	NITROGEN SURFACE AREA, m^2/g
A	> 191
B	161 to 190
C	136 to 160
D	106 to 135
E	71 to 105
F	< 70

typical of all rubber grade silicas. There does not exist a silica classification system, as is defined for carbon black in ASTM D 1765.

6.3 SURFACE AREA

Surface area is a measurement of particle size. It is that area of the aggregate that can be indirectly measured by the adsorption of specific molecules. Within the silica and rubber industries, three primary methods are used: single point BET Nitrogen Adsorption (D 5604); multipoint BET nitrogen adsorption (D 1993); and CTAB (cetyltrimethyl ammonium bromide) surface area (D 6845).

6.3.1 Surface Area by BET Nitrogen Adsorption

The most common method for determining the surface area is by measuring the nitrogen surface area either by single point or multipoint BET. The principle applied is that solids adsorb nitrogen and, under specific conditions, the adsorbed molecules approach a monomolecular layer. The quantity of gas adsorbed in the monomolecular layer can be calculated using the BET equation. From knowing the nitrogen molecule's area, an approximation of the total surface area of the silica can be calculated.

Before the surface area can be determined, it is necessary to remove any material that may already be on the surface. Removal of this material (usually by heating under vacuum) is essential because it can be the source of two potential errors. The first error can affect the mass and the second error can interfere with the nitrogen's access to the silica surface.

6.3.1.1 Surface Area by Single Point B.E.T. Nitrogen Adsorption (D 5604) This standard test method measures the surface based on a single partial pressure of 0.30 ± 0.01 kPa. The time required to run a single point test is less than that of the multipoint but can be less accurate due to the affect of the surface properties. However, because the equipment and test are simpler, it may be adequate for quality control depending on the requirements of the producer and the customer.

6.3.1.2 Surface Area by Multipoint B.E.T. Nitrogen Adsorption (D 1993) This standard test method measures the surface based on several (usually five) partial pressures of nitrogen. The time required to determine a multipoint test is greater than that of single point but provides a more accurate representation of the surface area. The level of accuracy and need to know the actual surface area is normally decided between the producer and the customer.

6.3.2 Surface Area by CTAB (Cetyltrimethylammonium Bromide)

6.3.2.1 CTAB (Cetyltrimethylammonium Bromide) Surface Area (D 6845) This is a new test method being defined within Subcommittee D11.20. It is based on D24's CTAB method D 3765. It is a method for measuring external surface area more closely related to the area available to rubber. It is based on the covering of the silica aggregate with a monolayer of CTAB molecules and then titrating the excess with dioctyl sodium sulfosuccinate. The amount of CTAB adsorbed can be related to the surface area available for reaction with rubber. This method is extremely sensitive to operator error and environmental conditions.

6.4 STRUCTURE (AGGREGATES AND AGGLOMERATES)

6.4.1 n-Dibutyl Phthalate Absorption Number (D 6854)

This procedure is currently under development and the exact conditions have not been finalized nor approved. But as with carbon black, this test method is more commonly referred to as DBP absorption and is the primary method for indirectly determining structure. The structure measured is the open areas of the aggregates where DBP can be absorbed by the silica. A high DBPA value may indicate either very large structures or numerous smaller structures with accessible voids.

The test is carried out using an absorptometer (commercially available from two manufacturers) that has a pre-defined mixing chamber volume with mixing blades set at 125 r/min and 250 r/min. DBP is titrated into the chamber using a constant-rate buret at 4 cm^3/min. As the void spaces are filled, the silica undergoes a transition from a free flowing powder to a semi-plastic agglomerated mass, resulting in a sharp rise in viscosity and a subsequent increase in the torque. The absorptometer and buret automatically shut off, at a selected torque level, and the DBPA value is reported as cm^3 of DBP/100 g of silica. An internal silica sample with a nitrogen surface area of 175 ± 10 m^2/g is used to set the torque limit alarm, which should correspond to approximately 70 % of the maximum torque, developed during the test.

6.5 GENERAL METHODS

6.5.1 Volatiles (D 6738)

The volatile content of silica is very important. Normally, precipitated hydrated silica contains 5–9 % volatile water. This is water that can be removed at 105°C, which differs from bound water. The amount of residual water can affect the compounding and the compound properties.

6.5.2 pH Value (D 6739)

The pH value of a silica is known to affect the vulcanization of some rubber compounds. The pH is measured in a 5 % aqueous slurry, which is measured after the pH has stabilized. Time is important because potential differences can be obtained based solely on how long the silica is in contact with the water. The pH value is just as important as particle size in determining final compound properties.

6.6 ORGANOSILANES

The use of organosilanes is critical to rubber compounding with silicas. Silica alone may not provide the necessary reinforcement and may require the use of a silane coupling agent. The improved properties obtained are based on a combination of the silica properties and type of coupling agent used.

6.6.1 Determination of Residue on Ignition (D 6740)

The residue on ignition, which consists essentially of SiO_2, is related to the silicon content of the silane. The method may be used to verify the composition of the silane. In this test method, a sample of the silane is carefully treated with hydrochloric acid and then ignited in a muffler furnace at 1000°C. The mass retained is expressed in % of the initial mass.

6.6.2 Determination of Sulfur in Silanes (D 6741)

The sulfur content can be used to characterize a silane or an admixture of silane and carbon black. There are two methods used to determine the amount of sulfur. The first is by oxygen combustion and titration of the resulting sulfate. The second is by combustion in a high temperature oven and then measuring the sulfur dioxide, using an infrared absorption detector. Automated equipment on the market favors using the second method over the first, as test time can be reduced to less than two minutes.

TABLE 6.2—List of ASTM Silica (Precipitated, Hydrated) and Organosilanes Test Methods.

ASTM DESIGNATIONS	ASTM TITLES
D 1993	Test Method for Precipitated Silica—Surface Area by Multipoint BET Nitrogen Adsorption
D 5604	Test Method for Precipitated Silica—Surface Area by Single Point BET Nitrogen Adsorption
D 6738	Standard Test Methods for Precipitated Silica—Volatile Content
D 6739	Standard Test Methods for Precipitated Silica—pH Value
D 6740	Test Method for Silanes Used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes)—Residue on Ignition
D 6741	Test Method for Silanes Used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes)—Sulfur Content
D 6843	Test Method for Bis-Triethoxysilylpropyl Sulfanes—Characterization by GC
D 6844	Test Method for Bis-Triethoxysilylpropyl Sulfanes—Characterization by HPLC
D 6845	Test Method for Silica, Precipitated, Hydrated—CTAB (Cetyltrimethylammonium Bromide) Surface Area
D 6854	Test Method for Precipitated Silica—*n*-Dibutyl Phthalate Absorption Number

6.6.3 *Silanes used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes): Characterization by High Performance Liquid Chromatography—(D 6843)*

This test method characterizes silanes of the type bis-(triethoxysilylpropyl)sulfane by high performance liquid chromatography (HPLC). In this test method, a sample of the silane is analyzed by HPLC to determine the polysulfide distribution. From the distribution, each sulfur chain and the average chain is calculated. Furthermore, from the chromatograph the amount of free elemental sulfur can be determined. The amount of additional components, reflects the purity of the product and, as a consequence, its behavior in a rubber compound.

6.6.4 *Silanes used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes): Characterization by Gas Chromatography—(D 6844)*

This test method covers the characterization of silanes of the type bis-(triethoxysilylpropyl)sulfane by Gas Chromatography (GC). In this test method, a sample of the silane is analyzed by GC in order to determine the amount of additional, volatile components. From the peak areas in the chromatograph, the amount (in weight %) is calculated taking into account individual response factors.

Table 6.2 lists all the current methods available for silica and silane usage in rubber compounding under the jurisdiction of Committee D11.

NOTE: Many of the significant uses and test descriptions are direct quotations from the methods themselves that can be found in ASTM's *Annual Book of ASTM Standards, Section Nine, Rubber, Vol. 09.01.*

7

Testing Mineral Fillers for Use in Rubber

by John S. Dick[1]

7.1 GROUND COAL

GROUND COAL IS USED AS A COMPOUNDING INGREDIENT mainly in the United States in certain rubber formulations. It is used as an inexpensive filler to partially replace carbon black or as an economical diluent in rubber compounds.

Even when used as a diluent in rubber formulations, this material, in many cases, should still conform to cited quality specifications to help partially ensure satisfactory product performance. To help ensure that the rubber industry receives ground coal of adequate quality, ASTM D11.20 Subcommittee on Compounding Materials in 1993 published a classification document as ASTM D 5377, which is shown in Table 7.1.

This standard classifies ground coal for use in the rubber industry, based on the following characteristics:

- Particle size
- Ash
- Alpha quartz
- Moisture
- Acidity
- Volatile matter
- Density

7.1.1 Particle Size

All ground coal grades that are used in the rubber industry as compounding ingredients go through some sort of grinding process. The more efficient or complete the grinding, usually the smaller the average particle size. If the grinding is not sufficient, there will be too many relatively large-size

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[1] Akron OH, www.rubberchemist.com

TABLE 7.1—Properties of Ground Coal.

Property (Maximum Values)	Grade I	Grade II	Grade III	Test Method
Average particle size (μm) not weighted	5	6	7	C 1070
Top particle size (μm)	20	24	28	C 1070
Retained on 325 mesh (g)	0.0100	0.0450	0.0950	[A]
Retained on 100 mesh (g)	0.0003	0.0005	0.0010	[A]
Ash,%	5	6	7	D 3174
Alpha quartz,%	1.0	1.50	2.0	X-Ray Diffraction
Heat loss, % (moisture)	0.5	0.75	1.0	D 3174
Acidity	0.02	0.02	0.02	D 1208
Volatile matter,%	20	20	20	D 3175
Density (Mg/m^3) (specific gravity)	1.35	1.45	1.55	D 4371

[A] Method is being letter balloted in Subcommittee D11.11. Values based on 100 g samples.

particles in the distribution that can cause stress points in a vulcanizate during normal deformations, resulting in tear initiation and propagation as well as poor flex fatigue. Also, by applying more effective grinding, the resulting average for the size distribution of the ground coal particles will be lower. A smaller average particle size means a higher surface area interfacing in the rubber medium when the ground coal is added as a compounding ingredient. This means that a finer particle-size grade of ground coal can impart better physical properties, such as tear strength, modulus, and ultimate tensile strength to the cured rubber compound. A finer particle-size coal may also increase a rubber compound's viscosity somewhat. This could have a small effect on processing in the factory.

ASTM D 5377 calls for particle-size distribution of ground coal grades to be measured by laser light scattering in accordance with ASTM C 1070. Several companies make test instruments that can measure the particle size of powders such as ground coal by this method. Each instrument manufacturer uses their own proprietary computer algorithm to convert the light-scattering data into particle-size distribution information. For ground coal, these algorithms are usually based on the optical theory of Fraunhofer Diffraction, which describes the low-angle scattering of light by particles, that are significantly larger than the wavelength of the incident light itself. (If the particles were close in size to the wavelength of light, a different theory called Mie Scattering would be applied.) Usually, the assumption of spherical equivalents is applied even though some of the measured particles may be quite nonspherical.

These light-scattering particle-size measurements are commonly made with different instruments throughout the world. Thus, it is not possible to achieve perfect agreement among laboratories. This is because ASTM C 1070 does not describe an accepted absolute standard. Some of the reasons for interlaboratory bias are given below.

1. Some instruments have "built in" ultrasonic baths to facilitate better dispersion, while others do not have such features. Otherwise, dispersions must be completed externally through ultrasonic probes, baths, etc.
2. Different instrument manufacturers use different computer algorithms to calculate particle size.

It should be noted that conditions of sample preparation in an aqueous medium can differ. Problems that can bias results include: (1) air bubbles, which will scatter light, and (2) reagglomeration of the filler, or settling of the particles while analysis is being performed.

From ASTM C 1070 testing, ASTM D 5377 classifies ground coal into Grade I, Grade II, and Grade III based on the average particle size (in μm units) and the "top particle size" (also in μm units).

7.1.2 *Sieve Testing*

This test is an inexpensive method of measuring the presence of very large particles that might be present in the ground coal. Typically, the percent retained on either a 325-mesh screen or the coarser 100-mesh screen is measured quantitatively. Sieve testing measures only the extreme end of the particle-size distribution; this method cannot measure or calculate the average distribution. However, from a quality perspective it is very important to know what weight fraction of the particles is over a certain dimension. This is because these very large particles (or impurities) can result in stress points and initiate cracks in a rubber product during dynamic deformations, which can cause premature failure. A percent of particles retained on a 325-mesh screen by definition means that particle sizes are bigger than 45 μm. From a rubber-compounding perspective, these large particles are like "boulders" and can result in deterioration of cured physicals. This is even more true with retains on a 100-mesh screen.

7.1.3 *Ash*

Percent ash is another test recommended by D 5377. Percent ash is important because a high value can indicate a higher specific gravity and can ultimately affect curing characteristics of the rubber compound.

ASTM Method D 3174, for measuring ash of coal and coke, is recommended. This method calls for the analytical weighing of a specified quantity of the ground coal and transferring it to a porcelain or platinum capsule. This capsule is placed in a special electric muffle furnace for coal set at room temperature. This furnace is programmed to rise in the first hour to about 450 to 500°C and then to a final temperature of 700 to 750°C by the end of the second hour. The heating of the sample continues at this final temperature for another 2 h, after which the capsule is removed, a cover is placed on the capsule, and it is cooled under conditions of minimum moisture exposure. After cooling, the capsule is reweighed.

High ash is usually a sign of inorganic impurities, including alpha quartz, which is discussed next.

7.1.4 *Alpha Quartz*

The alpha quartz is usually part of the ash results obtained from D 3174. However, it is important to determine exactly the actual amount in the ground coal because alpha quartz is recognized as an IARC carcinogen. (IARC stands for International Agency for Research on Cancer [1].) Therefore, there are government regulatory limits on the worker exposure level allowed for alpha quartz. For more details concerning these worker health and safety risks, consult the supplier's Material Safety Data Sheet (MSDS).

ASTM D 5377 recommends that an X-ray diffraction method be used to directly measure the amount of alpha quartz present in the ground coal being used.

7.1.5 *Heat Loss (moisture)*

This test can be used to monitor and control moisture content of shipments of ground coal received by a rubber fabricator. Excessive levels of water content can lead to blister problems with rubber products and also affect scorch characteristics of the rubber compound itself.

7.1.6 *Acidity*

This test, which measures the percent acid impurity that is present in a sample of ground coal, is conducted in accordance with ASTM D 1208 by a straightforward acid-base titration. As can be seen from the D 5377 classification document, the different grades of ground coal all have low levels of acidity. Any significant acidity content will drastically affect scorch and cure characteristics of a rubber compound.

7.1.7 *Volatile Matter*

This property is a characteristic feature of different types of coal [2]. It relates to the percent "gaseous products," excluding moisture vapor, which the coal contains. For example, different sources of bituminous coals may have a characteristic level of volatile matter. Variations in volatile matter can usually be associated with a density variation in the coal as well. According to ASTM D 5377, the ground coal grades that are used in rubber will typically have a volatile matter value of approximately 20 %. Coals with different volatile matter values may display different grinding characteristics while being processed into ground coal for rubber compounding use.

ASTM D 3175, used to measure the volatile matter in coal, employs a special electric furnace as shown in Fig. 7.1.

In performing this test, a ground coal sample is placed in a special platinum crucible with a closely fitting cover. This closely fitting cover is important. If it does not fit closely, the carbonaceous residue will burn off, giving erroneous results. This crucible is quickly placed in the special electric furnace, which is preset at 950°C. The covered crucible is kept in the furnace for exactly 7 min and then removed. Percent volatile matter is calculated from the percent weight loss minus the percent moisture loss.

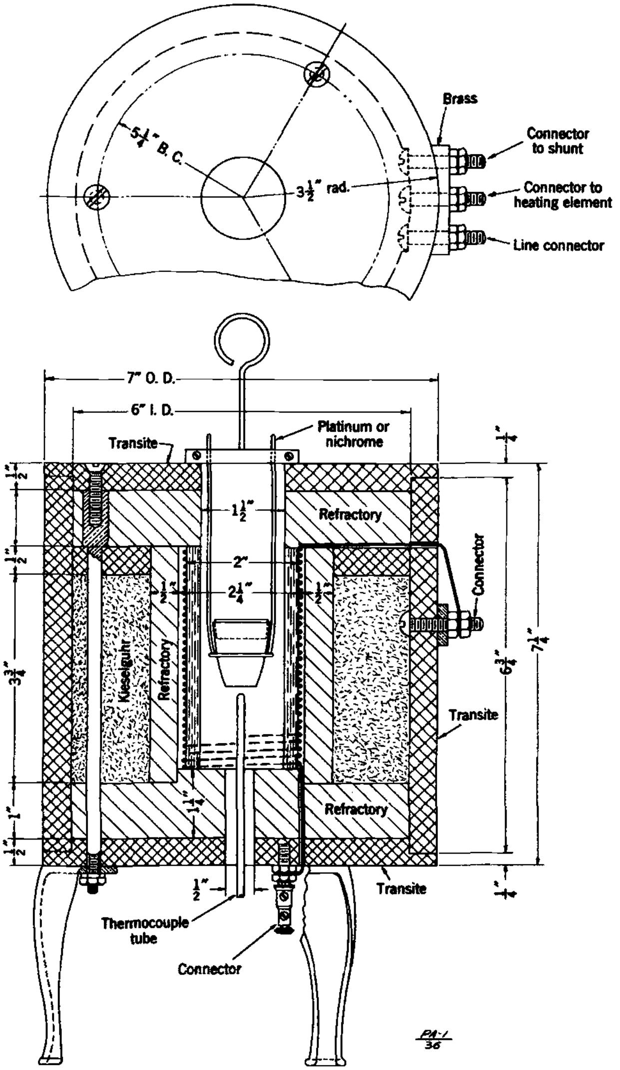

FIG. 7.1—Electric furnace for determining volatile matter.

7.1.8 Density

This is another characteristic property that differs with changes in grade of coal as well as impurities. Density or specific gravity is important to know, from a rubber compounding perspective, because this information is the basis for pound/volume cost calculations.

ASTM D 4371 is the method recommended for measuring the density of ground coal.

7.2 TITANIUM DIOXIDE

Titanium dioxide is used in rubber compounding as a white inorganic pigment with good "hiding power." This material is ideal as a whiting agent because it possesses a very high refractive index (much higher than the refractive index of rubber), which can scatter light. This property also imparts considerable "hiding power" over other darker ingredients that may also be present in the rubber formulation. Usually titanium dioxide grades are manufactured so they possess an average particle size of about 0.2 μm, which is about one half the wavelength of light, the optimum for light scattering [3].

There are two crystalline forms of titanium dioxide used in rubber compounding. One of these crystalline forms, called *anatase* TiO_2, is the softer form and easily chalks. This chalking characteristic makes it commonly the choice for some tire white sidewall compounds because it imparts a "self-cleaning" characteristic for a better white appearance outdoors.

The other crystalline form of TiO_2 commonly used in rubber compounding is the *rutile*, crystalline form. This form is harder than anatase and is somewhat chalk resistant. On the other hand, the rutile form has a higher refractive index (2.7) than the anatase (with a RI of 2.5). The greater the difference in refractive index between the titanium dioxide particles and the rubber medium of a compound, the greater the opacity imparted to the compound [4].

Table 7.2 presents the classification for titanium dioxide for use in rubber as described by ASTM D 4677.

The classification system given in the table for grades of titanium dioxide used in rubber is based mainly on purity and polymorphic form

TABLE 7.2—Properties of Titanium Dioxide (By Type).

	TEST METHOD	TYPE I (ANATASE)	TYPE II (RUTILE)	TYPE III (RUTILE)
TiO_2, min, %	D 1394	95	92	85
pH	D 1208	7–8.0	7–8.0	7–8.0
Coarse particles, max, %	D 185	0.2	0.2	0.2
Moisture, max, %	D 280	0.7	0.7	1.5
Rutile[a]	D 3720	1 % max	99 % min	99 % min
Tint Strength[b]	...	...	...	...
Brightness[b]	...	...	...	...

[a] Percent rutile as a percent of total TiO_2 content.

[b] Test methods to be developed and agreed upon by supplier and user. A basic white sidewall formula could be chosen to generate inherent color properties.

(crystalline structure). The three types of titanium dioxide listed in the table are described below.

Type I—Anatase, free chalking
Type II—Rutile, low/medium chalk resistance
Type III—Rutile, high-chalk resistance

The important properties of titanium dioxide for rubber use are discussed below.

7.2.1 Titanium Dioxide Purity

This property is determined by one of two wet analytical methods described in ASTM D 1394. One of these procedures is described as the Jones Reductor Method. It involves solubilizing TiO_2 in strong acid using the "Jones Reductor" and titrating with potassium permanganate. This procedure uses a redox reaction involving the use of zinc to quantitatively measure titanium. Interfering elements include the presence of iron, chromium, arsenic, and any other substance that is reduced by zinc and acid.

An alternate method given in D 1394 for measuring titanium dioxide purity is by the Aluminum Reduction Method. Reportedly, this method gives test results similar to the Jones Reductor Method.

Also part of ASTM D 1394 are wet procedures for directly measuring the aluminum oxide and silica content of commercial titanium dioxide samples. SiO_2 and Al_2O_3 are commonly found with titanium dioxide. Often, titanium dioxide particles are surface treated with silica and alumina as well as other agents. Sometimes the titanium dioxide manufacturer may apply certain additives to the titanium dioxide as dispersion aids.

7.2.2 pH Measurements

Titanium dioxide, under most situations, is chemically inert, with a pH imparted to an aqueous dispersion usually between 7 and 8. The pH procedure for measuring this property is quite simple and is described in ASTM D 1208.

Because the pH of titanium dioxide is close to neutral, this pigment may have only a small effect on cure characteristics of the rubber compound.

7.2.3 Coarse Particles

Even though the average particle size of titanium dioxide may be very small, it is possible that coarse particles or agglomerates, which could adversely affect cured physical properties of a rubber compound, may be present.

ASTM D 185 is recommended for measuring these large particle-size impurities that may be present. This standard specifies a wet sieve test to be performed with a 325-mesh (45-μm) screen.

7.2.4 Moisture Content

This is simply a method for determining the content of hygroscopic moisture by heat loss at 105 or 110°C. Excessive moisture can affect rubber curing. ASTM Method D 280 describes this procedure.

7.2.5 Rutile Content

For some applications with titanium dioxide, the rubber compounder may want chalking to occur. In other applications, the compounder may wish the grade of titanium dioxide to be chalk resistant. As stated earlier, the higher the rutile content, the more chalk resistant the rubber compound will probably be in service.

ASTM D 3720 calls for measurement of anatase and rutile crystalline forms of titanium dioxide by using X-ray diffraction techniques. The quantity of anatase and rutile are determined by measuring and determining the ratio of the intensity of the anatase diffraction peak to the intensity of the rutile diffraction peak. It is assumed that the purity of the titanium dioxide sample has already been determined by D 1394 (discussed above). So it is assumed that the titanium dioxide portion is either anatase or rutile polymorphic forms. (The only other polymorphic form would be Brookite; however, reportedly this crystalline form does not occur in commercial grades of titanium dioxide.) Some chemical compounds can interfere with this X-ray diffraction analysis. One potential interference could come from calcium sulfate; however, this impurity could be easily removed from the sample if it proves to be a problem. The use of X-rays can be hazardous if the proper safety precautions are not followed. All ASTM safety precautions in ASTM D 3720 as well as those given by NIST and the instrument manufacturer should be followed.

7.2.6 Tint Strength and Brightness

These properties to some extent relate to the "hiding power" of titanium dioxide. This is why TiO_2 is sometimes chosen over other less expensive white fillers such as calcium carbonate or water-washed clay. These other white fillers do not possess the hiding power, tint strength, and brightness that titanium dioxide can impart to a rubber compound. As discussed earlier, both anatase and rutile both possess a much higher refractive index than conventional mineral fillers such as calcium carbonate or clay. Also as stated earlier, the greater the difference between the refractive index of the particles and the rubber hydrocarbon medium, the more light scattering and the greater the opacity.

An effective method to determine if a new grade of titanium dioxide will impart to rubber the same degree of tint strength and brightness is to directly compare it to another approved source, side-by-side in a standard test formulation. This direct comparison could be made visually one-on-one or through the use of a reflectometer.

7.3 CLAY

Clays are siliceous fillers composed of a variety of aluminum silicates. Selected clays are commonly used as fillers in rubber compounding. Because of the relatively low price of clays compared to rubber, these fillers are mostly used to reduce the cost of the rubber compound. In North America, Kaolin clays are the most common type of clay, by far, which are used as rubber compounding ingredients. These clays are typically mined in Georgia and South Carolina and are processed to remove large particles and other foreign impurities before they are suitable for use in rubber formulations [5].

Kaolin clays used in rubber compounds are broadly divided into two categories based on the deposits from which they were mined. If the clay possesses a predominately finer particle size, it is called a *hard* clay because it produces a harder rubber compound. On the other hand, if the clay has a higher average particle size, then it is called a *soft* clay and will produce a softer rubber compound [6].

There are two high-volume processes that are commonly applied to separate impurities and larger-size particles from these clays. One process is separation by air flotation, while the other is separation by water washing. Air-floated clays are less expensive, but do not have as good a control of particle size or the removal of the large particle-size weight fraction [7]. Water-washed clays, however, usually have a smaller average particle size, a much lower large particle-size weight fraction, and a "whiter" color (usually because of the removal of iron oxide impurities). Generally, clay particles possess a flat plate-like shape that imparts higher hardness to a rubber compound than an equivalent loading of ground calcium carbonate (whiting). Clays also typically have an acidic surface chemistry that sometimes can retard a rubber cure (just as a precipitated silica can). For worker protection, one should avoid using clays that contain unsafe levels of silica impurities, such as alpha quartz (which is an IARC carcinogen).

As of this printing, there are no rubber standards under ASTM that classify, specify, or provide methods for testing clays intended for use in rubber. However, in 1981, The U.S. Technical Advisory Group to ISO TC45, under the administration of ASTM D11.45, worked with other ISO member nations to establish an ISO standard for the classification and testing of the clays used in the rubber industry worldwide. This standard was proposed for acceptance as ISO 5795. It denoted four different grades of clay based on average particle size and silica to alumina mass ratio.

Classification by particle size was supported by the United States TAG (Technical Advisory Group) because this system of classification is consistent with the existing industrial practice of using both soft clays (larger particle size) and hard clays (smaller particle size). This classification system divided clays into two broad categories based on those sources, i.e., at least 75 % of the particles less than 10 μm and 20 % less than 2 μm (soft clays) versus those sources that had at least 95 % of the particles less than 10 μm and 75 % less than 2 μm (hard clays). This classification was based on ISO 3262-9, Determination of Particle-Size Distribution by Sedimentation Method in Accordance with Stoke's Law. (This method is relatively easy to perform, and the equipment required is mostly inexpensive glassware.)

On the other hand, the United States TAG in 1981 did not support the classification of clay for use in rubber by using silica-to-alumina mass ratio. This standard proposed that clays with a silica/alumina ratio less than 1.50:1 were in one category, while those clays with a ratio greater than 1.50:1 were in a second category. The kaolin clays mined in the United States are mostly in the first category. In fact, U.S. manufacturers did not have any data showing if the clays in the second category would, in fact, perform the same as clays in the first category based upon cured physical properties when tested in a rubber compound.

The proposed ISO 5795 standard called for the measurement of silicon in clays by a chemical wet method called the molybdosilicate spectrometric method. This same proposed ISO standard called for the determination of aluminum content in a clay by an EDTA titrimetric method.

Other test methods in the proposed ISO 5795 standard to control the level of impurities contained in clays for use as rubber compounding ingredients are summarized below:

- Total percent iron by 2,2′-bipyridyl spectrometric method, Annex C
- Copper content by atomic absorption spectrometric method, Annex D
- Manganese content by atomic absorption spectrometric method, Annex E
- Percent residue on 45 μm sieve, ISO 3262-8
- pH of aqueous suspension, ISO 3262-13
- Percent volatile matter at 105°C, ISO 3262-10
- Percent ignition loss at 1000°C, ISO 3262-11
- Density, ISO 787-10
- Color, ISO 3262-7

High iron content can impart a yellowish color to a clay and in some cases can promote degradation. Copper and manganese are well known as pro-oxidants, which can promote rubber degradation, especially with natural rubber–based compounds. A pH test is needed because some clays can contain water soluble impurities that can interfere with cure. Volatile matter usually relates to the content of free water, while ignition loss relates to chemically bound water. Both of these can affect such rubber properties as electrical resistivity and conductivity. Density is important for compound pound-volume cost calculations.

No standard rubber test recipe for evaluating clays was accepted in ISO TC 45. However, one proposed test recipe which was submitted for comparing different clays in rubber is shown below.

INGREDIENT	PARTS PER HUNDRED RUBBER (PHR)
SBR 1500	100
Clay	70
Diethylene glycol	2
Zinc oxide	5
Stearic acid	1.5
Sulfur	2
TBBS accelerator	2

Using 70-phr clay instead of 100-phr may actually show greater sensitivity to subtle differences among the subject clays being evaluated. It was reported that 2 phr of DEG was required to help prevent adsorption of curative by the surface of the clay particles. This proposed test recipe used only one accelerator in order to reduce the chances of interlaboratory differences. It should be noted, however, that neither this test recipe for evaluating clays in rubber nor the proposed ISO 5795 document has been accepted by ISO TC 45 as of this publishing date.

7.4 NATURAL CALCIUM CARBONATE

Ground calcium carbonate (sometimes called "whiting") is commonly used as an economical diluent in rubber compounding to reduce the material cost of the compound [8]. Also, this filler will usually impart higher resilience to a rubber compound than clay imparts. In addition, it usually imparts a whiter color than clay to a given rubber compound. On the other hand, clay will usually impart a higher compound modulus.

Presently there are no ASTM standards that give classifications, specifications, or test methods for calcium carbonate grades for use in rubber compounding. However, in 1981, the USA Technical Advisory Group to ISO TC 45 on Rubber (administered by ASTM as Subcommittee D11.45) with representatives from other member nations supported the development of an ISO standard for this filler. This standard is now ISO 5796 with the official classification of natural calcium carbonate and typical physical and chemical properties given in Annex D. This established classification system is based on the particle size (or fineness of the grind) and purity.

Annex D classifies natural calcium carbonates for use in rubber as moderate grind (5 % max retained on a 45-μm screen and 0.1 % max retained on a 125-μm screen) and a very fine grind (0.5 % max retained on a 45-μm screen and 0.005 % max retained on a 125-μm screen). This standard only uses sieve tests to quantify the "finest of the grind" (which can only measure particle sizes at the upper portion of the particle size distribution). Very large particle sizes can do harm to a rubber vulcanizate while in service because they can create stress points that become points of crack initiation and tearing. Generally, the fewer large particles means the slower the rate of rubber degradation while in service. ISO 3262-1 describes the sieve test.

The second classifying characteristic used by Annex D of ISO 5796 is percent purity (minimum percentage of calcium carbonate). The original purity proposal was to have only purity levels of 98 and 96 %. However, United States TAG did a survey of American suppliers and found that 40 % of all natural calcium carbonate sources had purity levels greater than 98 %, while 29 % of sources had purity in the range of 96 to 98 %. It was also found that 25 % of the natural calcium carbonate sources to the U.S. rubber industry had purity levels between 94 and 96 %. From this survey, it was decided by the member nations to include all three purity levels instead of just two into the ISO 5796 Classification (Annex D). The purity of natural calcium carbonate is determined by ISO 3262-1.

Other properties described in ISO 5796 Annex D in the classification of natural calcium carbonate are given below.

- Heat loss at 105°C by ISO 787-2
- Ignition loss at 1000°C by ISO 3262-1
- Alkalinity as Na_2CO_3 by ISO 5796
- Copper content (atomic absorption method) by ISO 5796
- Manganese content (atomic absorption method) by ISO 5796
- Iron content by (atomic absorption method) ISO 5796
- Density

Heat loss indicates the level of moisture that could be present. Moisture can interfere with curing characteristics. On the other hand, ignition loss at 1000°C gives a characteristic value for calcium carbonate because it drives off carbon dioxide, leaving calcium oxide. This characteristic value in a crude way can help in determining the purity of the natural calcium carbonate. The dominant ignition loss reaction is given below.

$$\underset{\textbf{Calcium Carbonate}}{CaCO_3} \rightarrow \underset{\textbf{Calcium Oxide}}{CaO} + \underset{\textbf{Carbon Dioxide (gas)}}{CO_2\uparrow}$$

Copper, manganese, and iron can function as pro-oxidants. Even trace quantities of copper and manganese can accelerate the degradation of rubber, especially natural rubber. Lastly, density is important to enable the compound pound-volume costs to be calculated.

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8

Oils, Plasticizers, and Other Rubber Chemicals

by John S. Dick[1]

8.1 RUBBER PROCESSING AND EXTENDER OILS

PETROLEUM OILS ARE COMMONLY USED as extenders in styrene butadiene (SBR) and polybutadiene (BR) masterbatches purchased from synthetic rubber producers, as well as processing oils used in rubber formulations as a compounding ingredient. These oils differ in their chemical composition, which affects a rubber compound's processing behavior and its cured physical properties [1].

These oils used in rubber compounding differ in a variety of ways as noted below:

- Degree of aromaticity
- Average molecular weight
- Volatility
- Percent polar compounds
- Percent asphaltenes
- Wax content

8.1.1 Aromaticity

Because of the complexity of an oil molecule's structure, it is rare to find any two that are identical. All oil molecules, however, usually have three types of structures in common. These structures are: (1) aromatic, (2) naphthenic, and (3) paraffinic. Virtually all oils will contain all three of these structures. It is the proportional quantity (or number) of each structure that differs from one type of oil to another. A "typical" oil molecule, shown in Fig. 8.1, contains these three structures.

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[1] Akron, OH, www.rubberchemist.com

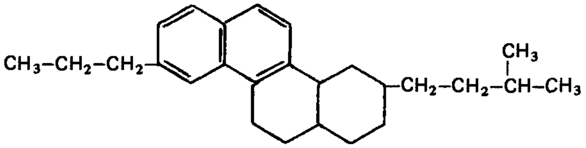


FIG. 8.1—A typical oil molecule containing the aromatic, naphthenic, and paraffinic structures.

One method to statistically relate to the dominant chemical structure of a petroleum oil is to use ASTM D 2501, Viscosity-Gravity Constant (VGC). The VGC is calculated from specific gravity and viscosity as shown in Eqs 8.1 and 8.2.

For kinematic viscosity measurements at 40°C:

$$VGC = [G - 0.0664 - 0.1154 \log (V - 5.5)] / [0.94 - 0.109 \log (V - 5.5)] \tag{8.1}$$

where

G = density at 15°C, g/mL, and
V = kinematic viscosity @ 40°C, cSt.

For kinematic viscosity measurements at 100°C:

$$VGC = [G - 0.108 - 0.1255 \log (V' - 0.8)] / [0.90 - 0.097 \log (V' - 0.8)] \tag{8.2}$$

where

G = density at 15°C, g/mL, and
V' = kinematic viscosity @ 100°C, cSt.

A classification scheme proposed to crudely classify oils into categories [2,3], is shown in Fig. 8.2.

This classification is based in part on the fact that a higher aromatic content means that the molecules will be more "compact," hence more dense. However, density is only an indirect method of measuring aromatic content. Naphthenic groups, which are saturated rings with six carbons, can also be somewhat dense compared to paraffinic molecular structures but are not as compact as aromatic structures. Variations in these chemical structures can affect the way the process oil behaves in a rubber compound. For example, a highly aromatic oil is very compatible and imparts very good processing quality to a rubber compound based on SBR. However, a highly paraffinic oil is more compatible with an EPDM-based compound and imparts better low-temperature properties.

VGC Scale 0.82 0.85 0.90 0.95

Paraffinic Oil	Relatively Naphthenic Oil	Naphthenic Oil	Relatively Aromatic	Aromatic

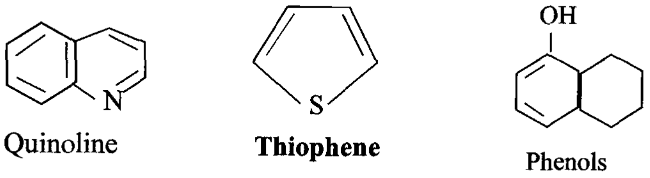
FIG. 8.2—Classification scheme to classify oils.

8.1.2 Average Molecular Weight

This property is also an important consideration in determining the effectiveness of an oil in rubber. Many times, oil viscosity is used as a crude measure of molecular weight. Higher average molecular weight (MW) oils with similar chemical structure will have a higher viscosity. Oil viscosity can affect the processability characteristics imparted to a rubber compound. Also, higher viscosity may impart better permanence and aging resistance to vulcanizates.

8.1.3 Volatility

Some oils contain an excessive weight fraction of low-molecular-weight components. When present in an oil, they can impart poor aging properties to a cured rubber compound. An excessive quantity of these low-molecular-weight components will cause the aged durometer hardness of a vulcanizate to rise or can cause shrinkage of the vulcanizate with aging. This can be detrimental to product performance.



Quinoline **Thiophene** Phenols

FIG. 8.3—Examples of "polar compounds."

8.1.4 Polar Compounds

These components in a petroleum oil can also be very important. These so-called polar compounds are commonly heterocyclic organic compounds based on oxygen, sulfur, and nitrogen as illustrated in Fig. 8.3 [4].

These types of polar components in oil have been reported in the literature to affect curing behavior of a rubber compound.

8.1.5 Asphaltenes

These materials are basically impurities in a rubber process oil. Asphaltic material is usually measured as insolubles in *n*-pentane. If an oil contains high quantities of this material, it will make a rubber vulcanizate more hysteretic in nature.

8.1.6 Wax Content

Waxes can also be an important characteristic for rubber process oil. Petroleum wax molecules can be very much like other oil molecules except they contain mostly the paraffinic structures and only a small number of naphthenic and aromatic rings. Therefore, waxes can crystallize at specific temperatures, are less compatible with rubber at lower temperatures, and may affect the bloom characteristics of a rubber compound.

8.1.7 ASTM Oil Classification

ASTM D 2226 gives a classification system for rubber extender and process oils based mainly on a column chromatographic method described in ASTM D 2007. Table 8.1 shows this ASTM classification for rubber petroleum oils.

8.1.8 ASTM Oil Tests

The following gives a general description of the ASTM oil tests commonly used to control the quality of petroleum oils used in extending raw rubbers or as compounding ingredients (processing oils).

8.1.8.1 Clay-Gel Analysis, A Column Chromatographic Method (D 2007) This test method is very important for classifying process oils for use in rubber compounding. It employs a column chromatograph consisting of a clay in the upper section and a specified silica gel in the lower section for quantitatively separating an oil into four components, i.e., asphaltenes, polar compounds, aromatics, and saturates. As discussed earlier, the asphaltenes are the insoluble materials that precipitate from a solution of the oil and *n*-

TABLE 8.1—Classification of Oil Types.

TYPES	ASPHALTENES, MAX, %[a]	POLAR COMPOUNDS, MAX, %	SATURATED HYDROCARBONS, %
101	0.75	25	20 max
102	0.5	12	20.1 to 35
103	0.3	6	35.1 to 65
104[b]	0.1	1	65 min

[a] Pentane-insoluble materials as determined by Test Method D 2007.

[b] Type 104 oils are further classified into two subtypes 104A and 104B for SBR polymers only. Type 104B oils are those that have a viscosity-gravity constant of 0.820 maximum (Method D 2501). Type 104A oils are those that have a viscosity-gravity constant greater than 0.820 (Method D 2501). It is recognized that certain Type 104 oils may not be satisfactorily classified for polymers other than SBR by this subclassification.

pentane. The polar compounds (also referred to as the polar aromatics) are the materials adsorbed on the clay. The aromatics are the materials that pass through the clay but are adsorbed onto the silica gel. Lastly, the saturates are the materials that pass through both the clay and silica gel without adsorbing onto either. Figure 8.4 below shows the Clay-Gel apparatus that is commonly used.

8.1.8.2 Viscosity-Gravity Constant (D 2501) This ASTM standard method defines the method for calculating the VGC of an oil from its measured density and viscosity. Two equations (8.1 and 8.2) were given above for calculating VGC. One uses viscosity measured at 40°C for free-flowing oils. The other is for highly viscous oils, which are difficult to measure at 40°C but can be measured easily at 100°C. Kinematic viscosity is the method of choice

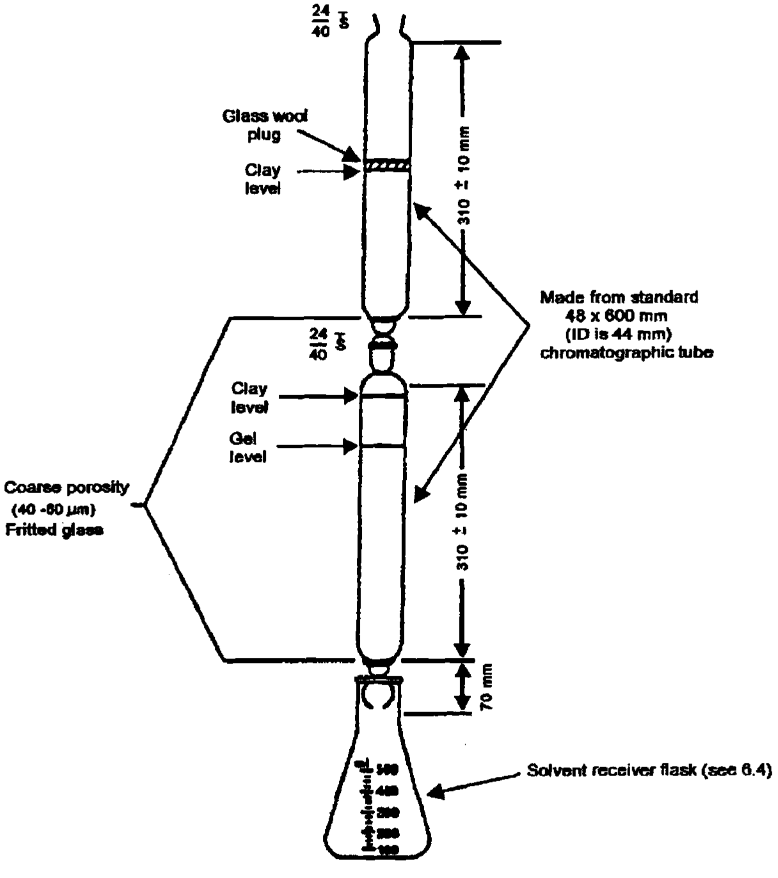


FIG. 8.4—Clay-gel percolating columns.

for measuring viscosity for VGC determination. However, the Annex of this method contains the equations for calculating the VGC values from the older *Saybolt* viscosity method. If the oil's calculated VGC value is near 0.800, this indicates that the test oil is paraffinic in character. However, if the oil's VGC value is close to 1.00, this indicates that the oil is more aromatic in nature with a preponderance of aromatic structures. VGC calculations are not applicable to oils that contain a high quantity of nonhydrocarbons. VGC calculations should not be applied to residual oils or asphaltic materials.

8.1.8.3 Kinematic Viscosity (D 445) This method determines the kinematic viscosity of a given process oil by measuring the time required for the oil to flow under gravity through a calibrated glass viscometer of capillary design. Using this procedure, the oil's dynamic viscosity, η, can be calculated by multiplying the kinematic viscosity ν by the oil density. Large changes in an oil's viscosity can affect a rubber compound's viscoelastic characteristics.

8.1.8.4 Aniline Point and Mixed Aniline Point (D 611) This test method is another simple method for quantifying the degree of aromaticity in a given oil. It works best with transparent oils; however, there are alternate procedures in this standard that allow one to see the end point for less transparent oils. Aniline is quite toxic. All the appropriate precautions should be followed when working with aniline and other hazardous chemicals. The method consists of mixing under controlled conditions, a specified quantity of aniline with the test oil, or aniline and *n*-heptane with the test oil. This mixture is heated under controlled conditions so that the temperature rises at a controlled rate until the two phases become miscible with each other. The mixture is then cooled under controlled conditions, and the temperature, at which the two phases begin to separate (becomes cloudy), is recorded as the aniline point (for aniline and oil) or the mixed aniline point (for aniline, *n*-heptane, and oil). It should be noted that highly aromatic oils have the lowest aniline points, while paraffinic oils give the highest aniline points. The apparatus that is commonly used for Method A is shown in Fig. 8.5.

8.1.8.5 Pour Point (D 97) This test procedure measures the temperature at which the test oil no longer flows from the force of gravity. In this method, the subject oil is heated well above its pour point. It is cooled, at a specified rate, and examined at 3°C intervals, for flow properties. Oils with high pour points could affect the low-temperature and dynamic properties of a rubber compound.

8.1.8.6 Acid and Base Number by Titration (D 974) This test method is an acid-base or base-acid titration procedure to quantify the acidic or basic constituents that may be present in an oil. The presence of either acidic or ba-

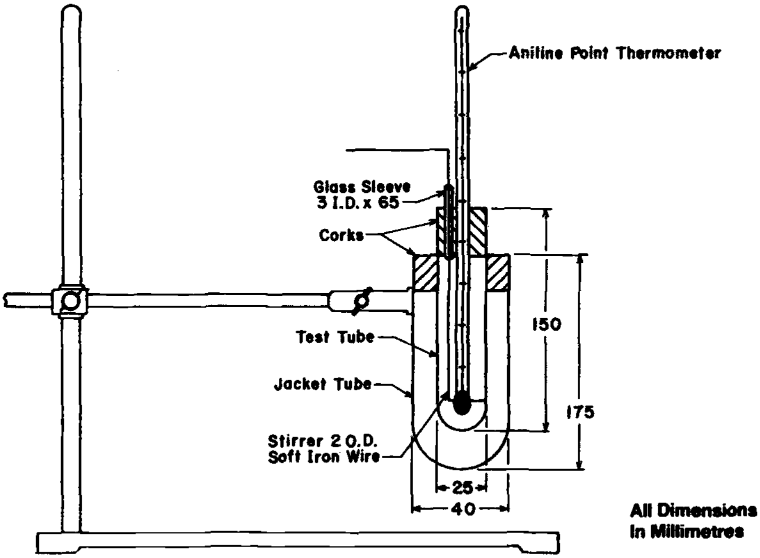


FIG. 8.5—Aniline point apparatus (Method A).

sic components in a process oil can affect the cure characteristics of a rubber compound. Acidic components in an oil could retard a conventional sulfur cure of a compound based on general purpose elastomers. This method can also be used to measure relative changes that might occur when an oil is stored under oxidizing conditions.

This test standard calls for the subject test oil to be dissolved in a specified mixture of toluene and isopropyl alcohol, containing a small quantity of water. This solution is titrated with either an alcoholic base or alcoholic acid solution, respectively, to a given color end-point change, based on using *p*-naphtholbenzein indicator (orange in acid; green-brown in base). In certain cases for a strong acid number, methyl orange indicator is used if a titration is performed on a separate portion of the sample, which has been extracted with hot water. *Acid number* is defined by this standard as "... the quantity of base, expressed in milligrams of potassium hydroxide per gram of sample that is required to titrate an oil to a specified end-point." Also, this standard defines a *base number* as "... the quantity of acid, expressed in milligrams of potassium hydroxide per gram of sample, that is required to titrate a sample to a specified end-point."

8.1.8.7 Density, Relative Density (Specific Gravity) or API Gravity (D 1298) This method involves the insertion of a glass hydrometer into a sufficient volume of sample oil at a specified temperature in order to measure the oil's density. The standard temperatures, which are commonly used, are

20°C, and 60°F. Generally, oils with greater aromatic content (a more compact chemical structure) tend to have a higher density (or specific gravity) than a more paraffinic oil. However, this relationship is not hard and fast. Knowing the density (in g/mL) of a given rubber process oil is very useful for converting a given volume into the mass quantity (weight) or vice versa. Also Equation 8.3 is used for converting specific gravity into *API Gravity.*

$$°\mathrm{API} = 141.5/(\mathrm{sp\ gr}\ 60/60°\mathrm{F}) - 131.5 \qquad (8.3)$$

where *specific gravity* is relative density or the ratio of the mass of a specified volume of liquid at a specific temperature to the mass of the same volume of pure water at the same or a different specified temperature. Figure 8.6 below shows the hydrometer in use.

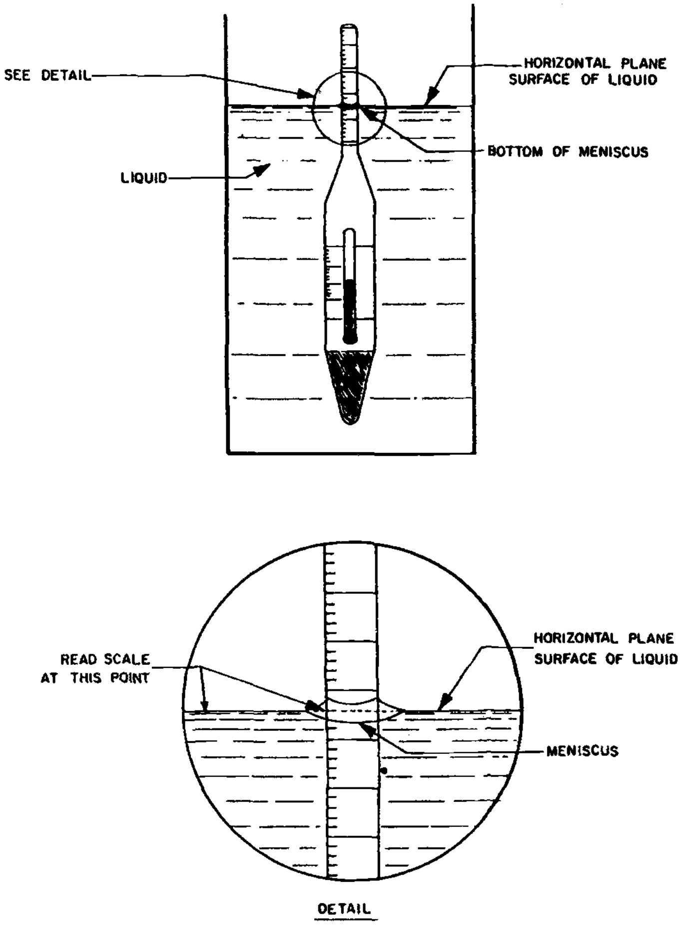


FIG. 8.6—Hydrometer seal reading for transparent liquids.

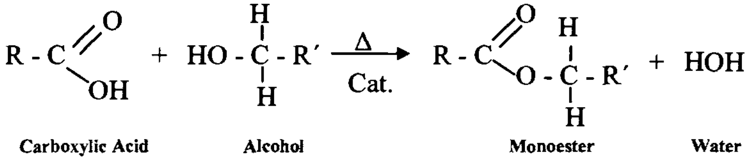
8.1.8.8 Color (D 1500) This method is simply comparing the subject oil sample to a set of standard colored glass disks using a standard common light source. This is called "ASTM Color" and can be measured with an "ASTM D 1500 Colorimeter" described in Annex 1 of this standard.

8.1.8.9 UV Absorbance (D 2008) This method calls for the measurement of the absorption spectra between 220 to 400 nm in wavelength. This provides a characteristic spectrum of the oil.

8.1.8.10 Flash Point Open Cup (D 92) This is defined by the ASTM standard as the lowest temperature (corrected for standard pressure of 760 mm Hg) where "the application of an ignition source causes the vapors of a test specimen [the process oil] to ignite under specified conditions of this test." This method uses the Cleveland Open Cup apparatus, which is to be used only for viscous petroleum oils with flash points above 79°C. The Flash Point can provide a characteristic value for a process oil or extender oil. According to this ASTM Standard, flash point should not be used alone but with a number of other appropriate properties and factors that should be considered in assessing the overall flammability hazard of the material.

8.2 SYNTHETIC PLASTICIZERS

Synthetic plasticizers are commonly used as compounding ingredients, usually with specialty polar elastomers such as NBR, CR, or ECO, for example. These plasticizers are usually somewhat polar in their molecular structure and are therefore commonly miscible in these polar elastomers. Often they are used not only to help plasticize the compound during processing, but also to improve the low temperature properties of the vulcanizate [5]. The ester plasticizers are the product of a chemical reaction usually of an organic acid (or anhydride) with an alcohol [6] as shown in Eq 8.4.

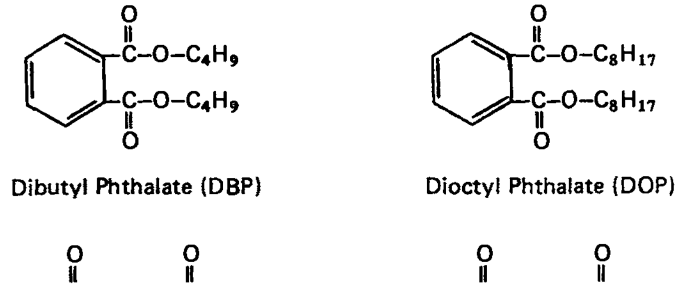


(8.4)

Examples of these ester plasticizers are given in Fig. 8.7

8.2.1 Standard Abbreviations

As given in ASTM D 3853, these standard abbreviations for commonly used synthetic plasticizers in the rubber industry are given in Table 8.2.



Dibutyl Phthalate (DBP) **Dioctyl Phthalate (DOP)**

$C_8H_{17}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-C_8H_{17}$

Dioctyl Sebacate (DOS)

$C_8H_{17}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-C_8H_{17}$

Dioctyl Adipate (DOA)

FIG. 8.7—Examples of ester plasticizers.

TABLE 8.2—Standard Abbreviations for Commonly Used Synthetic Plasticizers.

STANDARD ABBREVIATIONS	CHEMICAL NAME
BOP	butyl octyl phthalate
DBP	dibutyl phthalate
DBS	dibutyl sebacate
DCHP	dicyclohexyl phthalate
DEP	diethyl phthalate
DIBA	diisobutyl adipate
DIBP	diisobutyl phthalate
DIDA	diisodecyl adipate
DIDP	diisodecyl phthalate
DIOA	diisooctyl adipate
DIOP	diisooctyl phthalate
DMP	dimethyl phthalate
DMS	dimethyl sebacate
DOA	dioctyl adipate
DOP	dioctyl phthalate
DOS	dioctyl sebacate
DOTP	dioctyl terephthalate di-(2-ethylhexyl) terephthalate
DPCF	diphenyl cresyl phosphate
DPOF	diphenyl octyl phosphate
DPP	diphenyl phthalate
DUP	diundecyl phthalate
ELO	epoxidized linseed oil
ESO	epoxidized soya bean oil
ODA	octyl decyl adipate
TCEF	trichloroethyl phosphate
TCF	cresyl phosphate
TOF	triocyl phosphate
TOTM	trioctyl trimellitate

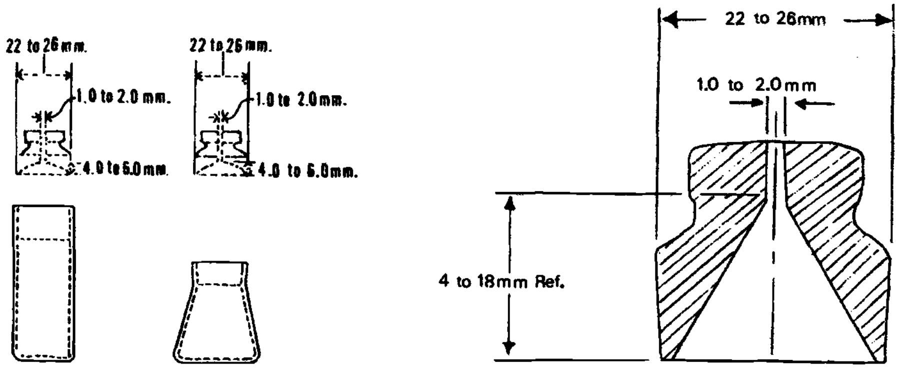
8.2.2 Standard Test Methods

ASTM D 1992 outlines the standard test methods that can be used for the quality control of synthetic plasticizers used in rubber compounding. These methods are discussed below.

8.2.2.1 Specific Gravity (D 70, D 891, and D 2111) ASTM D 70 uses a calibrated glass pycnometer to measure the density of a plasticizer at a specified temperature. ASTM D 891 allows either a hydrometer (Method A) or another pycnometer (Method B) to measure apparent specific gravity of liquids. Lastly, ASTM D 2111 is designed to measure halogenated liquids and again uses the hydrometer (Method A) and pycnometer (Method B). Density and specific gravity are characteristic values that can be used to help confirm that the proper plasticizer was received in shipments to a plant. Also, density can be used to convert the volume of a given plasticizer to weight (or vice versa). An example of a pycnometer used in D 70 is shown below in Fig. 8.8.

8.2.2.2 Color (D 1209 and D 1544) ASTM D 1544 simply calls for the visual comparison of a sample of the plasticizer in a standard glass tube against a set of *Gardner* glass standards as specified.

ASTM D 1209 calls for visual comparison of color from the plasticizer in 100 mL *Nessler* tubes against color standards made from different specified concentrations of potassium chloroplatinate (K_2PtCl_6) and cobalt chloride ($CoCl_2{\cdot}6H_2O$). This is a method for quantifying a "water-white" description. Preparation of these platinum-cobalt color standards was originally made by *A. Hazen*. In 1905 the American Public Health Association (APHA) adopted a version of this platinum-cobalt standard. While D 1209 is related to these color standards, it is *not* correct to refer to the color standard of D 1209 as ei-



(a) Pycnometers **(b) Stopper**

FIG. 8.8—Pycnometers and stopper.

ther the "APHA Color" or "Hazen Color." Instead it should be referred to as the "Platinum-Cobalt Color, Test Method D 1209."

High color in a synthetic plasticizer used in rubber can be a sign of impurities present. This can be very important in nonblack rubber compounds.

8.2.2.3 Refractive Index (D 1218) This method consists of using a Bausch & Lomb Precision Refractometer (or its equivalent) to measure the refraction of light at a specified wavelength and temperature in the plasticizer sample medium. Technically the refractive index is the "sine of the angle of incidence divided by the sine of the angle of refraction." Another way to define refractive index is the ratio of the light velocity in air divided by the light velocity in the plasticizer sample. Refractive index is a fundamental characteristic of a chemical and relates to its structure. For example, a chemical compound that contains aromatic rings will have a higher refractive index than a chemical compound with only an aliphatic structure. By using a characteristic property such as refractive index, and another characteristic property such as specific gravity, one can perhaps lessen the accidental use of the wrong plasticizer in the factory.

8.2.2.4 Saponification Value (D 1962) This method involves the reaction of a standard sample size of certain select ester plasticizers with an excess of standard alcoholic potassium hydroxide solution for 1 hour, under reflux conditions, which are described in the standard. The KOH reacts with the ester as follows in Eq 8.5:

$$\mathrm{RCOOR} + \mathrm{KOH} \rightarrow \mathrm{RCOOK} + \mathrm{ROH} \qquad (8.5)$$

After refluxing, the solution is cooled and titrated with a standard solution of either hydrochloric acid or sulfuric acid using phenolphthalein indicator for determining the end point in order to find the amount of KOH that did not react with the ester. From this titration the saponification value is calculated. The higher the saponification value indicates the higher the number of ester linkages, which makes it a characteristic test related to the structure of the specific plasticizer.

8.2.2.5 Brookfield Viscosity (D 2196) This test method consists of determining the apparent viscosity of a test plasticizer by inserting a *Brookfield* viscometer rotor of standard dimensions into the sample and measuring the viscosity from the force required to rotate the rotor at a specified speed. All Brookfield viscosity specifications must specify the Brookfield rotor size, rotor speed in revolutions per minute (rpm), and temperature. While the chemical structure of a plasticizer has a major effect on a rubber compound's characteristics, the viscosity of the plasticizer can affect the compound's processing characteristics and compound viscosity. Method A of this standard calls for the measurement of Brookfield viscosity at one standard rotor speed (one shear rate).

Method B of ASTM D 2196 calls for measuring Brookfield viscosity at two or more different rotor speeds (two or more different shear rates). This is done in order to measure the *shear thinning index.* This index is calculated by dividing the apparent viscosity at a low rotor speed by the viscosity measured at a rotor speed ten times greater. Typically, viscosity comparisons will be made between 2 and 20 rpm, 5 and 50 rpm, or 6 and 60 rpm. This STI calculation might be applicable to polymeric plasticizers used in rubber; however, it may not be as applicable for monomeric plasticizers.

8.2.2.6 Heat Loss (D 2288) This procedure, developed especially for synthetic plasticizers, calls for the heating of preweighed plasticizer samples at either 105 or 155°C for a period of 2, 4, and 24 h. After each of these time periods, the weight loss is measured and reported on a percent basis. The percent volatiles present in a plasticizer used in a rubber compound can be very important. High volatiles can cause such problems as porosity in a rubber compound. Fuming during compound processing can change the ultimate cured hardness of the compound. Also, high volatiles can damage the cured rubber's aging properties.

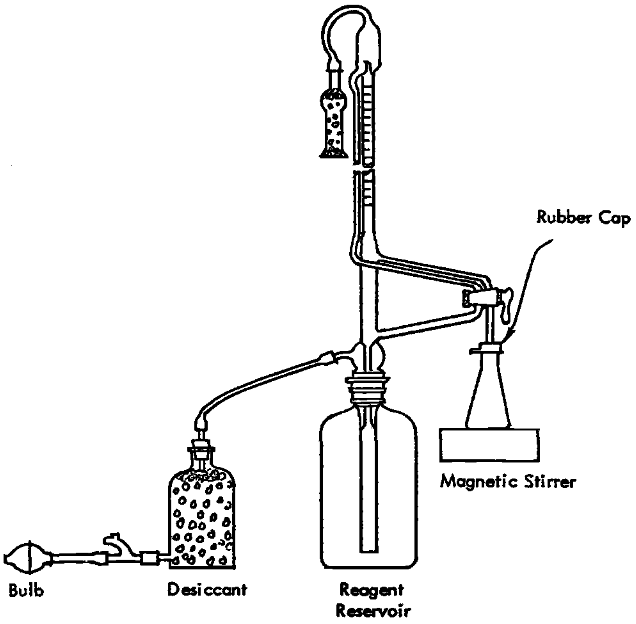
8.2.2.7 Karl Fischer (E 203) This method measures the amount of water present in certain plasticizers. With the proper adjustments and the correct selection of sample size as noted in this standard, moisture levels from as low as the parts per million range all the way to high percentages can be determined. This method consists of a titration of the sample plasticizer dissolved in an appropriate anhydrous solvent such as anhydrous methanol using a Karl Fischer (KF) reagent. This KF reagent usually consists of iodine, sulfur dioxide, and an organic base dissolved in an appropriate anhydrous solvent (such as methanol, ethylene glycol, or 2-methoxyethanol). The end-point in this titration is determined amperometrically using a platinum electrode, noting the sudden change in the cell resistance caused by the iodine being reduced by sulfur dioxide from the moisture present. The equation (8.6) for this reaction is given below.

$$H_2O + I_2 + SO_2 + R'OH + 3RN \rightarrow (RNH)SO_4R' + 2(RNH)I \qquad (8.6)$$

where:

RN = an organic base which is commonly pyridine, and
R'OH = an alcohol.

An advantage of this KF method for measuring water content is that it is very sensitive and effective at measuring moisture at very low levels. Unlike heat loss tests, this method directly measures the quantity of water present by reacting directly with the water. This method lends itself to automation.



NOTE—Not to scale.

FIG. 8.9—Example of a KF apparatus.

Disadvantages of the KF method are that it does involve the use of toxic chemicals and there are impurities in a test sample that can interfere with accuracy. All appropriate safety precautions should be followed. Also, the interfering compounds are listed in this ASTM standard. There are 14 other KF methods described in the *ASTM Book of Standards* that may or may not be applicable to determining water content in plasticizers. Moisture in a plasticizer can cause compounding problems such as porosity and alteration of cure characteristics. Figure 8.9 shows an example of a KF apparatus.

8.2.2.8 Flash Point Open Cup (D 92) See the comments in Section 8.1.8.10 for Process Oils. These comments are relevant for synthetic plasticizers as well.

8.3 CURATIVES

Curatives are compounding ingredients that are added to a rubber formulation to promote crosslinking and cure (also known as vulcanization). There are *vulcanizing agents* that are the actual curing agents themselves. Sulfur is the most commonly used vulcanizing agent in the rubber industry. The sulfur vulcanization reaction is made practical through the use of special organic chemicals called *accelerators* that speed the crosslinking reaction greatly. However, these accelerators must be activated by additional special compounding additives in order to perform effectively in curing. These additives are referred to as *activators*. The two most commonly used activators are zinc oxide and stearic acid. These two activators are commonly used together in the vast majority of rubber formulations used in the industry. They work by reacting with each other in the compound before and during cure. The stearic acid reacts with the zinc oxide, which solublizes the zinc ion so that it can react with the accelerator to enable it to perform better in the vulcanization reaction [7].

8.3.1 Sulfur

Tables 8.3 and 8.4 show the ASTM classification tables from ASTM D 4528 for different grades of sulfur used as a rubber compounding ingredient.

As can be seen from Tables 8.3 and 8.4, there are four grades (general purpose, fine, oiled, and conditioned) for the rhombic or ordinary ground type and four grades (flowers of sulfur; 60 % insolubles; 90 % regular insolubles; and 90 % insolubles oil-treated) for the insoluble or polymeric sulfur. The sulfur used by the rubber industry can vary in its particle size, level of oil treatment, and allotropic form (crystalline or noncrystalline). Particle size or fineness of the grind has a lot to do with how well the sulfur disperses during mixing and how uniformly it cures the rubber. (Sulfur particles should be significantly fine enough to help dissolve in the rubber medium during cure.) Oil treatment may help reduce the risk of a sulfur fire or explosion during mixing and aid in the incorporation during the mixing process. Lastly, whether the sulfur is in crystalline (rhombic) form or the insoluble polymeric form has a great effect on the reduction or elimination of sulfur surface "bloom" (exudation). This is because the insoluble or amorphous sulfur grades resist being solubilized by the rubber during processing. Therefore, at cooler temperatures after processing, there is less sulfur to separate out to the surface of the rubber forming an exudate called "bloom." This sulfur "bloom" can cause appearance problems as well as interfere with building tack and adhesion. Also, the selection of amorphous versus crystalline sulfur can affect a compound's scorch characteristics differently.

The following is a general description of chemical test methods which are used to monitor the quality of sulfur for rubber use.

8.3.1.1 Sulfur Insolubles (D 4578) The polymeric grades have limited storage stability and will revert to rhombic sulfur with time. This insolubles test provides a method of checking the concentration of polymeric sulfur that is present in a shipment. Method A calls for the use of carbon disulfide, while

TABLE 8.3—Typical Properties of Rhombic (Ordinary Ground) Sulfur.

Typical Properties	ASTM Test Method	Sulfur Grade			
		General Purpose	Fine	Oiled	Conditioned
Sulfur,%	...	99.8	99.8	98 to 99.5	95.5 to 99
Rubber process oil, %	D 4573	...	...	0.5 to 2	0 to 2.0
Additive, %	D 4574	...	...	...	up to 2.5
Acidity, % as H_2SO_4	D 4569	0.01	0.01	0.01	0.01
Ash, %	D 4574	0.02	0.02	0.02	depends on additive
Heat loss,%	D 4571	0.04	0.04	0.10	0.10
Fineness, Residue on standard sieve	D 4572				
180 µm,%		<0.3	<0.2	<0.3	<0.3
75 µm, %		5–15	0.5 to 1	variable [A]	variable [A]
45 µm,%		NA [B]	<2	variable	variable

[A] Oils and conditioning agents may be added to any grind without changing the sieve residues. Refer to the values given for the untreated ground sulfur.

[B] NA—not available.

TABLE 8.4—Typical Properties of Insoluble (Polymeric) Sulfurs.

Typical Properties	ASTM Test Method	Flowers of Sulfur	60 % Insoluble	90 % Insoluble	
				Regular	Oiled
Sulfur,%	...	99.8	99.8	99.8	78.8
Insoluble sulfur, %	D 4578	34.0	63.0	93.0	74.5
Rubber process oil,%	D 4573	...	...	...	19.0 *to* 21.0
Acidity, % as H_2SO_4	D 4569	0.1	0.01	0.01	0.01
Ash,%	D 4574	0.01	0.01	0.01	0.01
Heat loss, %	D 4571	0.10	0.20	0.20	0.30
Fineness,	D 4572				
Residue on standard sieve					
180 µm, %		0.2	0.2	0.2	0.2
150 µm,%		1.0	1.0	1.0	1.0

Method B uses toluene to measure insolubles. Using carbon disulfide in Method A is much more dangerous than the use of toluene in Method B. However, carbon disulfide, while much more dangerous, is more efficient as a solvent for rhombic sulfur.

8.3.1.2 Percent Oil (D 4573) Different grades of sulfur, used as rubber compounding ingredients, will commonly contain oil. This test method uses sulfur-saturated hexane to quantitatively determine the concentration of the oil in the sulfur.

8.3.1.3 Acidity (D 4569) Sometimes sulfur can contain acid, which could affect cure characteristics. This method uses a standard sodium hydroxide solution to titrate for acid content. This method involves titrating a water/sulfur suspension with standard NaOH solution to a pH of 7.0.

8.3.1.4 Wet Sieve (D 4572) This is a method for evaluating the particle-size distribution for the coarse fraction of a given sulfur shipment. Sulfur particles must be small enough to dissolve in the rubber medium during cure, otherwise a nonuniform crosslinked network could result, causing poor cured physicals. This method disperses the sulfur sample in water containing a detergent and passes it through sieves of specified mesh size. The quantitatively removed sulfur retains are then dried and weighed according to the procedure. An alternate method for sieve measurements of sulfur used in rubber is ASTM D 4570 (the dry sieve method). However, the dry sieve method is not applicable if the sulfur is very fine and the screens become clogged by caking.

8.3.1.5 Percent Ash (D 4574) This method is a simple test used to detect foreign inorganic impurities that might be present. It involves controlled burning of sulfur and then using a furnace at 600°C to ash. All appropriate safety precautions must be followed.

8.3.2 Rubber Accelerators

ASTM D 4818 is the classification standard for different rubber accelerators. This standard classifies these accelerators into six different groups. The descriptions for each of these groups are quoted directly from D 4818 and are given in Table 8.5.

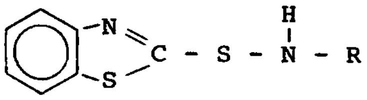
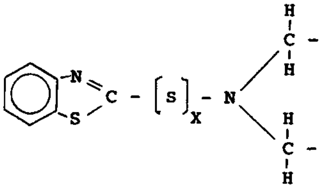
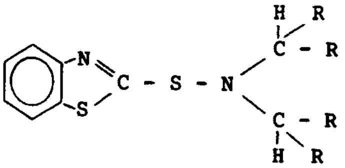
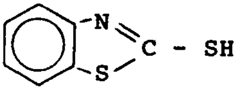
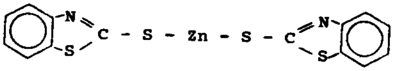
ASTM D 4818 also denotes the general chemical structures as shown in Table 8.6 given below.

As indicated from Table 8.6, the performance of the sulfenamides greatly depends on the nature of the substitutions around the sulfenamide nitrogen.

TABLE 8.5—Comparison of Accelerator Classes.

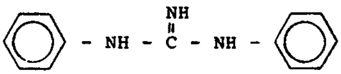
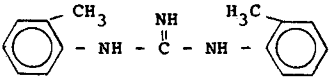
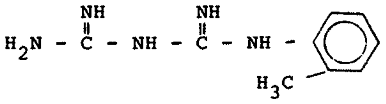
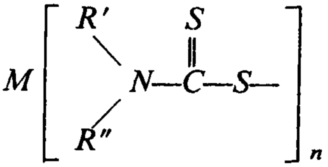
ACCELERATOR CLASS	ASTM D 4818 DESCRIPTION (GIVEN VERBATIM AS CITED IN THE STANDARD)
Class 1, Sulfenamides	"As a group, the 2-benzothiazyl sulfenamides are the principle sulfur vulcanization accelerators used in the rubber industry today. The role of these materials in vulcanization is dual. They provide scorch time (delay period) in the crosslinking or vulcanization operation at processing temperatures. The delay avoids premature crosslinking during the processing, for example, mixing, extruding, etc. Once the mixed rubber is at the curing temperature, these materials promote a rapid rate of curing (crosslinking, vulcanization). "The presence of certain impurities in this class of materials can affect their performance characteristics. The 2-benzothiazyl sulfenamides are subject to degradation on extended storage. Significant degradation can affect their performance characteristics. In particular, the quality of the material is a function of storage time, temperature, relative humidity, and the impurity profile of the material; for example, free amines, salts of 2-mercaptobenzothiazole, etc. Since sulfenamide degradation in storage is an autocatalytic process (degradation products accelerate further degradation), significant degradation may only occur after a long induction period.
Class 2, Thiazoles	"Thiazole derivatives are versatile vulcanization accelerators that are widely used in the rubber industry either alone or in combination with other accelerators.
Class 3, Guanidines	"The guanidines have little importance as primary vulcanization accelerators, except for thick sectioned goods, because of a typically slow vulcanization rate. As secondary accelerators, they are used with other accelerators of the thiazole class. These resulting combinations vulcanize faster and give higher levels of vulcanization than do their individual constituents, when used separately. The thiazole-guanidine combinations are frequently used for technical rubber goods.
Class 4, Dithiocarbamates	"Vulcanization with dithiocarbamates is faster than with thiurams. Dithiocarbamates are used as *ultra-accelerators* with normal sulfur levels. They are also employed as secondaries or activators for other accelerators.
Class 5, Thiurams (disulfides)	"Thiuram disulfide accelerators are used for vulcanization, without elemental sulfur, to produce rubber compounds which show essentially no reversion and which have low compression set and good aging characteristics. For low sulfur vulcanization, thiurams are normally used in combination with sulfenamides. With a normal amount of sulfur, thiurams act as ultra-accelerators.
Class 6, Thiurams (other than disulfides)	"This class contains other thiuram types which are not disulfides. They are used as ultra-accelerators with normal amounts of sulfur. Di, tetra, and hexasulfides can be employed without sulfur or with low sulfur levels to obtain rubber compounds with much reduced reversion tendencies."

TABLE 8.6—General Chemical Structures from ASTM D 4818.

CHEMICAL STRUCTURE TYPES	ASTM D 4818 DESCRIPTION (GIVEN VERBATIM AS CITED IN THE STANDARD)	CHEMICAL STRUCTURE
Sulfenamides of Primary Amines (Type I)	"These compounds have one hydrogen on the sulfenamide nitrogen, in addition to the generic R group. In general, this type, as a group, exhibits a somewhat shorter scorch time and higher cure rate than the other sulfenamides	Sulfenamides of Primary Amines 
Sulfenamides of Unhindered Secondary Amines (Type II)	"These compounds have two primary carbon attachments, each with at least two hydrogen atoms on the carbon bonded to the sulfenamide nitrogen. In this case, X can be one or two. This type, as a group, exhibits an intermediate scorch time and cure rate.	Sulfenamides of Unhindered Secondary Amines 
Sulfenamides of Hindered Secondary Amines (Type III)	"These compounds have two secondary carbon attachments to the sulfenamide nitrogen. This type, as a group, exhibits a longer scorch time and lower cure rate than the other sulfenamides	Sulfenamides of Hindered Secondary Amines 
Thiazoles	"There are three different thiazoles in common use. They all show a similar vulcanization effect. These three thiazoles are: Mercaptobenzothiazole (MBT); Zinc Salt of 2-Mercaptobenzothiazole (ZMBT); and Dibenzothiazyldisulfide (MBTS).	 MBT  ZMBT  MBTS

(continues)

TABLE 8.6—*(continued).*

CHEMICAL STRUCTURE TYPES	ASTM D 4818 DESCRIPTION (GIVEN VERBATIM AS CITED IN THE STANDARD)	CHEMICAL STRUCTURE
Guanidines	"There are two different types of guanidines in common use. They both show a similar vulcanization efficiency. These two types are Symmetric (Type I) and Asymmetric (Type II). Diphenylguanidine (DPG) and Di-Ortho-Tolyguanidine (DOTG) are examples of Type I, while Ortho-tolybiguanidine (OTBG) is an example of Type II.	 DPG  DOTG  OTBG
Dithiocarbamates	Examples of this group of ultra accelerators are shown in the right column	Dithiocarbamates  Where: R′ = alkyl groups such as amyl, butyl, ethyl, or methyl, or aryl groups such as phenyl or benzyl; R″ = alkyl groups such as amyl, butyl, ethyl or methyl, or aryl groups such as phenyl or benzyl; M = metals such as zinc, tellurium, copper, cadmium, nickel, bismuth, or lead; n = 2 in the case of zinc, copper, cadmium, nickel, and lead; = 3 in the case of bismuth; and = 4 in the case of tellurium or selenium

(continues)

TABLE 8.6—*(continued).*

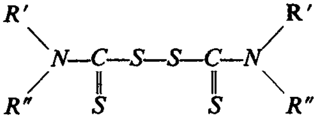
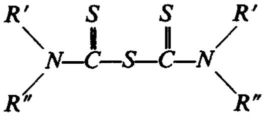
CHEMICAL STRUCTURE TYPES	ASTM D 4818 DESCRIPTION (GIVEN VERBATIM AS CITED IN THE STANDARD)	CHEMICAL STRUCTURE
Thiuram Disulfides	Examples of this group of ultra accelerators are shown in the right column	 Where: R′ = R″ = Alkyl group R′ = alkyl group R″ = aryl group, and R′ R″ = cyclic group R′ = R″ = methyl; tetramethyl thiuram disulfide (TMTD) R′ = R″ = ethyl; tetraethyl thiuram disulfide (TETD) R′ = methyl R″ = phenyl; dimethyl diphenyl thiuram disulfide (DMPTD)
Thiurams (Monosulfides)	Examples of this group of ultra-accelerators are shown in the right column	 Where: R′ = R″ = methyl; tetramethyl thiuram monosulfide (TMTM)

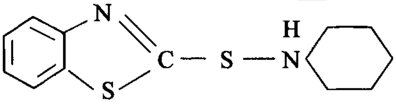
Table 8.7 gives the specific chemical structures for some rubber accelerators that are commonly used in industry [8].

Figure 8.10 shows the results of testing four different accelerators in the test recipe for SBR (ASTM D 3185) using a rotorless curemeter described in ASTM D 5289 with a sealed die design given in ASTM D 5289, (Fig. 4). This die design is reproduced again here in Figure 8.11.

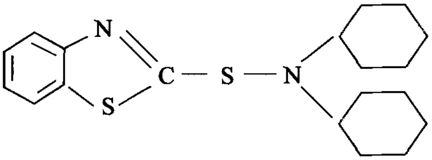
8.3.2.1 Standard Abbreviations As given in ASTM D 3853, these standard abbreviations for commonly used rubber accelerators in the rubber industry are given in Table 8.8.

8.3.2.2 Initial Melting Point (D 1519) This method discusses the use of a capillary tube containing the accelerator to measure the melting range. The initial melt point (first signs of liquid) can be a good measure of the relative purity of the accelerator. Significant amounts of other materials that are soluble in the accelerator cause a significant lowering of the initial melting point. This can be caused by naturally occurring impurities as well as the formation of degradation products. However, inorganic impurities or very high molecular weight material may not lower this initial melt point. There-

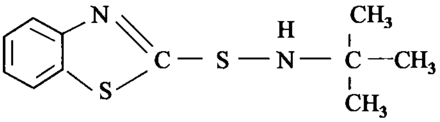
TABLE 8.7—Specific Chemical Structures for Some Rubber Accelerators Commonly Used in the Industry.



CBS



DCBS



TBBS

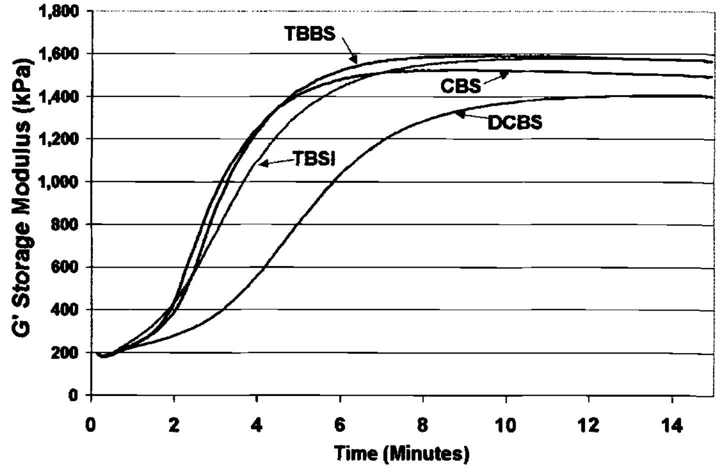


FIG. 8.10—Results of testing four different accelerators in the test recipe for SBR. (Mixed batches for comparative testing courtesy of Flexsys America)

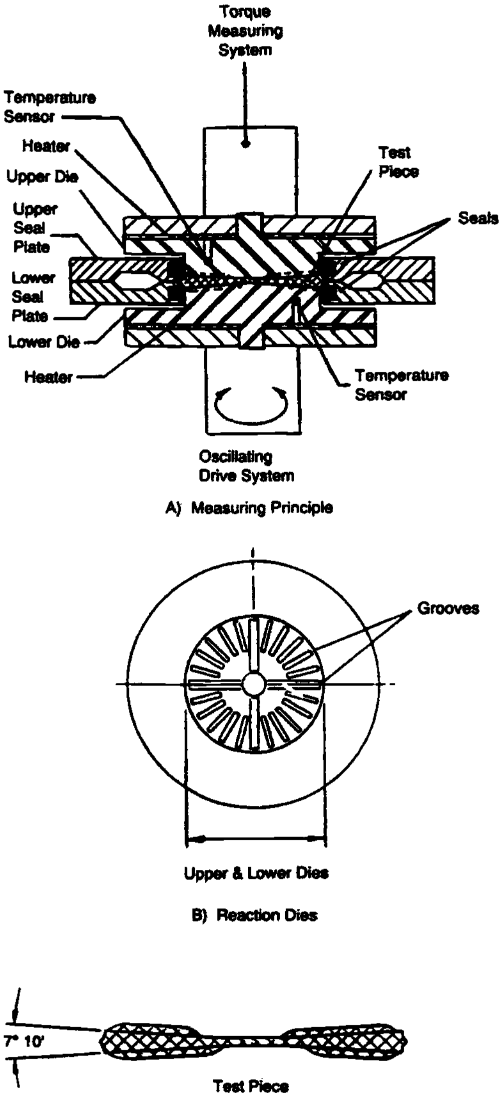


FIG. 8.11—Typical sealed torsion shear rotorless curemeter.

fore, while the melting point test can be a very important measure of the quality of an accelerator, it is not an absolute indication of the purity. Also, if the accelerator melts at a temperature above 300°C (such as with certain dithiocarbamates), this test may not be applicable.

8.3.2.3 Wet Sieve (Similar to D 4572) A wet sieve test is important for accelerators with a melting point higher than the mixing temperature of the

TABLE 8.8—Standard Abbreviations for Commonly Used Rubber Accelerators.

STANDARD ABBREVIATIONS	CHEMICAL NAME
BA	Butyraldehyde-aniline condensate
BiDMC	Bismuth dimethyldithiocarbamate
BMTS	Bis-morpholino-thiocarbamyl sulfenamide
CBS	N-cyclohexyl-2-benzothiazolesulfenamide
CdDEC	Cadmium diethyldithiocarbamate
CdDMC	Cadmium dimethyldithiocarbamate
Cd5MC	Cadmium pentamethylenedithiocarbamate
CEA	Cyclohexylethylamine
CuDIP	Copper diisopropyldithiophosphate
CuDMC	Copper dimethyldithiocarbamate
CuMBT	Copper 2mercaptobenzothiazole
DBA	Dibutylamine
DBQD	p,p′-dibenzoyl-p-benzoquinone dioxime or quinone dioxime dibenzoate
DBTU	1,3-dibutylthiourea
DBXD	Dibutyl xanthogen disulfide
DBzA	Dibenzylamine
DCBS	N,N-dicyclohexyl-2-benzothiazyl sulfenamide
DEPTD	Sym. Diethyldiphenylthiuram disulfide N,N′ Diethyl-N, N′-diphenylthiuram disulfide
DETU	1,3-diethylthiourea
DIBS	N,N-diisopropyl-2-benzothiazyl sulfenamide
DMPTD	Dimethyl diphenylthiuram disulfide
DOTG	Di- tolylguanidine
DPG	Diphenylguanidine
DPTD	Dipentamethylenethiuram disulfide
DPTH	Dipentamethylenethiuram hexasulfide
DPTM	Dipentamethylenethiuram monosulfide
DPTT	Dipentamethylenethiuram tetrasulfide
DTDM	Dithiodimorpholine
DTTU	N,N′-di-o-tolylthiourea
EFA	Ethyl chloride, formaldehyde, and ammonia reaction product
ETU	Ethylene thiourea
HMD	Hexmethylene diamine
HMDC	Hexamethylenediamine carbamate
HMMA	N,N′-hexamethylene-bis-methacrylamide
HMT	Hexamethylenetetramine
MBSS	4-morpholinyl-2-benzothiazyl disulfide
MBS	2-(morpholinothio)benzothiazole
MBSS	2-benzothiazole-N-morpholydisulfide
MBT	2-mercaptobenzothiazole
MBTS	Benzothiazyl disulfide
M-o-CA	4-4′-methylene-bis-(chloroaniline)
m-PBM	N,N′-m-phenylene-bis-maleimide
MPTD	N,N′-dimethyl-N,N′diphenylthiuram disulfide
MTT	3-methyl-thiazolidine-thione-2
NaDBC	Sodium dibutyldithiocarbamate
NaDMC	Sodium dimethyldithiocarbamate
NaDEC	Sodium diethyldithiocarbamate
NaIX	Sodium isopropylxanthate
OTBG	o-tolylbiguanide
OTOS	N-oxydiethylene thiocarbamyl-N′oxydiethylene sulfenamide
PbDAC	Lead diamyldithiocarbamate
PbDMC	Lead dimethyldithiocarbamate
PBQD	p-benzoquinone dioxime

(Continues)

TABLE 8.8—*(continued).*

STANDARD ABBREVIATIONS	CHEMICAL NAME
P5MC	Piperidinium pentamethylenedithiocarbamate
SeDEC	Selenium diethyldithiocarbamate
SeMDC	Selenium dimethyldithiocarbamate
TAC	Triallyl cyanurate
TAIC	Triallyl isocyanurate
TBBS	N- butyl-benzothiazolesulfenamide
TBSI	t-butyl-2-benzothiazole sulfenimide
TBTD	Tetrabutylthiuram disulfide
TBTU	1,1,3-tributylthiourea
TBzTD	Tetrabenzylthiuram disulfide
TCT	Tricrotonylidenetetramine
TeDEC	Tellurium diethyldithiocarbamate
TeDMC	Tellurium dimethyldithiocarbamate
TIBTD	Tetraisobutylthiuram disulfide
TETD	Tetraethylthiuram disulfide
TMTD	Tetramethylthiuram disulfide
TMTM	Tetramethylthiuram monosulfide
TU	Thiourea
ZnBX	Zinc butylxanthate
ZnDBC	Zinc dibutyldithiocarbamate
ZnDBzC	Zinc dibenzyldithiocarbamate
ZnDBP	Zinc dibutyldithiophosphate
ZnDEC	Zinc diethyldithiocarbamate
ZnDIBC	Zinc diisobutyldithiocarbamate
ZnDMC	Zinc dimethyldithiocarbamate
ZnEHBP	Zinc ethylhexyl-n-butyldithiophosphate
ZnEPC	Zinc ethylphenyldithiocarbamate
ZnEX	Zinc ethylxanthate
ZnIX	Zinc isopropylxanthate
ZnMBT	Zinc-2-mercaptobenzothiazole
Zn5MC	Zinc pentamethylenedithiocarbamate

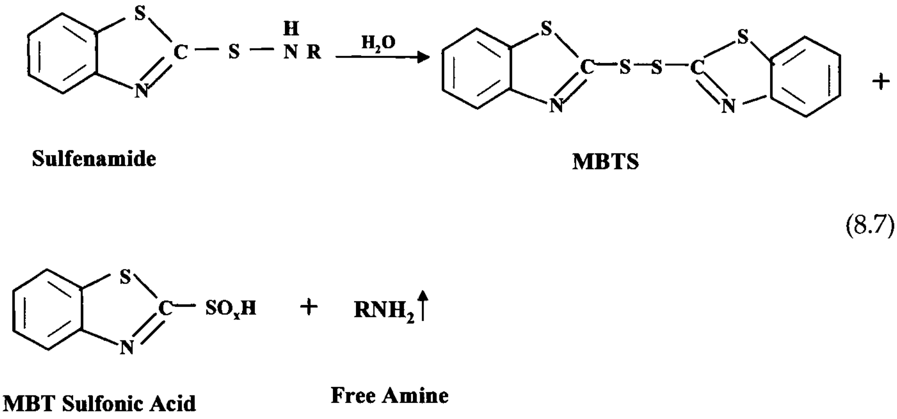
rubber compound. For an accelerator to be effective, it must uniformly disperse during the rubber mixing process and then dissolve at the cure temperatures. Thus it is critical for a high melting accelerator to have a fine particle size and be in an easily dispersible physical form. Unfortunately, this test cannot be used to test accelerators that are not in a powder form (such as masterbatches, pastes, etc.).

8.3.2.4 Percent Ash (D 4574) This is an impurity test, which will detect the presence of noncombustibles such as metallic or metallic oxide impurities. Siliceous "dirt" contamination might also be detected.

8.3.2.5 Percent Heat Loss (D 4571) This is a simple method to measure any moisture or other volatiles which might be present in the accelerator. For sulfenamide accelerators, this test may detect the presence of free amines, which are a product of the accelerator's decomposition. Excess moisture can affect a compound's cure characteristics.

8.3.2.6 Percent Moisture in Sulfenamides (D 4818) A direct measure of any moisture that might be present in a sulfenamide accelerator is quite important because sulfenamide degradation, while in storage, can be a result of hydrolysis.

8.3.2.7 Percent Insolubles in Sulfenamides (D 4934) By referencing Table 8.6, it can be seen that sulfenamide accelerators, as a class, are basically the MBT moiety attached to an amine. This bond, as shown in the chemical Eq 8.7 below, will break upon degradation, which might be promoted by moisture, impurities, heat, or long storage.



(8.7)

As can be seen, one of the products from this degradation reaction is MBTS [9]. The higher the concentration of MBTS means the further this degradation reaction has gone. MBTS is also a rubber accelerator; however, its presence in a sulfenamide is undesirable because it is more scorchy than the sulfenamides. Therefore, degraded sulfenamide accelerators may have significantly less scorch safety than fresh sulfenamide accelerators. MBTS is basically insoluble in either methanol or cyclohexane. Therefore ASTM D 4934 calls for methanol to be used as the solvent when measuring the percent insolubles in CBS, MBS, or TBBS. However, cyclohexane is used as the solvent when measuring insolubles in DCBS specimens. It is important to note that soluble species (by-products) can also be produced during sulfenamide degradation. Therefore, this insolubles test does not provide "an absolute measure of purity" for a sulfenamide. This is why the percent assay test may also be used to measure the purity of a sulfenamide.

8.3.2.8 Assay for Sulfenamides (D 4936) This is based on the principle of titrating the basic amines, which are freed from the sulfenamide accelerator upon the reduction of this accelerator with hydrogen sulfide gas. The dis-

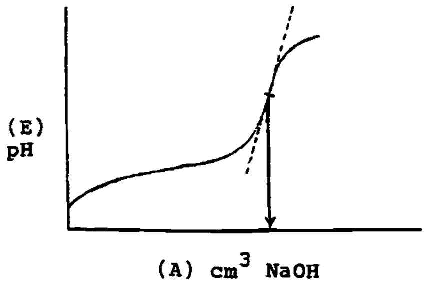


FIG. 8.12—Potentiometric titration using NaOH as the titrant, for MBT Assay, D 1991.

advantage of this method involves the use of hydrogen sulfide gas, which is very toxic. Because of the high toxicity of this gas and the required safety precautions, many laboratories have chosen to eliminate this test. However, there is now an alternate procedure that might be considered that uses MBT as the reducing agent.

8.3.2.9 MBTS Assay (D 5051) This is a common method for measuring the purity of MBTS accelerator. It is essentially the titration of liberated iodine from the reduction of the MBTS (using $Na_2S_2O_3$ solution with starch indicator) from the presence of potassium iodide in an acid medium.

8.3.2.10 Assay for DPG and DOTG (D 5054) This is an assay test for measuring the purity of DPG and DOTG accelerators. It consists of a titration of the "guanidine class" of accelerators with hydrochloric acid.

8.3.2.11 MBT Assay (D 1991) This is another assay test for monitoring the purity of MBT accelerator. It is a potentiometric titration of MBT using sodium hydroxide solution. The end-point is illustrated in Fig. 8.12.

8.3.3 Zinc Oxide

As mentioned earlier, zinc oxide is the principle chemical used to activate the accelerator for a sulfur cure. Therefore, its quality characteristics are very important [10]. Certainly not all "zinc oxides" are the same in regards to their performance in rubber. ASTM D 4295 classifies zinc oxide into different performance grades based on differences in chemical characteristics. Table 8.9 shows the established ASTM classification of different grades for zinc oxide used in rubber.

This table shows four different types of zinc oxides used in the rubber industry. These types are as follows:

- American Process or Direct Type
- French Process or Indirect Type (3 classes)

TABLE 8.9—Typical Properties of Zinc Oxide.

						SECONDARY TYPES		
	ASTM	AMERICAN TYPE	FRENCH TYPE (INDIRECT)				METALLURGICAL	
PROPERTY	METHOD	(DIRECT)	CLASS 1	CLASS 2	CLASS 3	CHEMICAL	CLASS 1	CLASS 2
% Zinc oxide	D 3280	99.0	99.5	99.5	99.5	95.0	99.0	99.0
% Lead	D 4075	0.10	0.002	0.002	0.002	0.10	0.10	0.10
% Cadmium	D 4075	0.05	0.005	0.005	0.005	0.05	0.05	0.05
% Sulfur	D 3280	0.15	0.02	0.02	0.02	0.15	0.02	0.02
% Heat loss at 105°C	D 280	0.25	0.30	0.25	0.25	0.50	0.25	0.25
% Sieve residue, 45 μm	D 4315	0.10	0.05	0.05	0.05	0.10	0.10	0.10
Surface area, m^2/g	D 3037	3.5	9.0	5.0	3.5	40.0	5.0	3.5

- Secondary Zinc Oxide Type—Chemical
- Secondary Zinc Oxide Type—Metallurgical (2 classes)

8.3.3.1 American Process or Direct Type This type of ZnO is produced from the reduction and reoxidation of a zinc bearing material, i.e., zinc ore, with carbonaceous fuel. This type can have broadly varying chemical and physical characteristics. Many times the nodular-type particle shape is preferred for rubber compounding. Because the properties for this type can vary greatly, it is difficult to generalize regarding its properties and characteristics.

8.3.3.2 French Process or Indirect Type This type of ZnO is produced from the burning of zinc vapor, which is formed from the boiling of zinc metal in a retort. Since this zinc oxide is from the metal and not directly from the ore, it is characteristically more pure (better than 99.9 % pure). Usually the zinc oxide particle shape from this process is nodular in shape. The three different classes of French Process ZnO, given in Table 8.9, represent different surface areas. The finer the average particle size results in a higher surface area. Higher surface area zinc oxide grades are more reactive because they have more surface area exposed at the interface in the rubber compound medium.

8.3.3.3 Secondary Zinc Oxide—Chemical Type This type of zinc oxide is produced as a by-product from a chemical reaction. The properties of these types of zinc oxide can vary greatly. Its quality is greatly dependent on the source of raw material and the nature of the reaction.

8.3.3.4 Secondary Zinc Oxide—Metallurgical This type is produced by burning zinc vapor from boiling scrap zinc. Since scrap zinc can vary greatly, the chemical and physical quality of this grade can also vary greatly. As noted from Table 8.9, there are two different grades of this type of zinc oxide based on surface area differences.

8.3.3.5 Zinc Oxide Treatment It is important to note that zinc oxide will commonly be treated with a fatty acid, which is usually propionic acid. This fatty acid treatment is typically about 0.5 %, which results in 0.5 % less zinc oxide. Sometimes, these treatments have been reported to improve the dispersion of the zinc oxide in certain rubber compounds.

8.3.3.6 Zinc Oxide Test Methods As noted from the classification table for different rubber grades of zinc oxide (Table 8.9), there are several standard tests that are commonly used to analyze the quality of zinc oxides used in rubber. Many of these are described in more detail in ASTM D 4315, Standard Test Methods for Rubber Compounding Material—Zinc Oxide.

8.3.3.6.1 Surface Area (D 3037 and D 4315)—This is perhaps one of the most important tests to perform when trying to predict how well a given grade of zinc oxide will perform in a rubber compound. The smaller the average particle size of a zinc oxide means the higher the effective surface area that will interface in the rubber hydrocarbon medium. This higher surface area will allow greater opportunity for the zinc oxide to react with the stearic acid present, solubilize the zinc ion, and activate the accelerator to initiate vulcanization. However, too fine a particle size, in some cases, might make it more difficult to achieve good dispersion, depending on the type of rubber mixing process. The method used to control average particle size is ASTM D 3037 (for measuring nitrogen adsorption surface area for carbon blacks), which can be run under modified conditions to also test zinc oxide in accordance with ASTM D 4315.

8.3.3.6.2 Percent Lead and Cadmium (D 4075 and D 4315)—This can be an important test to detect and quantify the presence of lead and cadmium, two impurities that are commonly found in zinc oxide. Both lead and cadmium can affect how a zinc oxide will activate a cure. Both lead and cadmium are very toxic. Therefore it is important to test for the presence of these metals and measure how much, if any, are present in order to control the uniformity of the cure and to know how to protect workers from any possible toxic exposure. The most common method for measuring lead and cadmium impurities is through the use of atomic absorption spectroscopy.

8.3.3.6.3 Percent Residue on 45 μm Sieve (D 4315)—This method detects any particles present that are larger than 45 μm in diameter. These particles could include zinc oxide itself as well as foreign contamination (such as dirt). Large particles are always undesirable because they can cause stress points when the cured rubber is stretched. These stress points could cause crack propagation and tearing.

8.3.3.6.4 Percent Heat Loss at 105°C (D 280)—Generally used to detect and measure volatile components, primarily moisture. Water can react with zinc oxide forming zinc hydroxide, thus reducing the activity of this compounding ingredient. It should be remembered that a typical propionic acid treated zinc oxide (commonly at 0.5 % treatment) may increase a heat loss value by around 0.2 %.

8.3.3.6.5 Percent Sulfur (D 3280 and D 4315)—These methods detail the chemical procedure for measuring sulfur impurities in zinc oxide.

8.3.3.6.6 Percent Zinc Oxide Purity (D 3280, D4295, and D 4315)—These methods cover determination of the assay for the purity of zinc oxide.

8.3.3.6.7 Test Recipe (D 4620)—This method specifies a standard rubber test recipe that can be used to evaluate the effective surface area of a specific grade of zinc oxide in rubber. The recipe used is based on a mercaptan modified chloroprene rubber, where zinc oxide functions more as a vulcanizing agent and not just an activator. Therefore, this recipe is more sensitive to subtle differences in the surface area among different grades of zinc oxide than a conventional recipe (where zinc oxide only functions as an activator). A lower surface area zinc oxide will impart a longer cure time to the compound, as seen by $t'90$ (defined in D 2084 for ODR and D 5289 for MDR). Test recipe is given in Table 8.10.

Since other factors besides surface area can effect the cure times, this method cannot be used for accurate surface area measurements. On the other hand, an apparatus for directly measuring the surface area of zinc oxide by nitrogen adsorption is usually quite expensive, and the majority of rubber laboratories do not have such an apparatus. However, if two or more different grades of zinc oxide were evaluated side-by-side in the cited recipe, in accordance with ASTM D 4620, then a fairly good ranking of these zinc oxide samples, in relation to their specific surface area, could be achieved.

8.3.4 Stearic Acid

This is the other principle activator that is used in the vast majority of rubber compounds with zinc oxide to activate the cure. It is generally known that stearic acid reacts with the zinc oxide in the rubber compound to produce a salt that reacts with the rubber accelerator to initiate an effective vulcanization. What the rubber industry calls "rubber grade stearic acid" is not pure stearic acid. The grade of "stearic acid" selected as a rubber compound-

TABLE 8.10—Recipe from ASTM D 4620 for Evaluating Zinc Oxide.

MATERIAL IDENTIFICATION	PARTS PER HUNDRED RUBBER (PHR)
Chloroprene-rubber (mercaptan modified) (Mooney viscosity ML 1 + 4' at 100°C by D 1646 is between 40 to 50 MU)	100
Octylated diphenylamine	1
Magnesium oxide (Scorchguard O)	4
N774 carbon black	30
Zinc oxide	5
3-methyl-thiazolidine-thione-2 (curative)	0.5
Total	140.5

TABLE 8.11—Typical Physical and Chemical Properties of Stearic Acid—Class Number 1^A.

Property	Test Method	Grade 1 Low-IV ^{B}	Grade 2 Med-IV ^{B}	Grade High-IV ^{B}
Ash, %	D 1951	0.2 max	0.2 max	0.2 max
Iodine value, g/100 g	D 1959	8 max	15 max	39 ± 5
Saponification value, mg KOH/g	D 1962	204.5 ± 5.0	204.5 ± 5.0	...
Unsaponification matter, %	D 1965	3.0 max	3.0 max	...
Acid value, mg KOH/g	D 1980	203.5± 4.5	203.0 ± 4.5	203.5 ± 4.5
Titer, °C	D 1982	56.0± 4.5	53.0 ± 3.0	48.5 ± 4.5
^{C}Trace metals, ppm	D 4075	varies from industry to industry		

^{A} The values listed in Table 8.11 are typical ranges and values.

^{B} IV-iodine value.

^{C} Trace metals such as nickel, iron, copper, and manganese can be determined in accordance with Test Method D 4075.

TABLE 8.12—Typical Physical and Chemical Properties of Stearic Acid—Class Number 2^A.

Property	Test Method	Grade 1, Palmitic/Stearic 50/40 ^{B}	Grade 2, Palmitic/Stearic 30/65
Ash,%	D 1951	<0.1	<0.1
Iodine, value, g/100 g	D 1959	1.0 max	1.0 max
Saponification value, mg KOH/g	D 1962	208.5 ± 2.5	203.5 ± 3.0
Unsaponification matter, %	D 1965	0.2 max	0.5 max
Acid value, mg KOH/g	D 1980	208.5± 2.0	203.0 ± 3.0
Titer, °C	D 1982	55.5± 1.0	60.0 ± 2.0
^{C}Trace metals, ppm	D 4075	varies from industry to industry	

^{A} The values listed in Table 8.12 are typical ranges and values.

^{B} Even though this grade contains more palmitic acid than stearic acid, this grade is still referred to as "stearic acid" in the rubber industry.

^{C} Trace metals such as nickel, iron, copper, and manganese can be determined in accordance with Test Method D 4075.

ing ingredient is usually a mixture of stearic acid, palmitic acid, and oleic acid as derived from hydrolysis of triglycerides from tallow or fats from other animal or vegetable sources. The ratio of these different fatty acid components determines how they will be classified as a rubber grade "stearic acid." The stearic acid producer can use various processes such as hydrogenation, crystallization, distillation, bleaching with diatomaceous earth, etc., to adjust the fatty acid composition in order to meet the chemical characteristics of a specific grade of stearic acid.

A classification of rubber grades of "stearic acid" in accordance with ASTM D 4817 is given above in Tables 8.11 and 8.12.

This classification is based mainly on unsaturation level (the iodine value) and the stearic/palmitic acid ratios. A high iodine value indicates high unsaturation. Unsaturation can usually be attributed to the presence of oleic acid (C18 fatty acid with one unsaturated site per molecule). It is also possible to have small quantities of polyunsaturated fatty acids such as linoleic acid and linolinic acid, which are more susceptible to oxidative attack and are much less stable than oleic acid. Overall, high unsaturation in a rubber grade stearic acid can affect the curing characteristics of the rubber compound. In some cases, high unsaturation can lead to higher hysteresis (heat buildup) of the vulcanizate. Also, high levels of unsaturation can affect the solubility of the "stearic acid" in rubber leading to migration to the surface ("bloom" or exudation).

The palmitic acid to stearic acid ratio can affect the titer point (or melt point) of the rubber grade "stearic acid." It is somewhat ironic that one of the grades of "stearic acid" given in Table 8.12 actually has more palmitic acid than stearic acid. Palmitic acid is a saturated C16 while stearic acid is a saturated C18 fatty acid. Chemically, stearic acid and palmitic acid are very similar, except palmitic acid is two carbon atoms shorter than the stearic acid chain.

One should check for metallic impurities in all stearic acid grades because many of these metallic impurities are transition metals, which are strong pro-oxidants that can accelerate degradation of a cured rubber compound while in service. What can be particularly harmful is that these metallic impurities will probably be present in the form of stearates, which are usually highly soluble in the rubber hydrocarbon medium. This solubilizes the metallic ion, which can cause great harm to the rubber. One should be on the lookout for nickel impurities since nickel is sometimes used as a catalyst in the production of rubber grade stearic acid. Also, copper and manganese are metallic impurities that are particularly harmful to rubber.

8.3.4.1 Iodine Value (D 1959) This is a good way to detect and partially quantify the presence of unsaturated fatty acids such as oleic, linoleic, or linolinic acid, which may be present with saturated fatty acids such as stearic acid and palmitic acids. This method consists of dissolving the fatty acid sample in a solvent, such as isooctane or fresh cyclohexane, which has replaced the extremely hazardous and toxic carbon tetrachloride, now banned in many states. Then a special Wijs solution is quantitatively added. This Wijs solution is a special preparation consisting of iodine monochloride and acetic acid. The sample flask and a blank are stored in the dark under specified conditions to allow the iodine to react with the unsaturation through an addition reaction. Afterwards, potassium iodide solution is added to liberate the unreacted excess iodine as shown below.

$$2\,ICl + 2KI \rightarrow 2KCl + 2I_2$$

The amount of liberated iodine is measured by titrating with standard sodium thiosulfate solution using a starch indicator solution. This is demonstrated below.

$$2I_2 + 4Na_2S_2O_3 \rightarrow 4NaI + 2Na_2S_4O_6$$

8.3.4.2 Titer (D 1982) As discussed above, rubber grade "stearic acid" contains a mixture of saturated and unsaturated fatty acids. The higher the level of nonstearic acid components, especially the unsaturated fatty acids, the lower the titer point (solidification point). This method is a relatively simple, indirect way to measure the purity of a "rubber grade" stearic acid. The method itself calls for the specimen to be dried under specified conditions, heated about 10°C above the anticipated titer point, and cooled under specified controlled conditions in a test tube until the temperature either remains unchanged for 30 s or rises. The actual titer point is defined as the highest temperature achieved during the temperature rise while cooling. Figure 8.13 shows the actual apparatus used for this test.

8.3.4.3 Acid Value (D 1980) Here, the fatty acid or rubber grade stearic acid activator is dissolved quantitatively in 95 % ethanol and titrated with sodium hydroxide solution to a phenolphthalein end point. This method reports what is called an "acid value." It relates to all acidic components, not just fatty acids. This method has value as a quality test for fatty acid materials.

8.3.4.4 Saponification Value (D 1962) This method was discussed under Synthetic Plasticizer Section, Part 8.2.2.4. Unlike acid value given above, saponification value relates to the total acid content as well as the ester content that is present (usually triglycerides).

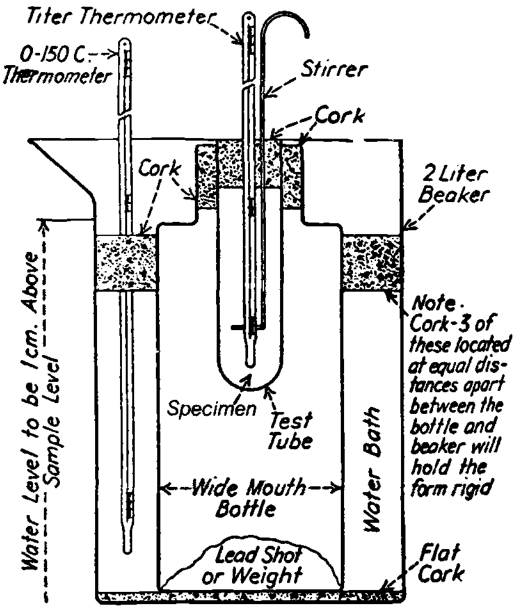


FIG. 8.13—Apparatus assembly for titer test.

8.3.4.5 Percent Ash (D 1951) This procedure involves igniting the fatty acid sample in a specified crucible, under controlled conditions, and quantitatively determining the residual ash. This is a simple way to quantify inorganic or non-combustible impurities which might be present.

8.3.4.6 Unsaponfication Matter (D 1965) This procedure measures "unsaponifiable matter" that might be present in the fatty acid sample. These are materials that cannot be saponified with either NaOH or KOH, yet are soluble in common "fat solvents." Examples of unsaponifiables include sterols, aliphatic alcohols, and other hydrocarbons. This method involves saponification of the sample with KOH for 1 h using a reflux condenser, followed by an extraction procedure with petroleum ether in a separatory funnel.

8.3.4.7 Trace Metal (D 4075) This method calls for the use of flame atomic absorption spectroscopy to measure the presence of trace quantities of these metals down to the parts per million level. Trace quantities of copper, manganese, iron, or cobalt might be particularly bad, in that they would probably be present in a rubber soluble form (as a soap). This would increase their degrading qualities to the rubber compound, since they are prooxidants in nature.

8.4 ANTIDEGRADANTS

Antidegradants are rubber compounding ingredients that are added to a rubber compound to protect the vulcanizate from oxidative attack. An antidegradant can function as an antioxidant (protecting against effects of oxygen) and/or an antiozonant (protecting the cured rubber from the surface attack of ozone) [11]. ASTM D 4676 classifies these rubber antidegradants into six different classes given below:

- P-Phenylenediamines (PPDs)
- Trimethyl-dihydroquinolines (TMQs)
- Phenolics
- Alkylated Diphenylamines (DPAs)
- Aromatic Phosphites
- Diphenylamine-Ketone Condensates

The following is a discussion of these six classes of antidegradants used in the rubber industry. Also Table 8.13 gives examples of chemical structures for each type.

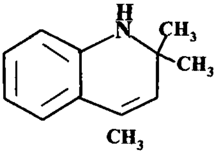
8.4.1 Class I: p-Phenylenediamine (PPDs)

This class of antidegradant is primarily used in tires and in some mechanical rubber goods as an antiozonant to give protection against ozone at-

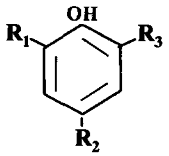
TABLE 8.13—Chemical Structures of Antidegradants.

Where R is Alkyl, Aryl, or both

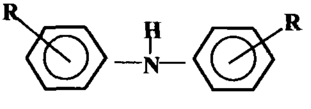
p-phenylenediamine (PPDs)



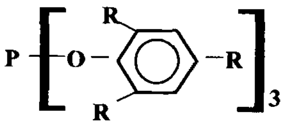
TMQ Type



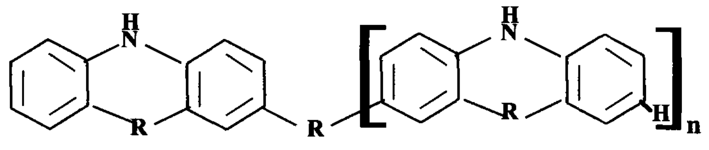
Phenolic AOs



Alkylated Diphenylamine AOs



Aromatic phosphites



n = 1-5

Diphenylamine-Ketone Condensate Type AO

tack while the rubber is flexing. These chemicals are also used for their antioxidant and antiflex fatigue characteristics that they impart to the compound. Unfortunately, these additives will impart staining and discoloration characteristics to a rubber compound as well. Different members of this class will impart different degrees of ozone resistance and flex resistance. These PPD compounds bloom to the surface of the rubber article in order to react with ozone and protect the rubber surface. Different types of PPDs have different degrees of chemical reactivity with ozone, different degrees of solubility, and different diffusion rates in the rubber compound. These characteristics determine how much protection a given PPD will impart to a rubber article and whether it will be long-term or short-term protection. There are three types of PPDs that are discussed below:

8.4.1.1 Type 1: N,N′-dialkyl-*p*-phenylenediamines Usually these additives have secondary alkyl groups (C6 or larger). These chemicals are usually liquids at room temperature.

8.4.1.2 Type II: N-alkyl-N′aryl-*p*-phenylenediamines These AOs are either used as a single chemical component or consist of a mixture of two or more components. They may be in either a liquid or solid state.

8.4.1.3 Type III: N, N′-diaryl-*p*-phenylenediamines These PPDs can consist of one chemical component or a mixture of three or more isomers. Usually, AOs in this class are in solid form at room temperature.

8.4.2 Class 2, Trimethyl-dihydroquinolines (TMQs)

These rubber additives are primarily used as general-purpose antioxidants to protect rubber products from atmospheric oxygen attack, especially at higher temperatures. This class represents some of the more popular antioxidants used in the rubber industry. They are the condensation products from the reaction of aniline and acetone. Because this polycondensation reaction is quite complicated and reaction conditions may vary, the AOs in this group may contain a small percentage of the TMQ itself, with a wide variety of other related oligomers (dimers, trimers, etc.), which are also effective AOs. Different commercial products in this category have different degrees of polymerization and different softening points as a consequence. Different TMQs are made with different ratios of aniline to acetone. These AOs are considered moderately staining.

8.4.3 Class 3, Phenolics

As compounding ingredients, these chemicals are used as relatively weaker antioxidants and are relatively nonstaining and nondiscoloring. These AOs are used in light colored mechanical goods and in tire white sidewall applications. There are three types of phenolic AOs that are discussed below:

8.4.3.1 Type I: Monofunctional Phenols These AOs are often referred to as "hindered phenols." While this type may be the best nondiscoloring, it is the weakest in antioxidant activity compared to the other phenolic types. Since this type has the lowest average molecular weight, it is therefore more volatile.

8.4.3.2 Type II: Bifunctional Phenols These AOs are also referenced as hindered bisphenols. This is the most important type of phenolic AO, which is used in the rubber industry.

8.4.3.3 Type III: Multifunctional Phenols This type of phenolic AO, as a rule, has a higher molecular weight than Type II and therefore lower volatility. However, this type also has equivalent AO activity compared to Type II.

8.4.4 Class 4, Alkylated Diphenylamines

This class of AO is manufactured as a complex reaction product of diphenylamine with various alkylating agents. The selection of reactants by the manufacturer is done to provide the best balance between cost and performance. This class is a good representation of substituted amine antioxidants used in rubber compounding and is generally considered moderately staining and discoloring in a compound.

8.4.5 Class 5, Aromatic Phosphites

These antioxidants are nonstaining relative to other classes of AOs. They are commonly used as stabilizers for synthetic elastomers.

8.4.6 Class 6, Diphenylamine-Ketone Condensates

This class of rubber antioxidant is generally manufactured as a reaction product of diphenylamine and an alkyl ketone, usually acetone. Some versions are further condensed with formaldehyde, yielding products of high molecular weight. This AO class protects the rubber from degradation resulting from oxidative attack and heat. Usually compounding additives from this AO class are in a liquid form or will consist of low melting resins with low volatility.

8.4.7 Standard Abbreviations

As given in ASTM D 3853, these standard abbreviations are commonly used for rubber antioxidants and antiozonants in the rubber industry as given in Table 8.14.

8.4.8 Test Methods for Antidegradants

The following is a discussion of ASTM standard test methods for testing rubber antidegradants.

8.4.8.1 Purity of *p*-Phenylenediamine Antidegradant by Gas Chromatography (D 4937) This is the standard method for measuring the purity of PPD antiozonants and is applicable to all three classes using gas chromatography (GC) detection and area normalization for data reduction.

8.4.8.2 Purity of Phenolic Antioxidants According to ASTM D 4676, the purity of these AOs can sometimes be measured by high pressure liquid chromatography (HPLC) and in some cases even gas chromatography (GC); however, no specific ASTM method for either one of these procedures has been developed as of this publication date. However, the melting point for these materials by ASTM D 1519 is commonly used as an indication of their purity. Refractive index for phenolic AOs, in the liquid form, by ASTM D 1218 and D 1747 can also be used.

TABLE 8.14—Standard Abbreviations Commonly Used for Rubber Antioxidants and Antiozonants in the Rubber Industry.

STANDARD ABBREVIATIONS	CHEMICAL NAME
AANA	Aldol-α-naphthylamine
ADPA	Acetone diphenylamine condensation product
APPD	N-alkyl-N'-Phenyl-p-phenylenediamine
p-BBp14	4,4'-butylidene-bis-(6-t-butyl-m-cresol)
BHA	Butylated hydroxyanisole
BHT	2,6-di-butyl-4-methylphenol (butylated hydroxy toluene)
CPPD	N-cyclohexyl-N'-phenyl-p-phenylenediamine
DAHQ	2,5-di-amylhydroquinone
DBHQ	2,5-di-tert-butylhydroquinone
DLTDP	Dilauryl thiodipropionate
i88PD	N,N'-bis-(1-methylheptyl)-p-phenylenediamine
DNPD	N,N'-di-2-naphthyl-p-phenylenediamine
DOPD	Dioctyl-p-phenylenediamine
DPA	Diphenylamine
DPPD	N,N'-diphenyl-p-phenylenediamine
DSTDP	Distearylthiodipropionate
DTPD	N,N'-ditolyl-p-phenylenediamine
ETMQ	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
o-IBBp11	2,2'-isobutylidene-bis-(4,6,-di-methylphenol)
p-IPBp(4)n	Polybutylated bisphenol A
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
MBI	2-mercaptobenzimidazole
o-MBp1C	2,2'-methylene-bis-(4 methyl-6-cyclohexylphenol)
o-MBp1(1C)	2,2'-methylene-bis[6-(1-methyl cyclohexyl)-p-cresol]
o-MBp14	2,2'-methylene-bis-(4-methyl-6-t-butylphenol)
o-MBp19	2,2'-methylene-bis-(4-methyl-6-nonylphenol)
o-MBp24	2,2'-methylene-bis-(4-ethyl-6-t-butylphenol)
p-MBp44	4,4'-methylene-bis-(2,6-di-t-butylphenol)
MMBI	Methyl-2-mercaptobenzimidazole
NiDBC	Nickel dibutyldithiocarbamate
8DPA	Octylated diphenylamine
PAN	N-phenyl-alpha-naphthylamine
PBN	N-phenyl-beta-naphthylamine
i-8PPD	N-phenyl-N'-2-octyl-p-phenylenediamine
P3DPA	p-isopropoxylateddiphenylamine
SPDA	Styrenated diphenylamine
SPH	Styrenated phenol
p-TBp14	4,4'-thio-bis-(2-t-butyl-m-cresol)
TMQ	2,2,4-trimethyl-1,2-dihydroquinoline (oligomer)
TNPP	Tri(nonylphenyl)phosphite
ZnMBI	Zinc-2-mercaptobenzimidazole
ZnMMBI	Zinc-methyl-2-mercaptobenzimidazole
6PPD	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine
7PPD	N-(1,4-dimethylpentyl)-N'-phenyl-p-phenylenediamine
77PD	N,N'-bis-(1,4-dimethylpentyl)-p-phenylenediamine
8PPD	N-octyl-N'-phenyl-p-phenylenediamine
88PD	N,N'-dioctyl-p-phenylenediamine
9DPA	Nonylated diphenylamine
29DPA	Ethylated/nonylated diphenylamine
48DPA	Butylated/octylated diphenylamine

8.4.8.3 Purity of TMQs, Alkylated Diphenylamines and Phosphite Antidegradants Basically these three classes of AOs are reaction mixtures and not well defined chemical structures. It is common practice to use HPLC or sometimes GC to measure the quality of these AOs; however, no specific standard ASTM method has been developed as of this publication date. Therefore, an indirect method is to use ASTM D 5376 to determine percent basic nitrogen. This method consists of a careful potentiometric titration of an acetone solution of TMQ with specified acids. Also ASTM D 4676 cites the use of UV spectroscopy with a standard to ascertain the purity of complex alkylated diphenylamine. ASTM D 2702 for infrared spectroscopy is recommended by D 4676 to relate to the purity of mixed aromatic phosphites. Lastly, D 4676 recommends that a melting point procedure be used for determining the purity of diphenylamine-ketone condensates.

8.4.8.4 Volatile Materials for PPDs The second part of ASTM D 4571 specifically outlines measurement of volatile materials in PPD antiozonants. This method determines the loss on heating at 70°C to measure volatile organics and moisture.

8.4.8.5 Percent Ash The second part of D 4574 can be used to test PPDs for ash content. It measures noncarbon components that remain after ashing in a muffle furnace, essentially the amount of inorganic impurities that are present.

8.4.8.6 Softening Point ASTM D 4676 also recommends that a softening point be performed on TMQs by either E28 or D3461. Since TMQ is amorphous (not crystalline), it does not have a sharp melt transition like crystalline materials. The softening point relates to the degree of oligomerization for a TMQ.

8.4.8.7 Hydrolysis Stability ASTM D 4676 recommends that this test be performed on aromatic phosphite antioxidants in order to measure their relative resistance to hydrolysis.

8.5 PROTECTIVE WAXES

As discussed earlier, *p*-phenylenediamine antiozonants are commonly used as a rubber compounding ingredient to protect the cured rubber article surface against ozone attack while being flexed (dynamic conditions). However, petroleum waxes are also used as rubber compounding ingredients to protect the cured rubber surface against ozone attack under *static* conditions (no flexing). Commercial blends of low-molecular-weight paraffin wax, higher-

TABLE 8.15—Protective Wax Classification.

TYPE	WAX DESIGNATION	MASS WAX OF BOILING POINT >538°C, %
A	paraffin	<1
B	modified paraffin	1–10
C	intermediate microwax content	10–30
D	high microwax content	>30

molecular-weight paraffin wax, and usually a certain amount of microcrystalline wax, are commonly used as rubber compounding ingredients for this purpose [12]. These waxes bloom to the surface of the rubber article at different rates, offering a wide range of protection. Once these waxes bloom, they can establish a protective physical barrier against ozone. Some petroleum microcrystalline wax is commonly used to impart flexibility to this wax barrier so that it is less likely to crack and lose its protective quality. Generally, a great deal of trial and error in compound development may be required before the correct blend of waxes, which will provide the best protection for a given rubber compound, is found. Once this blend of petroleum waxes is established for the proper compound, the wax tests described here should be used to characterize the blend and assure uniformity of all future wax shipments. Variations in the chemical composition of the wax can greatly affect its usefulness as an antiozonant. Table 8.15 from ASTM D 4924 shows an ASTM classification for waxes.

8.5.1 Test Methods

The following are standard test methods which are prescribed by ASTM D 4924 regarding the classification of petroleum waxes used in rubber. These methods are described below:

8.5.1.1 Boiling Point, Determination by GC Distillation (D 2887) This method uses the gas chromatograph to determine the boiling range distribution of waxes and some other petroleum products. Therefore, it should relate somewhat to the molecular weight distribution of the wax being used as a rubber compounding ingredient. These waxes used in rubber are usually blends of low MW, high MW, and microcrystalline waxes. This method is applicable to samples with fractions that have final boiling points as high as 538°C. This procedure is performed through gas chromatography (simulated distillation techniques), which is programmed to thermally ramp the column temperature in a linear manner. This method is the basis for the wax classification system given by ASTM D 4924.

8.5.1.2 Melting Point and/or Congealing Point (D 87, D 938, D 3944, D 4419) Method D 87 is applied to waxes that contain a significant amount of crystallinity. Here molten wax is placed in a test tube in an air bath, which, in turn, is held in a water bath set at 16 to 28°C. The temperature is plotted as the wax cools. Because of the crystalline content of the wax, there is a recrystallization exotherm that results when the molten wax sample is cooled to a sufficiently low enough temperature. When this happens, the heat from the recrystallization causes the cooling curve to plateau (giving up the heat of fusion). The end-point is defined as the temperature at which the first five points are within 0.1°C of each other when reading the temperature every 15 s. The test results are reported as the average of these last five readings as "Melting Point (Cooling Curve)."

ASTM D 938 is similar to ASTM D 87 in that it also ascertains a congealing point; however, D 938 determines the end-point from when a drop of wax on the end of a thermometer bulb stops moving around the bulb with the rotation of the thermometer. D 938 might possibly be a little more sensitive than ASTM D 87 to variations in the type and level of crystallinity that might exist with a wax: but ASTM D 87 may have a less subjective end point.

ASTM D 3944 is still another congealing point test that uses a thermocouple inserted into the wax sample. A chart recorder denotes the temperature drop as the sample cools. The first significant change in the curve's slope is defined as the "solidification point." This method is sometimes preferred for quality control of waxes because it is faster to perform than either ASTM D 87 or ASTM D 938.

ASTM D 4419 is used to quantify thermal transitions of waxes. This method calls for the use of the *differential scanning calorimeter* (DSC) to make these measurements. Waxes will display a first order thermal transition for the melt transition. There is some evidence that for the same series of waxes, wider molecular weight distribution will cause the width of the major first order transition to be wider at the base. Also, microcrystalline wax content will cause a shoulder to appear on these transition peaks as shown in Fig. 8.14.

8.5.1.3 Refractive Index (D 1747) This is similar to the method described earlier in Section 8.2.2.3—Synthetic Plasticizers, except this procedure is designed for measuring refractive index for melted solids (such as melted waxes) at an established temperature between 80 and 100°C. Refractive index will provide a characteristic value, which is affected by microcrystalline content. In fact, one wax producer has plotted the melting point of a variety of waxes against their refractive index. In theory, the higher average molecular weight of a wax series of perfectly normal (no branching) specimens, the proportionally higher the melt point and refractive index. A theoretical "normality" line for these waxes could be plotted on an MP/RI plot. Waxes that contain highly branched material or microcrystalline content will deviate from this line. Therefore, a MP/RI plot might be an interesting method for comparing different waxes.

8.5.1.4 Percent Oil (D 721) This procedure involves dissolving the preweighed wax sample in methyl ethyl ketone (MEK) and cooling the solution to −32°C in order to precipitate the wax and remove it by filtration. The percent oil is calculated by weighing the oil residue left after the MEK has evaporated away. High oil content in a wax can affect the hardness and flexibility of a wax as well as its melting point.

8.5.1.5 Viscosity (D 445) This is the kinematic viscosity test which was discussed in Section 8.1.8.3 under Process Oils.

8.5.1.6 Color (D 1500) This method was discussed earlier in Section 8.1.8.8 under Process Oils.

8.5.1.7 Needle Penetration (D 1321) This method is commonly used in characterizing different waxes. It is simply the depth of penetration into a wax sample that a standard needle achieves under a defined load and time. The instrument used to make this measurement is called a *penetrometer*. This is a common method to measure the hardness of a given wax. The extent of crystallinity as well as other qualities affects the hardness of a wax. Variations in these wax qualities could also affect performance in a rubber compound. Therefore the Needle Penetration Test has some usefulness for qual-

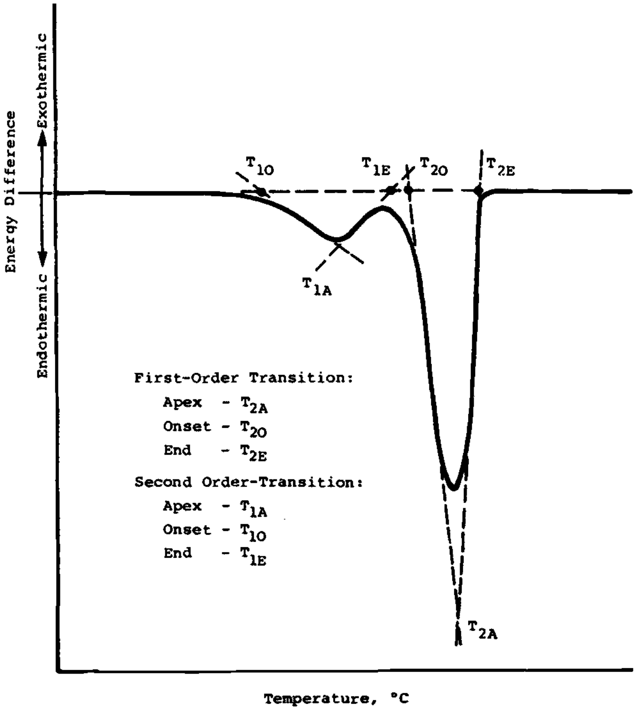


FIG. 8.14—DSC curve.

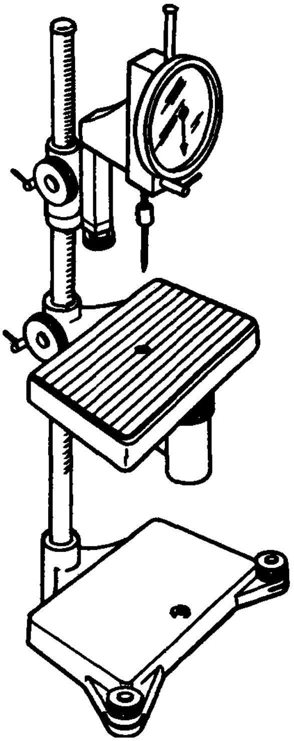


FIG. 8.15—Penetrometer used in Standard D 1321.

ity assurance testing of waxes used in rubber applications. Figure 8.15 shows the penetrometer used in this standard.

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9

Recycled Rubber

by Krishna C. Baranwal[1]

9.1 DEFINITIONS AND RUBBER RECYCLING PROCESSES

ACCORDING TO ASTM STANDARD CLASSIFICATION for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber (ASTM D 5603-01):

- *Recycled rubber* is defined as recyclable, vulcanized rubber that has been processed to give particulates or other forms of different shapes, sizes, and size distributions.
- *Parent Compound:* original compound used in rubber product.
- *Vulcanizate:* cured (vulcanized) rubber.

Various techniques are used to generate recycled rubber. Major processes are briefly discussed below.

9.1.1 Reclaiming

This is done by a chemical digestion process. Aryl sulfides and other chemicals are added to rubber, and then the mixture is chemically digested. This process does not produce crumb rubber. Rather, it generates coherent chunks or lumps that can be shipped in the bale form. Over the years, there have been significant decreases in use of reclaim rubber. Currently, consumption is significantly curtailed and only two companies in the United States are in the rubber reclaiming business, one dealing with butyl reclaim and the second with VMQ, EPDM, and other specialty reclaim rubbers. Another international company sells low-odor reclaim rubber from whole tire, NR, and butyl rubber.

9.1.2 Ground Rubber

Here, vulcanized scrap rubber is first reduced to approximately 2.5-cm

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[1] Akron Rubber Development Lab Inc., 2887 Gilchrist Road, Akron, OH 44305.

by 2.5-cm to 5 cm by 5-cm chips by shredding. This material is further reduced in size by use of ambient grinding mills. The finer the particle size needed, the longer the rubber must be milled. Multiple grinds reduce the particle size. Any fiber is removed by air and metal is removed by magnetic separation. The production rate is about 550 kg/h for 30 to 40 mesh size crumb rubber. The heat generated in this process can degrade rubber if the product is not cooled properly before storage or shipping.

9.1.3 Cryogenic Ground Rubber

In this process, small rubber chips or crumb rubber, 10 to 20 mesh, are cooled by a chiller using liquid nitrogen and then put through a grinding mill. For finer particles, multiple cooling and grinding are usually needed. A typical production rate is 1800 to 2700 kg/h for 60 to 80 mesh material. Little heat is generated in the process, thereby decreasing possible degradation of the rubber. All fiber and steel are separated by freeze-grinding to give a higher yield of usable product.

9.1.4 Wet Ground Rubber

Here ground rubber is produced by passing a water suspension of rubber particles through a flour-grinding-type mill. Mesh sizes from 60 to 120 are typical.

9.1.5 "Devulcanization" Process

In sulfur-accelerator vulcanization of diene rubbers, sulfur-sulfur bonds are formed. "Devulcanization" is the reverse process in which either via external energy (ultrasonic) or by the addition of chemicals some of the sulfur-sulfur bonds are broken. There may also be cleavage of some C-S and C-C bonds in these processes.

In ultrasonic "devulcanization" [1,2], a crumb rubber is exposed to ultrasonic vibrations. Presumably, the energy absorbed by the rubber breaks the sulfur-sulfur bonds. The resulting devulcanized rubber can be compounded as is, or mixed with virgin rubber and recured. Chemical "devulcanization" involves addition of certain accelerators and sulfur to the crumb rubber on a mill or in a Banbury.®[2]

9.1.6 Need for Standards

Since recycled rubber is produced using different processes, it is important to have standards for different particle sizes and chemical tests for characterization.

[2] Farrel Corporation, Ansonia, CT.

In early 1995, ASTM Subcommittee D11.26 on Recycled Rubber was formed. By late 1996 ASTM approved two standards: ASTM Standard Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber (ASTM D 5603-96) and ASTM Standard Test Methods for Rubber Compounding Materials—Determination of Particle Size Distribution of Recycled Vulcanizate Particulate Rubber (ASTM D 5644-96) developed by the subcommittee. These standards were revised and reissued as D 5603-01 and D 5644-01.

ASTM D 5603-01 includes classification of crumb rubber based on parent compounds, specifications for the first two screens for particle size determination for particles 100 mesh and larger, limits on chemical test results and maximum limits for fiber and metal content. ASTM D 5644-01 describes a mechanical sieve shaker technique to determine particle size and particle size distribution of crumb rubber for coarser particles and ultrasonic and light optical microscope technique for 80 mesh or finer particles.

In late 1997, the Chicago Board of Trade [3] (CBOT) published a document on definition of terms, chemical tests, and particle size specification based on ASTM D 5603-96 for buying and selling crumb rubber. Thus, there are now specifications available for recycled rubber that vendors and customers should use to ensure material quality.

9.2 STORAGE, QA SAMPLING, AND TEST PLANS

9.2.1 *Material and Safety Data Sheets (MSDS)*

Recycled rubber processors should provide MSD sheets to their employees and to the end-users. Information for MSDS can be generated at either the processor's laboratory or at an independent laboratory. An MSDS should include information on chemical reactivity, storage, disposal, and physical hazards.

9.2.2 *Crumb Rubber Storage*

Recycling rubber from whole tires into chips and crumbs can generate heat up to 115°C in the ambient grinding process. This can, on storage, without sufficient cooling, lead to spontaneous combustion. The presence of iron (Fe) in natural rubber compounds, can catalyze the oxidation process, causing rubber degradation. This degradation is accelerated with heat. During processing, generation of crumbs and storage, volatiles and hot fumes may be generated.

Thus, the materials must be sufficiently cooled, either by water or air, to avoid spontaneous combustion. Crumbs should be stored at ambient temperatures in dry areas, but not in tin sheds or tin roof warehouses.

9.2.3 Sampling and Test Plans

Each rubber recycling plant may have its own sampling procedures. A typical sampling procedure is given here. Two samples, about 125 g each of each skid (1000 to 1200 kg), are taken by the bagger at the time of bagging recycled rubber. Random samples are taken by the laboratory personnel for quality checks. Frequency and sampling procedures may vary, but should be agreed upon between vendor and customer.

After sampling, the following tests, described in ASTM D 5603-01, are carried out: % extractables, % ash content, % moisture (heat loss), % natural rubber, % rubber hydrocarbon, and % carbon black. Two samples per truck load (five skids) are tested for % moisture. The remaining tests are one sample per truck load shipment. All these tests are carried out according to ASTM D 297. For ambient ground materials, moisture content and bulk density measurements are made on every skid because of possible moisture content variation in feedstock. Fiber and metal contents should be reported as agreed upon between vendor and customer.

Particle size and particle size distribution measurements are made according to ASTM D 5644-01. ASTM D 5603-01 should be used to determine if the material meets the size specification for the top two screens.

Analysis results are shipped along with the materials meeting customer's specifications.

9.3 TEST METHODS

ASTM D 5603-01 defines classification of crumb rubber based on parent compounds (see Table 9.2). Below is a summary:

Grade 1	Crumb rubber from passenger car, truck, and bus tires from which metal and fibers have been removed.
Grade 2	Crumb rubber from tread only from passenger car, truck, and bus tires.
Grade 3	Crumb rubber from tread and shoulder area buffing (in retreading operation) from passenger car, truck, and bus tires.
Grade 4	Crumb rubber from passenger car, truck, and bus tire retreading where the buffing from tires includes tread, shoulder area, and sidewalls.
Grade 5	Crumb rubber from off-the-road tires, large equipment tires, industrial tires, forklift tires, and farm implement tires. This excludes car, bus, and truck tires.
Grade 6	Crumb rubber from nontire rubber products.

9.3.1 Particle Size (PS) and Particle Size Distribution (PSD)

PS and PSD measurements are made according to the procedure described in ASTM D 5644-01 using six screens and a mechanical sieve shaker,

TABLE 9.1—Recycled Rubber Product Designation (ASTM D 5603-01).

NOMINAL PRODUCT DESIGNATION	EXAMPLE ASTM D 5603 DESIGNATION	ZERO SCREEN µm	PERCENT RETAINED ON ZERO SCREEN	SIZE DESIGNATION SCREEN µm	MAXIMUM PERCENT RETAINED ON DESIGNATION SCREEN
10 Mesh	Class 10-X	2360 (8 Mesh)	0	2000 (10 Mesh)	5
20 Mesh	Class 20-X	1180 (16 Mesh)	0	850 (20 Mesh)	5
30 Mesh	Class 30-X	850 (20 Mesh)	0	600 (30 Mesh)	10
40 Mesh	Class 40-X	600 (30 Mesh)	0	425 (40 Mesh)	10
50 Mesh	Class 50-X	425 (40 Mesh)	0	300 (50 Mesh)	10
60 Mesh	Class 60-X	300 (50 Mesh)	0	250 (60 Mesh)	10
70 Mesh	Class 70-X	259 (60 Mesh)	0	212 (70 Mesh)	10
80 Mesh	Class 80-X	250 (60 Mesh)	0	180 (80 Mesh)	10
100 Mesh	Class 100-X	180 (80 Mesh)	0	150 (100 Mesh)	10
120 Mesh	Class 120-X	150 (100 Mesh)	0	128 (120 Mesh)	15
140 Mesh	Class 140-X	128 (120 Mesh)	0	106 (140 Mesh)	15
170 Mesh	Class 170-X	106 (140 Mesh)	0	90 (170 Mesh)	15
200 Mesh	Class 200-X	90 (170 Mesh)	0	75 (200 Mesh)	15

TABLE 9.2—Properties for Recycled Rubber (Grades 1–6) (ASTM D 5603-01).

PROPERTY	%	TEST METHOD
(a) *Grade 1–4*		
Acetone Extractables	8–22	D 297, Sec. 17,18, 19
Ash, max	8	D 297, Sec. 34, 35, 36, 37
Carbon Black	26–38	D 297, Sec. 38, 39
Loss on Heating, max	1	D 1509
Natural Rubber	10–35	D 297, Sec. 52, 53
Rubber Hydrogen Content (RHC), min	42	D 297, Sec. 11
(b) *Grade 1–6*		
Metal Content, max	0.1	See 7.3.2
Fiber Content, max (Grades 1, 4, 5, 6)	0.5	See 7.4
Fiber Content, max (Grades 2, 3)	Nil	See 7.4

usually the Ro-Tap sieve shaker. The first two top screens, zero screen and designation screens, are defined in ASTM D 5603-01 for sizes 10 to 200 mesh. The remaining four screens for these sizes can be agreed upon by vendor and customer.

In a PS and PSD test, screens are stacked on a shaker in order of increasing mesh size with the coarsest mesh screen on top and the finest mesh at the bottom. Approximately 100 g of crumb rubber is mixed with talc powder, about 5 g of talc for coarser than 50 mesh, and 15 g for finer particles. The mixture is put on the zero screen and the shaker started. After the specified time, the shaker is stopped, and the material retained on each screen is weighed. The weight percent retained on a designated screen determines the crumb size (see Table 9.1). Weight percents retained on all six screens when plotted as a function of screen size gives the particle size distribution.

The mechanical shaker is suitable for coarser particle sizes. For 80 mesh and finer particles, it is recommended that the ultrasonic and light microscope technique, described in Section 12 of ASTM D 5644-01, be used.

9.3.2 Particle Size Classification (ASTM D 5603-01)

Table 9.1 defines particle size classification of crumb rubber for sizes 10 to 200 mesh. The crumb rubber size designation is the mesh size based on the size of designation sieve screen, which allows a range for the upper limit of material retained on that screen. No crumb rubber is retained on the zero screen.

The overall classification of recycled crumb rubber is based on particle size distribution and origin (Grades 1–6, previously listed). Other size designations, not listed in Table 9.1, can be agreed upon by vendor and customer.

9.3.3 Chemical Analysis (ASTM D 5603-01)

Table 9.2 lists properties, their limits, and ASTM test methods for crumb rubber.

Based on ASTM procedures, the following are brief descriptions of test methods.

9.3.3.1 Percent Extractables (ASTM D 297, Section 19) About 2 g of crumb rubber is extracted with hot acetone for 16 h. Acetone is evaporated from the extract over a steam bath and the dried extract is weighed. Percent extract is calculated based on the original mass of the samples.

9.3.3.2 Percent Ash (ASTM D 297, Section 35) A known amount of sample is heated at 550 ± 25°C in air for 1.5 h or until all carbonaceous material is burned off to give residue or ash. Ash may be due to zinc oxide, silica, clay, or some other inorganic material in crumb rubber.

9.3.3.3 Percent Carbon Black (ASTM D 297, Section 39) A known amount (X g) of crumb rubber is extracted with solvent, usually acetone. Extracted rubber is pyrolyzed at 800 to 900°C in nitrogen in an electrically heated tube furnace. It is then cooled and weighed (Y g). The pyrolysis sample is then heated at 800 to 900°C in air in a muffle furnace for 2 h. The resulting material is cooled and weighed (Z gms).

$$\text{Percent carbon black is} = \frac{Y - Z}{X} \times 100 \tag{1}$$

9.3.3.4 Percent Moisture Content (ASTM D 1509–2000) or Heating Loss About 2 g of weighed recycled rubber is heated at 125°C for 1 h, cooled, and weighed. Percent mass loss is the moisture content. Typically, moisture content in crumb rubber is less than 1 %, which is the current accepted maximum level.

Too much moisture can cause caking and may inhibit free flow in processing. Anti-caking agents such as calcium carbonate can be used. Moisture buildup can lead to acidic conditions, giving slower cure rates in compounds.

9.3.3.5 Percent Natural Rubber Content (ASTM D 297, Section 53) A known amount of cured rubber is extracted with hot methyl ethyl ketone and dried in an oven at 100°C for 1 h. The extracted rubber is digested in chromic acid solution to quantitatively oxidize the rubber, resulting in acetic acid formation. The acetic acid is separated by distillation. It is then aerated to remove carbon dioxide. The amount of acetic acid is determined quantitatively by titration with 0.1 M, NaOH solution. A blank titration should also be determined. Percent isoprene is calculated as:

$$\text{Isoprene Polymer \%} = \frac{9.08\,(A - B)M}{C} \tag{2}$$

where

A = volume of NaOH solution required for titration of the specimen.
B = volume of NaOH solution required for titration of the blank.
M = molarity of NaOH solution.
C = grams of specimen used.

This procedure is currently used for reclaimed rubber, even though it has been found to give consistently lower than previously accepted estimates of the isoprene polymer content.

9.3.3.6 Percent Rubber Hydrocarbon (ASTM D 297) By determining percentages of extractables, ash, moisture, and carbon black, rubber hydrocarbon (RHC) can be calculated as:

$$\begin{aligned}\%\,\text{RHC} = 100 - (&\%\,\text{Extractables} + \%\,\text{Ash}\\ &+ \%\,\text{Moisture} + \%\,\text{Carbon Black})\end{aligned} \tag{3}$$

9.3.3.7 Iron and Fiber Content (ASTM D 5603-01, Section 7) Crumb rubber may contain metal particles remaining from recycling radial tires, wire-reinforced hoses, belts, etc. To determine iron content, about 100 g of crumb rubber is weighed and spread on a flat nonmagnetic surface. A small horseshoe magnet is passed over the specimen for 60 s to pick up iron particles. All iron fragments are removed and weighed. The percentage of iron is then calculated.

Loose fiber in crumb rubber may come from recycling fiber-reinforced tires, hoses, belts, etc. Fiber content determination can be made after normal mechanical shaker sieve analysis procedure according to ASTM D 5644-01. After sieve analysis, any free fabric would result in the form of "fabric balls," which can be removed from each screen. "Fabric balls" are weighed and fabric content is calculated as percentage of initial sample mass used for sieve analysis.

9.4 EVALUATION OF RECYCLED RUBBER IN COMPOUNDS

Recycled rubber is blended with virgin rubber compound in two ways: (1) the total elastomer content from the virgin compound plus recycled rubber is kept at 100 phr (parts per hundred rubber) or (2) the recycled rubber is added on top of the virgin compound, whereby the total elastomer content becomes more than 100 phr. W. Dierkes [5] found that at more than 20 phr natural rubber reclaim, tensile strengths are higher when reclaim rubber is added on top of 100 phr than when elastomer content of the blend is constant at 100 phr. This is according to expectations. Higher elastomer content can lead to more crosslinked rubber and, hence, can give higher tensile strength.

The amount of recycled rubber used in a rubber compound must be optimized. Experiments can be used to determine the effects of varying amounts of recycled rubber on desired properties. Table 9.3 shows the effects

TABLE 9.3—Effect of Cryogenically Ground Butyl Rubber on Innerliner Compound[a] Properties [6].

		GROUND BUTYL[b] ADDED, %			
PROPERTIES		0 (CONTROL)	5	10	15
Masterbatch, phar		188.0	178.6	169.2	159.8
Cryo Ground Butyl, phar		...	9.4	18.8	26.2
Cure Time t90, min	ASTM D 2084	47.5	46.3	47.0	46.5
Cure Rate, lbf in./min		0.59	0.58	0.55	0.56
Tensile Strength, psi	ASTM D 412	1410	1350	1290	1280
300% Modulus, psi		1120	1040	1000	950
100% Modulus, psi		415	410	365	365
Air Permeability[c], Q		4.71	4.70	4.47	4.16

[a] Formulation: Butyl HT-1066, 80.0; RSS No. 1, 20; N-650 Carbon Black, 65.0; Mineral Rubber, 4.0; Durez 29095, 4.0; Sunthene 410, 8.0; Stearic Acid, 2.0; Zinc Oxide, 3.0; Devil A Sulfur, 0.5; MBTS, 1.5. Total recipe = 188.0.

[b] 80 mesh.

[c] $Q \times 10^3$ (cubic ft/0.001 in./°F psi/day).

of 0 (control), 5, 10, and 15 phr cryogenically ground butyl rubber on tensile properties [6].

In this case, the virgin rubber compound, formulation given at the bottom in Table 9.3, was mixed, cured, and cryogenically ground. The ground recycled rubber was added to the virgin rubber compound at different levels. It appears that 5 phr ground butyl rubber content (or 9.4 phr cryo-ground) is the optimum level. At 10 and 15 phr, tensile properties and air permeability are reduced significantly. Because of the addition of ground butyl rubber, air permeability of a compound is reduced, which is desirable.

Phake, Chakraborty, and De [7] observed that natural rubber compound containing 30 phr recycled rubber had shorter scorch time, higher cure rate, and lower maximum torque than the control compound with no recycled rubber. In a more recent study, Gibala and Hamed [8] got similar results for SBR compounds. Based on experimental results, they proposed that migration of sulfur takes place from the matrix to the recycled rubber giving, overall, lower torque, and that migration of accelerator from the recycled rubber to the matrix, causes shorter scorch time and faster cure rate.

Therefore, when compounding with recycled rubber, curatives should be adjusted accordingly.

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10

Standard Test Methods—Insuring High-Quality Output

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10.1 INTRODUCTION

MEASUREMENT AND TESTING PLAY key roles in society. Decisions based on testing for scientific, technical, commercial, environmental, and health purposes are everyday occurrences. Measurement and testing for research and development, for producer-user transactions, and for ongoing control of production processes are important elements of a larger organized effort that may be called a technical project. The assurance that the output data are of the highest quality, consistent with the stipulated goals and objectives, is the key to a successful technical project.

Quality for a technical project test system has two major components: (1) how well the measured parameters relate to the properties involved in the decision process, and (2) the magnitude of the uncertainty for the measured parameters; the higher the uncertainty, the lower the quality. Both of these depend on the equipment, the test method, the technicians, the test environment, and the decision process itself. The purpose of this chapter is to give some elementary background on how to assess and assure the quality of physical and chemical property measurements in the rubber and carbon black manufacturing industries.

This chapter, that addresses Committee D11 standards for rubber testing and Committee D24 standards for carbon black testing that relate to test quality, is divided into three parts. Part 1, The Fundamentals of Testing Operations, presents a general test operation background and gives the fundamentals of testing procedures that use certain standards to assure good measurement practices. Part 2, Testing—Using Specific Standards, lists various combined committee standards that may be used for specific testing

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programs. Part 3, Recent Developments in Test Method Technical Merit, is a review of some of the latest standardization and technical developments in the topics addressed in Part 1. These developments have the overall goal of improving testing for any technical project, especially those that involve interlaboratory testing. Part 3 also contains a discussion of Appendix 2, which lists the precision of the current D11 and D24 test method standards.

For brevity, all Committee D11 and D24 standards are cited in the text by their D number. The D number and the full title of all referenced standards are listed in Appendix 1 in two sequences: (1) for the three operations—(a) selecting test methods, (b) sampling, and (c) conducting measurements, which includes reference materials, classifications, process indexes, and statistical analysis, roughly the order as discussed in the chapter, and (2) in numerical order by the D number. This appendix is an important element of the chapter and provides ready reference to all D11 and D24 standards devoted to quality output for test method standards. ASTM or other standards (ISO) that are not part of D11 or D24 are cited as general references in the Reference section at the end of the chapter.

10.2 PART 1: FUNDAMENTALS OF TESTING OPERATIONS

A technical project may involve a local testing domain within a particular laboratory, or it may involve a global testing domain, two or more locations or laboratories, domestic or international. The project may be: (1) the development of a new compound or product; (2) the solution or investigation of a production or process problem; (3) product testing and acceptance in producer-user relationships. All of these have certain common operational characteristics that require testing and data acquisition. Successful execution of any technical project requires good organization with a number of steps that must be undertaken in a specified order. The steps involve: (1) planning the project; (2) selecting test methods with defined measurement capability or technical merit with appropriate supporting calibration procedures; (3) selecting a sampling procedure or protocol; (4) conducting the measurements and reporting data followed by analysis and appropriate statistical evaluation. Steps (2) and (3) are addressed in Appendix 1.

For global testing, which may be an ongoing project, these five steps have to be undertaken in the start-up process. For both local and global projects, the steps must be carried out with careful execution and control for a complex project, especially if it involves interlaboratory testing. The chapter begins by addressing each of these five steps on the basis of using applicable D11 and D24 standards to perform the necessary actions to accomplish the stated goal.

10.2.1 Step 1—Planning

The required topics that must be addressed are: overall project organization, objectives, resources, measurement methodology, and performance criteria, as well as selection of decision procedures. A set of well-designed and coordinated standard operating procedures must be selected. All the elements of the project required for a successful solution need to be specified. The use of standard test methods is imperative for any project; especially if it involves a global testing domain. A response model, defined as the simplified representation of a physical or chemical system, should be developed in an easily interpreted symbolic mathematical format. The model may be theoretical or empirical, but the formulation of an accurate model is a requirement for the successful solution of any problem. An appropriate statistical model for any testing program is described in Annex A1 of ASTM D 6085. This may be used in addition to any response model in the analysis of any testing problems that might arise in a test program.

10.2.2 Step 2—Measurement Methodology: Selecting Test Methods

The selection of a measurement system for testing is usually made on the basis of technical merit. Four important technical merit characteristics are: (1) precision and bias (uncertainty in test results); (2) test sensitivity, (3) useful range, and (4) ease of calibration. Secondary characteristics are low-cost, rapid testing, and/or automated procedure, test ruggedness, and ease of operation. Frequently only one test method may exist for any desired measurement. When only one test method is available for any test, it is important to know the technical merit of that method. Test method precision and sensitivity provide that evaluation.

10.2.2.1 Precision This technical merit attribute is indicated by the inverse of test result standard deviation; thus, precision is good when the standard deviation is low. Bias exists when a test result has a systematic deviation or is offset from the true or reference value. Good precision and low or zero bias equate to good or high accuracy. The statistical term *uncertainty* (in distinction to the general term meaning "lack of trust") is also frequently used as a surrogate for accuracy in an inverse sense, i.e., low or acceptable uncertainty is equivalent to high accuracy. Statistical "uncertainty" is not the full equivalent of accuracy, and it is currently being addressed by technical committees on metrology and other similar organizations.

Uncertainty is a characteristic of a local testing domain; each local domain for any defined test may have a different uncertainty value. Precision, both repeatability or within-laboratory variation and reproducibility or between-laboratory variation, is characteristic of a global testing domain. The precision values obtained in any interlaboratory test program are intended for universal application to a number of laboratories as a group or to the entire industry. The basic precision standard for D11 and D24 test methods is ASTM D 4483. This standard has been recently fundamentally revised in terms of the procedures to obtain precision that are representative of well-controlled and competent testing laboratories. The essentials of the newly revised standard are described in more detail in Part 3. ASTM D 4821 outlines procedures to monitor precision for carbon black test methods as an ongoing operation. Some information on troubleshooting is also presented to assist in improving precision.

10.2.2.2 Sensitivity This attribute is related to the discrimination and fidelity of a measurement process. It is the ratio of two technical merit characteristics: (1) the ability to detect small differences in the measured property and/or the fundamental inherent property, and (2) the precision of the measurement process expressed as a standard deviation. A newly adopted standard on test sensitivity, directed mainly to D11 test methods, is ASTM D 6600. More details on ASTM D 6600 and the concept of sensitivity and its relation to precision are found in Part 3. The useful range is the range over which there is direct instrument response, i.e., the presence of a linear relationship between instrument output versus level of measured property.

10.2.2.3 Calibration This is a requirement basic to all measurement systems. For purposes of this chapter it is defined as the act of comparing a measured test value to an accepted true value. This true value may be a reference or standard value or object. The purpose of calibration is the elimination of bias or systematic deviation of measured values so they correspond exactly with true or reference values. Once the bias is known, an adjustment of the testing device is made to generate the true value.

The requirements for calibration include: (1) an estimate of the accuracy (precision, bias) required in the output measurement, (2) the availability of documented calibration standards, (3) the presence of a state of statistical control for the test system, and (4) a fully documented procedure or protocol along with experienced personnel. Decisions on the frequency of calibration are made by balancing the cost of the calibration vs. the risk of biased test output. When in a state of statistical control, repetitive instrument responses for each standard value should be randomly distributed about a mean. For a series of true values, the response means vs. true values should give a linear least-squares regression relationship. This gives confidence intervals on the slope and the intercept and for selected points on the line in the calibration range.

10.2.2.4 Traceability This is defined as the ability to trace or accurately record the presence of an unbroken and documented pathway from fundamental standards or standard values to the measurement system of interest. Traceability is a prerequisite for the assignment of limits of uncertainty to the output or response measurement, but it does not imply any level of quality, i.e., the magnitude of the uncertainty limits. Physical standards with certified values are available from national standardization laboratories such as the National Institute of Standards and Technology or NIST (formerly NBS) in the United States or from the corresponding national metrology laboratories for all developed countries.

10.2.3 Step 3—Basic Sampling Principles

10.2.3.1 Sampling This is very important in any testing operation. Good sampling technique ensures that all samples represent the population under consideration. A review of basic sampling procedures is given in ASTM D 6085, which describes elementary principles and gives definitions for sampling terms. This standard also contains a statistical model for testing operations. One of the key issues is the distinction drawn between two types of intrinsic variation: (1) production variation, the variation in the process that generates any material or product, and (2) measurement variation, the variation in the actual action of measurement.

A sampling plan should generate an objective estimate of any measured parameter by using strict probabilistic or statistical sampling or some variant of such operations that gives objective decisions. However, there are situations where this plan would be excessively costly for the importance level of the decisions to be made. In such cases an alternative approach using subjective elements or technical judgment is usually employed.

A comprehensive sampling plan should provide estimates of (1) the population (lot) mean and confidence limits on the mean, (2) tolerance interval for a given percentage of the units of the population, and (3) the sample size (samples, specimens) to establish the above intervals with a selected confidence level. Since there is a wide range of projects from simple to complex, three generic types of sampling plans may be used.

10.2.3.2 Intuitive Sampling This operation is conducted using developed skill and judgment together with prior information on the lot or population as well as past sampling experience. The decisions made are based on a combination of the skill and experience. Strict probabilistic conclusions are not warranted.

10.2.3.3 Statistical Sampling This technique is based on strict statistical sampling procedures and provides for authentic probabilistic conclusions. Population estimates may be obtained and hypothesis testing may be conducted, inferences drawn, and predictions made about future system or process behavior. Usually a large number of samples are needed if the significance of small differences is of importance.

10.2.3.4 Protocol Sampling This special operation uses specific plans tailored for decision purposes in a given situation. Regulations (of the protocol) usually specify the type, size, frequency, and period of sampling and the test methods. A combination of intuitive and statistical considerations may be used, and true population estimates may be obtained depending on the protocol. Testing for conformance with producer-user specifications for commercial transactions is typical for this approach. Any sampling plan should (1) be based on a stable (nonchanging) population and (2) utilize individual samples independent of each other. When these sampling conditions are met, the sampling system is said to be in a stable condition or in statistical control.

The number of specimens required to estimate the sample mean to some degree of precision or uncertainty is an important aspect of sampling. Increasing the sample size increases the precision or reduces the uncertainty. The cost of this extra work increases linearly with sample size, while the precision increases at a much slower rate with the square root of the number of samples. Sample size problems are approached on the basis of the total uncertainty in the mean. There are two criteria that must be specified to calculate a sample size, n: (1) the value of E, the maximum ($\pm$) uncertainty (error) of estimation of the mean, and (2) the required level of confidence of the maximum uncertainty. To be able to calculate n, given some E, requires a value for the standard deviation of the individual unit measurements under a specified sampling and testing condition. See ASTM D 6085 for more details on sampling operations.

10.2.4 Step 4—Measurement, Data Reporting and Analysis

The appropriate methodology or test methods for conducting the selected measurements should be chosen and completely described. Standard test methods should be used, and if modifications are made on a standard method they should be clearly documented. The methodology should be validated as to its precision and sensitivity and if possible bias or accuracy, see Step 1. Model development and calibration, in distinction to test method calibration, is essential for a good technical project. It is important to perform the model calibration over a substantially large range of the operating or independent variables. Model validation is a process whereby the influence of the relevant input variables are observed for rational model output. The validation program should be based on input-output response generated from a separate testing and evaluation operation after all model development is concluded.

Once the above issues have been addressed, the next step is to conduct the measurements and report the data. For simple projects, the as-measured data may be of primary concern. If this is the case, the averages or means for the data are given usually at some confidence level for a specified uncertainty interval. Analysis and other statistical operations, using any developed precision model for guidance, may be conducted on the raw data. However, the measured parameter(s) may be used as input to a mathematical expression that gives some derived parameter that is used to assess system performance and make decisions. A typical example is the use of one test or reference material as a control to express the performance of the tested candidate materials, usually as an index obtained by dividing the candidate-measured parameter by the control-measured parameter. When this is the case, the statistical parameters obtained by analysis of the raw data will not apply to these derived performance parameters or properties. Under these conditions, the use of propagation of error algorithms is required to determine the variation or error of the derived property or parameter in terms of the measured parameter(s).

Standard techniques on statistical analysis may be used to analyze the data generated in project testing. For more sophisticated or complex analysis procedures, dedicated statistical software computer programs may be used. Most projects will involve some form of iteration involving successive measurement operations to arrive at a satisfactory solution. Reference materials and a new group of standards called classification standards are important for good measurement technology, and some additional details on these are provided in the next section.

10.2.4.1 Reference Materials: ASTM D 4678 and D 5900 All measurement operations can benefit from any procedure that reduces or eliminates bias. Since bias represents a general measurement uncertainty that cannot be reduced or eliminated by replication, the concept of reference materials is important. The use of a reference material in any testing operation may provide for calibration, adjustment, or ongoing monitoring of the test data output in a quality control sense. Reference materials have a long history in all types of commercial as well as scientific testing. In 1948 the National Institute for Standards and Technology or NIST began a program to develop reference materials designated as "standard reference materials" or SRMs for the rubber and carbon black industries. The list of SRMs included zinc oxide, sulfur, stearic acid, several carbon blacks, accelerators, SBR and IIR or butyl rubber. In the middle 1980s this program was phased out as budgeting for these activities was terminated.

As the SRMs were being phased out, Committee D11 began a program to develop two types of reference materials that covered a range of rubber manufacturing industry raw materials: (1) industry reference materials or IRMs that have a comprehensive testing procedure to establish uniformity and well-defined physical or chemical properties, and (2) common reference materials, or CRMs, materials for less critical applications that have been prepared to be as uniform as possible, but that do not have established properties. ASTM D 4678 was developed to organize this activity. It provides instructions and techniques to prepare candidate IRMs and CRMs and to test and accept the IRMs. These are given in the standard proper and in a series of annexes. Also included are the documentation procedures as well as suggested ways to use IRMs. For each candidate IRM, a producer prepares a lot or mass of the material according to the procedures as specified in Section 4 of the standard. The prepared IRM lot is then sampled according to Annex A2 of ASTM D 4678, or sampling may be conducted after it has been packaged also using Annex A2. Testing for homogeneity according to Annex A3 completes this part of the procedure.

Once the uniformity or homogeneity of the candidate IRM is ascertained to the required degree, an interlaboratory test program or ITP is organized using Annex A4 to determine the "accepted reference value" or AR value. This is defined as the expected value that any laboratory should obtain in conducting a test on the IRM. The AR value is normally the grand average as obtained from all the laboratories in the ITP after any outlier values have been deleted. Limits on the AR-value are established on the basis of ±2 or ±3 standard deviations.

ASTM D 5900 lists the physical and chemical properties for the current seven established IRMs: tetramethyl thiuram disulfide (TMTD), IRM1; Benzothiazyl disulfide (MBTS), IRM 2; napthenic process oil, IRM 43; zinc oxide, IRM 91; butyl rubber, IRM 241; petroleum oil, IRM 901 and 902. These two oils replace the former ASTM No. 1 and No. 2 oils. Tables 10.1 to 10.7, originally from ASTM D 5900, are shown below. See also the ASTM website, *www.astm.org*, for an up-to-date list of IRMs.

TABLE 10.1—Specification for IRM 1—Tetramethyl Thiuram Disulfide (TMTD).

PROPERTY	ASTM DESIGNATION	LIMITS
Melting point, °C	D 1519	142 min
Ash, %	D 4574	0.10 max
Loss on heating at 105°C, % loss	D 4571	0.5 max
Wet sieve analysis, % retaining on 100 mesh screen	D 4572	0.05 max

TABLE 10.2—Specification for IRM 2—Benzothiazyl Disulfide (MBTS).

PROPERTY	ASTM DESIGNATION	LIMITS
Melting point, °C	D 1519	165 min
Ash, %	D 4574	0.7 max
Loss on heating at 105°C, % loss	D 4571	0.5 max
Wet sieve analysis, % retained on 100 mesh screen	D 4572	0.1 max

TABLE 10.3—Specification for IRM 43—Napthenic Process Oil.

PROPERTY	ASTM DESIGNATION	LIMITS/TARGETS
Clay-gel absorption chromatographic analysis	D 2007	
% Asphaltenes		0.3 max
% Polar compounds		6.0 max
% Saturated hydrocarbon		35.1 to 65.0
Viscosity @ 100°C, mm^2/s	D 88 and D 2161	16.8 ± 1.2
Viscosity-gravity constant	D 2501	0.889 ± 0.002

TABLE 10.4—Specification for IRM 91—Zinc Oxide (ZnO).

PROPERTY	ASTM DESIGNATION	LIMITS/TARGETS
Surface area, m^2/g	D 4315 and D 3037	4.3 ± 0.3
% Zinc oxide	D 3280	99.5 min
% Lead	D 4075	0.08 max
% Cadmium	D 4075	0.08 max
Loss on heating @ 105°C % loss	D 280	0.50 max
Wet sieve analysis, %, retains on 45 μm	D 4315	0.10 max

TABLE 10.5—Specification for IRM 241—Butyl Rubber.

PROPERTY	ASTM DESIGNATION	LIMITS/TARGETS
Mooney Viscosity mL 1 + 8 125°C (unmassed)	D 1646	50.0 ± 1.0
Mooney Viscosity mL 1 + 4 100°C (unmassed)	D 1646	73.5 ± 2.0
Volatile matter, %	D 1416	0.30 max
Ash. %	D 1416	0.50 max

TABLE 10.6—Specification for IRM 902—Petroleum Oil.

PROPERTY	ASTM DESIGNATION	LIMITS/TARGETS
Viscosity: cst @ 99°C	D 445	20.35 ± 1.15
Gravity, API @ 16°C	D 287	20.0 ± 1.0
Flash pt. COC, °C	D 92	240 min
Aniline point, °C	D 611	93.0 ± 3.0
Viscosity-gravity constant	D 2140	0.865 ± 0.005
Naphthenics Cn%	D 2140	35 min
Paraffinics Cp%	D 2140	50 max

TABLE 10.7—Specification for IRM 903—Petroleum Oil.

PROPERTY	ASTM DESIGNATION	LIMITS/TARGETS
Viscosity: cst @ 38°C	D 445	33 ± 1.1
Gravity, API @ 16°C	D 287	22.0 ± 1.0
Flash pt. COC, °C	D 92	163 min
Aniline point, °C	D 611	70.0 ± 1.0
Viscosity-gravity constant	D 2140	0.880 ± 0.005
Naphthenics Cn%	D 2140	40 min
Paraffinics Cp%	D 2140	45 max

IRMs have several uses. They can be used for self evaluation in any laboratory to determine if it is biased with respect to the AR value and other similar laboratories. If the average from approximately ten test results (to reduce random error) are well within either the ±2 or ±3 standard deviation limits, then the laboratory is operating with minimal or no bias. If the average of ten is outside the limits, investigation of the potential cause is indicated. Producer-user operations can profit from IRMs and AR values. Each laboratory can gain an estimate of its bias, and the joint bias between a producer and consumer laboratory can be determined. The highest use IRM is butyl rubber, IRM 241. Currently the third lot, IRM 241c, has been produced and as for the two previous lots, 241a and 241b, is in use as an IRM for Mooney viscosity testing.

Classification standards for compounding materials give useful information on such topics as: individual classes or types of the material, manufacturing methods, background on their use in rubber compounding in addition to typical chemical and physical properties for all classes of any material. ASTM D 1765 is the classification standard for carbon blacks, ASTM D 4295 for zinc oxide, ASTM D 4528 for sulfur, ASTM D 4676 for antidegradents (antioxidants), ASTM D 4817 for stearic acid, ASTM D 4818 for accelerators and ASTM D 5603 on particulate (or ground) rubber.

10.2.4.2 Reference Materials: D 3324, D 4122 ASTM D 3324 is directed to the improvement of reproducibility in carbon black testing by the use of standard reference blacks or SRBs. Six SRBs, A to F, are listed with target values and ± 3 standard deviation limits for a number of tests: Iodine number, DBP absorption, CTAB, BET nitrogen surface area, tint strength, and multipoint surface area. These six span the range from N326 to N683 type blacks. ASTM D 4122 is the standard used to prepare industry reference blacks, designated as IRBs. A series of new and replacement IRB lots totaling approximately 270 000 kg (600 000 lb) have been prepared over the past 40 years and used to assess internal laboratory testing as well as interlaboratory testing quality. A battery of physicochemical tests, Iodine number, DBP absorption, compressed DBP, tint strength, multipoint BET surface area, pour density, and statistical surface area are evaluated in addition to rubber tensile and modulus properties.

10.3 PART 2: TESTING—USING SPECIFIC STANDARDS

10.3.1 Natural and Synthetic Rubber, Carbon Black

ASTM D 1485, sampling for natural rubber, provides guidance for selecting the sampling plan, for sample size, and deriving a test portion from the sample and preparation of the test portion for the actual testing. It gives the procedures for lot acceptability using quality indexes based on specification limits as agreed on by the producer and the user. ASTM D 3896, sampling for synthetic rubber, is a standard that parallels the procedures as set forth in D 1485.

ASTM D 1799 is a standard practice that gives the sampling procedures for packaged shipments of carbon black. The design of the sampling device is specified as well as sample preparation and handling operations. ASTM D 1900 is the standard practice for sampling bulk shipments of carbon black. The specific locations for drawing samples from the sample ports on hopper cars are outlined in addition to the sample preparation and handling steps. ASTM D 5817 is devoted to the reduction and blending operations for gross samples of pelleted carbon black. Details on the riffle sample splitter and the reduction of sample size diagram are given along with the procedures for the reduction and splitting process.

10.3.2 Process Performance and Capability Indexes

ASTM D 5406, for rubber testing, is used to evaluate the operation of production processes by calculating two parameters. The first designated as Pp′, the producer's process performance index, is equal to the ratio of the difference, (upper specification limit–lower specification limit), (USL-LSL), and the total process variation or six standard deviations, 6S. The second, Ppk′, an additional producer's performance index, is equal to the ratio of the minimum of either (USL—process mean) or (process mean—LSL), to the total process variation or 6S. The use of Ppk′ along with Pp′ determines how well the process is operating, especially in terms being centered on the target of the production process. These indexes may be used when special cause variation is present and when the process is not in a state of statistical control.

ASTM D 4583 for carbon black testing sets forth directions for the use of quality control data to evaluate process capability for individual production runs. In simple terms, the metric for process capability is the percentage of the specification range or bandwidth, (max-min) that is used by the process. This standard makes use of the Pp and Ppk indexes as described above as well as the usual Cp index, which is the ratio of (USL - LSL) to 6S when the process is in a state of statistical control and the CpK index which is an analog of Ppk. Cpk is an index that indicates how well the process is centered on the production target. The main difference in the two sets of variability indexes (Pp′, Ppk′ vs Cp, Cpk) is the magnitude of the underlying or active variability, i.e., the 6S. For Pp′ and Ppk′, 6S includes special cause variations that usually occur due to unintended process perturbations of a short-term, long-term, or transient nature. For Cp and Cpk, the value of 6S corresponds to a state of statistical control where only common cause variations exist.

10.4 PART 3: RECENT DEVELOPMENTS IN TEST METHOD TECHNICAL MERIT

10.4.1 Test Method Precision: D 4483

10.4.1.1 Background The newly revised ASTM D 4483 uses the basic one-way analysis of variance or ANOVA algorithms for each material as developed in the ASTM generic precision standard, E 691[5]. See also ISO 5725 [6], a similar standard. A generic standard like ASTM E 691 (and ISO 5725) attempts to accommodate a broad range of testing communities but cannot really do an adequate job because of the various unique needs of some of these communities such as D11 and D24. The new ASTM D 4483 is organized to accommodate the requirements of the rubber and carbon black manufacturing industries; it has three new features that provide for a more structured analysis of interlaboratory test program or ITP data. First, it provides an improved treatment for detecting outliers that cause poor precision, especially poor between laboratory agreement. Second, after outlier deletion, it provides a way to retain the nonoutlier data (for any material-laboratory combination) to permit inclusion of the nonoutlier data in the precision calculations, thus giving a broader database for precision. Third, it sets forth a procedure for calculating replacement values for deleted outliers in ITPs that have only a few participating laboratories. This is important since many ITPs are in this category.

One of the overriding issues with precision evaluation over the past several decades is the frequent discovery that reproducibility or between-laboratory standard deviation for many test methods is quite large. This very poor agreement for many test methods fundamental in the industry has been the subject of much discussion and consternation. A number of publications have addressed the "poor reproducibility problem" in industrial technology. Youden [1,2] pioneered in this type of investigation over 40 years ago. Veith [3] reported on this topic in 1987, and later in 1993 proposed a new approach to evaluating interlaboratory precision [4]. This latter report as well as overall experience has shown that poor reproducibility is most often caused by only a small number or percentage of the laboratories participating in any ITP. These few laboratories differ substantially from the remainder of the laboratories that give fairly good agreement with each other. The frequent occurrence and the attendant detrimental effects caused by outliers has prompted the development of analysis procedures over the past 15 years given the general name "robust statistics." Although terminology for this topic is still being developed, robust statistics as it applies to ITP work may be generically defined as "an approach to statistical analysis that eliminates or substantially reduces the effect of outliers."

The recognition and removal of outliers in any precision database is a subject with some controversy. If true outliers are not removed and their magnitude is substantial, seriously inflated values may be obtained for both repeatability and reproducibility. However, caution must be exercised to ensure that high (or low) magnitude, but *bona fide* values, not be deleted. If such values are removed, the precision estimates will be too optimistic. The procedures as presented in the new ASTM D 4483 standard are in essence a middle ground position, designated as a "robust analysis" procedure. Outliers frequently occur in one of two general appearance patterns: (1) none or infrequent—only a few outliers; one or two for every 20 laboratory-material combinations or data cells in the usual laboratory by material table of ITP results, or (2) extensive—outliers occur in greater numbers, three, four, or more for every 20 data cells in several of the materials tested for any laboratory. When outliers are extensive, they may frequently be of substantial magnitude. There are of course intermediate cases between these two extremes.

10.4.1.2 Outlier Detection There are two points of view on the significance level for declaring a value as an outlier. An extremely conservative approach maintains that outliers should rarely be eliminated in any ITP. This is based in part on the concept that in the preliminary stages of test method development, outlier rejection will lead to an overly optimistic impression of the quality of the method. This approach usually adopts a probability significance level of 0.5 % ($p = 0.005$), for outlier rejection. This approach has some limited merit for the initial stages of development for any test method, especially when only a few laboratories participate in an ITP. This significance level is specified by ASTM E 691. However, this approach has some serious limitations.

For well-established test methods, experience has taught that there is a distribution of skill and testing competence, from poor to good. This capability range argues for a more realistic approach to the outlier issue, the use of a 5 % significance level, $p = 0.05$ (or a 95 % confidence level) for declaring incompatible values as outliers. This is the usual level for most statistical significance tests and will in general reject the results of laboratories that have poor quality control for their internal testing and are in need of improved operating procedures.

Allowing a few "poor" laboratories to inflate the evaluated precision gives a false negative impression of the true precision defined by laboratories with good control of testing operations. The precision of the "good" laboratories, the majority of those participating, should be the *benchmark* for industry-wide precision level for any test method. The newly revised ASTM D 4483 uses two robust analysis approaches: a General Procedure for D11 rubber test methods and a Special Procedure for D24 carbon black test methods. Both of these use objective algorithms to delete outliers. Employing these procedures to identify poor quality-control laboratories can lead to a general industry-wide improvement for any test method provided that feedback is employed to encourage the poor-performing laboratories to improve testing operations.

10.4.1.3 Outlier Rejection Two types of outliers are reviewed: (1) repeatability outliers or test values (for a laboratory-material combination or cell) that show poor agreement; and (2) reproducibility outliers, cell averages that show poor agreement with the typical values averaged across the laboratories in the ITP. This review is conducted using the statistics as defined in ASTM D 4483 and as originally developed for ASTM E 691 designated as h-values and k-values. The h-value is the ratio of the test result difference or deviation, d, of each individual laboratory cell average from the overall cell average for all laboratories divided by the standard deviation among the cell averages across all the laboratories.

Large *h* values (+ or −) indicate substantial discrepancy from the overall (across all laboratories) cell average. After an *h* value is calculated for each laboratory for each material, the values are reviewed to determine if any of the calculated *h*-values exceed a certain critical 5 % significance value or *h*-crit, and if so this signifies that each cell average exceeding *h*-crit is an outlier. The *h*-crit value depends on the number of laboratories in the ITP.

The *k*-value is the ratio of the within-laboratory individual cell standard deviation to the pooled within-laboratory standard deviation across all laboratories. A comparison similar to the *h*-value procedure identifies any 5 % significance level cell standard deviations that exceed *k*-crit and thus are outliers. If any outliers are found at the 5 % significance level, their removal has now generated a second database with substantially reduced "across all laboratories" or denominator standard deviation for either the *h* or *k* statistics or both. When outliers are deleted, the resulting revised database is one that might have been obtained had the outlying laboratories not volunteered for the ITP.

This second or revised database can now be again reviewed for outliers using cell values and calculated "across all laboratory" standard deviations for the revised database. However, to guard against the generation of an excessively optimistic precision, the significance level for this second review needs to be more rigorous than for the initial review and is conducted at the 2 % significance level. The outcome of this "dual process" robust analysis review is a database that represents those laboratories that have developed a high level of competence and good internal control in their testing operations.

10.4.1.4 Outlier Deletion or Replacement If outliers are found at either significance level, there are two options: delete the outliers and thereby generate the revised reduced size database or replace the outliers in a way that essentially preserves the distribution of the nonoutlier data. For any ITP with a substantial number of laboratories (approximately nine or ten or more) and with three or more materials and with only a few outliers, the simplest choice is deletion. However when outliers are found with a small database (limited number of laboratories, six or less), replacing outlier values, rather than deleting them, preserves the size of the database. The procedure to calculate replacement values, however, must be one that is consistent with the observed "data distribution" in the database. The replacement procedure as described in the new ASTM D 4483 fulfills this objective.

When ITP cell averages for any material are sorted from low to high across all laboratories and the sorted values plotted vs. the corresponding ascending order laboratory number for each cell average, a positive slope straight line relationship is found with some minimal point scatter about the line. If any outliers are present, they will be at either end of the plot and will show substantial negative or positive departure from the straight line, i.e., more than minimal point scatter, as established by the central data point region. This central region contains the laboratories that give good agreement: the nonoutlier laboratories. The analogous cell standard deviation plot may contain more curvature from the low end (which may contain zero values) toward the central point region, but it will also clearly show the outliers as positive departures at the high value end of the plot. Such plots are designated as "ascending order trend" or AOT plots.

For any laboratory that has an outlier for a material, a replacement value is calculated that substantially preserves the distribution of the central region of the straight line as illustrated by the ascending order trend plots. This is designated as an AOT replacement. Each AOT replacement value is in essence a predicted value, one that would be expected for the laboratory in question, absent the unexpected perturbation that generated the outlier de-

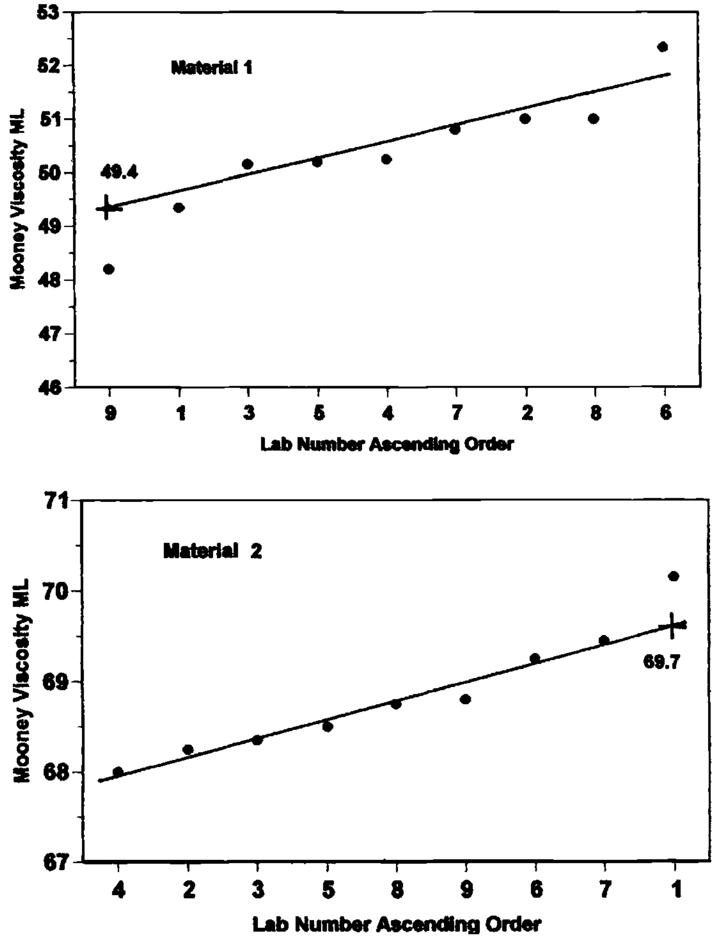

FIG. 10.1—AOT Plots: Mooney Viscosity Averages each Lab; Matl 1 & 2.

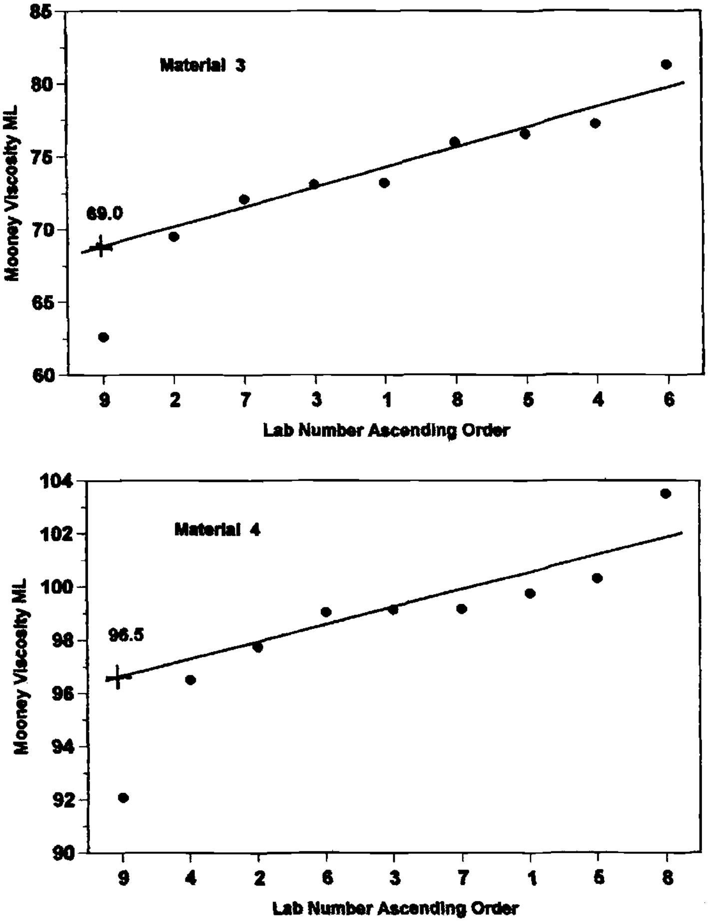

FIG. 10.2—AOT Plots: Mooney Viscosity Averages each Lab; Matl 3 & 4.

parture illustrated in the AOT plot. Figures 10.1 and 10.2 show AOT plots for cell average values for Mooney viscosity for an ITP with four materials (rubbers) and nine laboratories. A typical regression straight line is visually fitted through the points; this establishes the general trend as developed by the underlying distribution, i.e., end points omitted. The + symbol on the line with an appended numerical value identifies the value that would have been expected absent the perturbation.

Committee E11 has developed a computer program that can be used to calculate precision [7]. As currently structured, this program requires that the data across all materials for each laboratory be complete; each cell must contain the same number of replicates. If any outliers are deleted or if data values are not submitted for that material in the ITP, this generates an incomplete database (with one or more "data holes"), and the E11 analysis program cannot handle this database. Rejecting the remaining nonoutlier data for that material imposes a burden on the analysis of ITPs with only a few laboratories; it reduces the database and the degrees of freedom for the analysis. The new ASTM D 4483 provides instructions to set up computer spreadsheet algorithms that can analyze an incomplete database (the option with outliers deleted) and thus utilize all of the nonoutlier data.

Appendix 2 presents a review of the current state of precision evaluation for D11 and D24 test methods. It lists values for repeatability or within-laboratory precision and for reproducibility or between-laboratory precision. The total number of test method standards for D11 and D24 is 178, and currently 104 test method standards have precision sections. Thus 58 % of test methods in the two committees have been evaluated for precision. Most test methods generate data that can be used to calculate two basic precision parameters for both repeatability and reproducibility. For repeatability, the first parameter is r, the repeatability in measurement units. The second repeatability precision parameter is (r) and this is, simply, r expressed as a percent of the mean value of the measured property (for any material), i.e., a relative precision. For proper test operation, two test results should have a difference, less than r, in measurement units and less than (r) expressed as a percentage of their average. Analogous parameters for reproducibility are R, in measurement units, and (R) expressed as a percentage. The same application reasoning applies to R and (R) in terms of differences in two test results obtained from two separate laboratories, testing the same material and using the same test method.

The use of relative precision parameters (r) and (R) permits an "across the board" comparison of test methods. The precision for all D11 test methods in the ASTM Book of Standards, Vol 09.01, that have tabulated precision parameters is contained in four Appendix 2 tables, Tables 10.A1 to 10.A4. The precision results are listed in numerical order of their D number designation. For some test methods, the precision is given in terms of absolute precision parameters, r and R, rather than (r) and (R). These methods have mean values of the measured test property that are small or close to zero that makes the relative precision quite large and not really meaningful. A better appreciation of precision for these particular methods can be gained from r and R. The precision values listed in Appendix 2 are pooled or averaged values (average across all the materials as tested) for each test method. Table 10.A5 and 10.A6 give the precision for Vol. 09.01 standards that are devoted to the evaluation of natural rubber and various synthetic rubbers.

One additional topic is the type of precision evaluated in an interlaboratory test program or ITP. A Type 1 precision is one where the materials (or products) tested are distributed to all laboratories in the ITP in a ready-to-test state. No processing or other operations are needed prior to testing. A Type 2 precision is one where processing or other operations are required to prepare what is tested prior to testing. Typical Type 2 precision is the evaluation

TABLE 10.A1—Comparison of Precision for ASTM D 11 Test Method Standards (Vol. 09.01).Relative Precision = (*r*) and (*R*) in %; Absolute Precision = *r* and *R* in Meas. Units.

ASTM Designation	(D297 to D1053) Measured Test Property	Within-Lab Precision(a) (r)	Between-Lab Precision(a) (R)	Type Precision
D297	Rubber Density	0.23	0.44	1
D412	Stress-Strain Testing	(r)	(R)	
	Ten Str; dumbbells	6.5	18.7	1
	% Elong; dumbbells	7.9	12.4	1
	Mod100; dumbbells	15.5	33.1	1
	Ten Str; rings	16.7	33.3	1
	% Elong; rings	8.7	25.2	1
D430	Flex Life, Meth B	(r)	(R)	
		67.5	107.1	1
D454	Aging 30hr, % change:	r	R	
	Ten Str; dumbbells	12.7	43.2	2
	% Elong; dumbbells	6.3	43.7	2
D471	Immersion 70 hr @ temp			
Note 3	Various oils/rubbers:	r	R	
	Change Ten Str, %	10.3	19.1	1
	Change % Elong	10.6	17.4	1
	Vol Change, %	2.1	6.9	1
D572	Aging 48 hr @ 70C	r	R	
Note 3	Ten Str; dumbbells	21.4	27.8	2
	% Elong; dumbbells	16.0	22.6	2
D573	Aging 72 hr @ 100C	r	R	
Note 3	Ten Str; dumbbells	9.0	11.0	2
	% Elong; dumbbells	14.7	18.4	2
D575	Compression Prop	(r)	(R)	
	Method A , kPa	6.3	20.5	1
	Method B, % defl	7.5	14.9	1
D623	Flexometer Testing			
	Various rubbers	(r)	(R)	
	delta T, deg C (15 - 40C level)	14.3	86.1	1
		r	R	
	% Per Set (2 - 12% level)	1.3	7.9	1
D624	Tear Testing	(r)	(R)	
	Die B	16.6	75.8	1
	Die C	16.2	48.2	1
D813	DeMattia Flexlife	(r)	(R)	
	Flexlife to 12.5 mm	15.8	96.1	1
	Flexlife to 3x Pierced Cut	37.3	108.0	1
	Flexlife to 6x Pierced Cut	25.8	78.0	1
D865	Aging, Test Tube @ 100C	r	R	
	Change Ten Str % (1 to - 60% level)	15.2	19.7	2
	Change Elong % (-5 to -65% level)	10.5	13.2	2
D926	Plasticity-Recovery	(r)	(R)	
	Plasticity @ 70C	11	31.1	2
	Plasticity @ 100C	10.2	14.7	2
	Recovery @ 70C	54.0	105.0	2
	Recovery @ 100C	40.6	54.0	2
D945	Yerzley Oscillograph	(r)	(R)	
Note 1	Yerzley Resilience %	1.5	8.7	1
	Yerzley Hystersis %	1.7	6.4	1
	Dyn Modulus, MPa	11.0	63.0	1
D1053	Low Temp Stiffness	(r)	(R)	
	Method A , T2 deg K	1.40	2.90	1
	Method A , T5 deg K	0.50	2.10	1
	Method A , T10 deg K	0.40	2.40	1
	Method A , T100 deg K	0.60	2.70	1

(a) The reported values are pooled or averaged over several typical materials
Note 1 : Precison results obtained prior to use of D4483 protocols; only approximate values
Note 2 : For precision program with small number pf labs ; use with caution
Note 3 : The absolute test values are numerically small, this inflates (r) and (R)
Note 4 : These results are for an international ITP conducted in ISO TC45
Note 5: Broad range of mean property values ; r and R give better indication of precision

TABLE 10.A2—Comparison of Precision for D11 Test Method Standards (Vol. 09.01).Relative Precision = (*r*) and (*R*) in %; Absolute Precision = *r* and *R* in Meas. Units.

ASTM Designation	(D1148 to D2084) Measured Test Property	Within-Lab Precision(a)	Between-Lab Precision(a)	Type Precision
D1148	Rubber UV Discoloration			
	Colorimeter, delta L	r	R	
	White Rubbers	0.80	2.00	1
	Blue Rubbers	0.50	0.57	1
	Green Rubbers	0.34	0.85	1
D1229	Comp Set @ Low Temp	(r)	(R)	
Note 1	Comp Set, 10s release	1.9	8.2	1
	Comp Set, 30min release	6.6	23.2	1
D1329	Retraction @ Low Temp	(r)	(R)	
Note 2	TR10 to TR70 Range	0.52	3.4	1
	TR(70-10) Diff	7.7	54.0	1
D1415	Hardness	(r)	(R)	
	IRHD	1.89	14.0	1
D1417	Rubber Latices, Synthetic	(r)	(R)	
	Total Solids, %	0.35	0.47	1
	Volatile Unsat, %	30.0	47.0	1
	pH value	1.4	3.1	1
	Sur Tension, Mn/M	2.1	5.5	1
	Viscosity, mPa*S	4.9	19.6	1
	Coaguium Mass, %	9.4	99.0	1
	Mooney Vis	7.9	10.9	1
	Mech Stability, %	27.6	67.9	1
D1519	Rubber Chemicals	(r)	(R)	
	Capillary Melt range,	1.8	3.5	1
	DSC Melt range	1.82	5.7	1
D1630	Abrasion, NBS	(r)	(R)	
	Abrasion Index	26.9	95.6	1
D1646	Mooney Testing	(r)	(R)	
	Viscosity, clear, no mill	3.0	6.7	1
	Viscosity, clear, milling	5.1	8.8	1
	Viscosity, BMB, no mill	4.3	9.7	1
	Viscosity, BMB, milling	9.2	20.0	1
	Stress Relax, slope	8.4	24.0	1
	Intercept, ML units	10.1	19.8	1
	PreVulcan, min Vis	4.3	9.5	1
	Scorch Time	7.7	30.9	1
	Cure Index	15.2	30.4	1
D1917	Shrinkage, SBR	(r)	(R)	
	% Shrinkage, Meth A	17.7	17.7	1
D1991	MBT Assay	(r)	(R)	
	Avg %	0.83	4.9	1
D1993	Precipitated Silica, Mult BET	(r)	(R)	
	Mean, hm^2/kg	3.4	4.7	1
D2084	Osc Disc Curemeter	(r)	(R)	
	M(L)	5.4	45.8	1
	M(H)	1.5	16.6	1
	t(S)1	9.0	18.7	1
	t(50)	6.7	15.0	1
	t(90)	5.6	16.7	1
	Avg for All	*5.6*	*22.6*	
	M(L)	7.0	23.9	2
	M(H)	2.5	18.4	2
	t(S)1	6.7	20.6	2
	t(50)	5.8	29.0	2
	t(90)	3.2	25.0	2
	Avg for All	*5.0*	*23.4*	
Note 4	M(L)	12.7	60.0	1
	M(H)	5.5	22.8	1
	t(S)1	12.4	39.5	1
	t(50)	8.4	20.4	1
	t(90)	9.1	22.6	1

(a) The reported values are pooled or averaged over several typical materials

Note 1 : Precison results obtained prior to use of D4483 protocols; only approximate values

Note 2 : For precision program with small number pf labs ; use with caution

Note 3 : The absolute test values are numerically small, this inflates (r) and (R)

Note 4 : These results are for an international ITP conducted in ISO TC45

Note 5: Broad range of mean property values ; r and R give better indication of precision

TABLE 10.A3—Comparison of Precision for D11 Test Method Standards (Vol. 09.01). Relative Precision = (r) and (R) in %; Absolute Precision = r and R in Meas. Units.

ASTM Designation	(D2137 to D4573) Measured Test Property	Within-Lab Precision(a)	Between-Lab Precision(a)	Type Precision
D2137	Rubber Brittleness	(r)	(R)	
	Brittle Temp	0.90	4.0	1
D2228	Abrasion, Pico	(r)	(R)	
	Abrasion Loss, cm3	9.9	58.1	1
	Abrasion Index	16.1	21.3	1
D2240	Hardness, Durometer	(r)	(R)	
	Type A Hardness	3.1	9.3	1
	Type D Hardness	3.6	15.7	1
	Type M Hardness	4.3	9.9	1
D2632	Resilience Vert Rebound	(r)	(R)	
	Percent rebound	3.4	12.2	1
D3194	Plasticity Retention Index	(r)	(R)	
	PRI , %	9.8	34.5	1
D3314	SBR - Styrene Blocks	(r)	(R)	
	Mean, % blocks	14.5	20.2	1
D3346	Processing SBR : Delta Mooney	r	R	
	Delta ML Meth A, massed	2.4	3.9	1
	Delta ML Meth A, unmass	1.6	2.1	1
	Delta ML, Meth B, unmass	0.90	1.4	1
D3616	Gel, Swelling, Dil Sol Vis	r	R	
Note 5	% Gel	1.21	4.6	1
	Swelling Index, %	3.3	7.5	1
	Dilute Solution Viscosity	0.14	0.28	1
D3629	Rubber Cut Growth	(r)	(R)	
	Flex Life to 10 mm	8.6	11.3	1
		r	R	
	Log Flex Life to 10mm	0.52	0.74	1
D3900	Det Ethylene Units in EPM, EPDM			
	Avg Test Meth A, B, D	(r)	(R)	
	Non-OE, Eth %	2.9	6.3	1
	Test Meth D			
	OE , Eth %	8.3	13.9	1
D4004	Det Metal Content by Flame			
	Atomic Absorp Anal (AAS)	(r)	(R)	
Method C ==>	Zinc (3% Level)	10.7	11.6	1
Method C ==>	Lead (1% Level)	9.8	25.6	1
		r	R	
Method C ==>	Zinc (12 ppm Level)	3.7	7.6	1
Method C ==>	Lead (13ppm Level)	2.3	4.7	1
Method D ==>	Copper (10 ppm Level)	0.32	1.35	1
Method E ==>	Manganese (15 ppm Level)	0.46	1.53	1
D4026	SBR , Det Residual Styrene	(r)	(R)	
	Styrene, (2500 ppm Level)	20.6	32.6	1
D4075	Det Metals in Zinc Oxide, AAS	r	R	
	Copper (7 ppm Level)	1.3	2.6	1
	Cadmium (2 ppm Level)	3.0	4.0	1
	Lead (12 ppm Level)	2.0	5.1	1
	Cadmium (240 ppm Level)	15.1	78.0	1
	Lead (930 ppm Level)	26.7	178	1
D4569	Det Acidity in Sulfur,			
	% Acidity, (0 to 4% level)	r	R	
	Oil Treated, 90% Insol Sulfur A	0.66	0.68	1
	Oil Treated, 90% Insol Sulfur B	0.99	0.99	1
	Gen Purpose Grd Sulfur	0.92	2.3	1
D4571	Rubber Chemicals - % Volatile	r	R	
	In Sulfur, Gen Purpose, Insol	0.087	0.34	1
	In p-Phenylenediamine	0.044	0.06	1
D4572	Wet Sieve Analysis - Sulfur			
	Gen Purpose, Insoluble, % thru	r	R	
	250 micro-m mesh	0.020	0.020	1
	180 micro-m mesh	0.027	0.13	1
	150 micro-m mesh	0.069	0.31	1
	75 micro-m mesh	0.30	4.6	1
D4573	Det Oil Content , Treated Sulfur	(r)	(R)	
	% Oil , (Treated), (ca 20% Level)	0.60	2.3	1

(a) The reported values are pooled or averaged over several typical materials

Note 1 : Precison results obtained prior to use of D4483 protocols; only approximate values

Note 2 : For precision program with small number pf labs ; use with caution

Note 3 : The absolute test values are numerically small, this inflates (r) and (R)

Note 4 : These results are for an international ITP conducted in ISO TC45

Note 5: Broad range of mean property values ; r and R give better indication of precision

TABLE 10.A4—Comparison of Precision for D11 Test Method Standards (Vol. 09.01). Relative Precision = (*r*) and (*R*) in %; Absolute Precision = *r* and *R* in Meas. Units.

ASTM Designation	(D4574 to D6370) Measured Test Property	Within-Lab Precision(a)	Between-Lab Precision(a)	Type Precision
D4574	Rubber Chemicals, Ash %	r	R	
	in Antideg, Accelerators, %	0.020	0.028	1
D4578	Sulfur, Insoluble Content	(r)	(R)	
	% Insoluble, (75% Level)	0.47	0.68	1
D4934	2-Benzothiazyl Sulfenamide	r	R	
	% Insoluble (0.6 % Level))	0.11	0.35	1
D4936	Mercaptobenzothiazole			
	Sulfenamide , Assay %	(r)	(R)	
	Proc A (CBS,TBBS,MBSS,MBS)	1.72	2.2	1
	Proc B (DIBS, DCBS)	0.71	3.9	1
	Proc C use of MBT reducing agent	0.41	1.8	1
D4937	p-Phenylenediamine - Purity			
Note 2	by Gas Chromatography	(r)	(R)	
	% Assay	0.68	4.9	1
D5044	Free MBT in MBTS	r	R	
	% MBT (0.2 % Level)	0.017	0.10	1
D5051	MBTS Assay	(r)	(R)	
	% MBTS (97% level)	0.39	1.2	1
D5054	DPG and DOTG Assay	(r)	(R)	
	% DPG (98% level)	0.60	1.6	
	% DOTG (97% level)	0.41	1.9	
D5289	Rotorless Curemeters	(r)	(R)	
	M(L)	1.90	14.2	1
	M(H)	0.73	13.0	1
	t(S)1	1.43	10.4	1
	t(50)	0.73	7.2	1
	t(90)	0.97	8.0	1
D5297	Accelerator Purity by High Perf			
	Liquid Chromatography	(r)	(R)	
	Method A , assay %	1.51	3.5	1
	Method B , assay %	0.66	2.6	1
D5376	Det % Nitrogen in Pol TMQ	(r)	(R)	
	% Nitrogen (7.5 % Level)	0.87	4.2	1
D5666	p-Phenylenediamine - Purity by			
	High Perf Liq Chromatography	(r)	(R)	
	% Assay (95% level)	1.0	1.31	1
D5670	Det Residual Unsaturation in HNBR			
	by Infrared Spectrophotometry	r	R	
	% Unsaturation (3% Level)	0.39	0.63	1
D5774	Rubber - Chemical Anal Extractables	(r)	(R)	
	% Total Extractables	0.92	2.3	
	% Organic Acid (5% Level)	3.9	8.8	
		r	R	
	% Soap (0.04% level)	0.024	0.12	
D5902	Det Residual Unsaturation in			
Note 2	HNBR by Iodine Value	(r)	(R)	
	Residual Unsat, % (35 % level)	6.4	9.0	1
D5963	Rotary Drum Abrader, Abrasion Loss	(r)	(R)	
	Meth A , Non-Rotating Test Piece	11.5	22.7	1
	Meth C, Non-Rotating Test Piece	15.6	24.6	1
	Meth D , Rotating Test Piece	102	19.3	1
D6047	Det 5-Ethylidenenorbornene (ENB)			
	or Dicyclopentad(DCPD) in EPDM	(r)	(R)	
Note 2	ENB, % (4 to 10 % level)	2.6	11.0	1
	DCPD, % (2 to 10 % level)	1.9	6.3	1
D6147	Det of Force Decay (Stress Relax)			
	in Compression (24, 96,168 hr)	(r)**	(R)	
Note 2	Meth B, Washer Test, R(t) @70C	32.0	47.0	1
	Meth B, Button Test, R(t) @ 70C	30.0	39.0	1
	** Between specimens 1 day only			
D6370	Compositional Analysis by			
	Thermogravimetry (TGA)	(r)	(R)	
	% Organics, (65% level)	0.77	3.4	1
	% Carbon Black (35% level)	1.2	5.6	1
		r	R	
Note 5 ==>	% Ash (0.2 to 2% level)	0.33	0.50	1

(a) The reported values are pooled or averaged over several typical materials
Note 1 : Precison results obtained prior to use of D4483 protocols; only approximate values
Note 2 : For precision program with small number pf labs ; use with caution
Note 3 : The absolute test values are numerically small, this inflates (r) and (R)
Note 4 : These results are for an international ITP conducted in ISO TC45
Note 5: Broad range of mean property values ; r and R give better indication of precision

TABLE 10.A5—Comparison of Precision for D11 Test Method Standards (Vol. 09.01). For Material Evaluation Test Methods: Rubbers (a). Relative Precision = (*r*) and (*R*) in %; Absolute Precision = *r* and *R* in Meas. Units.

ASTM Designation	Material and Measured Test Property	Within-Lab Precision(b)	Between-Lab Precision(b)	Type Precision
D3185	Evaluation SBR (Black)	(r)	(R)	
ODC	M(L)	6.1	15.2	2
Note 1	M(H)	5.7	16.4	2
	t(S)1	8.8	45.2	2
	t(50)	6.9	25.3	2
	t(90)	9.1	21.1	2
	Mod 300	15.6	39	2
	Tensile Strength	9.8	16.6	2
	Elong %	8.3	34.7	2
	Mooney ML1+4 100C	6.4	27.9	2
D3186	Evaluation SBR-BMB	(r)	(R)	
ODC	M(L)	6.6	35.6	2
	M(H)	5.8	22.7	2
	t(S)1	8.6	40.0	2
	t(50)	8.2	21.6	2
	t(90)	7.5	16.2	2
D3187	Evaluation NBR (Black)	(r)	(R)	
ODC	M(L)	8.9	16.9	2
	M(H)	5.8	14.6	2
	t(S)1	8.2	40.9	2
	t(90)	11.8	31.5	2
	Mod 300	13	22.9	2
	Tensile Strength	7.5	12.4	2
	Elong %	7.1	16.8	2
	Mooney ML1+4 100C	4.6	27.8	2
D3188	Evaluation IIR(Black)	(r)	(R)	
ODC	M(L)	4.3	10.2	2
	M(H)	4.3	10.0	2
	t(S)1	14.4	26.5	2
	t(50)	3.9	8.7	2
	t(90)	10.2	15.1	2
D3189	Evaluation BR (Black)	(r)	(R)	
ODC	M(L)	10.4	36.3	2
	M(H)	10.4	28.3	2
	t(S)1	5.9	44.6	2
	t(50)	9.8	25.3	2
	t(90)	6.8	28.2	2

(a) Excludes Carbon Black , as an Evaluation Material

(b) The reported values are pooled or averaged over several typical materials

Note 1: ODC = Oscillating Disc Curemeter (D2084) ; MDC = Moving Die Curemeter

Black = Rubber mixed with carbon black for testing

NB = Rubber evaluated as gum mix

TABLE 10.A6—Comparison of Precision for D11 Test Method Standards (Vol. 09.01). For Material Evaluation Test Methods: Rubbers (a). Relative Precision = (r) and (R) in %; Absolute Precision = r and R in Meas. Units.

ASTM Designation	Material and Measured Test Property	Within-Lab Precision(b)	Between-Lab Precision(b)	Type Precision
D3180	Evaluation CR			
ODC	Both Black and NB			
	CR - Sulfur Grade, NB	(r)	(R)	
	M(L)	15.6	61.8	2
	M(H)	4.7	14.7	2
	t(S)1	11.4	31.3	2
	t(90)	7.2	57.4	2
	Mod 300	9.6	14.8	2
	Tensile Strength	12.1	18.7	2
	Elong %	4.4	8.7	2
	CR - Sulfur Grade, Black			
	M(L)	14.0	56.7	2
	M(H)	5.3	15.4	2
	t(S)1	28.6	66.7	2
	t(90)	16.8	44.1	2
	Mod 300	9.8	14.2	2
	Tensile Strength	8.3	17.8	2
	Elong %	7.8	15	2
	CR - Mercaptan Grd NB			
	M(L)	11.2	55.7	2
	M(H)	5.8	10.5	2
	t(S)1	23.8	37.8	2
	t(90)	36.1	56.4	2
	Mod 300	12.2	20.2	2
	Tensile Strength	21.9	32.2	2
	Elong %	9.3	10.4	2
	CR - Mercaptan Grd Black			
	M(L)	10.1	37.9	2
	M(H)	4.1	19.5	2
	t(S)1	12.9	41.1	2
	t(90)	24.6	69.8	2
	Mod 300	13.4	22.8	2
	Tensile Strength	14.2	17.4	2
	Elong %	15	21.7	2
D3403	Evaluation IR (Black)	(r)	(R)	
ODC	M(L)	7.3	20	2
	M(H)	6.1	15.8	2
	t(S)1	10.3	21.9	2
	t(50)	9.1	12.4	2
	t(90)	10.6	12.8	2
MDC	M(L)	29.8	37.4	2
	M(H)	3.5	12.1	2
	t(S)1	9.4	13.8	2
	t(50)	8.3	10.9	2
	t(90)	6.2	14.0	2
	M300	13.9	25.8	2
	Tensile Strength	15.9	16.4	2
	Elong %	7.9	11.0	2
	ML1+4 100C	12.2	16.1	2
D3484	Evaluation OESBR (Black)	(r)	(R)	
ODC	M(L)	1.6	20.8	2
Note 2	M(H)	6.1	21.8	2
	t(S)1	13.1	20.6	2
	t(50)	11.8	12	2
	t(90)	8.8	10.7	2
MDC	M(L)	19.1	24.1	2
Note 2	M(H)	8.4	15.4	2
	t(S)1	13.5	25.1	2
	t(50)	12.1	12.6	2
	t(90)	10.4	15.3	2
Note 2	M300	13.5	15.3	2
	Tensile Strength	17.5	20.3	2
	Elong %	14.6	19.6	2
	ML1+4 100C	12.2	12.5	2

(R) Excludes carbon black, as an Evaluation material.

Note 1: ODC = Oscillating Disc Curemeter (D2084) ; MDC = Moving Die Curemeter

Note 2 : Precision = Avg for Formula 1 & 2

Black = Rubber mixed with carbon black for testing

NB = Non-Black, Rubber evaluated as gum mix

TABLE 10.A7—Comparison of Precision for D11 Test Method Standards (Vol. 09.02). Relative Precision = (*r*) and (*R*) in %; Absolute Precision = *r* and *R* in Meas. Units.

ASTM Designation	Measured Test Property	Within-Lab Precision(a)	Between-Lab Precision(a)	Type Precision
D380	Rubber Hose			
	Burst Strength , MPa	(r)	(R)	
	Type Hose = 500	12.0	23.0	1
	Type Hose = 800	18.0	23.0	1
	Type Hose = 1600	10.4	23.0	1
	Type Hose = 2500	5.2	15.0	1
	Type Hose = 8000	5.7	10.1	1
	Type Hose = 14000	7.4	8.6	1
	Type Hose = 20000	9.0	19.0	1
D751	Coated Fabrics	(r)	(R)	
Note 2	Grab Breaking Strength (Warp)	17.0	42.0	1
	Grab Breaking Strength (Fill)	21.0	48.0	1
	Cut Strip Brk Strength (Warp)	16.0	27.0	1
	Cut Strip Brk Strength (Fill)	17.0	36.0	1
		r	R	
	Burst Str Diaph Test, (1 - 4 MPa level)	0.44	0.63	1
	Proc A, Pendulum Tear (Warp), (3 - 30 N level)	1.6	2.4	1
	Proc A, Pendulum Tear (Fill), (3 - 20 N level)	1.9	2.9	1
		(r)	(R)	
	Proc B, Tongue Tear (Trans or Fill)	29.0	61.0	1
	Proc B, Tongue Tear (Warp or Longitudinal)	26.0	57.0	1
	Proc A, Hydrostatic Resistance	54.0	73.0	1
	Peel Adhesion (Warp Side 1)	4.9	24.0	1
	Peel Adhesion (Warp Side 2)	14.0	26.0	1
	Peel Adhesion (Fill Side 1)	17.0	17.0	1
	Peel Adhesion (Fill Side 2)	13.0	24.0	1
	Reinforced Coating, Peel Adhesion (Warp)	27.0	58.0	1
	Reinforced Coating, Peel Adhesion (Fill)	39.0	81.0	1
		r	R	
	% Change Brk Str, Cut Strip Warp (-11 to 3 level)	28.0	36.0	1
	% Change Brk Str, Cut Strip Fill (-12 to 4 level)	8.7	31.0	1
	% Change Brk Str, Grab, Warp (- 8 to -3 level)	15.0	18.0	1
	% Change Brk Str, Grab, Fill (- 15 to -3 level)	19.0	25.0	1
D1414	Rubber O-rings	r	R	
	Tensile Str, Ring Specimen (7 -17 MPa level)	1.2	1.8	1
	Tensile Str, Strip Specimen (7 -17 MPa level)	1.2	2.7	1
	Stress 100% (Modulus) Rings (3 - 7 MPa level)	0.46	0.59	1
	Stress 100% (Modulus) Strips (3 - 7 MPa level)	0.53	2.1	1
	% Elongation at Break, Strips (180 - 350 Level)	25.0	53.0	1
	Shore A Hardness, Strips (72 - 80 level)	1.6	6.6	1
D3389	Coated Fabrics Abrasion (Rot Platform-Dbl Hd)	(r)	(R)	
Note 2	Mass Loss per Rev	30.0	132.0	1
D3492	Rubber Contraceptives (Male Condoms)	r	R	
Note 1	Burst Pressure (1.7 - 1.9 kPa level)	0.58	0.62	1
	Burst Volume (28 -38 dm3 level)	14.0	16.0	1
D5712	Anal Extractable Protein in NR - Mod Lowry	(r)	(R)	
Note 1	Protein Content, micro-g / g	23.0	88.0	1
D6124	Residual Powder on Medical Gloves	(r)	(R)	
	Proc 1 - Powder Free Gloves. (Resid = 0.4 mg)	66.0	105.0	1
	Proc 2 - Powder on Gloves, (110-225 mg level))	21.0	45.0	1
D6499	Immunological Meas Antigenic Protein in NR	(r)	(R)	
	Protein Content, Powdered Exam Gloves	31.0	73.0	1
	Protein Content, Powdered Surgical Gloves	35.0	84.0	1
D6515	Rubber Shaft Seals - Det of Recovery: Bending	(r)	(R)	
	Lab Specimens :Recovery from Bending,	1.4	3.0	1

(a) The reported values are pooled or averaged over several typical materials

Note 1 : Precison results obtained prior to use of D4483 protocols; only approximate values

Note 2 : For precision program with small number of labs ; use with caution of rubbers as given in Tables 10.A5 and 10.A6. Their evaluation requires that rubbers be mixed with other compounding materials (accelerators, ZnO, sulfur, carbon black, etc.) and cured sheets or other test specimens or samples prepared for each rubber. To evaluate a realistic (overall) precision for rubbers, the variation inherent in the mixing, curing, and sample preparation must be included in the overall variance of the test. Table 10.A7 lists the precision for all test methods in Book of Standards, Vol. 09.02, which is mainly directed to product testing and product specifications.

Table 10.A8 contains the precision results for all the D24 carbon black test methods. Note the Type 2 precision for ASTM D 3191 and ASTM D 3192, the evaluation of carbon black in SBR and NR.

These two standards also require mixing, curing, and other specimen or sample preparation for the materials tested, i.e., carbon blacks. Table 10.A9 presents some results for comparing certain test methods for their relative precision. Part 1 contains data for the comparison of oscillating disc curemeter, ODC, testing vs. stress-strain testing. Precision for the ODC parameters, M(L), M(H), t(S1), t(S50), and t(S90) is listed (see ASTM D 2084 for definitions) along with the stress-strain parameters Mod300 (stress at 300 % elongation), tensile strength, and percent elongation at break. The tabulated data are averages for the rubber evaluation methods ASTM D 3185 to D 3484 as indicated in the footnote. To compare the two classes of test, ODC vs. stress-strain, averages are given across all the parameters for each class of testing. For within-lab testing, the ODC has a slight edge on the stress-strain testing, 9.9 vs. 11.8. For between-lab operations, stress-strain testing has a substantially smaller avg (*R*) of 19.4 compared to 29.8 for ODC testing. These are numerical differences; no statistical analysis has been conducted to declare significance. Perhaps stress-strain testing appears to be superior to ODC testing in between-lab operations, because it is an older and more established test technique.

Part 2 of Table 10.A9 allows a comparison for non-black (NB) and black (B) testing. On an overall basis there is no substantial precision difference, NB vs. B, for within-lab testing. For between-lab operations or testing, the overall difference of −2.2 favors the NB testing. The incipient cure time *t*(*S*1) seems to be the most sensitive parameter for NB vs. B; it has the maximum individual difference for both NB and B. Part 3 of this table permits a comparison of the ODC with the newer type of rotorless curemeter designated as a moving die curemeter or MDC. Even though Table 10.A10 shows MDC overall has better precision than the ODC, the difference column in Table 10.A9 shows that the ODC has an edge of −3.6 for within-lab testing and a smaller difference of −1.2 for between-lab testing. Here in this specific situation the older established test, the ODC, seemed to be slightly better than the MDC. Again all the difference results in Table 10.A9 are numerical. No statistical analysis has been conducted to declare significance. Also there were different compounds and different laboratories involved in this comparison as well. The results of the table are offered as general interest comparisons.

TABLE 10.A8—Comparison of Precision for D24 Carbon Black Test Method Standards (Vol. 09.01). Relative Precision = (*r*) and (*R*) in %; Absolute Precision = *r* and *R* in Meas. Units.

ASTM Designation	Carbon Black Measured Test Property	Within-Lab Precision(a) (r)	Between-Lab Precision(a) (R)	Type Precision
D1506	Carbon Black , % Ash	16.0	30.0	1
D1508	Carbon Black	(r)	(R)	
	5 Minute Fines, %	44	51	1
	Attrition, %	37	85	1
D1509	Carbon Black	r	R	
	Heat Loss. % @ 125C	0.070	0.36	1
D1510	Carbon Black	(r)	(R)	
	Iodine Number. g/kg	1.5	3.5	1
D1511	Carbon Black, Pellet Size	(r)	(R)	
	% Retained, Sieve 10	33	119	1
	% Retained, Sieve 18	12	35	1
	% Retained, Sieve 35	10	32	1
	% Retained, Sieve 60	24	55	1
	% Retained, Sieve 120	42	105	1
	% Retained, pan	63	126	1
D1512	Carbon Black	(r)	(R)	
	pH of water slurry, Meth A	7.7	24.0	1
	pH of water slurry, Meth B	6.5	18.0	1
D1513	Carbon Black	(r)	(R)	
	Pour Density, kg/cu meter	1.7	3.7	1
D1514	Carbon Black	(r)	(R)	
Note 2	Sieve res ,mg/kg, No 325	66	154	1
D1618	Carbon Black -Toluene Extract	(r)	(R)	
	Transmittance, extract	1.6	3.6	1
D1619	Sulfur Content	(r)	(R)	
	Percent Sulfur	5.5	21.6	1
D2414	Carbon Black,Oil Absorption	(r)	(R)	
	Absorption, cm3/100g	1.8	4.0	1
D2663	Carbon Black Dispersion	(r)	(R)	
	Meth C, Disp Index	9.6	18.5	1
D3191	Carbon Black, Eval in SBR			
Note 1	Diff from IRB 6	r	R	
Note 3	Mod 300, Mpa	0.87	1.85	2
	Tensile Strength, Mpa	2.0	3.3	2
	Elong %	48	65	2
D3192	Carbon Black, Eval in NR			
Note 1	Diff from IRB 6	r	R	
Note 3	Mod 300, Mpa	0.85	1.23	2
	Tensile Strength, Mpa	1.3	1.87	2
	Elong %	31	44	2
D3265	Carbon Black, Tint Strength	(r)	(R)	
	Tint units	2.8	5.7	1
D3313	Carbon Black, Pellet Hardness	(r)	(R)	
	Mean, mN	26	74	1
D3493	Carbon Black, Oil Absorp			
	Compressed Sample	r	R	
Note 3	cc/100g Absorption	2.0	4.0	1
D3765	Carbon Black, CTAB Surf Area	(r)	(R)	
	Surf Area, cm3/100g	1.2	3.5	1
D4527	Carbon Black, Solv Extractables	r	R	
Note 2	with Toluene, %	0.09	0.13	1
D5230	Carbon Black, Auto Pellet Hard	(r)	(R)	
	Hardness, cN (gf)	5.4	14	1
D6556	Carbon Black,Total & Ext Surface			
	Area by Nitrogen Adsorption	(r)	(R)	
	NSA, (m2/g)	1.9	4.4	1
	STSA, (m2/g)	3.0	3.8	1

(a) The reported values are pooled or averaged over several typical materials

Note 1 : The absolute measured values are numerically small; r and R give better indication of precision

Note 2 : Precison results obtained prior to use of D4483 protocols ; only approximate

Note 3: No relative precision listed for this test

TABLE 10.A9—Precision Comparison: Selected Test Methods.

Part 1 — **Oscillating Disc Curemeter (ODC) vs Stress Strain Testing**

Within Lab - Precision (r)			Between Lab - Precision (R)	
Measured Property	Avg (r)		Measured Property	Avg (R)
M(L)	8.7		M(L)	33.4
M(H)	5.8		M(H)	17.2
t(S)1	13.3		t(S)1	37.9
t(50)	8.3		t(50)	17.6
t(90)	13.6		t(90)	33.0
Avg (r)	*9.9*		Avg (R)	*29.8*
Mod 300	12.6		Mod 300	21.9
Tensile Strength	13.4		Tensile Strength	19.0
Elong %	9.30		Elong %	17.2
Avg (r)	*11.8*		Avg (R)	*19.4*

Note: Average Precision for D3185, 3186, 3187, 3188, 3189, 3190, 3403, 3484
See also - D2084, D412

Part 2 — **Non-Black (NB) vs Black (B) Compounds - CR (Rubber)**

	Within Lab - Precision (r)			Between Lab - Precision (R		
Measured Property	(NB) Avg (r)	(B) Avg (r)	Difference (NB - B)	(NB) Avg (R)	(B) Avg (R)	Difference (NB - B)
M(L)	13.4	12.1	1.4	58.8	47.3	11.5
M(H)	5.3	4.7	0.5	12.6	17.5	-4.9
t(S)1	17.6	20.8	-3.2	34.6	53.9	-19.4
t(90)	21.7	20.7	0.9	56.9	57.0	-0.1
Avg (r)	14.5	14.6	-0.1	40.7	43.9	-3.2
Mod 300	10.9	11.6	-0.7	17.5	18.5	-1.0
Tensile Strength	17.0	11.3	5.8	25.5	17.6	7.9
Elong %	6.9	11.4	-4.6	9.6	18.4	-8.8
Avg (r)	11.6	11.4	0.2	17.5	18.2	-0.7
		Grand Avg ==	*0.0*		Grand Avg ==	-2.2

See D3190 data

Part 3 — **Oscillating Disc Curemeter (ODC) vs Moving Die Curemeter (MDC)**

	Within Lab - Precision (r)			Between Lab - Precision (R)		
Measured Property	ODC Avg (r)	MDC Avg (r)	Difference (ODC - MDC)	ODC Avg (R)	MDC Avg (R)	Difference (ODC - MDC)
M(L)	4.5	24.5	-20.0	20.4	30.8	-10.4
M(H)	6.1	6.0	0.1	18.8	13.8	5.1
t(S)1	11.7	11.5	0.3	21.3	19.5	1.8
t(50)	10.5	10.2	0.2	12.2	11.8	0.4
t(90)	9.7	8.3	1.4	11.8	14.7	-2.9
Avg ==>	*8.5*	*12.1*	*-3.6*	*16.9*	*18.1*	*-1.2*

See - D2084, D5289

TABLE 10.A10—Distribution of Relative of Precision for D11 Test Method Standards (Vol. 09.01). For Test Methods with Multiple Measured Properties, (*r*) and (*R*) are Method Averages Both within Lab Avg (*r*) and Between Lab Avg (*R*) are Sorted Low to High.

ASTM Designation	Measured Test Property	Avg (r)	ASTM Designation	Measured Test Property	Avg (R)
D297	Rubber Density	0.23	D297	Rubber Density	0.44
D5051	MBTS Assay	0.39	D4578	Sulfur, Insoluble Content	0.68
D4578	Sulfur, Insoluble Content	0.47	D5051	MBTS Assay	1.2
D5054	DPG and DOTG Assay	0.51	D5666	p-PPD Purity HPLC	1.3
D4573	Det Oil Content Treated Sulfur	0.60	D5054	DPG and DOTG Assay	1.8
D4937	p-PPD - Purity Gas Chrom	0.68	D4573	Det Oil Content Treated Sulfur	2.3
D1053	Low Temp Stiffness	0.73	D1053	Low Temp Stiffness	2.5
D1991	MBT Assay	0.83	D4936	Mercaptoben -Sulfen As %	2.6
D5376	Det % Nitrogen in Pol TMQ	0.87	D5297	Accel Purity by High Perf Liq Chr	3.1
D2137	Rubber Brittleness	0.90	D2137	Rubber Brittleness	4.0
D4936	MBT -Sulfenamide Assay %	0.95	D5376	Det % Nitrogen in Pol TMQ	4.2
D6370	Comp Anal Thermogavimetry	0.99	D6370	Comp Anal Thermogavimetry	4.5
D5666	p-PPD Purity HPLC	1.0	D1519	Rubber Chemicals	4.6
D5297	Accel Purity by High Perf Liq Chr	1.1	D1993	Prec Silica, Mult BET	4.7
D5289	Rotorless Curemeters	1.2	D4937	p-PPPD - Purity Gas Chrom	4.9
D1519	Rubber Chemicals, Melt Range	1.8	D1991	MBT Assay	4.9
D1415	Hardness	1.9	D5774	Rubber - Chem Anal Extractables	5.5
D6047	Det 5-Ethylidenenorbornene (ENB)	2.3	D6047	Det 5-Ethylidenenorbornene (ENB)	8.7
D5774	Rubber - Chem Anal Extractables	2.4	D5902	Det Residual Unsaturation in	9.0
D5044	% MBT (0.2 % Level)	2.8	D3900	Det Ethylene Units in EPM, EPDM	10.1
D2632	Resilience Vert Rebound	3.4	D5289	Rotorless Curemeters	10.6
D1993	Prec Silica, Mult BET	3.4	D3629	Rubber Cut Growth	11.3
D2240	Hardness, Durometer	3.7	D2240	Hardness, Durometer	11.6
D1329	Retraction @ Low Temp	4.1	D2632	Resilience Vert Rebound	12.2
D1229	Comp Set @ Low Temp	4.3	D1415	Hardness	14.0
D3900	Det Ethylene Units in EPM, EPDM	5.6	D1229	Comp Set @ Low Temp	15.7
D5902	Det Res Unsat HNBR, I - Number	6.4	D5044	% MBT (0.2 % Level)	17.2
D2084	Osc Disc Curemeter	6.8	D575	Compression Prop	17.7
D575	Compression Prop	6.9	D1917	Shrinkage, SBR	17.7
D1646	Mooney Testing	7.5	D1646	Mooney Testing	17.8
D3629	Rubber Cut Growth	8.6	D4004	Det Metal Cont Flame AAS	18.6
D3194	Plasticity Retention Index	9.8	D3314	SBR - Styrene Blocks	20.2
D4004	Det Metal Cont Flame AAS	10.3	D5963	Rot Drum Abrader, Abrasion Loss	22.2
D1417	Rubber Latices, Synthetic (all)	10.5	D412	Stress-Strain Testing	24.5
D412	Stress-Strain Testing	11.1	D2084	Osc Disc Curemeter	26.3
D5963	Rot Drum Abrader, Abrasion Loss	12.4	D1329	Retraction @ Low Temp	28.7
D2228	Abrasion, Pico	13.0	D1417	Rubber Latices, Synthetic	31.7
D945	Yerzley Oscillograph	14.2	D4026	SBR Det Residual Styrene	32.6
D3314	SBR - Styrene Blocks	14.5	D3194	Plasticity Retention Index	34.5
D624	Tear Testing	16.4	D2228	Abrasion, Pico	39.7
D1917	Shrinkage, SBR	17.7	D6147	Det of (Stress Relax, Comp)	43.0
D4026	SBR Det Residual Styrene	20.6	D926	Plasticity-Recovery	51.2
D623	Flexometer Testing	21.3	D624	Tear Testing	62.0
D813	DeMattia Flexlife	26.3	D945	Yerzley Oscillograph	78.1
D1630	Abrasion, NBS	26.9	D623	Flexometer Testing	91.3
D926	Plasticity-Recovery	29.0	D813	DeMattia Flexlife	94.0
D6147	Det of (Stress Relax, Comp)	31.0	D1630	Abrasion, NBS	95.6
D430	Flex Life, Meth B	67.5	D430	Flex Life, Meth B	107

Note: Avg (r) and (R) are obtained by averaging the precison for any two or more individual test parameters for any test method

Table 10.A10 addresses the distributional aspects of precision for Vol. 09.01 methods that have their precision expressed in relative terms—the good, the intermediate, and the bad. The left side of the table presents the sorted precision Avg (*r*) from the lowest value at the top, 0.23, to the highest at the bottom, 67.5, a ratio of 293. The right side of the table gives analogous results for Avg (*R*). Both Avg (*r*) and Avg (*R*) are precision averages for the two or more test properties for any test method, when more than one property is measured. The min vs: max values for Avg (*R*) are 0.44 vs. 107, a ratio of 243. In general, analytical chemical testing, both wet and instrumental methods, is near the top with good precision and flex life; abrasion and simple rheological tests are near the bottom, with the highest Avg (*r*) and (*R*). Hardness, curemeter tests (both ODC and MDC), compression set, Mooney testing, resilience, and some less precise wet chemical and analytical tests for

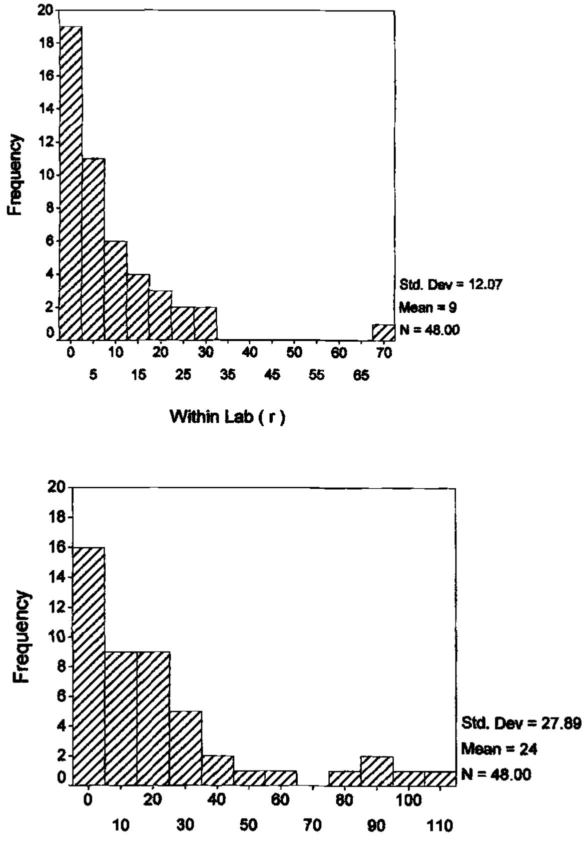

FIG. 10.3—Histograms: (r), (R) for D11 test methods.

rubber chemicals and monomers are near the middle of the distribution. Figure 10.3 contains two histograms, for Avg (*r*) and Avg (*R*). They both have the same general shape, with the maximum number of test methods in the lowest (*r*) and (*R*) group (0 to 2.5). There is an apparent sharper drop in bar height or frequency (left to right, as (*r*) and (*R*) increases) for within-lab (*r*) compared to between-lab (*R*). The (*r*) distribution has a cutoff at 30 % with one extreme value in the 67.5 to 72.5 group. The (*R*) distribution has no apparent cutoff and has a larger number of test standards with high (*R*) values compared to the (*r*) distribution. This illustrates the overriding precision issue of poor between-lab agreement.

10.4.2 Test Sensitivity: D 6600

10.4.2.1 Background The concept of test sensitivity has taken on added importance in the past decade due in part to the appearance of new tests for certain physical and chemical properties and in part as a desire to increase the efficiency of testing. Test sensitivity as it applies to rubber testing was first introduced by Mandel and Stiehler [8] and later further developed by Mandel [9]. A generic definition for test sensitivity is—a derived quantity that indicates the level of technical merit of a test method; it is the ratio of the test discrimination power, i.e., the magnitude of the change in the measured property for some unit change in the fundamental property being evaluated to the standard deviation of the measured property. For a comprehensive understanding of test sensitivity, a brief background on the previous history of test sensitivity evaluation and on the measurement process is required.

One index of sensitivity technical merit frequently used in the past has been test method precision. The precision is usually expressed as some multiple of the test measurement standard deviation for a defined testing domain. Although precision is a required quantity for test sensitivity, it is an incomplete characteristic (only one half of the necessary information) since it does not consider the discrimination power for the fundamental property (or constituent) being evaluated.

Any attempt to evaluate relative test sensitivity for two different test methods on the basis of test measurement standard deviation ratios or variance ratios, which lack any discrimination power information, constitutes an invalid quantitative basis for sensitivity technical merit evaluation. Coefficient of variation ratios (which are normalized to the mean) may constitute a valid test sensitivity evaluation only under the special condition where the two test methods under comparison are directly proportional or reciprocally related to each other. If the relationship between two test methods is nonlinear or linear with a nonzero intercept, the coefficient of variation ratios are not equivalent to the true test sensitivity.

10.4.2.2 The Measurement Process A measurement process involves three components: (1) a (chemical or physical) measurement system, (2) a chemical or physical property to be evaluated, and (3) a procedure or technique for producing the measured value. The fundamental property to be determined or evaluated, FP, has two associated adjuncts: a measured quantity or parameter, MP, that can take on a range of numerical values, and a relationship between FP and MP of the general functional form $MP = f(FP)$. An implicit assumption is that the procedure or technique must be applicable across a range of material or system property values.

The fundamental property may be a defined characteristic, such as the percentage of some constituent in a material or it may be defined solely by the measuring process itself. For this latter situation the measurement and the property are identical, and $MP = FP$ or $f = 1$. This is the usual case for many strictly technological measurement operations or tests, e.g., the modulus of a rubber. The $MP = f(FP)$ relationship must be monotonic and must be specific for any particular measuring process or test. If there are two different processes or tests for evaluating the fundamental property, the relationship is generally different for each test.

10.4.2.3 Test Sensitivity Concepts There are two classifications for test sensitivity; Class 1 is absolute test sensitivity, where the word absolute indicates that the measured property can be related to the fundamental property by a relationship that gives absolute values for the fundamental property, FP, from a knowledge of the measured property, *MP*. In evaluating test sensitivity for this class, two or more calibration materials (CMs) are used, each hav-

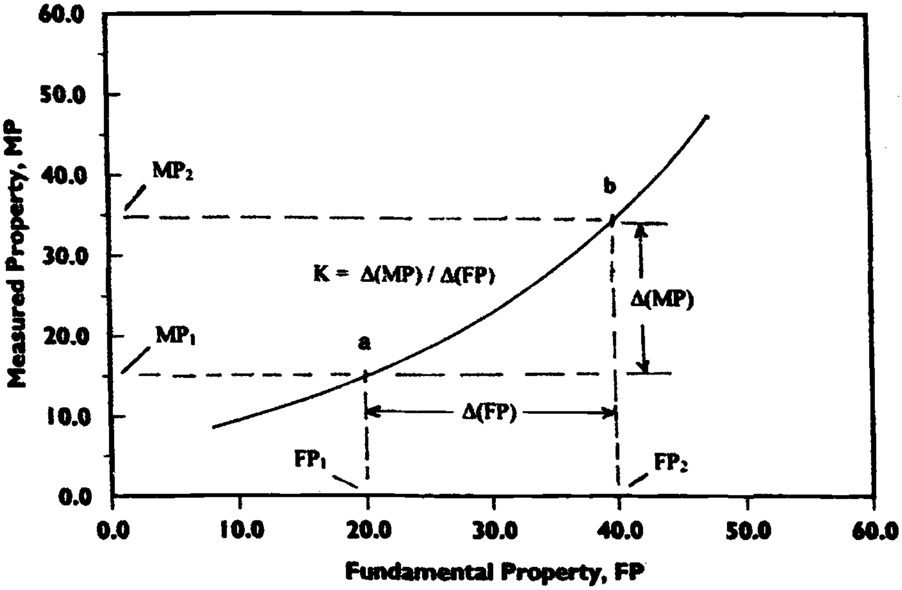

FIG. 10.4—Measured vs. fundamental property relationship.

ing documented different values for the fundamental property, *FP*. Class 2 is relative test sensitivity, where the test sensitivity of Test Method 1 is compared to Test Method 2, on the basis of a ratio, using two or more reference materials (RMs) with different measured property (*MP*) values. This class is used for physical test methods where no fundamental properties can be evaluated.

Absolute test sensitivity is defined in a simplified manner by the use of Fig. 10.4, a plot of two types of properties, a fundamental property, *FP*, the value of which is established by the use of a calibration material or CM, and a measured property, *MP*, obtained by applying the test method to the calibration material.

A relationship or functionality exists between the measured property and fundamental property that may be nonlinear. In the application of a particular test, FP_1 corresponds to MP_1 and FP_2 corresponds to MP_2. Over a selected region of the relationship, designated by points *a* and *b*, the slope, *K*, of the illustrated curve is approximated by the relationship $K = \Delta(MP)/\Delta(FP)$. If the test measurement standard deviation for *MP*, denoted as S_{MP}, is constant over this *a* to *b* range, the absolute test sensitivity designated as Ψ_A is defined by Eq 1.

$$\Psi_A = |K|/S_{MP} \tag{10.1}$$

For the selected region of interest, test sensitivity will increase with the increase of the numerical (absolute) value of the slope, $|K|$ and sensitivity will increase the more precise the measured property measurement or the smaller the standard deviation.

Relative test sensitivity is evaluated for typical physical test methods when a relationship between *MP* and *FP* using calibration materials (CMs) is not feasible or possible. This can be accomplished without knowledge of the $MP = f(FP)$ relationship for each test method. Standard D 6600 gives the derivation for relative test sensitivity as indicated by Eq 2.

$$\Psi_{R(T1/T2)} = |Ko|/[S_{MP1}/S_{MP2}] \tag{10.2}$$

where

$\Psi_{R(T1/T2)}$ = the relative test sensitivity of Test 1 to Test 2,
$|Ko|$ = absolute value of the slope of a plot of Test 1 measured property, *MP*1 vs. Test 2 measured property, *MP*2,
S_{MP1} = standard deviation of *MP*1, and
S_{MP2} = standard deviation of *MP*2.

If $\Psi_{R(T1/T2)}$ is above unity, Test 1 is more sensitive than Test 2; if it is below unity, Test 2 is more sensitive than Test 1. Again, the relative test sensitivity is applicable to a particular range of MP_1 and MP_2 values unless the plot of MP_1 vs. MP_2 is linear and the ratio (S_{MP1}/S_{MP2}) is constant across the experimental range under study. *Ko* may be evaluated without any knowledge of the fundamental properties; the requirements are (1) the relationship between *MP*1 and *MP*2 must be empirically known and (2) the measurements MP_1 and MP_2 must be made on the same set of reference materials or RMs, each of which has a different fundamental property or *FP* value that may or may not be known.

There are two categories for test sensitivity; Category 1 is designated as a limited range or "spot check" test sensitivity, an assessment of test sensitivity by a procedure that uses two (or perhaps three) different calibration materials (CMs) or reference materials (RMs). Category 2 is an extended range test sensitivity, a more comprehensive evaluation assessment over a substantial part or all of the entire working range of *MP* vs. *FP* values or *MP*1 vs. *MP*2 values, as customarily used in routine testing. Category 2 test sensitivity may or may not be uniform or constant across a broad range of the measured property.

There are two types of Category 2 sensitivity; uniform or Type 1 test sensitivity is a sensitivity that is uniform or constant across the entire experimental range as investigated. This requires a constant value for the (S_{MP1}/S_{MP2}) ratio across this range. Nonuniform or Type 2 test sensitivity depends on or is correlated with the value of either measured property (*MP*) across the experimental range. The ratio (S_{MP1}/S_{MP2}) can usually be expressed as a linear function of either measured property in the *MP*1 vs. *MP*2 relationship. See D 6600 for more details on test sensitivity and its evaluation.

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[9] "The Statistical Analysis of Experimental Data," see Chapters 13, 14; Mandel, J., Interscience Publishers (John Wiley & Sons), 1964.

APPENDIX 1

List of D11 and D24 Standards for Insuring High Quality Output

Part 1—Standards Arranged by Topic

(Standards may appear in more than one category)

1. Selecting ASTM Test Methods

Rubber Testing: Compound and Product Development, Acceptance-Rejection Plans

D 4483	Standard Practice: Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries
D 4678	Standard Practice, Rubber: Preparation, Testing, Acceptance, Documentation and Use of Reference Materials (IRMs)
D 5900	Rubber: Specifications for Physical and Chemical Properties of Industry Reference Materials (IRMs)
D 6600	Standard Practice, Rubber: Evaluating Test Sensitivity for Rubber Test Methods

Carbon Black Testing: Product Development, Acceptance-Rejection Plans

D 3324	Standard Practice, Carbon Black: Improving Test Reproducibility Using ASTM Reference Blacks
D 4122	Standard Practice, Carbon Black: Evaluation of an Industry Reference Black
D 4483	Standard Practice—Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries
D 4821	Standard Guide, Carbon Black: Validation of Test Method Precision and Bias

2. Sampling

Rubber Testing: Compound and Product Development, Acceptance-Rejection Plans

D 1485	Test Method, Rubber from Natural Sources—Sampling and Sample Preparation
D 3896	Test Method, Rubber from Synthetic Sources—Sampling
D 6085	Standard Practice, Sampling in Rubber Testing—Terminology and Basic Concepts

Carbon Black Testing: Product Development, Acceptance-Rejection Plans

D 1799	Standard Practice, Carbon Black—Sampling Packaged Shipments
D 1900	Standard Practice, Carbon Black—Sampling Bulk Shipments
D 5817	Standard Practice, Carbon Black—Reduction and Blending of Gross Samples

3. Conducting Measurements: Reference Materials, Classifications, Process Indexes and Precision (Statistical) Analysis

Reference Materials

D 4678	Standard Practice, Rubber: Preparation, Testing, Acceptance, Documentation and Use of Reference Materials (IRMs)
D 5900	Standard Specification—Physical and Chemical Properties for IRMs
D 4122	Standard Practice, Carbon Black: Evaluation of an Industry Reference Black
D 3324	Standard Practice, Carbon Black: Improving Test Reproducibility Using ASTM Reference Blacks

Classifications

D 1725	Standard Classification: Carbon Blacks Used in Rubber Products
D 4295	Standard Classification: Rubber Compounding Material—Zinc Oxide
D 4528	Standard Classification: Rubber Compounding Material—Sulfur
D 4676	Standard Classification: Rubber Compounding Material—Antidegradents
D 4817	Standard Classification: Rubber Compounding Material—Stearic Acid
D 4818	Standard Classification: Rubber Compounding Material—Vulcanization Accelerators

D 5603	Standard Classification: Rubber Compounding Material—Vulcanized Particulate Rubber

Process Indexes

D 5406	Standard Practice, Rubber: Calculation of Producer's Process Performance Index
D 4583	Standard Practice, Carbon Black: Calculation of Process Indexes from an Analysis of Process Control Data

Precision/Sensitivity

D 4483	Standard Practice—Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries
D 4821	Standard Guide: Carbon Black—Validation of Test Method Precision and Bias
D 6600	Standard Practice, Rubber: Evaluating Test Sensitivity for Rubber Test Methods

Part 2—Standards Numerically Arranged by D-Number

D 1485	Test Method, Rubber from Natural Sources—Sampling and Sample Preparation
D 1725	Standard Classification: Carbon Blacks Used in Rubber Products
D 1799	Standard Practice, Carbon Black—Sampling Packaged Shipments
D 1900	Standard Practice, Carbon Black—Sampling Bulk Shipments
D 3324	Standard Practice, Carbon Black: Improving Test Reproducibility Using ASTM Reference Blacks
D 3896	Test Method, Rubber from Synthetic Sources—Sampling
D 4122	Standard Practice, Carbon Black: Evaluation of an Industry Reference Black
D 4295	Standard Classification: Rubber Compounding Material—Zinc Oxide
D 4483	Standard Practice, Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries
D 4528	Standard Classification: Rubber Compounding Material—Sulfur
D 4583	Standard Practice, Carbon Black: Calculation of Process Indexes from an Analysis of Process Control Data
D 4676	Standard Classification: Rubber Compounding Material—Antidegradents
D 4678	Standard Practice, Rubber: Preparation, Testing, Acceptance, Documentation and Use of Reference Materials (IRMs)
D 4817	Standard Classification: Rubber Compounding Material—Stearic Acid
D 4818	Standard Classification: Rubber Compounding Material—Vulcanization Accelerators
D 4821	Standard Guide, Carbon Black: Validation of Test Method Precision and Bias
D 5406	Standard Practice, Rubber: Calculation of Producer's Process Performance Index
D 5603	Standard Classification: Rubber Compounding Material—Vulcanized Particulate Rubber
D 5817	Standard Practice, Carbon Black—Reduction and Blending of Gross Samples
D 5900	Standard Specification—Physical and Chemical Properties for IRMs
D 6085	Standard Practice, Rubber: Sampling in Rubber Testing—Terminology and Basic Concepts
D 6600	Standard Practice, Rubber: Evaluating Test Sensitivity for Rubber Test Methods

MNL39-EB/Aug. 2003

APPENDIX—ASTM TEST METHODS

Chap_1.5		
	D 6204-01	Test Method for Rubber—Measurement of Unvulcanized Rheological Properties Using Rotorless Shear Rheometers
	D 5289-95 (2001)	Test Method for Rubber Property—Vulcanization Using Rotorless Cure Meters
	D 6601-02	Test Method for Rubber Properties-Measurement of Cure and After-Cure Dynamic Properties Using a Rotorless Shear Rheometer
Chap_1.6		
	D 1765-03	Classification System for Carbon Blacks Used in Rubber Products
	D 5605-94 (2002)	Practice for Styrene-Butadiene Rubber (SBR)—Establishing Raw Mooney Viscosity Target Values
1.8.4	D 4821-03	Guide for Carbon Black—Validation of Test Method Precision and Bias
1.8.5	D 4678-94 (2001)	Practice for Rubber—Preparation, Testing, Acceptance, Documentation, and Use of Reference Materials
	D 3324	Standard Practice for Carbon Black—Improving Test Reproducibility Using ASTM Standard Reference Blacks, Replaced By D 4821
1.9	D 6204-01	Test Method for Rubber—Measurement of Unvulcanized Rheological Properties Using Rotorless Shear Rheometers
	D 5289-95 (2001)	Standard Test Method for Rubber Property—Vulcanization Using Rotorless Cure Meters
	D 1646-03	Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)
	D 6601-02	Test Method for Rubber Properties-Measurement of Cure and After-Cure Dynamic Properties Using a Rotorless Shear Rheometer
	D 2084-01	Test Method for Rubber Property-Vulcanization Using Oscillating Disk Cure Meter
	D 5899-98 (2002)	Classification System for Rubber Compounding Materials for Use in Computer Material Management Systems

Chap_2

2.1.2	D 3182-89 (2001)	Practice for Rubber—Materials, Equipment, and Procedures for Mixing Compounds and Preparing Vulcanized Sheets
2.1.3	D 3182-89 (2001)	Practice for Rubber—Materials, Equipment, and Procedures for Mixing Compounds and Preparing Vulcanized Sheets
2.1.4	D 3182-89 (2001)	Practice for Rubber—Materials, Equipment, and Procedures for Mixing Compounds and Preparing Vulcanized Sheets
2.2.1	D 1646-03	Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)
2.2.1.1.	D 3185-99	Test Methods for Rubber-Evaluation of SBR (Styrene-Butadiene Rubber) Including Mixtures With Oil
	D 3186-97 (2002)	Test Methods for Rubber-Evaluation of SBR (Styrene-Butadiene Rubber) Mixed With Carbon Black or Carbon Black and Oil
	D 1418-01a	Practice for Rubber and Rubber Latices-Nomenclature
2.2.1.2	D 1646-03	Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)
2.2.1.3	D 1646-03	Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)
	D 1349-99	Practice for Rubber-Temperatures For Testing
	D 1418-01a	Practice for Rubber and Rubber Latices-Nomenclature
2.2.2.	D 2084-01	Test Method for Rubber Property-Vulcanization Using Oscillating Disk Cure Meter
2.2.2.1	D 2084-01	Test Method for Rubber Property-Vulcanization Using Oscillating Disk Cure Meter
2.2.3	D 5289-95 (2001)	Standard Test Method for Rubber Property—Vulcanization Using Rotorless Cure Meters
	D 2084-01	Test Method for Rubber Property-Vulcanization Using Oscillating Disk Cure Meter
2.2.4.6	D 6204-01	Test Method for Rubber—Measurement of Unvulcanized Rheological Properties Using Rotorless Shear Rheometers
2.2.5	D 1412-98a (2002)e1	Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension
2.2.6	D 6601-02	Test Method for Rubber Properties-Measurement

		of Cure and After-Cure Dynamic Properties Using a Rotorless Shear Rheometer
	D 6204-01	Test Method for Rubber—Measurement of Unvulcanized Rheological Properties Using Rotorless Shear Rheometers
2.2.7.1	D 624-00e1	Test Method for Tear Strength of Conventional Vulcanized Rubber and Thermoplastic Elastomers
2.2.7.2	D 573-99	Test Method for Rubber-Deterioration in an Air Oven
	D 865-99	Test Method for Rubber-Deterioration by Heating in Air (Test Tube Enclosure)
2.2.7.3	D 623-99	Test Methods for Rubber Property-Heat Generation and Flexing Fatigue In Compression
	D 6601-02	Test Method for Rubber Properties-Measurement of Cure and After-Cure Dynamic Properties Using a Rotorless Shear Rheometer
	D 430-95 (2000)	Test Methods for Rubber Deterioration-Dynamic Fatigue
2.2.7.4	D 430-95 (2000)	Test Methods for Rubber Deterioration-Dynamic Fatigue
2.2.7.5	D 471-98e1	Test Method for Rubber Property-Effect of Liquids
2.2.7.6	D 395-02	Test Methods for Rubber Property—Compression Set
2.2.7.7	D 2240-02b	Test Method for Rubber Property—Durometer Hardness
	D 5289-95 (2001)	Test Method for Rubber Property—Vulcanization Using Rotorless Cure Meters
2.2.7.8	D 2228-02	Test Method for Rubber Property-Relative Abrasion Resistance by the Pico Abrader Method
2.2.7.9	D 1053-92ae1 (2001)	Test Methods for Rubber Property—Stiffening at Low Temperatures Flexible Polymers and Coated Fabrics
	D 2137-94 (2000)	Test Methods for Rubber Property-Brittleness Point of Flexible Polymers and Coated Fabrics
2.2.7.10	D 1171-99	Test Method for Rubber Deterioration-Surface Ozone Cracking Outdoors or Chamber (Triangular Specimens)
2.2.8	D 412-98a (2002)e1	Test Methods for Vulcanized Rubber and Thermoplastic Elastomers—Tension
	D 2240-02b	Test Method for Rubber Property—Durometer Hardness
	D 573-99	Test Method for Rubber-Deterioration in an Air Oven
	D 2000-01	Classification System for Rubber Products in Automotive Applications

Chap_3

3.2	D 1485-86 (2002)	Test Methods for Rubber from Natural Sources-Sampling and Sample Preparation
3.3	D 2227-96 (2002)	Specification for Natural Rubber (NR) Technical Grades
3.4	D 1278-91a (2002)	Test Methods for Rubber from Natural Sources-Chemical Analysis
3.4.1	D 1278-91a (2002)	Test Methods for Rubber from Natural Sources-Chemical Analysis
3.4.2	D 1278-91a (2002)	Test Methods for Rubber from Natural Sources-Chemical Analysis
3.4.3	D 4004-93 (2002)	Test Methods for Rubber—Determination of Metal Content by Flame Atomic Absorption (AAS) Analysis
3.4.4	D 4004-93 (2002)	Test Methods for Rubber—Determination of Metal Content by Flame Atomic Absorption (AAS) Analysis
3.4.8	D 3533-90 (2001)	Method of Rubber—Nitrogen Content
3.5	D 3194-99	Test Method for Rubber From Natural Sources-Plasticity Retention Index (PRI)
3.6	D 3157-84 (2001)	Test Method for Rubber from Natural Sources—Color
3.7	D 3184-89 (2001)	Test Methods for Rubber-Evaluation of NR (Natural Rubber)
3.8	D 6204-01	Test Method for Rubber—Measurement of Unvulcanized Rheological Properties Using Rotorless Shear Rheometers

Chap_4

4.1	D 1418-01a	Practice for Rubber and Rubber Latices-Nomenclature
4.2	D 5605-94 (2002)	Practice for Styrene-Butadiene Rubber (SBR)—Establishing Raw Mooney Viscosity Target Values
4.3	D 1646-03	Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)
	D 6204-01	Test Method for Rubber—Measurement of Unvulcanized Rheological Properties Using Rotorless Shear Rheometers
4.4	See tables 4.5 to 4.13	

4.5	D 3346-00	Test Methods for Rubber Property-Processability of SBR (Styrene-Butadiene Rubber) With the Mooney Viscometer
4.6.1	D 5774-95 (2000)	Test Methods for Rubber From Synthetic Sources-Chemical Analysis of Extractables
4.6.2	D 5668-99	Test Methods for Rubber From Synthetic Sources-Volatile Matter
4.6.3	D 5667-95 (2000)	Test Method for Rubber From Synthetic Sources-Total and Water Soluble Ash
4.6.4	D 5805-00	Test Method for Rubber from Synthetic Sources—Carbon Black in Masterbatches
4.6.5	D 3616-95 (2000)	Test Method for Rubber, Raw-Determination of Gel, Swelling Index, and Dilute Solution Viscosity
4.6.6	D 3533-90 (2001)	Method of Rubber—Nitrogen Content
4.6.7.1	D 5902-96 (2001)	Test Method for Rubber-Determination of Residual Unsaturation in Hydrogenated Nitrile Rubber (HNBR) by Iodine Value
	D 1959-97	Test Method for Iodine Value of Drying Oils and Fatty Acids
4.6.7.2	D 5670-95 (2000)e1	Test Method for Rubber-Determination of Residual Unsaturation in Hydrogenated Nitrile Rubber (HNBR) by Infrared Spectrophotometry
	D 5902-96 (2001)	Test Method for Rubber-Determination of Residual Unsaturation in Hydrogenated Nitrile Rubber (HNBR) by Iodine Value
4.6.8.1	D 6047-99e1	Test Methods for Rubber, Raw—Determination of 5-Ethylidenenorbornene (ENB) or Dicyclopentadiene (DCPD) in Ethylene-Propylene-Diene (EPDM) Terpolymers
4.6.9.1	D 5775-95 (2000)	Test Method for Rubber from Synthetic Sources-Bound Styrene in SBR
4.6.10.1	D 3566-96 (2001)	Practice for Rubber—Determination of Bromine in the Presence of Chlorine by Oxygen Combustion
4.6.11	D 4004-93 (2002)	Test Methods for Rubber—Determination of Metal Content by Flame Atomic Absorption (AAS) Analysis

Chap_5

5.1.2	D 1510-02a	Test Method for Carbon Black—Iodine Adsorption Number
	D 6556-02a	Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption

	5.2.1	D 1765-03 Classification System for Carbon Blacks Used in Rubber Products
	D 4820	Standard Test Methods for Carbon Black-Surface Area by Multipoint B.E.T. Nitrogen Adsorption (Withdrawn 2000), Replaced by D 6556
	D 1510-02a	Test Method for Carbon Black—Iodine Adsorption Number
	D 2414-02a	Test Method for Carbon Black—Oil Absorption Number
	D 6556-02a	Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption
	D 3493-01	Test Method for Carbon Black—Oil Absorption Number of Compressed Sample
	D 3265-02	Test Method for Carbon Black—Tint Strength
	D 1513-99ae1	Test Method for Carbon Black, Pelleted-Pour Density
	D 3192-02	Test Methods for Carbon Black Evaluation in NR (Natural Rubber)
	D 3182-89 (2001)	Practice for Rubber—Materials, Equipment, and Procedures for Mixing Compounds and Preparing Vulcanized Sheets
	D 3493-01	Test Method for Carbon Black—Oil Absorption Number of Compressed Sample
	D 2414-02a	Test Method for Carbon Black—Oil Absorption Number
5.3.1	D 3324	Standard Practice for Carbon Black—Improving Test Reproducibility Using ASTM Standard Reference Blacks, Replaced By D 4821
	D 4821-01	Guide for Carbon Black—Validation of Test Method Precision and Bias
5.3.2	D 1510-02a	Test Method for Carbon Black—Iodine Adsorption Number
	D 2414-02a	Test Method for Carbon Black—Oil Absorption Number
	D 3493-01	Test Method for Carbon Black—Oil Absorption Number of Compressed Sample
	D 4820 Standard	Test Methods for Carbon Black-Surface Area by Multipoint B.E.T. Nitrogen Adsorption (Withdrawn 2000), Replaced By D 6556
	D 3265-02	Test Method for Carbon Black—Tint Strength
	D 5816	Standard Test Methods for Carbon Black-External Surface Area by Multipoint Nitrogen Adsorption (Withdrawn 2000), Replaced By D 6556
5.4.1	D 1510-02a	Test Method for Carbon Black—Iodine Adsorption Number

5.4.2	D 6556-02a	Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption
5.4.3	D 3765-02	Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area
	D 6556-02a	Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption
5.4.4	D 3849-02	Test Method for Carbon Black-Morphological Characterization of Carbon Black Using Electron Microscopy
5.5.1	D 2414-02a	Test Method for Carbon Black—Oil Absorption Number
5.5.2	D 3493-01	Test Method for Carbon Black—Oil Absorption Number of Compressed Sample
	D 2414-02a	Test Method for Carbon Black—Oil Absorption Number
5.5.3	D 6086-97	Test Methods for Carbon Black—Compressed Volume Index
5.6.1	D 1514-01	Test Method for Carbon Black—Sieve Residue
5.6.2	D 1511-00e1	Test Method for Carbon Black-Pellet Size Distribution
5.6.5.3	D 1937-98	Test Method for Carbon Black, Pelleted-Mass Strength
5.7.1	D 3191-02	Test Method for Carbon Black in SBR (Styrene-Butadiene-Rubber)-Recipe and Evaluation Procedures
	D 3192-02	Test Methods for Carbon Black Evaluation in NR (Natural Rubber)

Chap_6

6.2.2	D 1765-03	Classification System for Carbon Blacks Used in Rubber Products
6.3	D 1993-03	Test Method for Precipitated Silica-Surface Area by Multipoint BET Nitrogen Adsorption
	D 5604-96 (2001)	Test Methods for Precipitated Silica—Surface Area by Single Point B.E.T. Nitrogen Adsorption
	D 6845-02	Test Method for Silica, Precipitated, Hydrated—CTAB (Cetyltrimethylammonium Bromide) Surface Area
6.3.1.1	D 5604-96 (2001)	Test Methods for Precipitated Silica—Surface Area by Single Point B.E.T. Nitrogen Adsorption
6.3.1.2	D 1993-03	Test Method for Precipitated Silica-Surface Area by Multipoint BET Nitrogen Adsorption

6.3.2.1	D 3765-02	Test Method for Carbon Black—CTAB (Cetyltrimethylammonium Bromide) Surface Area
6.4	D 6854-03	Test Method for Silica—>n-Dibutyl Phthalate Absorption Number
6.5.1	D 6738-01	Test Method for Precipitated Silica—Volatile Content
6.5.2	D 6739-01	Test Method for Silica—pH Value
6.6.1	D 6740-01	Test Method for Silanes Used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes): Residue on Ignition
6.6.2	D 6741-01	Test Methods for Silanes Used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes): Sulfur Content
6.6.3	D 6843-02	Test Method for Silanes Used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes): Characterization by Gas Chromatography (GC)
6.6.4	D 6844-02	Test Method for Silanes Used in Rubber Formulations (bis-(triethoxysilylpropyl)sulfanes): Characterization byHigh Performance Liquid Chromatography (HPLC) See tables 6.2

Chap_7

7.1	D 5377-93 (2002)	Classification for Rubber Compounding Materials—Ground Coal
7.1.1	C 1070-01	Test Method for Determining Particle Size Distribution of Alumina or Quartz by Laser Light Scattering
	D 5377-93 (2002)	Classification for Rubber Compounding Materials—Ground Coal
7.1.2	D 5377-93 (2002)	Classification for Rubber Compounding Materials—Ground Coal
	D 3174-02	Test Method for Ash in the Analysis Sample of Coal and Coke from Coal
7.1.4	D 3174-02	Test Method for Ash in the Analysis Sample of Coal and Coke from Coal
	D 5377-93 (2002)	Classification for Rubber Compounding Materials—Ground Coal
7.1.6	D 5377-93 (2002)	Classification for Rubber Compounding Materials—Ground Coal
	D 1208-96 (2002)	Test Methods for Common Properties of Certain Pigments
7.1.7	D 3175-02	Test Method for Volatile Matter in the Analysis Sample of Coal and Coke

	D 5377-93 (2002)	Classification for Rubber Compounding Materials—Ground Coal
7.1.8	D 4371-91 (1998)	Test Method for Determining the Washability Characteristics of Coal
7.2	D 4677-87 (2002)	Classification for Rubber Compounding Materials—Titanium Dioxide
7.2.1	D 1394-76 (1999)	Test Methods for Chemical Analysis of White Titanium Pigments
7.2.2	D 1208-96 (2002)	Test Methods for Common Properties of Certain Pigments
7.2.3	D 185-84 (1999)	Test Methods for Coarse Particles in Pigments, Pastes, and Paints
7.2.4	D 280-01	Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments
7.2.5	D 1394-76 (1999)	Test Methods for Chemical Analysis of White Titanium Pigments
	D 3720-90 (1999)	Test Method for Ratio of Anatase to Rutile in Titanium Dioxide Pigments by X-ray Diffraction

Chap_8

8.1.1	D 2501-91 (2000)	Test Method for Calculation of Viscosity-Gravity Constant (VGC) of Petroleum Oils
8.1.7	D 2226-93 (2002)	Classification for Various Types of Petroleum Oils for Rubber Compounding Use
	D 2007-02	Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay—Gel Absorption Chromatographic Method
	D 2501-91 (2000)	Test Method for Calculation of Viscosity-Gravity Constant (VGC) of Petroleum Oils
8.1.8.1	D 2007-02	Test Method for Characteristic Groups in Rubber Extender and Processing Oils and Other Petroleum-Derived Oils by the Clay—Gel Absorption Chromatographic Method
8.1.8.2	D 2501-91 (2000)	Test Method for Calculation of Viscosity-Gravity Constant (VGC) of Petroleum Oils
8.1.8.3	D 445-01	Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)
8.1.8.4	D 611-01b	Test Methods for Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents
8.1.8.5	D 97-02	Test Method for Pour Point of Petroleum Products

8.1.8.6	D 974-02	Test Method for Acid and Base Number by Color-Indicator Titration
8.1.8.7	D 1298-99e1	Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method
8.1.8.8	D 1500-02	Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)
8.1.8.9	D 2008-91 (2001)	Test Method for Ultraviolet Absorbance and Absorptivity of Petroleum
8.1.8.10	D 92-02b	Test Method for Flash and Fire Points by Cleveland Open Cup Tester
8.2.1	D 3853-03e1	Terminology Relating to Rubber and Rubber Latices—Abbreviations for Chemicals Used in Compounding
8.2.2	D 1992-91 (2001)	Guide for Testing Synthetic Plasticizers Used in Rubber
8.2.2.1	D 70-97	Test Method for Specific Gravity and Density of Semi-Solid Bituminous Materials (Pycnometer Method)
	D 891-95 (2000)	Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals
	D 2111-02	Test Methods for Specific Gravity and Density of Halogenated Organic Solvents and Their Admixtures
8.2.2.2	D 1209-00	Test Method for Color of Clear Liquids (Platinum-Cobalt Scale)
	D 1544-98	Test Method for Color of Transparent Liquids (Gardner Color Scale)
8.2.2.3	D 1218-02	Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids
8.2.2.4	D 1962-85 (1995)	Test Method for Saponification Value of Drying Oils, Fatty Acids, and Polymerized Fatty Acids
8.2.2.5	D 2196-99	Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield type) Viscometer
8.2.2.6	D 2288-97 (2001)	Test Method for Weight Loss of Plasticizers on Heating
8.2.2.7	E 203-01	Test Method for Water Using Volumetric Karl Fischer Titration
8.3.1	D 4528-88 (2002)	Classification for Rubber Compounding Materials—Sulfur
8.3.1.1	D 4578-89 (2002)	Standard Test Methods for Rubber Chemicals—Determination of Percent Insoluble Sulfur by Solvent Extraction

8.3.1.2	D 4573-98	Test Method for Rubber Chemicals-Determination of Oil Content in Oil-Treated Sulfur
8.3.1.3	D 4569-02	Test Method for Rubber Chemicals—Determination of Acidity in Sulfur
8.3.1.4	D 4570-02	Test Method for Rubber Chemicals—Determination of Particle Size of Sulfur by Sieving (Dry)
	D 4572-89 (1999)	Test Method for Rubber Chemicals-Wet Sieve Analysis of Sulfur
8.3.1.5	D 4574-02	Test Methods for Rubber Chemicals—Determination of Ash Content
8.3.2	D 4818-89 (1999)	Classification for Rubber Compounding Materials-Vulcanization Accelerators
	D 5289-95 (2001)	Test Method for Rubber Property—Vulcanization Using Rotorless Cure Meters
8.3.2.1	D 3853-03e1	Terminology Relating to Rubber and Rubber Latices—Abbreviations for Chemicals Used in Compounding
8.3.2.2	D 1519-95 (2000)	Test Method for Rubber Chemicals-Melting Range
8.3.2.3	D 4572-89 (1999)	Test Method for Rubber Chemicals-Wet Sieve Analysis of Sulfur
8.3.2.4	D 4574-02	Test Methods for Rubber Chemicals—Determination of Ash Content
8.3.2.5	D 4571-02	Test Methods for Rubber Chemicals—Determination of Volatile Material
8.3.2.6	D 4818-89 (1999)	Classification for Rubber Compounding Materials-Vulcanization Accelerators
8.3.2.7	D 4934-02	Test Method for Rubber Compounding Materials: 2-Benzothiazyl Sulfenamide Accelerators—Insolubles
8.3.2.8	D 4936-96 (2001)	Test Method for Mercaptobenzothiazole Sulfenamide Assay by Reduction/Titration
8.3.2.9	D 5051-02	Test Method for Rubber Chemicals-Benzothiazyl Disulfide (MBTS)-Assay
8.3.2.10	D 5054-90 (2000)	Test Method for Rubber Chemicals-Diphenyl Guanidine (DPG) and Di-o-tolyl-guanidine (DOTG) Assay
8.3.2.11	D 1991-96 (2001)	Test Method for Rubber Chemicals—2-Mercaptobenzothiazole (MBT)—Assay
8.3.3	D 4295-89 (1999)	Classification for Rubber Compounding Materials-Zinc Oxide
8.2.2.6	D 4315-94 (2001)	Test Methods for Rubber Compounding Material—Zinc Oxide

8.3.3.6.1	D 3037	Test Methods for Carbon Black-Surface Area by Nitrogen Adsorption (Withdrawn 1999), Replaced
	D 4315-94 (2001)	Test Methods for Rubber Compounding Material—Zinc Oxide
8.3.3.6.2	D 4075-02	Test Methods for Compounding Materials-Flame Atomic Absorption Technique-Determination of Metals
	D 4315-94 (2001)	Test Methods for Rubber Compounding Material—Zinc Oxide
8.3.3.6.3	D 4315-94 (2001)	Test Methods for Rubber Compounding Material—Zinc Oxide
8.3.3.6.4	D 280-01	Test Methods for Hygroscopic Moisture (and Other Matter Volatile Under the Test Conditions) in Pigments
8.3.3.6.5	D 3280-85 (1999)	Test Methods for Analysis of White Zinc Pigments
	D 4315-94 (2001)	Test Methods for Rubber Compounding Material—Zinc Oxide
8.3.3.6.6	D 3280-85 (1999)	Test Methods for Analysis of White Zinc Pigments
	D 4315-94 (2001)	Test Methods for Rubber Compounding Material—Zinc Oxide
	D 2084-01	Test Method for Rubber Property-Vulcanization Using Oscillating Disk Cure Meter
	D 5289-95 (2001)	Test Method for Rubber Property—Vulcanization Using Rotorless Cure Meters
	D 4620-02	Test Method for Evaluating the Effective Surface Area of Zinc-Oxide in Rubber
8.3.4.1	D 1959-97	Test Method for Iodine Value of Drying Oils and Fatty Acids
8.3.4.2	D 1982-85 (1999)	Test Method for Titer of Fatty Acids
8.3.4.3	D 1980-87 (1998)	Test Method for Acid Value of Fatty Acids and Polymerized Fatty Acids
8.3.4.4	D 1962-85 (1995)	Test Method for Saponification Value of Drying Oils, Fatty Acids, and Polymerized Fatty Acids
8.3.4.5	D 1951-86 (1995)e1	Test Method for Ash in Drying Oils and Fatty Acids
8.3.4.6	D 1965-87 (1998)	Test Method for Unsaponifiable Matter in Drying Oils, Fatty Acids, and Polymerized Fatty Acids
8.3.4.7	D 4075-02	Test Methods for Compounding Materials-Flame Atomic Absorption Technique-Determination of Metals

8.4	D 4676-94 (2001)	Classification for Rubber Compounding Materials—Antidegradents
8.4.7	D 3853-03e1	Terminology Relating to Rubber and Rubber Latices—Abbreviations for Chemicals Used in Compounding
8.4.8.1	D 4937-96 (2001)	Test Method for p-Phenylenediamine Antidegradants Purity by Gas Chromatography
8.4.8.2	D 4676-94 (2001)	Classification for Rubber Compounding Materials—Antidegradents
	D 1519-95 (2000)	Test Method for Rubber Chemicals-Melting Range
	D 1218-02	Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids
	D 1747-99	Test Method for Refractive Index of Viscous Materials
8.4.8.3	D 4676-94 (2001)	Classification for Rubber Compounding Materials—Antidegradents
	D 2702-94 (1998)	Practice for Rubber Chemicals-Determination of Infrared Absorption Characteristics
8.4.8.4	D 4571-02	Test Methods for Rubber Chemicals—Determination of Volatile Material
8.4.8.5	D 4574-02	Test Methods for Rubber Chemicals—Determination of Ash Content
8.4.8.6	D 4676-94 (2001)	Classification for Rubber Compounding Materials—Antidegradents
8.4.8.7	D 4676-94 (2001)	Classification for Rubber Compounding Materials—Antidegradents
8.5.1	D 4924-89 (1999)	Classification for Petroleum Waxes for Use in Rubber Compounding
8.5.1.2	D 87-87(1999)	Test Method for Melting Point of Petroleum Wax (Cooling Curve)
	D 938-92 (1998)	Test Method for Congealing Point of Petroleum Waxes, Including Petrolatum
	D 3944-88 (2000)	Test Method for Solidification Point of Petroleum Wax
	D 4419-90 (2000)	Test Method for Measurement of Transition Temperatures of Petroleum Waxes by Differential Scanning Calorimetry (DSC)
8.5.1.4	D 721-02a	Test Method for Oil Content of Petroleum Waxes
8.5.1.5	D 445-01	Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity)
8.5.1.6	D 1500-02	Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)
8.5.1.7	D 1321-02a	Test Method for Needle Penetration of Petroleum Waxes

Chap_9

9.1	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber -01
9.1.6	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber -96
	D 5644-01	Test Method for Rubber Compounding Materials—Determination of Particle Size Distribution of Vulcanized Particulate Rubber -96
	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber -01
	D 5644-01	Test Method for Rubber Compounding Materials—Determination of Particle Size Distribution of Vulcanized Particulate Rubber -01
9.2.3	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber -01
	D 297-93 (2002)e1	Test Methods for Rubber Products-Chemical Analysis
	D 5644-01	Test Method for Rubber Compounding Materials—Determination of Particle Size Distribution of Vulcanized Particulate Rubber -01
9.3	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber -01
9.3.1	D 5644-01	Test Method for Rubber Compounding Materials—Determination of Particle Size Distribution of Vulcanized Particulate Rubber -01
	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber -01
9.3.2	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber -01
9.3.3	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber -01
9.3.3.1	D 297-93 (2002)e1	Test Methods for Rubber Products-Chemical Analysis
9.3.3.2	D 297-93 (2002)e1	Test Methods for Rubber Products-Chemical Analysis
9.3.3.3	D 297-93 (2002)e1	Test Methods for Rubber Products-Chemical Analysis
9.3.3.4	D 1509-95 (2000)	Test Methods for Carbon Black-Heating Loss
9.3.3.5	D 297-93 (2002)e1	Test Methods for Rubber Products-Chemical Analysis
9.3.3.6	D 297-93 (2002)e1	Test Methods for Rubber Products-Chemical Analysis

9.3.3.7	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber -01
	D 5644-01	Test Method for Rubber Compounding Materials—Determination of Particle Size Distribution of Vulcanized Particulate Rubber -01

Chap_10

10.2.1	D 6085-97 (2002)	Practice for Sampling in Rubber Testing—Terminology and Basic Concepts
10.2.2.1	D 4483-99	Practice for Determining Precision for Test Methods in the Rubber and Carbon Black Industries
	D 4821-03	Guide for Carbon Black—Validation of Test Method Precision and Bias
10.2.2.2	D 6600-00e2	Practice for Evaluating Test Sensitivity for Rubber Test Methods
10.2.3.1	D 6085-97 (2002)	Practice for Sampling in Rubber Testing—Terminology and Basic Concepts
10.2.3.4	D 6085-97 (2002)	Practice for Sampling in Rubber Testing—Terminology and Basic Concepts
10.2.4.1	D 4678-94 (2001)	Practice for Rubber—Preparation, Testing, Acceptance, Documentation, and Use of Reference Materials
	D 5900-98 (2002)	Specification for Physical and Chemical Properties of Industry Reference Materials (IRM)
	D 1765-03	Classification System for Carbon Blacks Used in Rubber Products
	D 4295-89 (1999)	Classification for Rubber Compounding Materials-Zinc Oxide
	D 4817-88 (1999)	Classification for Rubber Compounding Materials-Stearic Acid
	D 4818-89 (1999)	Classification for Rubber Compounding Materials-Vulcanization Accelerators
	D 4528-88 (2002)	Classification for Rubber Compounding Materials—Sulfur
	D 5603-01	Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber
10.2.4.2	D 3324	Standard Practice for Carbon Black—Improving Test Reproducibility Using ASTM Standard Reference Blacks, Replaced By D 4821 Standard Practice for Carbon Black—Improving Test Reproducibility Using ASTM Standard Reference Blacks, Replaced By D 4821
	D 4122-02	Practice for Carbon Black—Evaluation of an Industry Reference Black

10.3.1	D 1485-86 (2002)	Test Methods for Rubber from Natural Sources-Sampling and Sample Preparation
	D 1900-94 (2002)	Practice for Carbon Black—Sampling Bulk Shipments
	D 5817-03	Practice for Carbon Black, Pelleted-Reduction, Blending, and Drying of Gross Samples for Testing
	D 3896-85 (2001)	Practice for Rubber From Synthetic Sources-Sampling
	D 1799-02	Practice for Carbon Black—Sampling Packaged Shipments
	D 4583-95 (1999)	Practice for Carbon Black-Calculation of Process Indexes From an Analysis of Process Control Data
10.4.1	D 4483-99	Practice for Determining Precision for Test Methods in the Rubber and Carbon Black Industries
10.4.1.2	D 4483-99	Practice for Determining Precision for Test Methods in the Rubber and Carbon Black Industries
10.4.1.3	D 4483-99	Practice for Determining Precision for Test Methods in the Rubber and Carbon Black Industries

Index

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John Dick has over 30 years of experience in the rubber industry. He was with BF Goodrich and later Uniroyal Goodrich Tire Co. as a Section Manager and Development Scientist in R&D until 1991 when he joined Alpha Technologies (formerly Monsanto's Rubber Instruments Group) as a Senior Marketing Technical Service Specialist. Mr. Dick has authored over 45 journal and magazine publications and three books on polymer technology. He received the Monsanto Master Technical Service Award in 1994, the American Chemical Society Rubber Division "Best Paper Award" in 1995, and a University of Akron Appreciation Award in 1998 for Teaching Polymer Compounding Courses in their Continuing Education Program. He is a Fellow in ASTM International, receiving the Award of Merit in 1990. Also he has represented the United States as a delegate to the International Standards Organization (ISO) for the last 20 years. He was appointed in 1992 to be the leader of the U.S.A. Delegation to ISO TC-45 on Rubber. He teaches rubber technology courses at both University of Akron and University of Wisconsin Continuing Education Departments. He is a member of American Chemical Society, Society of Rheology, and the American Society for Quality with a CQE. He is also a representative to the RMA. Mr. Dick received his B.S. degree from Virginia Polytechnic Institute in 1970 and an M.A. from the University of Akron in 1979. His hobbies include photography and amateur radio.

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