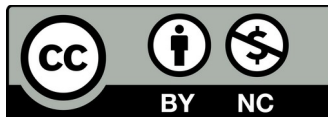


Rubber Boots – Understanding an Industry

by Jon Nicholson, President
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2022 Jon Nicholson

Preface

Intended audience: This handbook is intended for the use of anyone who is curious about the materials or methods connected with rubber or rubber boots. It may be of special interest to personnel working for importers, trading companies, and distributors in the footwear industry, who may include rubber boots in their product line. Rubber boots constitute a tiny niche in the footwear industry, but if your company distributes them you will benefit from having a basic understanding of the relevant technology. This understanding will help you and your company make rational decisions about sourcing the right products for your business, and avoiding possible problems in the future.

The rubber industry is a thriving branch of industry that has a history reaching back to the mid 19th century. While some rubber products have been normal items of daily life for a long time, many others are innovative products making use of the most advanced materials technologies available, and those technologies continue to be developed at major university and industrial institutions.

My field, rubber footwear, lies more at the “mature” end of the technology spectrum. However, even in my field, there are always new developments in design and materials. I, myself, have participated in developing technology to produce new and more capable products, with a focus toward safety footwear. I specialize in the chemistry of rubber compounds and the structural design of boots, to push performance of rubber footwear to higher levels. I continue this work every day.

I started my career in rubber footwear in 1977, spending 24 years at The LaCrosse Rubber Mills Co. Inc. (later known as LaCrosse Footwear, Inc.), a company founded in 1897. After two years of general factory work, I was able to advance to Laboratory Technician, to Development Chemist, and to Product Development Manager (Occupational Footwear). During my 24 years there, I studied the manufacturing process “from the ground up”. Since my LaCrosse Footwear days, I’ve worked independently with a variety of rubber boot factories in Asia, and I’ve consulted for various North American footwear distributors. What seems like the relatively unexciting field of rubber boots has provided me with a very satisfying and interesting career. It illustrates the old wisdom: you benefit from an experience in proportion to what you put into it.

Because American companies moved to source products more cheaply from Asia, the last remaining rubber footwear production ceased in the United States in 2010. As production dwindled and factories closed, the personnel who understood rubber boot manufacturing either retired or moved on to other jobs. As a result, when American distributors want to source rubber footwear, there are no longer many people around who understand the product from a technical point of view. Rarely does anyone on the American side of the equation know anything about rubber chemistry, structural engineering related to rubber footwear, or aspects of the

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manufacturing process that may affect the longevity of the boots. Mainly, U.S.-based personnel understand the product from the cosmetic standpoint, and where the product should fit into a marketing plan – and little else.

The story is almost as bad on the sourcing side. (Here, I’m specifically drawing from my own – admittedly limited – experience in Southeast Asia and China.) When representatives arrive from an American customer, they ask for a rubber boot – hopefully at a specific price. They provide a few requirements from the customer’s side, and the factory seeks to provide something that meets their request. The essential fact, though, is that the factory typically lacks technical details from the customer, other than that the product should look like a boot, have some (preferably low) cost, and be made out of “rubber”. As I will show later, “rubber” is a very general term that can mean many things.

So the Americans tend to only know the general design, cosmetic appearance, and price-point that they want, and the foreign factories try to give them what they asked for – usually with only a superficial understanding of the performance demands of the boots. Consequently, they guess about the technical details, and about how to hit the desired price-point. Even when the customer can provide testing specifications (like tensile strength, abrasion-resistance, etc.), there are many ways to reach specified test numbers that may not meet the actual field performance needed by the end-user.

I give a lot of guidance to my Chinese colleagues in order that they can understand the difference between a generic rubber boot and a rubber boot that meets a certain performance profile. On the other hand, American customers also need some help to understand their own requirements for rubber boots. They need the tools to better collaborate with foreign factories in order to make the right product. **Bringing some clarity to both parties is one of the most important aspects of my business, and I’m writing this handbook because I won’t be around forever!**

Jon Nicholson

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Introduction

I've been an expert witness in a couple of lawsuits and other legal proceedings, including a criminal case for the Illinois State Police. Whereas rubber boots seem like a very mundane product, they (like anything) can become an issue in people's lives -- in their safety and in their financial welfare.

I was a witness in one lawsuit where a commercial agent was being sued. He had been asked to source some rubber boots for an American distributor. The Americans gave him some sketchy information about what they wanted. He found a Chinese factory to produce the boots at the required price. After that, the distributor made some large orders, received the boots, sold them, and experienced a market disaster when a large percentage of the boots were returned as defective goods, failing from flex cracking.

In this instance, neither the distributor, the agent, nor (apparently) the factory had any clue about what they were doing. There were no functional specifications provided by the distributor, just cosmetic specs. The agent only arranged for a factory to fill the order, he knew nothing about rubber boots. The factory – I am guessing that they did whatever was necessary to make the boots at the specified price, and did not have the competence to foresee the result. At trial, I testified about various aspects of the defective products, but also pointed out that no standard of quality had been provided by the distributor, and no contracts existed that would assign responsibilities. Moreover, the distributor had failed to provide any data about the actual longevity or wear environments of the boots that failed, so they couldn't establish that the boots hadn't been "serviceable" on delivery. My client was found to be not liable for damages.

What made an impression on me was how amazingly careless all three parties were about products that had cost hundreds of thousands of dollars to bring into the country. Why hadn't anyone taken more care to evaluate the boots, before the order was placed? It seemed clear that for many people, if an object looks like a boot and it made of "rubber", then it qualifies as a rubber boot – and few people have the ability to look farther than that.

Real knowledge is important. The more aspects of a product that you can identify, the more likely you will find vulnerabilities that need attention. Science is about the material world, facts that can be observed, and their interrelationships and possible significance. Everything fits into that framework, including rubber boots. The science and technology of rubber as a crucial material in our lives has been thoroughly developed, most of all for the tire industry. So there is no reason that we have to accept a superficial point of view when addressing the rubber boot industry. In fact, rubber boots can be addressed with a fairly basic framework of chemical and physical concepts. It helps to be inventive with those concepts, but the concepts themselves are well-studied, and not too complicated to apply.

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When readers of this handbook start seeing text about the chemistry and structural engineering of rubber boots, I hope that it's not too off-putting. I've tried to ease the reader's efforts by including some of my diagrams that I've worked out over time, to illustrate different aspects of rubber boot technology to my clients. The ideas presented here are basically my "brain dump" from over 45 years in my field. These ideas do not all look like they did when I first came up with them – I've had to refine my understanding over time.

I had the good luck to move cross-country when I was much younger, necessitating that I get a factory floor job in a rubber boot factory – the only job I could find in my new location. Whereas many people with a college degree avoid factory work like the plague, I found it to be good honest work. And, like most work situations, if you apply yourself you can usually rise in the organization. Also, I was extremely fortunate to have a couple of excellent bosses in my earlier years, who told me what they wanted, then let me go do it without much interference.

This "handbook", as I think of it, is based on my experiences and ideas. The business niche I work in is tiny, and I don't know of anyone who knows more about it, or thinks more deeply about it, than I do – but such people might exist. If they do exist, and they read this handbook, I would be happy to know if they have additional or even better insights than the ones I've presented here. I'm on LinkedIn – message me!

Jon Nicholson, 2022-03-21

Disclaimer:

While the advice and information in this book are believed to be true and accurate at the date of release, the author can not accept any legal responsibility for any errors or omissions that may be made.

Chapter 1: Terms and Definitions

Rubber boots can be common rainboots, utility boots (for general work), farm boots, or sometimes (conforming to higher cosmetic standards) a fashion accessory. They can also serve specialized protection needs like steel toe safety work boots, firefighter boots, chemical protection boots, etc. Since they are made of rubber, it's important to understand the definitions of things related to rubber and the associated manufacturing terms.

Definitions:

Polymer – Polymers, both natural and synthetic, are created by chemically joining many small molecules, known as **monomers**, end-to-end to make very large molecules, or macromolecules, composed of many repeating subunits. The monomers can be all of the same type so that they make a simple polymer (like the “polyisoprene” in Natural Rubber, abbreviated as “NR”), or they can be of more than one type, which results in a “co-polymer”. In a Hevea rubber tree (see “Latex rubber” below), the biochemistry that operates inside the tree's cells perform the polymerization reaction.

The various synthetic rubber types that can be made artificially include:

- SBR – styrene butadiene rubber
- BR – butadiene rubber
- EPDM – ethylene propylene diamine monomer rubber
- CR – polychloroprene (neoprene) rubber
- NBR – acrylonitrile (nitrile) rubber
- IIR – isobutylene-isoprene (butyl) rubber

Each type of rubber has its own specific physical and chemical properties. We select the type of rubber to meet the expected performance demands on manufactured products, and sometimes we make blends of different types of rubber to achieve special requirements.

Currently, world consumption of rubber breaks down into approximately these percentages: 40% NR (solid and latex), 20% SBR (solid), 12% SBR (latex), 12% BR, 5% EPDM, 2% CR, 2% NBR, and 7% other synthetic types. It's interesting to note that, typically, up to 70% of the polymer rubber in an automobile tire can be natural rubber (NR), *an agricultural product*. There are many applications where natural rubber has a unique mix of physical properties that make it the preferred polymer to use.

Latex rubber – This is a liquid produced by plants, normally from the “rubber tree” (*Hevea brasiliensis*), a native tree of South America. The Hevea tree sap contains microscopic particles of the natural rubber polymer “polyisoprene”. The white, milky sap from the tree is collected

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in buckets and concentrated to remove part of the water along with some of the dissolved materials from the tree. This concentrates the rubber content to about 60% of the liquid volume. The concentrate is then stabilized by the addition of an ammonia solution, and can be used to produce latex products, like gloves, condoms, etc. Most commercial natural rubber latex comes from plantations in Southeast Asia.

Dry raw rubber – Natural rubber latex as it comes from the tree is coagulated (with formic acid), then repeatedly “milled” and water-washed before being dried at high temperature. This raw rubber is formed into solid bales and sheets, which are blended with other materials to prepare dry rubber compounds for manufacturing. There are many grades that are distinguished from each other based on collection method, cleanliness, and post harvest treatments.

Rubber compound – Solid raw rubber is not usable for finished rubber products, since it is difficult to handle, the solid shape is easy to distort, and it can quickly degrade due to oxidation. Raw rubber has to be mixed with various other materials in order to make it easily processible on standard rubber machinery. It also needs to be mixed with certain materials to modify its physical properties, and to allow it to be “cured” or “vulcanized” into a finished product with good strength. A rubber compound will typically use any or all of the following materials in the final mixture:

- Polymer rubber – Natural Rubber (NR) and/or a selection from the synthetic types mentioned above.
- Vulcanization chemicals – Vulcanization (or “curing”) is the chemical reaction process in which rubber is turned from a sticky, soft material into a material that has good strength and resilience. Vulcanization chemicals are materials that *cross-link independent polymer rubber molecules* into a *continuous network*. These include sulfur (which builds cross-links between rubber molecules), vulcanization promoters (like zinc oxide and fatty acids), and accelerators (which speed up vulcanization, and improve final properties).
- Antidegradants – These chemicals prevent or slow down the deterioration of rubber by heat, oxygen, ozone, acid attack, fire or other causes of rubber deterioration.
- Fillers – These materials are used to improve processing, reduce cost, or increase strength or other desired properties in the final product. Commonly used fillers include ground limestone, clay, silica powder, carbon black, and there are many others. Plasticizer oils, colorants/pigments, resins and other special purpose materials can also be considered as fillers.

Sole – the part of a footwear item that is located between the foot and the floor or ground. It is composed of variable sub-layers, including (but not limited to):

- **Insole** – the uppermost layer of the sole package, on which the foot rests.

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- Midsole – if present, it may consist of 1 or more layers designed to distribute stress within the sole package, or protect or insulate the foot.
- Outsole – the outermost rubber layer of the sole, which contacts the ground.

Upper – The part of a footwear item that extends above the sole elements. It is normally composed of various parts, including (but not limited to):

- Lining – the textile that lines the inner surfaces of the footwear upper.
- Vamp reinforcement – a rubber or rubberized fabric piece that covers the forefoot area.
- Counter – a reinforcement piece that surrounds and stabilizes the heel area of the footwear.
- Toe cap – a reinforcement piece that surrounds and stabilizes the toe area of the footwear.
- Gusset – an expandable pocket built into the upper which allows the leg area to open wider, to receive the foot easily.
- Upper rubber – The exterior waterproof rubber barrier layer of a rubber boot, designed to encapsulate and protect interior layers of the upper.

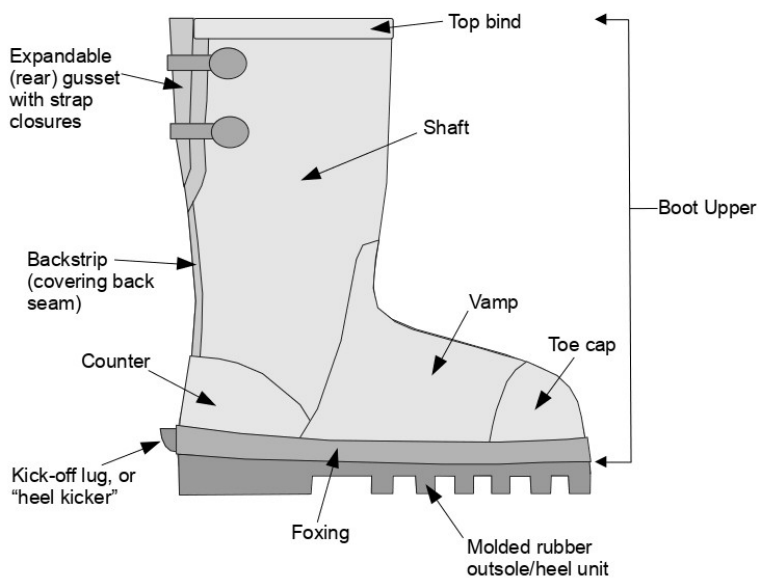


Figure 3: Diagram of typical boot zones and parts

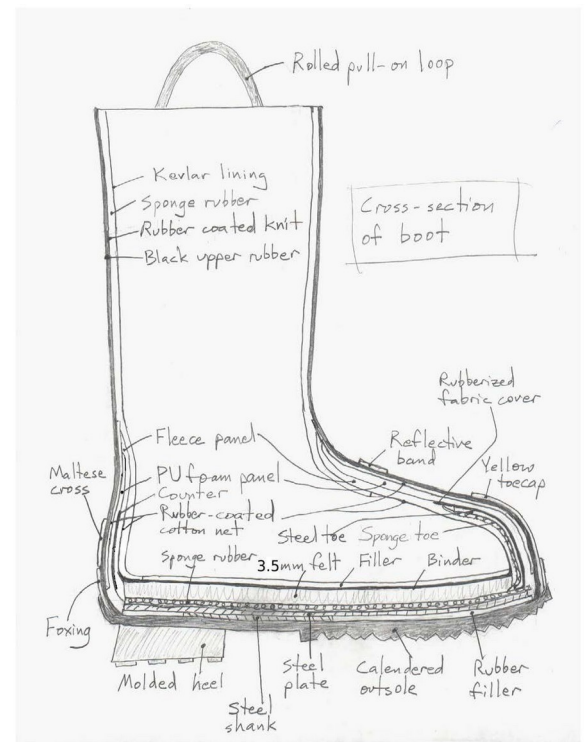


Figure 4: Cross-sectional sketch of high-performance firefighter boot, showing complex engineering that is possible with "hand laid" construction – and impossible to achieve with injection-molded PVC.

Chapter 2: Manufacturing

Compound mixing – Rubber and other materials are mixed together in a very precise way, to achieve good dispersion of the materials, and uniformity from batch to batch. Mixing is usually done on an open mill, or in an enclosed “Banbury” mixer. In either method, two steel rollers or screws, rotating inward toward each other, work the materials into a cohesive and uniform mass. Cooling or heating can usually be applied to the mixing machine to control temperature, so that the rubber compound can be mixed in a “plastic” state, when it is soft and “workable”.

Rubber “milling” and compound mixing can be seen at this Youtube web page:
https://www.youtube.com/watch?v=7Ju7J9zJ1Ow&ab_channel=JonNicholson

Calendering – A rubber “calender” (related to the word “cylinder”) is a machine with 2 or more steel rollers that can squeeze an unformed mass of rubber compound into a thinner sheet material, which can then be cut into a flat shape. Sometimes the sheet material is smooth, and sometimes it has a pattern embossed on it. The shaped parts that are cut from the sheet material all are designed to be applied by hand to build up the rubber boots. It should also be noted that calendering can be used to pre-laminate rubber with rolled fabric that is fed into the calender along with the rubber. This produces rubberized fabric that is much stronger than simple thin sheet rubber by itself. This rubberized fabric is often used for boot linings or reinforcing parts of the boot, where rubber by itself would not be resilient enough.

An example of a very simple calendering operation can be seen at this Youtube web page:
https://www.youtube.com/watch?v=yGzF9yXPMIU&ab_channel=JonNicholson

Molding – Everyone understands what molding is. In the context of rubber boots, molding is used to press rubber into the shapes of heels or soles or other parts of a boot. The molds are heated, so that the rubber softens quickly and fills the mold to take on the mold shape. The heat of molding also provides the heat needed to vulcanize the molded rubber shape. When the molded rubber is pulled out of the mold, it has been thoroughly vulcanized, so that the molded piece has achieved its greatest strength properties, and even when hot it will retain its shape.

An example of some molding operations can be see at this Youtube web page:
https://www.youtube.com/watch?v=n7ga5drI3is&ab_channel=JonNicholson

Last – A 3-dimensional form that looks like a lower leg and foot, and which is the form that boots and shoes are built around. Note that rubber boots are not normally molded – they are built up in layers around the last, by hand, of thin parts made of calendered rubber sheeting and rubberized fabrics. This action is called “lasting”.

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“Jack” assembly -- A “jack” is an assembly line devoted to footwear production. The cut sheet parts and molded parts are prepared, then delivered to the assembly jack. At the jack, these parts are applied by hand to the last, along with other parts – for example, steel midsole plates or steel toes. Sometimes the natural stickiness of rubber is enough to join parts together, but often some adhesive application is also used. The final result is the un-vulcanized finished boot.

An example of “lasting” and jack assembly can be seen at this Youtube web page:
https://www.youtube.com/watch?v=H0nDuWIp3K0&ab_channel=JonNicholson

Vulcanizer – As stated above, “vulcanization (or ‘curing’) is the chemical reaction process in which rubber is turned from a sticky, soft material, into a material that has good strength and resilience.” The essential operation after boot assembly is to load racks of finished boots into a “vulcanizer”. A vulcanizer is a large, heated, pressurized autoclave, that creates the conditions necessary to cure the rubber to its fully vulcanized state. After vulcanization, individual long polymer molecules have been cross-linked into a stable, strong network of molecules. This molecular network is so unified that you could consider a rubber boot to be one immensely huge molecule. The conditions inside a vulcanizer can be described by the parameters of temperature/pressure/time:

- The temperature inside a vulcanizer is typically in the range of 280-305 degrees Fahrenheit (approximately 138-152 degrees Celsius).
- The air pressure inside is typically set at about 10-20 psi (0.07-0.14 MPa) above the ambient air pressure, and this is done by injecting extra air into the vulcanizer at the beginning of a cycle.
- A vulcanizer cycle would normally last about an hour, *after* proper air pressure and temperature is reached.

A cycle of rubber boot vulcanization can be seen at this Youtube web page:
https://www.youtube.com/watch?v=Bgk4c4IpKBY&ab_channel=JonNicholson

Post vulcanization operations – These would normally include inspection and leak testing, packing into retail boxes and shipping cartons, and transfer into inventory in a warehouse, pursuant to loading into containers for shipping.

A brief example of post vulcanization operations can be seen on this Youtube web page:
https://www.youtube.com/watch?v=h4oqRSaG7Q&ab_channel=JonNicholson

Vulcanized Rubber vs. Injection-molded Plastic – If you have read the above and viewed the Youtube videos, you already have a reasonable idea of how rubber boots are manufactured. Perhaps the amount of hand labor surprised you. Vulcanized rubber boots are made quite differently from injection-molded boots made out of PVC. PVC boots are manufactured using a

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continuous process of injecting melted plastic into 2-piece molds (an outer mold shell and inner last) under pressure. Vulcanized rubber boots are made by the “hand laid” process that requires many steps between initial mixing of the rubber and final vulcanization of the finished boots, in batches. As you can imagine, the simpler injection-molding method means that most plastic boots are cheaper. Why, then, would anyone buy vulcanized rubber boots?

Compared to vulcanized rubber boots:

- The design of hand-built rubber boots can be modified. If a style needs to have more or less insulation, added reinforcements, added straps (or all of these things removed) it can be modified simply. The last defines the foot and leg area, but nothing limits what you can add or subtract regarding parts and layers outside of the last. A molded plastic boot must always fit the outer mold shell after it is designed and made – you can’t add extra boot parts because there is not available space inside the mold shell to do that.
- Vulcanized rubber boots remain flexible at cold temperatures, and have very little change in hardness with any temperature change. PVC boots are thermoplastic -- PVC compound is not chemically cross-linked into a stable network, it is a firm "gel", made of crystalline PVC resin and plasticizer oils. PVC boots are thermally unstable -- they lose flexibility in cold work conditions, and become soft and weak when exposed to excessive heat (the molecules will start flowing past each other). This, for example, explains why there are no PVC boots used in firefighting situations or metals foundries.
- PVC boots are usually not as comfortable as rubber. This is most noticeable in the energy absorption of the heel seat region -- because PVC soles are fairly hard and not rubbery, they return a lot of the walking impact shock to your heel and lower leg. Vulcanized rubber soles usually absorb most of that shock.
- PVC boots can be heavy, due to the chlorine content of PVC molecules.
- PVC boots often have a somewhat sloppy fit. Since PVC boots do not have the stretchiness of rubber, the molds must be designed to allow the foot to enter the interior of the boot without the boot material stretching to fit. Vulcanized rubber boots, being made from a stretchy material, can have a more form-fitting design.
- PVC usually has mediocre or poor slip resistance on wet or oily surfaces (interior smooth surfaces, like tile or concrete). In cold conditions, PVC becomes less flexible, less comfortable, and the slip resistance becomes worse. Molded-vulcanized rubber boots are lighter weight, and the flexibility of rubber is better for slip resistance -- rubber is better able to conform to and grip a surface texture.
- PVC boots may contain plasticizers that are considered regulatory problems – for example, being carcinogenic, teratogenic, or mutagenic. Especially with plastic boots of foreign manufacture, the safety of the plasticizers may not be verified.

Chemical resistance:

PVC (polyvinylchloride) -- Resistant to a large variety of fuels, oils and fats, corrosives (acids and bases) and non-polar solvents like heptane. However, PVC will absorb and deteriorate from contact with polar solvents and oils (like acetone, MEK, ester oils, etc.).

Vulcanized Rubber -- Different kinds of rubber can be molded for targeted applications, and resistance to chemicals varies between the types:

- Natural rubber (NR) is resistant to polar liquid chemicals, and it is generally very resistant to acidic and basic corrosives, but vulnerable to petroleum fuels and oils, non-polar solvents and animal fats and vegetable oils.
- Butyl rubber (IIR, BIIR and CIIR) is the premier polymer for resisting gas-warfare agents. It has the highest all-round resistance to permeation by all gases. Resistance to liquid chemicals and corrosives is similar to Natural Rubber.
- Neoprene rubber (CR) has resistance properties to oils, fats, and solvents similar to PVC. Neoprene has (in general) the best all-round chemical-resistance properties of all categories of rubber. Neoprene has good resistance to strong acids and bases. Neoprene is inherently flame-resistant.
- Nitrile rubber (NBR) has similar oil, fat, and solvent resistance properties to PVC. Nitrile rubber is best of all for resistance to petroleum-based fuels. Nitrile is compatible with strong bases, but it is very vulnerable to acid attack.



Figure 1: RSS (Ribbed Smoked Sheet) is a very clean grade of raw Natural Rubber (NR) which shows excellent physical properties.



Figure 2: SBR 1502 is a general-purpose grade of synthetic rubber, often used in blends with other rubber types.

Chapter 3: Basic Chemistry and Physics of Rubber

Natural Rubber in it's various molecular conditions

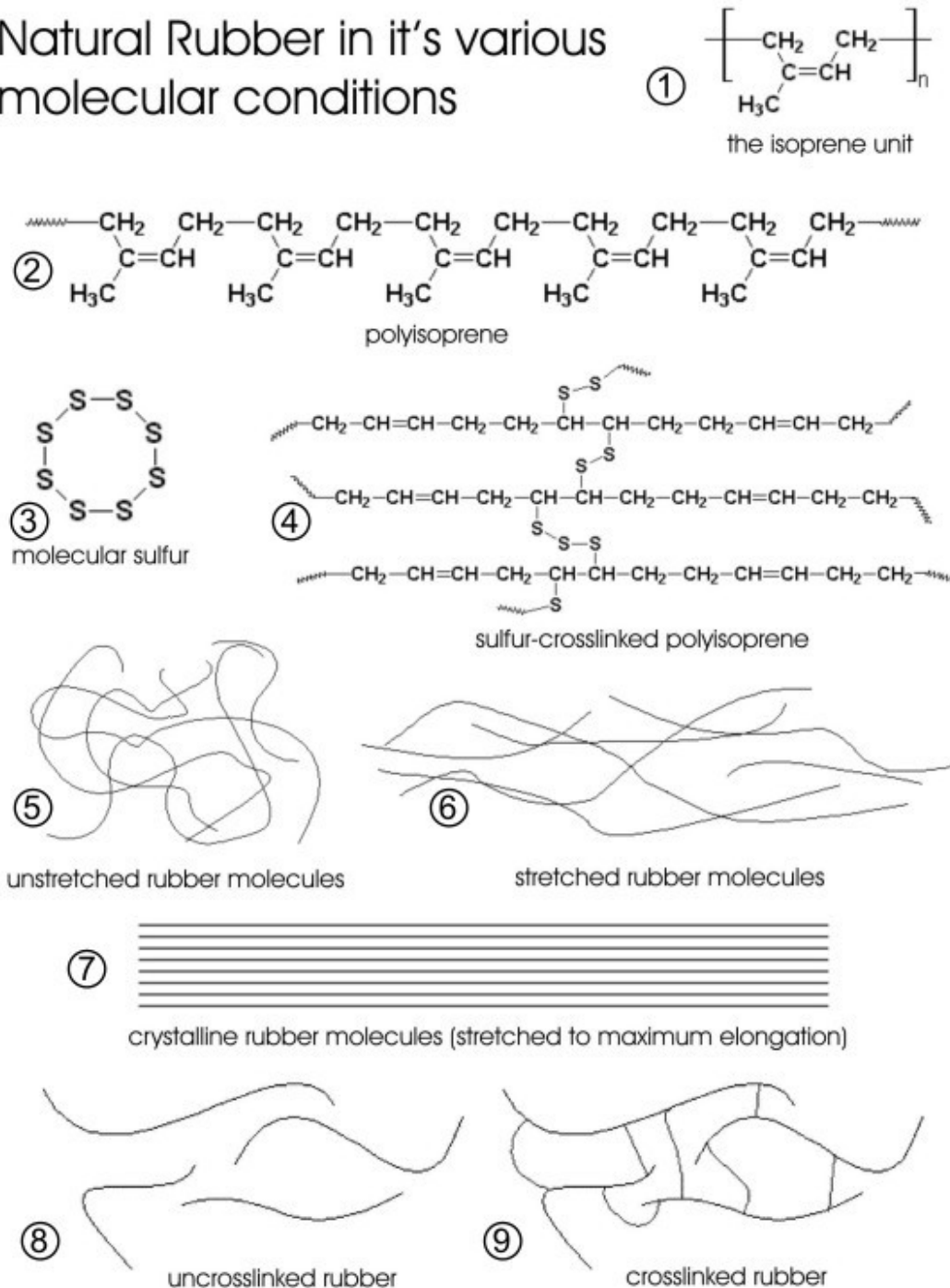


Figure 3: Refer to the following discussion for each diagram.

Someone who has taken General Chemistry in school will probably understand the general meaning of the diagrams in the preceding graphic. If you haven't gained that knowledge you may still be able to understand these explanations. Starting from the top of the graphic:

1. Raw rubber is a material that is a polymer – each smaller molecule is linked together with other small molecules in order to make a larger, chain-like, longer molecule. **In the case of Natural Rubber (NR), many smaller “isoprene” molecules are linked together to produce a “polyisoprene” molecule.** Natural Rubber was the first available type of rubber, and the chemistry of producing it is a part of the Hevea rubber tree's natural biology. It took some years before chemists understood the role of isoprene monomer, and then were able to think about making synthetic types of rubber.
2. If you look at the graphic of the polyisoprene molecule, you'll see that it is not totally straight – it has a zig-zag sort of shape. **This zig-zag, kinked structure allows the molecule to be stretched out farther, but when the stretching force is released, the molecule will rebound to its shorter natural shape.** This allows natural rubber to act as a spring – this spring-like property is something that Natural Rubber does better than any synthetic rubber, and it makes Natural Rubber the preferred polymer for many applications.
3. The element Sulfur is extremely important in rubber vulcanization. For some kinds of rubber, Sulfur is the crosslinking chemical that makes a structural bridge between separate polymer chains. (Other crosslinking chemicals exist, but are not discussed here.) The normal condition of Sulfur is as a ring-shaped molecule containing 8 atoms.
4. In the diagram showing “sulfur-crosslinked polyisoprene”, you can see that during vulcanization, this Sulfur ring breaks up and reacts with the rubber to build bridges (“crosslinks”) between polymer chains – usually these bridges are composed of 4-6 Sulfur atoms, but other numbers are encountered.
 - i. If you look at **diagram #2**, you will see double lines between some of the Carbon (“C”) atoms – “C=C”. **These double lines represent 2 electrons in close proximity.** Since the negative charges on electrons repel each other, C=C double bonds are less chemically stable than the single electron bonds represented as single lines – “C-C”. **Because the C=C double bonds between Carbon atoms are unstable, they are more vulnerable to Sulfur grabbing one of those electrons.**
 - ii. Therefore, when a Sulfur crosslink bonds to the rubber chain in **diagram #4**, the double bond disappears – it becomes a single bond between Carbon atoms (C-C) and another single bond between a Carbon atom and a Sulfur atom (C-S). **This is the chemical basis for Sulfur-based vulcanization.**
5. This diagram shows unvulcanized, raw rubber, in an unstretched state. Normally the long molecular chains will have a somewhat random arrangement. However, this raw rubber has no Sulfur crosslinks – the chains are independent units, separate from each other. Imagine a box full of steel Slinky toys, which have been jostled around so that they are tangled up with each other, without being permanently bonded to each other.

6. Stretched rubber molecules (again, this diagram shows raw rubber with no crosslinks) will start becoming more parallel as you start pulling the mass of rubber apart. As they become more parallel, the main bodies of the chains start approaching each other.
7. As rubber becomes very stretched and the molecules become very parallel, the electrostatic forces that are present along the molecular chains begin to attract the matching electrostatic forces on neighboring chains. The rubber chains align in a regular way and this will cause the rubber to form a crystal structure. This structure will persist as long as the chain is stretched. The crystal structures are strong, causing the rubber to reach a higher level of stiffness and strength that was not present in the unstretched rubber mass. This is called “strain-induced crystallization”, and is a valuable property of Natural Rubber and some synthetic rubber types, like Neoprene (polychloroprene, CR).
8. Uncrosslinked rubber has independent molecules, so that the rubber chains can slide past each other and flow like a liquid, when warm. If it flows like a liquid, it can’t be molded, because it will not retain a permanent shape. If the temperature of the rubber is increased, it can’t form strain-induced crystals and never develops any high strength. In general, unvulcanized rubber is not used for finished products because it can’t deliver any useful degree of performance.
9. Crosslinked rubber has strong Sulfur bridges bonding the molecular chains to each other. This prevents the chains from separating or sliding past each other. Being all bound together in a stable network, they mutually support any stress that is applied to the vulcanized rubber mass. Vulcanized rubber can be stretched, compressed or otherwise deformed and still return to its original shape. This is the vulcanized rubber that has proven reliable for so many applications like tires, gaskets, and (of course) rubber boots.

Anisotropy:

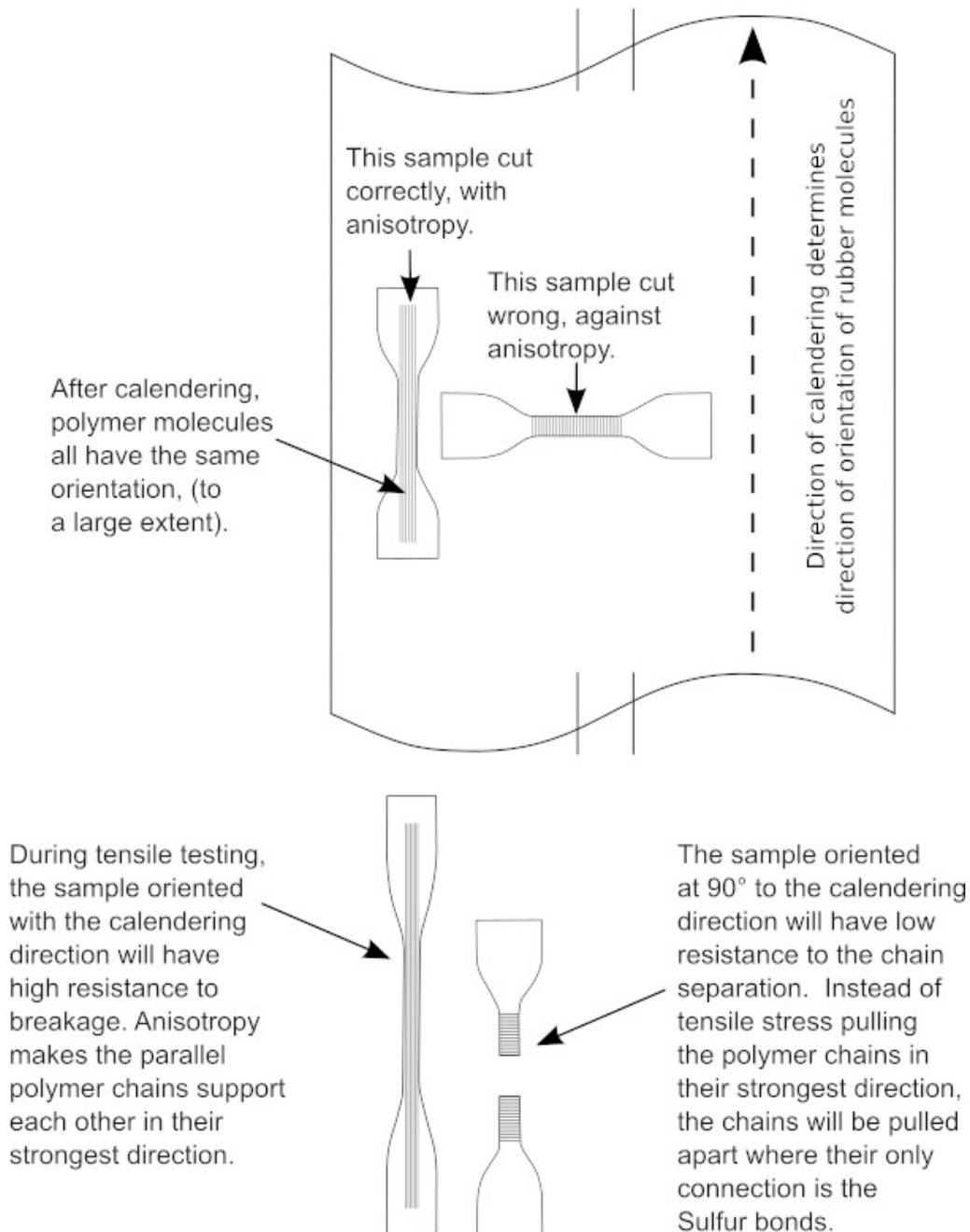
Anisotropy is the property of a material which allows it to change or assume different properties in different directions. This directionality becomes very important when cutting test pieces for lab testing of rubber.

In Chapter 2, you saw the operation called “calendering”. Imagine a pot of cooked spaghetti with the pasta still floating in the water. If you plunge your fingers into the water (wait until it’s not hot!) and rake your fingers in a straight line, many of the pasta strands will be pulled along, with the main part of the strands trailing out behind the direction of motion – parallel with other strands. This is the same orientation mechanism that happens when 2 calender rollers grab long polymer molecules and drag them through a narrow gap between each other.

The strongest orientation of rubber molecules is along the axis of the repeating units. Compared to this, the Sulfur bonds between molecules, and any electrostatic attraction between the molecules, are rather weak. Because of this, it is important that testing samples be cut along

the strongest axis, and that this is done consistently, so that any comparison of test results will always be comparable with other test results. Furthermore, anisotropy can be used to guide how you cut calendered parts for rubber boots. You can analyze where the stresses will be the greatest, and cut parts to take advantage of the strongest orientation.

The Effect of Anisotropy on Tensile Stress of 2 Sample Test Pieces at 90° Rotation to Each Other



Chapter 4: Rubber Compounding

Now that we have a view of what rubber looks like on the molecular level and understand some of its properties, we can look at the method used to create those Sulfur crosslinks between independent rubber molecules – the method to achieve vulcanization. But to understand the rubber product that we have after vulcanization, we also need to look at the other materials that are mixed with raw rubber to modify its properties to meet certain needs. The easiest way into that subject is to look at actual rubber formulas used to describe compounds. We'll start with an easy one. But first – disclaimer time!

While the advice and information in this book are believed to be true and accurate at the date of release, the author can not accept any legal responsibility for any errors or omissions that may be made. The rubber formulas provided here can not be guaranteed to be serviceable and free of hazard, and are provided solely to demonstrate standard formulation practices.

Formula Name: RUBBER BAND

<u>Materials</u>	<u>PHR</u>
RSS #3 (Natural Rubber)	80
SBR 1502 (Styrene-Butadiene Rubber)	20
Active Zinc Oxide (ZnO)	4
Stearic acid	1
Active Sulfur (S)	1.5
Accelerator CBS (CZ)	1.2
Accelerator M (MBT)	0.8
Titanium dioxide (TiO ₂)	2
Paraffin wax	1
Antioxidant MB (MTI)	1
Calcium Carbonate (CaCO ₃ , Ground Limestone)	5
Calcium grease	1
Mineral oil	8
Total:	126.5

Under the “Materials” heading, you can see that this rubber compound requires 13 different ingredients – you may be surprised that a simple rubber band requires more than just Natural Rubber and Sulfur!

Under the “PHR” heading, the numbers represent weights of each ingredient. The numbers could be any unit that you choose – pounds, kilograms, grams. I will discuss the actual meaning of “PHR” later.

Rubber: As you can see, this formula contains 2 kinds of polymer rubber: Natural Rubber, a very clean grade with the longest polyisoprene chains, called RSS #3; and SBR rubber.

SBR is a synthetic form called a “copolymer”. **A copolymer is composed of 2 or more different types of monomer.** Back in the “Definitions” section of Chapter 1, I discussed the small molecules (monomers) that are joined together repeatedly to make long polymer chains.

- For polyisoprene (Natural Rubber), the repeating monomer is the isoprene molecule.
- For SBR rubber, there are 2 kinds of monomers that are joined randomly to build the polymer chain: Styrene (like the plastic in foamed coffee cups) and Butadiene.

Rather than discuss these monomer chemicals, I’ll just say that Styrene plastic (polystyrene) is a hard plastic, while Butadiene rubber (polybutadiene – “BR”) has properties similar to Natural Rubber (NR). With styrene and butadiene monomers in the SBR polymer chain, the combination gives SBR some rubbery property, but also a thermoplastic property (crystallizing when cooled, and melting when hot). This combination helps rubber compound to process smoothly. The BR part of the SBR rubber vulcanizes with Sulfur, along with the NR.

Zinc Oxide, Stearic acid and Sulfur: Rubber vulcanizes extremely slowly if you are only using Sulfur as the curing (crosslinking) agent. The first large improvement in rubber technology was in the addition of other materials to improve curing time. Zinc Oxide and Stearic Acid (a fatty acid that is a major component of animal fat) were discovered to be necessary for improving the curing time and the physical strength of vulcanized rubber.

Accelerators: CBS and MBT are two “organic” chemicals that are used to vastly reduce the vulcanization time of rubber compounds. There can also be various improvements to the physical properties of the vulcanized rubber compound, depending on which accelerators are chosen.

Note: To chemists, “organic” doesn’t mean “healthy” or “natural” – in the science of chemistry, “organic” refers to any molecule that contains carbon-carbon or carbon-hydrogen bonds. Methane, carbon tetrachloride, petroleum products, white sugar, fats, proteins and any number of both beneficial or unhealthy chemicals can be categorized as “organic”.

Titanium dioxide: A white powdered pigment, to cause the rubber band to have a uniform, lighter color that you would have without the pigment. It does not participate in any chemical reactions in the rubber compound.

Paraffin wax: This lubricates the rubber molecules, to allow the mixing action to smoothly incorporate and disperse the non-polymer ingredients (most of them in powder form) into the rubber compound. It does not participate in chemical reactions in the rubber compound.

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Antioxidant: Oxygen (O₂) in the atmosphere will absorb into rubber and break the polymer chains into shorter segments. This causes the rubber to become softer, weaker, and sticky. Perhaps you've seen this effect in old rubber bands that have been stretched around some object – the rubber degrades from oxygen attack, becoming weak, sticky and somewhat crumbly. In the formula above, Antioxidant MB (aka MTI) is a general-purpose antioxidant that will slow this deterioration.

Calcium Carbonate (CaCO₃, Ground Limestone): This powdered mineral filler will help make the rubber process more smoothly. It does not participate in chemical reactions in the rubber compound.

Note: 5 PHR of a mineral filler powder like Calcium Carbonate is an extremely small amount. However, the main job of a rubber band is to stretch, and the greater the weight of filler in the formula, the less stretchy the rubber becomes. Therefore, to retain stretchiness of the rubber band, the minimum amount of filler is used, just enough to have the desired effect.

Calcium grease: This is just a general-purpose lubricant grease. Added to a rubber compound, it helps the rubber mix smoothly, and it also slightly softens the final product.

Mineral oil: This is identical to household mineral oil. It is added as a softener, but it also aids the compound mixing process.

Summary: So many ingredients to make a rubber band! But each one was added for a purpose, and this formula (not one of mine!) was probably built up from fewer ingredients. In other words, it probably started with fewer ingredients, but some additional ingredients were probably added after experience showed the need for improvement. That is the typical procedure in designing rubber compounds.

Formula Name: BLACK OUTSOLE - NON-MARKING

<u>Materials</u>	<u>PHR</u>
NR3 (Natural Rubber)	85
BR 9000 (Butadiene Rubber)	15
Active Zinc Oxide (ZnO)	5
Stearic Acid (StAc)	1
Active Sulfur (S)	2.5
Accelerator DM (MBTS)	1.2
Accelerator M (MBT)	0.75
Accelerator D (DPG)	0.5
Antioxidant 264 (BHT)	1.5
HAF (N330) Carbon Black	12
WCB (Precipitated Silica)	25
Si-69	1.5

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Diethylene glycol	2
Paraffin wax	0.5
PE Wax (Polyethylene wax)	0.5
Solid Coumarone-Indene Resin	4
Transformer Oil	10
Total:	168

An outsole has to resist abrasion and tearing in contact with rough floor or ground surfaces, provide some cushioning, and provide some slip-resistance. The compound formula above is a moderately high-performance outsole formula.

Rubber: In this formula, a blend of Natural Rubber (NR) and Butadiene Rubber (polybutadiene – BR) is useful in generating high strength. BR bonds strongly with both “Carbon black” and “Precipitated Silica”, which substantially improves abrasion-resistance.

Note: From now on, I will only use the standard abbreviations “NR” for Natural Rubber, “SBR” for Styrene-Butadiene Rubber and “BR” for Butadiene Rubber.

Zinc Oxide, Stearic acid and Sulfur: The main vulcanizing chemicals, as discussed above.

Accelerators: The rubber band formula used CBS and MBT, but other choices of accelerators are also used, and usually in combination. This outsole formula uses Accelerators DM (MBTS), M (MBT) and D (DPG). All of the ingredients of a rubber compound will have some effect on the final state of the vulcanized rubber. Therefore, a rubber chemist uses industry practices and personal experience to decide on the types and the amounts of accelerators that will cure the rubber properly.

Antioxidant: For this formula, a single general-purpose antioxidant, Antioxidant 264 (BHT) was considered sufficient. 264/BHT has the added advantage of being a food-grade antioxidant, so it is safer for the factory personnel to handle it.

Fillers and Si-69:

- HAF (N330) Carbon Black is produced from incomplete combustion of petroleum oil. It is a dry, black powder that actively bonds to and reinforces various types of rubber polymers, especially BR.
- WCB is a precipitated silica, which comes in powder form. It is amorphous silica, not crystalline – crystalline silica dust would present a serious health risk to your lungs, and is a known carcinogen. “WCB” is an abbreviation for White Carbon Black (an abbreviation used mostly in China, where my boots are made). It is not Carbon Black at all, but it serves a similar function – bonding and reinforcing polymer rubber, especially BR. It’s a little less reinforcing than Carbon Black, and increases hardness more than

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Carbon Black does – which is often not a welcome effect. WCB also improves wet slip resistance in rubber compounds.

- Why use both HAF Carbon Black and WCB silica? If you use too much Carbon Black, the boot outsoles can mark interior floors with black streaks. Therefore, it is advisable to use a smaller amount of Carbon Black and a larger amount of WCB silica to achieve the strength properties that you need.
- Si-69 is a “bonding agent” that crosslinks with WCB silica particles and rubber, especially BR. This significantly improves the strength properties of rubber containing WCB.

Diethylene glycol: This is a liquid that lubricates WCB silica powder so that it can quickly and completely disperse into the rubber compound.

Paraffin wax and PE (polyethylene) wax: These lubricate the powdered materials to help them blend in to the rubber compound. Furthermore, since the Black Outsole Rubber compound will be molded into outsoles, these waxes will act as “mold release” agents – helping the rubber to mold accurately and release from steel molds easily, without sticking.

Solid Coumarone-Indene Resin: This material helps the rubber materials to blend together smoothly, and improves the stickiness of the rubber to hold the rubber mass together. It also improves slip resistance of the vulcanized outsole.

Transformer oil: This is a lubricating oil that helps the rubber to mix thoroughly, and resists becoming volatile and smoking at elevated temperatures – like vulcanization temperature.

Summary: Compared to the rubber band formula, this outsole formula makes some different choices in chemicals. The performance demands are quite different between rubber bands and outsoles, so it’s no surprise that the chemicals that shape the final physical properties will be different.

Just 1 more formula!

Formula Name: COATING RUBBER FOR TEXTILE

<u>Materials</u>	<u>PHR</u>
NR3 (Natural Rubber)	68
BR 9000 (Butadiene Rubber)	18
High Styrene Resin (High Styrene-content SBR)	10
SBS (Styrene-Butadiene-Styrene block copolymer)	4
Active Zinc Oxide (ZnO)	3
Stearic Acid (StAc)	1

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Active Sulfur (S)	2.1
Accelerator M (MBT)	0.8
Accelerator DM (MBTS)	1.2
Accelerator CBS (CZ)	0.5
Accelerator TS	0.3
Antioxidant SPC	3
Antioxidant 264 (BHT)	1
WCB (Precipitated Silica)	20
Calcium Carbonate (CaCO ₃ , Ground Limestone)	65
Diethylene glycol	0.6
Total:	198.5

Rather than step through the ingredients, I will just note the more significant differences between this coating rubber and the previous rubber formulas.

- We see 4 different rubber types here, and both High Styrene Resin and SBS (Styrene-Butadiene-Styrene block copolymer) appear for the first time. **Coating rubber must penetrate into the textile interstices in order to make a good bond to the textile. For that reason, High Styrene Resin and SBS are used here because they are highly thermoplastic and help the rubber compound to flow into the textile weave when the rubber is hot and under pressure.** Heat and pressure are supplied by the rubber coating calender – a machine similar to what you saw in a video in Chapter 1, under the section “Calendering”.
- Accelerator TS shows up here for the first time. This formula requires 4 accelerators, all of which work a little differently. It also uses 2.8 units of accelerator – more than the others. **This more complicated accelerator combination and the larger quantity of accelerator are partly related to the large amount of Calcium Carbonate (CaCO₃, Ground Limestone).** Calcium Carbonate is inert in rubber compounds – it helps to reduce cost of the rubber, and it helps the rubber process smoothly on standard processing equipment. It reduces the strength properties of the rubber, but a smooth and penetrating rubber coating is more important than strength when you are coating textile. **Although this amount of inert filler is necessary for the rubber to do its job, it also dilutes the cure chemicals substantially. Therefore, more accelerator and a more aggressive mix of accelerators is needed in this formula.**

Note –

When I write “inert” in this document, I mean that a material has virtually no involvement in chemical reactions resulting in the finished product. Several common fillers (especially CaCO₃ [Ground Limestone], ground clay, talc, etc.) match that description. Other fillers (like Carbon Black or WCB [precipitated silica]) have a measurable bond to rubber molecules, and also affect the chemical reactions of other materials, like accelerators.

“PHR”: I’ll explain the “PHR” method of showing units in a rubber formula. “PHR” means “Parts per hundred of rubber”. In other words, amounts shown in a formula are always in reference to the amount of polymer rubber, which is always considered to be 100 PHR. The polymer rubber is the basis of a formula, and the other ingredients all act on the polymer in some way. The rubber industry has a large body of knowledge about how ingredients act on polymer rubber and what the usage amounts should be.

Therefore, polymer rubber always remains 100 PHR, and when formulas are written or changed, the other ingredients are set at some number of PHR compared to the polymer content, not referring to the total batch. If you compare PHR to percent, you can see that editing a formula by percentage increases the complexity of maintaining a formula – the total batch would constitute 100%. Using percentage, every time you changed the weight of a single ingredient, you would change the weight of the total batch, which changes the percentage of every other ingredient – for a simple weight change of one ingredient, the number of calculations for percentages of the other ingredients would be a burden.

The ACTUAL formulas used in the factory, for workers to weigh out ingredients, are written as some proportion of the PHR formula – all ingredients (including the polymer rubber) are multiplied by the same factor to give you the weight of each material needed to make an actual batch of rubber compound. Rubber batch sizes are not standard, because rubber mixing machinery varies widely in capacity. Of course, the factory version of the formula would include units like pounds or kilograms.

Volume: In the Coating Rubber formula, there was 100 PHR of combined rubbers (as always), and 65 PHR of Calcium Carbonate (CaCO_3). However, polymer rubbers are usually less dense than fillers. In fact, polymer rubber are usually less dense than water – most rubber polymers will float in water. The density can be expressed as “specific gravity” – the density of a material compared to the density of water. If we consider this rubber mixture to have a specific gravity of 0.95, and the Calcium Carbonate to have specific gravity of 2.71, we can see that Calcium Carbonate will be concentrated in a much smaller volume for the equal weight of polymers.

To see the effect on an imaginary batch of rubber containing only polymer rubber and CaCO_3 , let’s say that the PHR is actually weight in grams:

Weight calculation –

100 g. polymer + 65 g. CaCO_3 = 165 g. (total batch weight); $65\text{g.}/165\text{ g.} = 0.39$ or **39% of the mixture total weight is CaCO_3**

Volume calculation – based on specific gravity values of 0.95 for the polymer and 2.71 for the CaCO_3 . Let’s say that the PHR is actually in grams, and the volume is in milliliters:

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- 100 g. of polymer has a volume of $100\text{g.}/0.95\text{ g./ml.} = 105\text{ ml.}$
- 65 g. of CaCO_3 has a volume of $65\text{g.}/2.71\text{ g./ml.} = 24\text{ ml.}$
- $105\text{ ml.} + 24\text{ ml.} = 129\text{ ml.}$ (total volume of batch); $24\text{ ml.}/129\text{ ml.} = 0.19$, or **19% of the total volume of the mixture is CaCO_3**

Therefore, calculations of volumes may show the amounts of fillers in the rubber to be less drastic than you would otherwise think, if you are just looking at weights.

Volume calculations are important for several reasons. The main reason is that the mixing equipment in different factories (or even within a factory) may have different internal capacities. The batch size needs to be adjusted so that all of the ingredients can fit into the mixing equipment and experience good mixing action. Technical staff will adjust the weight units of each formula to be compatible with the desired batch volume.

A Widespread Rubber Compounding Problem – Blooming:

Bloom is the condition that happens on the surface of rubber when some chemical that is contained in the rubber migrates from the interior of the rubber article to the surface of the rubber. Typically, bloom appears as a layer of small – even microscopic -- crystals, giving a rubber surface a cloudy or dusty appearance. If the blooming material is liquid (or attracts water to form a liquid), it can appear as a wet, oily-feeling layer on the surface.

Theory: Rubber is a semi-liquid material, so on the molecular level it has some similar properties to water and other liquids. Because of its chemical properties, rubber will act as a liquid solvent for many “organic” (carbon-based) chemicals. To understand how blooming happens, think about adding sugar to water:

If you have a glass of water at room temperature, you can dissolve sugar in it. Keep adding and stirring sugar into the glass of water, and eventually you reach a point where the sugar just sits on the bottom of glass -- the water already holds the maximum amount of dissolved sugar. We call that a "saturated solution".

- You can make the water hold more sugar -- by heating the water. The hotter the water, the more sugar it can hold in solution. There is a maximum concentration of sugar in water for every temperature.
- If you let a hot saturated sugar/water solution become cool, the water will contain more sugar than it can hold at the lower temperature. The sugar will “fall” out of the solution, and solid sugar crystals will form (on the bottom and side of the glass).

When a batch of polymer rubber is forcefully mixed with other materials (cure chemicals, resins, fillers, oils, etc.), it becomes very hot due to frictional heating. You can add rubber chemicals to hot rubber, and those chemicals will be dissolved in the rubber. However, if you

add too much of any chemical, then the mixture will become “supersaturated” with that chemical, when the temperature returns to ambient temperature. When the rubber cools down, some of the chemical (the excess amount) will form crystals in the rubber (or simply separate, if the chemical is a liquid).

- Crystals that grow inside the rubber are under stress from the rubber molecules that surround the crystals. The rubber matrix becomes stretched tighter around the crystals, as the crystals grow larger.
- Tension from the stretched rubber surrounding the crystals forces some of the crystalline chemical to re-dissolve, and over time the excess chemical will migrate to the surface of the rubber, where crystals can grow free from the elastic stress found in the interior of the rubber article. This forms a thin, visible layer of the excess chemical on the rubber surface, which we call "bloom".

Rubber compounds are usually blends of different types of polymer rubber.

- Natural rubber will have different abilities to dissolve various chemicals than a synthetic rubber like SBR, or Nitrile rubber. One chemical may not be very soluble in one type of rubber, but it might be very soluble in another kind of rubber.
- Also, when you add materials to the rubber batch that are not soluble in rubber – these chemicals will never dissolve. **Examples of materials that will not dissolve in rubber (and therefore can never bloom from rubber) are fillers, like carbon black, ground limestone, clay, silica, etc.**

Examples of chemicals that can bloom: A typical rubber compound could contain 10 to 20 (or more) different materials, and might contain some of these.

- Waxes (paraffin or micro-crystalline polyethylene) make it easier to handle and process rubber, when the rubber is hot. So, waxes are popular to use in rubber compounds -- often they are too popular, and people use too much of them.
- Paraffinic "mineral oil", or "white oil" makes rubber processing easier, and it also increases the flexibility of the rubber. However, rubber cannot dissolve large amounts of "white oil", so often people use too much, and it causes an oily-greasy film after vulcanization. The same thing can happen with “ester”-type oils, which are often used with chemically “polar” polymers, like Nitrile or Polyurethane (PU).
- Vulcanization is a set of chemical reactions that make rubber a strong and stable material. Vulcanization chemicals cross-link the rubber chains to “cure” rubber. If the vulcanization chemical reaction is not completed, or if too much of these chemicals are added to the rubber, these chemicals can bloom out of rubber after vulcanization.
- Other chemicals that can bloom are antioxidants, salts, by-products of the vulcanization chemical reactions, and more.

Prevention: The best way to prevent bloom is to use the smallest possible amount of any chemical which could cause bloom. Or, you can eliminate that chemical – perhaps replace it

with another chemical that is effective at a smaller dose, or one that is more soluble in the polymer rubber. In my own rubber formulations, I stopped using waxes or paraffinic mineral oil long ago – any amount of these will eventually bloom.

An example follows showing how we can use information about rubber chemicals to avoid overdosing rubber compounds, and causing blooming to happen:

Here is a table of common rubber accelerators, showing their maximum solubility in unvulcanized rubber, at a normal room-temperature range. After vulcanization, some of these amounts will have been consumed by the vulcanization reaction. For example, Sulfur (S) is commonly used at higher PHR than 1.5. If you use 2 PHR, the concentration of Sulfur after vulcanization will be much less than 2 PHR, because most of the sulfur will be chemically bound up in the cross-linked rubber networks.

UPPER LIMIT OF RUBBER CURATIVES SOLUBILITY

Solubility in NR, SBR, BR or EPDM compounds

(Non-polar rubber types)

	<u>Maximum PHR</u>
TMTD	0.5
PVI/CTP	0.5
TMTM	0.7
ZDEC	0.8
S	1.5
ZDBC	2
Stearic	
Acid	2
CBS	2.5
TBBS	2.5
MBT	3
MBTS	3

Solubility in NBR
(Highly polar rubber
type)

	<u>Maximum PHR</u>
TMTD	2.0 – 3.0
TMTM	2.0 – 3.0

Table taken from website: <http://www.sinrubtech.com/short%20notes/Short%20Notes%203.htm>
Sin Rubtech® manufactures polymer-bound predispersed chemicals

Contrary to a claim that I've read by one distributor, blooming is not a natural process. It is completely the result of how a factory formulates their rubber compounds. Why do factories continue to make boots that bloom?:

- Rubber compounders often, unfortunately, have little understanding of the mechanism of blooming in rubber. In that case, they try to avoid any major reformulation of their rubber compounds, and just try to tweak their formulas in an indecisive way, hoping that something works.
- Blooming takes time. An order of rubber boots can leave the factory in perfect condition, but start blooming during shipment to the customer. Or the boots can bloom after they are placed on a store shelf, or bloom at the home or workplace of the end-user. A factory should not assume that they don't have a blooming problem, even if the boots are shipped in perfect cosmetic condition.
- Imagine a production lot of boots that are shipped in early Spring or Summer, when the shipping temperatures are warm. Imagine that those boots arrive in perfect condition, with no blooming. Now imagine a shipment of identical boots in a container on a ship crossing the ocean during Autumn or Winter. This shipment can experience temperatures that are even cooler than the boots might be exposed to at their destination. An entire shipment of boots can severely bloom in less than 24 hours when the weather is cool. A container of boots can leave the port of origin in good condition and arrive at the port of destination completely bloomed.

Suggestions for preventing blooming on rubber boots:

1. A company producing rubber boots should analyze their rubber compounds to make sure that they do not use excess amounts of chemicals, more than needed to achieve the required properties of the rubber.
2. Factories should eliminate any chemicals that are not strictly necessary for the rubber compound to do its job.
3. Factories should confirm that vulcanization is complete on their products. If vulcanization is not complete, excess free chemical loadings will remain in the rubber. The factory should increase vulcanizer times and/or temperatures to completely cure the boots, if this seems necessary.
4. Technical staff sometimes think that susceptibility to blooming can be tested using an "Environmental Test Chamber" that exposes rubber samples to heat, light, humidity, etc. Factories should understand that blooming mostly depends on temperature, but not high temperature. In my experience, for most blooming problems, the most effective test is to hold rubber for 1 week at room temperature, then to be placed in a normal refrigerator for 1 week – I recommend the temperature range 2-4°C (36-39°F). Note:
 - i. If the temperature is colder than this range, it can immobilize the excess chemicals, so that they are not mobile enough to bloom to the rubber surface.

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- ii. Different chemicals respond to temperature differently, not all blooming at the same temperature. **The best method to test for blooming might be leaving boots outside at night so that they can experience a very slow, continuous temperature drop overnight.** Multiple nights might be necessary with this method. I have used this method before, and it seems to work well.

Blooming is characterized by this hazy, blotchy, usually white-ish coating appearing on the rubber surface over time. Sometimes it appears quite quickly.



Chapter 5: Standards and Testing

Hand-built rubber boots are primarily made using calendered rubber sheeting, molded rubber parts, and textiles. The quality of the materials used can vary widely between boot factories, and even within a factory different materials may be used in different styles of boots.

Furthermore, factories are known to change suppliers of their materials sometimes, without informing their customers – maybe even without proper testing of the materials from the new source. Unless a foreign customer is specifying the rubber compounds and the textile sourcing, they will be operating on blind trust of the factory that's making their product. In either case, access to physical testing data will be highly advisable for the foreign customer.

It is essential that the factory producing rubber boots have a testing protocol with regular monitoring. It is advisable that their customers understand this testing protocol, regularly receive test result data, and also feel free to question the testing that happens (maybe request different tests), as well as set their own requirements for the test results.

Rubber footwear is a sort of hybrid between the leather/textile sewn shoe industry and the rubber industry. Rubber boots have their own set of performance demands that are not always shared by standard footwear. Consequently, there is a specific set of tests that seem to be commonly valued among technicians working in rubber boot factories. The following is my own protocol that I normally use, with recommended outcomes. For some tests, I recommend methods and conditions that deviate from the official methods. I have found that my modifications/deviations seem to provide better testing and better reproducibility of the results.

But first – my disclaimer!

While the advice and information in this book are believed to be true and accurate at the date of release, the author can not accept any legal responsibility for any errors or omissions that may be made. The specifics provided about test methods, and the suggested test result outcomes, are strictly based on the author's own admittedly limited career experience and opinions formed therefrom. Thank you for your attention! – Jon Nicholson

Preliminary notes about testing:

- Setting some standard fixed number as a required test result for a certain property may not guarantee good (or bad) quality. The way that a boot is designed -- and the way it is used -- has a big effect on the stress put on the rubber. A required test result number for one type of boot or one formula of rubber should be decided on carefully, in reference to the product's use. That same test result number may be irrelevant for others.
- Usually, rubber samples should be prepared for testing **according to the method of actual use** (calendered or milled rubber for calendered parts; molded rubber samples

only for molded parts). For example, the chemical reactions of vulcanization for upper rubber are different when cured while exposed to air (the way the upper rubber on the boot is actually cured) compared to curing the same rubber in a mold which excludes air. Therefore, molding every sample of rubber for testing is not in agreement with the principle of making tests mimic reality as much as possible.

MATERIALS TESTING:

Hardness: ASTM D 2240 (Shore A Durometer) – Test all rubber compounds used.

- Use Type A durometer.
- All specimens should be molded. No specimens laminated to fabric.
- The test result requirement will be different for different kinds of rubber compounds.

Tensile: ASTM D 412 – Test rubber sheeting and molded rubber

- Use a "Dumbbell" specimen, section 11 of the standard.
- Cut the specimens so that the long dimension of the samples is aligned parallel with the direction of calendering (if using calendered rubber). For milled or calendered sheet rubber, the thickness should be 1.5mm-3mm, as smooth as possible. For molded rubber, any thickness is acceptable.
- No samples laminated to fabric! Never! And if you pull the rubber off of a rubber-textile lamination to test the rubber, this will also give worthless test results.
- Record “300% Modulus” (tensile stress at 300% elongation), ultimate tensile stress at break, and ultimate elongation.
- Elongation at “rupture” should be a minimum of 400% (for upper rubber) and 300% for outsole rubber (100% is the original distance between markings).
- For upper rubber, tensile stress at rupture should be 8 Mpa (1,160 psi) minimum. Any test result below 9 Mpa (1,305 psi) should be considered as an alarm to monitor and improve the rubber formula or processing.
- Standards for tensile test results will vary with the specific kind of rubber compound.

Tear: ASTM D 624 – Test rubber sheeting

- Perform the test according to the standard, except ignore the “molded sample” requirement of section 7. Samples should be milled or calendered rubber sheet, vulcanized flat, in normal vulcanizer conditions. No molded samples, no samples laminated to fabric – they are not relevant to rubber compounds for rubber boots, and will produce misleading results.
- The rubber thickness should be between 1 and 3 mm thick, as smooth as possible.
- Use "Die C".

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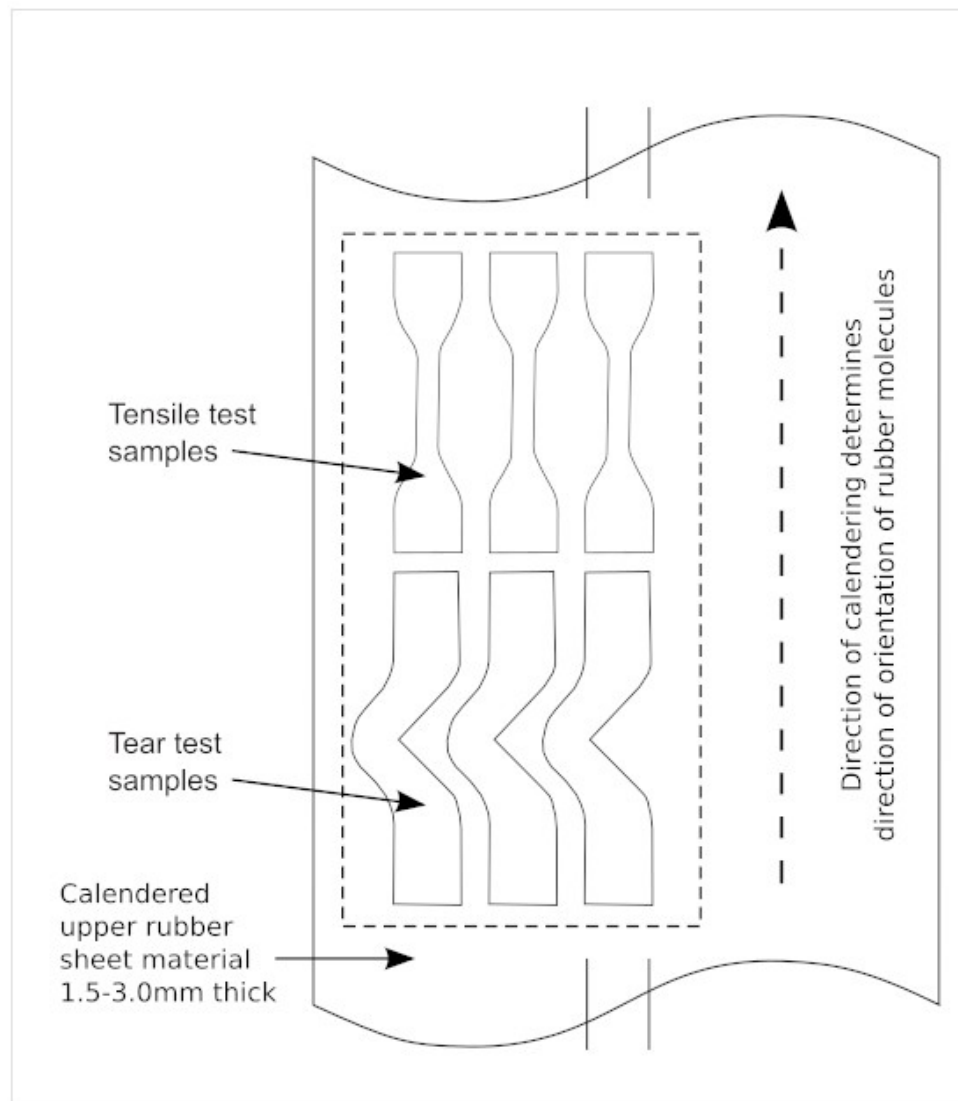
- Cut the samples so that the long dimension of the samples is aligned parallel with the direction of calendering.
- Minimum for upper rubber is 14 kg/cm (80 lb./in.). However, standards for tear test results will vary with the specific kind of rubber compound.

Please note this illustration, below, of the correct way to cut samples according to the direction of processing of the rubber, which causes “anisotropy” (which I explained in Chapter 3):

Tensile test (ASTM D 412) or **Tear test** (ASTM D 624) samples:

When testing upper rubber or any rubber which is calendered, follow the orientation of the cut samples as shown below.

When testing rubber which is molded in production, no orientation of the samples is needed -- molding tends to randomize molecular orientation.



Adhesion: ASTM D 751 – Test rubber coated fabrics.

- Perform the test according to the standard, Sections 50 through 53.
- If testing is done for QC purposes, 3 samples should be cut from the each roll of rubber-coated fabric, tested and reported separately. Samples should be representative (not taken from the far edges of the fabric).
- Use rubber adhesive to bond the rubber-coated fabric samples (the rubber side) to a separate sheet of milled rubber or calendered rubber (2mm-3mm thick). After they are bonded, vulcanize the laminated material, then cut the specimens.
- The specimens should be 2.5 cm wide, 15 cm long. The length of the specimens should be aligned parallel to the direction of calendering.
- Adhesion testing should be performed at a speed of approximately 30cm/minute (12 in/minute).
- The minimum acceptable lining adhesion should be 1.2 kg/cm (6.71 lb./in.). If the adhesion is less than 1.4 kg/cm (7.83 lb./in.), this fact should be considered as an “alarm” to monitor and improve the rubber formula or processing, or to provide a primer or pre-treatment to the fabric surface bonded to the rubber. In special cases (where the fabric will not separate, but the rubber or sponge splits), a lower test result can be acceptable.

NBS Abrasion: ASTM D 1630 – Test outsole and heel rubber only.

- Perform the test according to the standard.

In general, a high abrasion-resistance outsole has an Abrasion Index above 90; medium abrasion-resistance is 70 to 89. The tread pattern of an outsole is important – the less rubber that is in contact with a flat surface, the more concentrated the abrasion is, for that tread pattern, so the greater the need is for abrasion resistance. For sporting boots (medium performance), an Abrasion Index of 70 is probably a minimum allowable. For work/safety boots, I would require a minimum of 100.

Rotary Drum Abrasion: ASTM D 5963 – Test outsole and heel rubber, and other rubber compounds if needed.

- Perform the test according to the standard.

In general, a high abrasion-resistance outsole has a Volume Loss Abrasion Index at 200 or below; medium abrasion-resistance is above 200 to 250. The tread pattern of an outsole is important – the less rubber that is in contact with a flat surface, the more concentrated the abrasion is, so the greater the need is for abrasion resistance. For sporting boots (medium

performance), an Abrasion Index of 230 should probably be a maximum allowable. For work/safety boots, I suggest a maximum of 190.

Note: It's always interesting to compare 2 different tests that supposedly measure the same physical property. Below you'll see a small chart showing a comparison I made between 3 different rubber compounds. I obtained their abrasion-resistance test results using the **2 different abrasion-testing methods discussed above.**

Compound	Rotary Drum	NBS
1	220.3	87.1
2	97.6	199.1
3	91.7	227.2

You can see that as the Rotary Drum Abrasion test (ASTM D 5963) value **decreases** (becomes more abrasion-resistant), the NBS test (ASTM D 1630) value **increases** (also becomes more abrasion-resistant). It is a consistent trend between the two tests (although obviously only a limited sample of tests). **Anyway, it suggests that they are really measuring the same thing, with comparable sensitivity, even if they use reversed scales.** If you have to choose between these 2 different testing machines (for example, maybe a testing lab has one but not the other), this correspondence indicates that your test will probably provide reliable information.

Flex Crack Growth: ASTM D 813 –

- Perform the test according to the standard.
- Check samples twice daily, report time periods required for crack growth to reach 4mm, 8mm, 12mm, 16mm and 20 mm.

Ozone: **ASTM D 1149** – Only for upper rubber – it is very rare for ozone attack to be a problem for outsoles. I recommend that the ozone test should be run as a development test or occasional random check. If you use it for a QC test, expecting to get a "pass/fail" reading, interpretation becomes very important. If you run ozone testing with the "bent loop" specimens, (Method B, Procedure B2), test results tend to be unreliable, highly sensitive to specimen thickness, and difficult to reproduce. I highly recommend Method B, Procedure B3.

- Method B, Procedure B3—Exposure of Tapered Specimens. Use the Die Cut Tapered specimen, section 21.
- Samples should be milled or calendered rubber sheet, vulcanized flat, in normal vulcanizer conditions. No molded samples. Cut the samples so that the long dimension of the samples is aligned parallel with the direction of calendering.

- Specimen thickness should be 1.5mm-3.0mm. When comparing different compounds, thicknesses should be as uniform as possible.
- Specimens should be tested under 20% overall elongation (static elongation).
- 50 pphm ozone concentration at 40°C for 72 hours.
- Check the samples for cracking twice a day.
 - Preferred result: no cracking or hazing.
 - Acceptable result: light surface hazing or small cracks extending from the narrow end of the samples to no more than 30% of the length toward the wide end of the samples, at 72 hours.
 - Cracking at the clamps is not significant! Cracking at the clamps means that the clamp pressure was too high. Re-testing is advised, with closer attention to clamp pressure.

If you follow my recommendation for the ASTM D 1149 ozone test, you will be out of step with normally accepted practice at most commercial test labs. The “Bent Loop” version of the test is widely assumed to be the only version worth doing. However, I personally have performed the 72 hour ozone test series many times – certainly over 500 times, maybe 1,000 times. It was my experience/opinion that the bent loop test is too sensitive to sample thickness, and it’s even sensitive to whether a sample has fabric backing or not – because the fabric causes the bend to be more gradual compared to a sample of equal thickness but lacking fabric backing. My opinion is that the Die Cut Tapered specimen and its test method is more consistent.

I’m devoting a lot of attention here to the ozone test because I feel that it can lead people to make unjustified conclusions about their rubber formulas. I will let the text of ASTM D 1149 have the last word:

“1.3 The specified conditions of exposure to ozone in the controlled environments are accelerated in comparison to outdoor exposure. These accelerated ozone test methods may not give results which correlate with outdoor exposure tests or service performance.”

Textile Breaking Strength/Elongation (Grab Test): ASTM D 5034 – I do not personally use this test often, but if a measure of textile strength is needed, this is the test that I recommend.

Moving Die Rheometer: ASTM D 5289 – This is not a test that a customer normally orders, but rather a QC test that a factory should be running daily to confirm that their rubber is curing as expected. It requires a testing machine that is designed to measure selected vulcanization characteristics of rubber compounds in all stages of the curing process. The output of this testing machine is a chart showing a curve that represents the “state of cure over time” of the rubber being tested. The chart will also show key physical data at various points in the test. It is extremely useful, and I recommend that a customer should require that this test is run

frequently at the factory, a selection of charts is sent to the customer (digitally), and also that the customer learn to read the test curve to understand how their rubber cures – and recognizes when there is an unexplained variation.

WHOLE BOOT TESTING:

This is especially used on styles for the PPE (Personal Protective Equipment) market. Such styles would, at a minimum, incorporate a protective toe unit of some kind (steel toe, aluminum toe, composite toe).

Standard Test Methods for Foot Protection: ASTM F 2412

Performance Requirements for Protective (Safety) Toe Cap Footwear: ASTM F 2413

The test result requirements for these standards are integral to the standard, not open for modification.

Whole Boot Flex Test: SATRA TM92 – Test to at least 150,000 flexes, some people prefer larger numbers like 250,000 or even 1 million flexes.

Whole Boot Slip Resistance: ASTM F 2913 – A Coefficient of Friction test result of .40 is the official pass/fail requirement under the standard ASTM F3445

What can possibly go wrong?! I will share some cases where testing was not performed correctly or interpreted correctly, and corrections were needed.

Example #1: I once sent samples to a testing lab for NBS Abrasion testing (ASTM D 1630). The results came back unbelievably bad. Being sceptical, I contacted the lab and asked for details about how the test was performed. It turned out that during the test, the weighted arms of the testing machine were bouncing up and down constantly. This was a totally non-standard behavior, due to my rubber compound having poor vibration damping behavior – which was not relevant to my development work. The lab technician merely reported his testing results, without notifying anyone about the odd behavior. I asked the lab to re-run my tests, with a thick rubber band interposed between the NBS testing machine arms and the weights – to act as vibration dampers. The weight of the rubber bands was negligible, so it did not compromise the test validity. But the rubber bands suppressed the vibration, allowed the abrasion test to proceed normally, and produced believable results.

Example #2: Again, I had a fully qualified lab technician (at my own laboratory) run NBS Abrasion testing. The test results were amazingly good, the best ever seen! Again, being sceptical, I examined the testing apparatus and test samples. It turned out that the rubber compound was not fully vulcanized, therefore the rubber was unusually soft and somewhat gummy. As the abrasion test proceeded, the rubber heated up from friction against the

sandpaper-covered rotating drum. It then melted and filled the sandpaper surface with a smooth layer of rubber. This effectively prevented any further abrasion from happening, so that my test results (wrongly) looked fantastic. It didn't occur to my lab technician to comment on that when presenting the test results.

Example #3: Some of my boots were sent to a commercial laboratory for various tests, including leak tests. The specified test required filling the boot with water inside, then watching for water to leak outside – the opposite of real-life use, in which you wear a rubber boot to prevent water from passing outside-to-inside. One of the test sample boots leaked water – not through the rubber-covered walls of the boot, but by wicking up a tiny interior channel in the back seam of the lining, then spilling over the top of the boot – to the outside. The lab tech called this a failure. To avoid making new samples and paying to re-test, I challenged the test lab on their interpretation of the test:

- The purpose of the test was to detect water leaks through the rubber-covered sidewalls of the boot. Instead, their lab tech terminated the test because of a channel over the top of the boot, which had no relationship with the waterproof rubber barrier layer.
- The design of the test was rather questionable, since it was similar to how boots leak, but the direction of possible leakage was reversed. By putting the water on the inside, this created the opportunity for anomalous effects due to the interior structure of the boot. The failure of my sample because of this anomaly did not constitute the kind of leak that the test was intended to detect.

Considering my arguments, the lab reversed their reading of the test and logged it as a “pass”.

In the 3 previous examples, the lab test was wrongly concluded as a “pass” or “fail” due to lab technicians who were not curious enough to question the test procedure when something odd occurred. Now let's consider the cases where trained lab technicians just perform the tests wrong!

Example #4. A commercial laboratory was testing some of my boots with steel toes, using ASTM F2312/F2413. Most of the steel toe samples failed the impact and compression tests. I requested that the lab send all of the toe samples to me, for my examination. During the steel toe tests, a clay cylinder is placed inside the toe and in a very specific position. When the test occurs, the steel toe is pushed down sharply, pressing this soft clay cylinder into the insole fabric, and leaving a characteristic mark – a round clay residue. When I examined the tested steel toes that were returned to me, I could see that the clay residue marks were too far forward in the steel toe, in an area with constrained height. I challenged the testing lab and they agreed that the toes had been tested incorrectly. They re-tested new samples at no cost, and that set of samples passed easily.

Example #5. A commercial lab tested some puncture-resistant midsole plates to meet the flex testing requirement of ASTM F2412/F2413. The midsole plates failed, which I didn't think was plausible. I challenged the result, and the laboratory discovered that a steel pin on their testing machine was severely worn, which altered the flexing action of the machine. After repairing the machine and re-testing, the midsole plates were approved with no problem.

Keep in mind that the test labs (or individual technicians) can make a mistake in testing procedure, or else may be somewhat confused about the test results. All of these tests are invented by people for specific testing purposes, but the test designers may not always foresee how something could go wrong when a test is performed or interpreted.

It is your right as a customer to challenge test results, if you think the test results may be wrong. It is a good idea to request that tested samples be returned to you rather than discarded where the test was performed. If you have the failed samples in hand, you can try to confirm that the test was conducted properly – and if not tested properly, to challenge the results.

My point is **not** that testing labs are incompetent. *If your samples fail the tests you ordered, I would bet on the lab being right.* Rather, the point is that individuals sometimes make mistakes, as we all do, including in testing lab settings. Given the stakes involved in product testing, I simply want to urge caution in accepting a single lab testing report as being the final word on the subject.

You can purchase .pdf copies of any of these test standards on the astm.org website.

Chapter 6: Failure Modes of Rubber Cracking

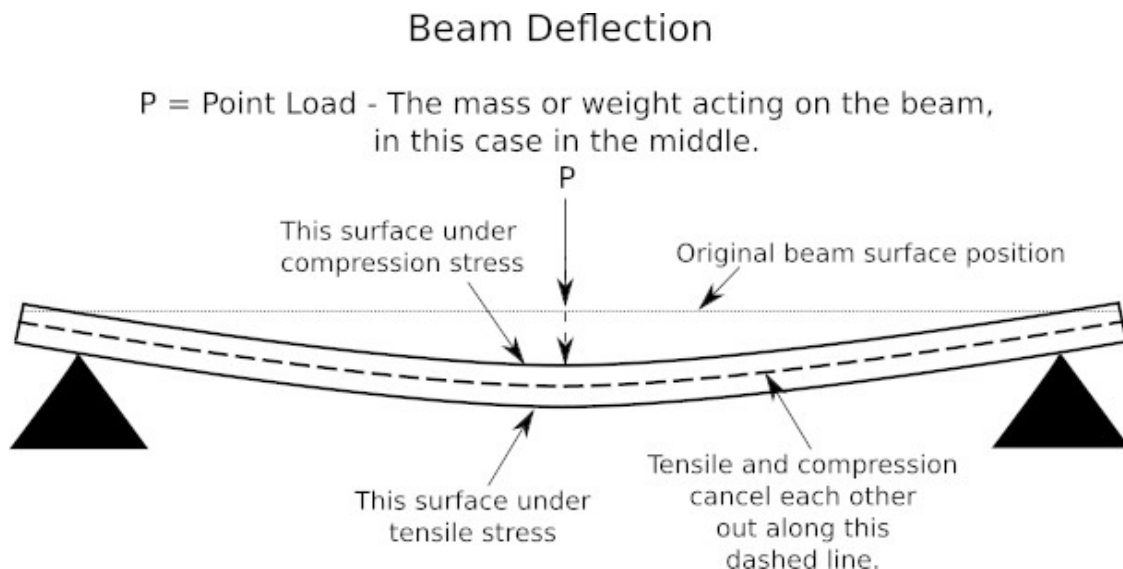
Failure mode: The specific pathway of events leading to failure of a machine, equipment, or system.

Rubber boots should be durable. The material is naturally waterproof, the design should (and usually does) provide a continuous barrier against water, and our technical knowledge is advanced enough to allow us to manufacture rubber boots strong enough to resist years worth of hard use. So it is especially unnerving when your boots deteriorate and leak within a year, or even within a couple of months. Usually the culprit in premature rubber boot failures is cracking of the upper rubber, the rubber barrier layer that surrounds the leg and foot areas of a boot.

There are basically 4 kinds of failure mode that involve rubber cracking, for boots made using NR rubber (which is usually mixed with 1 or more synthetic rubbers):

- Ozone cracking
- Flex cracking
- Barnyard acid cracking (in agricultural use)
- Cold cracking
- “Sun checking” (included here, but not really a rubber failure mode)

The most common sources of flexing failure are ozone cracking and flex cracking. Before proceeding, I need to discuss the concept of “beam deflection”. In structural engineering, a “beam” is a structural element that primarily resists loads applied laterally to the beam's axis. Its mode of deflection is primarily by bending. Under a bending load, one side is under tension and the other side is under compression. This idea helps to understand bending stress in boots.



Ozone cracking:

Most rubber boots fail by cracking. Ozone cracking is far and away the primary cause of premature failure of rubber boots. For rubber boots that are otherwise made well, ozone cracking is an “Achille’s heel”. This is due to poor understanding among technical staff of how ozone cracking happens, and lack of familiarity of corrective methods.

We will look at photos of what ozone cracking actually looks like, and briefly review the chemistry of ozone and the history of how ozone affects the rubber boot industry.

Ozone is a molecule made up of three oxygen atoms, O_3 . One of the ways that ozone is formed is by heat and sunlight causing chemical reactions between oxides of nitrogen (NO_x) and Volatile Organic Compounds (VOCs), aka “hydrocarbons”. This reaction can occur both near the ground and high in the atmosphere. Additionally, ozone can form from any sparking, for example brush-type electrical motors or “bug zappers” – or lightning. Another cause is “corona discharge” from electrical fields in power transmission lines, transformers or other electrical equipment.

Ozone high up in the atmosphere, specifically in the stratosphere, is beneficial to life on earth, because it shields us from dangerous UV light from the sun. On the other hand, ozone harms human health, the environment, *and rubber boots (!)* when it forms close to the ground. So, the air around us always contains some ozone – but more now than was the case before the mid-1970’s.

As a result of the U.S. 1970 Clean Air Act, most gasoline-powered vehicles (beginning with the 1975 model year) have been equipped with catalytic converters. These devices have had a huge impact on cleaning up automobile pollution. However, in order for gasoline engines to work properly with catalytic converters, manufacturers had to increase the combustion temperatures in automobile engines. The consequence of this was that emissions of hydrocarbon air pollution were reduced (as intended), but the higher combustion temperatures increased the generation of nitrous oxides (NO_x) in automobile exhaust (not intended).

As noted above, nitrous oxides react with VOCs and sunlight (NO_x) to produce ozone (O_3). Therefore, since about 1975, there has been an increasing trend in which catalytic converters cleaned up one kind of air pollution problem, but caused another one – increasing the ozone concentration in the air down here near the ground. In the late 1970’s, we began to see increased ozone cracking affecting our rubber boots at LaCrosse Footwear, so we began intensive research on finding the right strategies to protect our products from ozone attack.

Fortunately, one part of the solution had been commercially available since the 1960’s –

Rubber Boots – Understanding an Industry



#1 shows 2 boots left outside in open air. In the summer, in most regions, open air will provide adequate ozone exposure for whole-boot testing.

Note that one boot is flexed, and the other boot is not flexed -- this will differentiate between ozone attack and any effect that sunlight or weathering may have on the rubber.



#2 shows a view of the flexed boot after testing is complete (about 10 days). Fine network cracking is the distinguishing feature of ozone cracking. Many times this cracking may not be visible until you flex the affected area by hand.



#3 shows a closer view of the boot, in a slightly different location. You can see that the cracks are very sharp and well-defined, and cover the affected area rather uniformly. This shows that everywhere there was flexing stress on the boot during the test, ozone was actively attacking the rubber.

Note that ozone did not attack the rubber in any area that was not flexed!

EPDM rubber, “Ethylene-Propylene (with Diene Monomer)”. This is a highly ozone-resistant synthetic rubber, but it is not possible to build hand-laid boots using EPDM as the only rubber polymer. It is extremely difficult to calender into flat sheets, and it has no stickiness (unlike NR), so it’s not possible to assemble separate boot parts into one item. At LaCrosse Footwear, starting about 1978, we began blending EPDM with NR to make rubber boots that carried protection against ozone attack but still retained most of NR’s desirable properties.

Here are some important facts about ozone and rubber:

1. The natural ozone in the stratosphere is heavier than air, and it falls over time. Since ozone is a highly reactive chemical, it is mostly destroyed before it reaches the Earth’s surface, reacting with volatile gases in the atmosphere, dust particles, bacterial and mold spores, etc. – anything it encounters. However, natural ozone is found at higher altitudes in mountainous regions. Therefore, long before catalytic converters became significant, the problems of ozone attack on rubber items had already been known in connection to aircraft, and for high-altitude cities like Denver, Colorado or Bogota, Colombia.
2. Ozone from industrial and automotive air pollution stays down here with us at Earth’s surface. It moves widely over the landscape, propelled by wind. For example, ozone pollution from the Los Angeles/West Coast area can be routinely detected in Wisconsin (this from a University of Wisconsin isotopic study of ozone conducted several decades ago).
3. Ozone will only attack “unsaturated” rubber bonds. That basically means, $-C=C-$ double bonds as I previously discussed in connection to NR molecules. Other “unsaturated” rubber types are SBR and NBR, for example. Because of these double bonds, these polymers all vulcanize with Sulfur, and also can all be attacked by ozone.
4. Ozone will only attack vulcanized rubber that is stretched or flexed, which causes the $-C=C-$ bonds to become more unstable. If a boot is flexed and left in a **statically** flexed state, ozone will attack the rubber surface. If a boot is **dynamically** flexed (as in walking) ozone will attack it even faster. But if a boot is just static, unflexed in any way (like on a display shelf of a store), it will never be attacked by ozone.
5. In vulcanization Sulfur attacks rubber’s double electron bonds, but only reacts with 1, leaving the second electron alone. In ozone attack, ozone grabs both electrons in $C=C$, forming a short-lived molecule called an “ozonide”. It also cuts the long polymer chain into 2 independent, shorter sections. Eventually, ozone cracks will form.
6. Some people see ozone cracking on rubber boots and call it “dry rot”. “Dry rot” is fungal deterioration of wood, and it has nothing to do with the chemical deterioration caused by ozone.
7. Some people see “sun checking”, or “sun scald” and think that is a rubber cracking problem. “Sun checking” is a cosmetic defect resulting from prolonged exposure of rubber boots to sunlight. That causes deterioration of the boot lacquer, a clear external lacquer coating that is often used for a cosmetic finish for rubber boots. The crinkly,

checkered appearance of the lacquer can be alarming, but it does not penetrate into the boot rubber, and does not constitute a rubber failure.

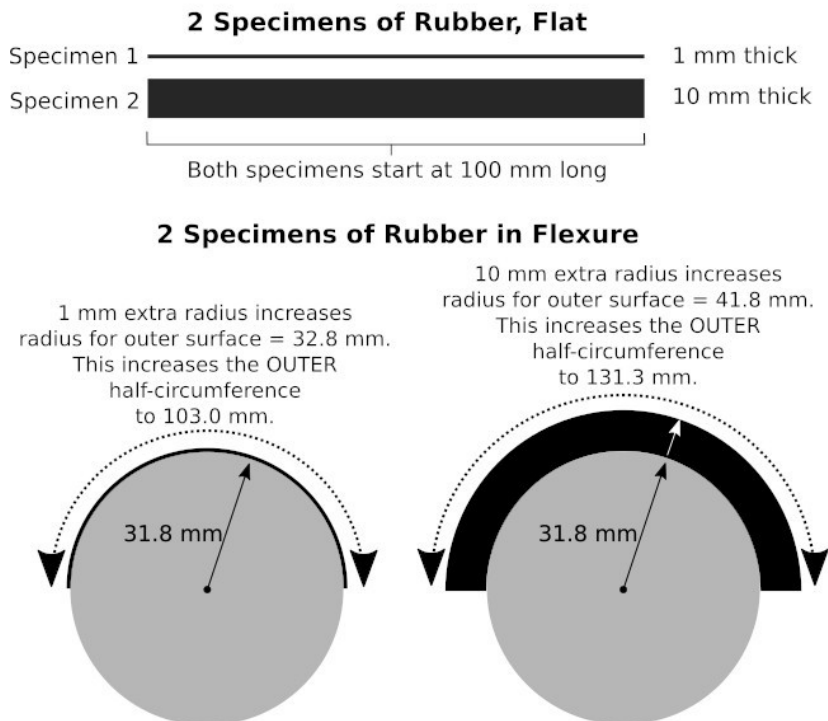
8. Sun light does not (directly) cause ozone cracking – never! Often in the industry you can see recommendations to avoid excess sunlight exposure. Or you can see that testing is performed in an environmental testing chamber (alternating intense heat, light, water shower, repeat!). None of this has any relation to ozone creation or ozone cracking or (as far as I know) any other failure mode of rubber boots. You may **rot** the lining with so much water and heat, but the actual rubber is invulnerable to those challenges.
9. When EPDM rubber is blended with NR, it acts as a physical bridge, so that if NR chains are cut by ozone, the EPDM molecular chains (which are already entangled with the NR chains) will tend to hold the incipient crack closed.
10. EPDM is very slow to cure, compared to NR. Therefore, when NR-EPDM rubber is vulcanized, the NR cures quickly and the EPDM **never** cures. Since EPDM does not co-cure with NR, it weakens the physical properties of the NR-EPDM rubber blend – similar to adding an inert filler like Calcium Carbonate (CaCO_3). Therefore, the rubber chemist has to make compromises in order to get ozone protection with EPDM, and needs to be very careful about the PHR of EPDM that is used in the formulas.
11. Other anti-ozone solutions are also available.
 - i. There are some solid chemicals that are well-known for their anti-ozone properties. These are in the chemical class “p-phenylene-diamine”. They are especially effective in combination with EPDM rubber, but they cause problems, too. They themselves are dark, staining resins, and they work by combining with wax to migrate over time to the surface of the rubber, forming an ozone-neutralizing coating. This seriously darkens rubber, and even if worn or washed away, the process of migrating to the surface of the rubber continues.
 - ii. The absolutely worst solution to ozone attack on rubber boots is to add excess paraffin wax to the rubber, so that wax constantly migrates to the rubber surface to form a barrier to ozone exposure. This only works for statically flexed rubber, and fails for dynamically flexed rubber, where the wax barrier is continuously broken open. Also, it is supremely ugly – see the section “Blooming” in Chapter 4. However, I must note that this absolutely worst solution is also very popular – especially with Asian factories.
12. For “my” rubber boots (the ones that my partner factories make for my customers), I use a specific PHR of EPDM rubber combined with NR, along with a certain non-darkening chemical combination to defeat ozone attack. It works very well.
13. One important strategy to reduce ozone cracking is to avoid designing boots with too much thickness in areas that you expect to be high-flex areas, like the vamp area, in the region behind the toe. When designing for strength to resist tears and punctures in the boot upper, always favor thinner rubber-coated fabrics under the upper rubber (and make that thin also!), instead of relying on thicker rubber parts. According to the concept of a “deflected beam” in engineering, thick cross-sections of rubber will generate more

tensile stress to the outer surface during flexure, therefore are more vulnerable to ozone cracking.

Rubber thickness and flexing as a mechanical factor in ozone cracking:

The illustration below tries to model flexing of thin and thick cross-sections of rubber, by forming a half-circle flex. It is very much simplified/idealized. Actually, just like you see if you stretch a normal rubber band, the rubber will become narrower and thinner as you pull the rubber band to be longer, and the force you have to use to keep stretching the rubber band becomes greater. So in the model below, the amount that each sample wraps around the cylinders is the same, but in reality it will result in some thinning and narrowing of the thick rubber specimen, as well as generating a large amount of “bending moment” – the reaction force that strongly pulls back against your stretching/wrap-around action. When tensile stress is applied to vulnerable rubber molecules containing C=C double bonds, they become more vulnerable to ozone attack. **Too much rubber thickness aggravates this vulnerability.**

Theoretical Asymmetry of Surface Length and Tensile Stress on Flexed Rubber -- Comparison by Thickness



Theoretically, if the rubber samples did not distort under this flexure, the outer surface of the thicker sample would have to be stretched 10X more than the outer surface of the thinner sample stretches. Therefore the **tensile stress** on the outer surface of the thicker sample would be much greater than on the outer surface of the thinner sample.

The inner surfaces of the rubber samples are subject to compressive stress, but that is not important for the ozone discussion.

Calculations showing the increase in half-circumference of the upper surfaces of 2 rubber samples at 2 thicknesses:

Consider two specimens of different thicknesses, but the same length. Here are the data:

- Specimen 1 -- a rectangular piece of rubber 1mm thick
- Specimen 2 – a rectangular piece of rubber 10 mm thick.
- Both specimens have the same length -- exactly 100 mm

Both pieces will be bent around cylinders to make a half-circle (180° arc). Since the circumference of a full circle is $2 * \pi * \text{radius}$, the half-circumference of a semi-circle or half-circle will be $\pi * \text{radius}$. Therefore, to make exactly a half circle of these two samples, the radius of the cylinder should be 31.8 mm ($\pi * 31.8 \text{ mm} = 100 \text{ mm}$).

If we bend both specimens into a half-circle/semi-circular loop over the outer surface of a cylinder having a 31.8 mm radius:

Thin rubber specimen --

- Making a half-circle with Specimen 1, the inner surface length of this thin rubber will remain 100 mm. **But the outer surface of the rubber specimen will have to stretch slightly**, because it will cover a longer distance.
 - The radius of the half-circle for the outer surface will now be 31.8 mm + 1 mm (the radius for the outer surface increases by adding the extra thickness of the thin rubber -- 1 mm more).
 - The outer surface of the sample has a new half-circumference (**length**) of $(31.8 + 1.0) * \pi = 103.0 \text{ mm}$.

Thick rubber specimen –

- Making the half-circle with Specimen 2, the inner surface length will remain (just like the thin rubber inner surface) 100 mm in length. **But the outer surface will now have to stretch significantly**, because it will cover a significantly longer distance
 - The radius of the half-circle for the outer surface will be 31.8 mm + 10 mm (the radius for the outer surface increases by adding the much greater thickness of the thick rubber – the radius increases by 10 mm).
 - The outer surface of the sample has a new half-circumference (length) of $(31.8 + 10.0) * \pi = 131.3 \text{ mm}$ – compared to 103.0 mm for the thin sample.

Again, this model is theoretical, for the purpose of illustrating that:

- The **outer surface** (exposed to the air) of the thicker sample becomes significantly more stressed, compared to the thinner sample.
- The more the surface is under tensile stress, the more aggressively ozone attacks unsaturated (-C=C-) rubber.

- Alleviate this problem by avoiding thick cross-sections of materials in rubber boot uppers. Instead of relying on thick rubber sheet parts for strength (tensile and tear strength), consider laminating thinner rubber parts with rubber-coated fabric parts. This is commonly done, and highly effective.

Flex Cracking:

Flex cracking is distinct from and simpler to discuss compared to ozone cracking. Flex cracking is a result of several different mechanisms. For rubber boots, the main cause is low cohesion between the different materials in a rubber compound. If a rubber compound has too much inert filler, or if it has a mixture of incompatible rubber types, the rubber matrix may not be strong enough to hold together the dissimilar materials in the mixture. Under flexing stress, there can be widespread separation of the incompatible polymers, and/or separation of the polymers from the filler particles.

At this point, I have to define “polarity” as a property of polymers:

- A molecule is 2 or more atoms joined by a shared electron bond, called a “covalent” bond. The positively charged atom nuclei share the negatively charged electrons, but if the atoms are different they may not share the electrons equally. The electrons will be denser around one of the atoms. This makes that end more negatively charged than the other end, creating a negative pole and a positive pole (aka “dipole”). The molecule is “polar”. If a molecule lacks this kind of electron concentration, it is called “non-polar”.
- The polarity of a molecule affects the attraction between molecular chains, which affects the structure of the polymer. If you mix polar polymers together (or non-polar polymers together), you can usually expect to have good cohesion (“holding together”) for that mixture. If you mix polar and non-polar polymers together, however, you can expect the mixture to have a tendency to fall apart easier – it lacks good cohesion!

If we mix NR with SBR rubbers, they are both non-polar, therefore the different polymers do not have strong compatibility problems. But if we mix NR with NBR (Nitrile), NR is non-polar and NBR is highly polar, and there are no strong attractions between those different rubber molecules. It can cause this rubber to be weak after vulcanization. It is also “dose-dependent” – if you use a small amount of NBR in a mixture with NR, the incompatibility problems will be weak, but a larger amount of NBR mixed with NR can have a degrading effect on physical properties.

Inert mineral fillers like ground limestone (CaCO_3) can’t bond with polymers very easily. Therefore, a particle of CaCO_3 mixed into a rubber matrix sits there merely occupies volume and forces polymer molecules to detour around it. It is incompatible with the polymers, and promotes weakness in the rubber matrix. Its effect on the rubber matrix is also dose-dependent – a smaller amount will have a smaller degrading effect on the rubber matrix strength.

Examples of the Flex Cracking Failure Mode



Rubber Boots – Understanding an Industry

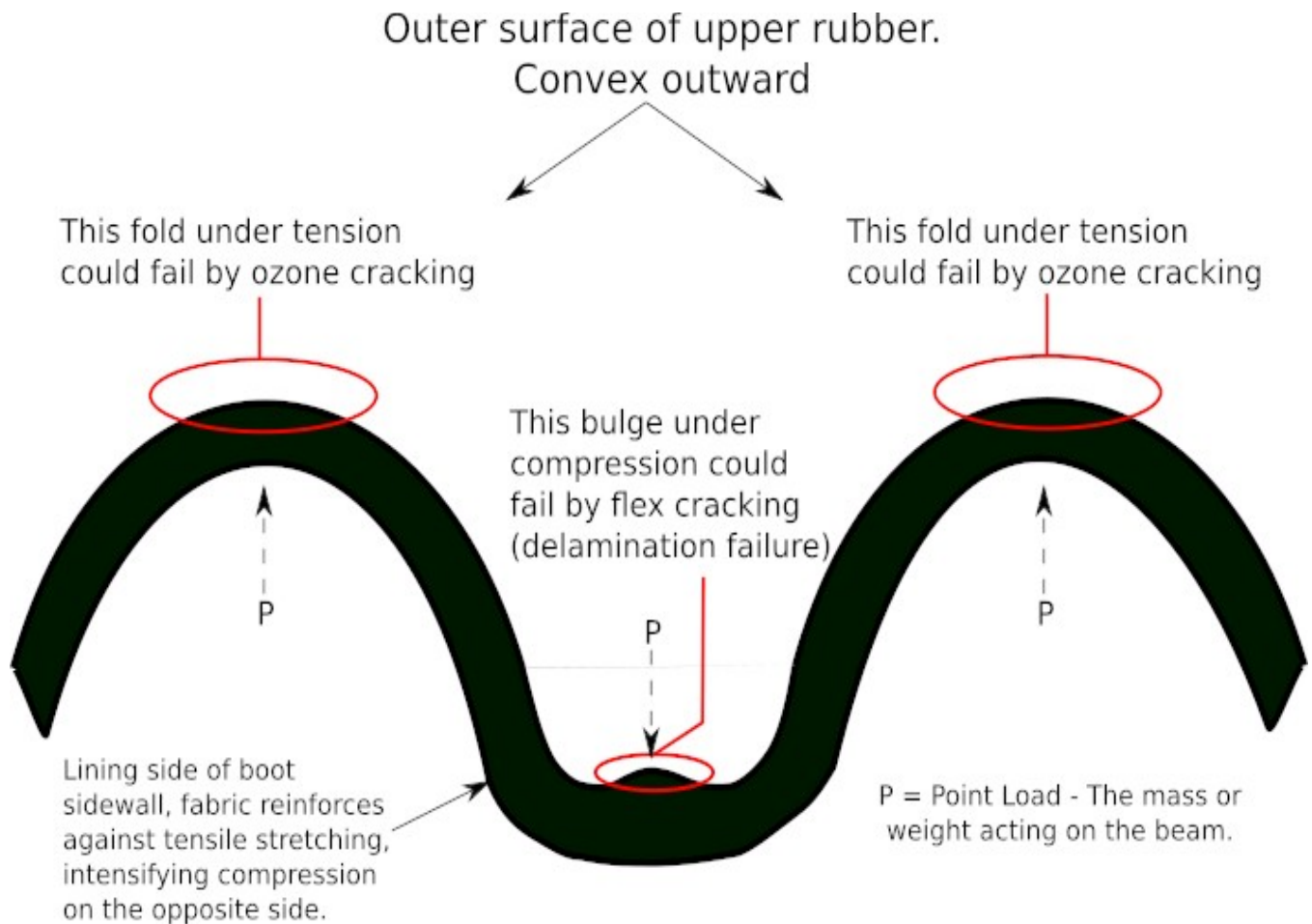
Flex cracking is caused by these kinds of incompatibility, and is also promoted by oxidation, which can cut polymer chains, and initiate a crack. On the previous page are a few photos of flex cracking, which show how its appearance differs from ozone cracking.

Flex cracking will **only** occur on products where dynamic flexing is happening – unlike ozone cracking, which can happen when a boot is either statically or dynamically flexed. **Flex breaks are larger and more ragged and irregular than ozone cracking breaks. Flex cracked areas will usually show streaks of delamination of the surface of the rubber, adjacent to the cracks.** The top and middle photos show 2 boots of the same style from the same source. They demonstrate the quick and drastic flex failure that happens when upper rubber compounds are highly dosed with inert filler, for the purpose of cutting cost of the rubber. The rubber just split open throughout the rubber layer, shortly after the end users began using the boots.

The bottom photo shows a boot where the rubber quality was higher, but still too much filler was used, which eventually induced flex cracking. If you zoom in and look at the top end of the crack (near the center of the foot area), you will see a few tiny blisters. These are delaminations within the rubber layer, and are very indicative of slower-developing flex cracking. A flex-cracked area will show very little of the fine “network” appearance of ozone cracking. However, in a boot that has failed by flex cracking, you may also see some ozone cracking alongside the flex cracking.

In the diagram on the next page, there are 2 folds that are pushed outward as a boot is flexed. For example, these folds often are pushed up on the vamp while walking. The convex (bulging outward) folds are subject to ozone cracking, as previously discussed. The inward facing fold between them has fabric on the inside surface – this would be a convex bulge if looked at from the inside of the boot.

- As noted above, in structural engineering, a “beam” is a structural element that primarily resists loads applied laterally to the beam's axis. Under a bending load, one side is under tension and the other side is under compression.
- In our discussion of bending rubber, the rubber acts like a beam. In this diagram, the concave fold has fabric on the tension side, and rubber on the compression side. Since the fabric does not readily deform compared to rubber, the lateral deformation of the rubber is increased, possibly resulting in delamination.



Inner surface of upper is the lining side.
This concave fold has the lining side under tensile stress, but the fabric resists stretching compared to rubber. The rubber is on the compression side of this "deflected beam", intensified by restricted stretching by fabric, also compressed by the 2 flanking folds. The resulting bulge can fail by delamination.

The preventative for flex cracking is always to change the balance of the rubber matrix in favor of more compatibility:

- Use less inert filler (like CaCO_3 , clay, talc, to name some common inert fillers).
- Talc has a “platey” aspect ratio – flat, broad particles. Of all the inert fillers, talc is the worst for initiating flex cracking. Anisotropy during rubber processing tends to orient the flat particles of talc parallel to the surface of the rubber, therefore talc particles act as a sort of template for delamination when the rubber is under flexing stress. Never use talc as a filler for a rubber article that receives a lot of dynamic flexing.
- If you are using a lot of structural fillers like carbon black or WCB (precipitated silica), use a bonding agent to create more compatibility – for example, a silane like Si-69 or an “organometallic” like titanate or zirconate coupling agents.
- If you are mixing polar and non-polar polymers (like NR and EPDM), try to shift the proportion of one polymer so that the NR percentage is more dominant. Make tensile tests to confirm that the rubber strength is not degraded by the proportions you’re using.
- If you are mixing polar and non-polar polymers, another option is to use a structural filler with a bonding agent (like WCB coupled with Si-69) to act somewhat like a bridge between the incompatible polymers.

Barnyard Acid Cracking:

A barnyard or feedlot containing livestock will also contain livestock’s waste product, manure. Manure not only includes animal dung, but also urine and whatever else is present on the ground. A significant problem with manure in contact with footwear is related to acid formation – “barnyard acid”, which can potentially be as acidic as lemon juice. The chemicals present in animal waste mix together, and are exposed to conditions leading to formation of “barnyard acid”, especially moisture and bacteria.

In conditions of plant growth, like a farm field or a garden, the interaction of manure or other fertilizer and plants usually maintains a stable chemical balance. The agricultural practice of “liming” adds ground limestone to the soil, which restores proper acid/base balance, when needed. However, in a feedlot or other livestock confinement situation, the concentration of these manure chemicals becomes highly unbalanced, creating acidic conditions. For example:

- Livestock urine adds a high concentration of urea (and/or uric acid) to the manure, and these sources of organic nitrogen are readily converted to nitric acid (HNO_3) by bacteria in the soil.
- There are 22 amino acids that build proteins necessary to life, and 2 of these (methionine and cysteine) contain the element sulfur (S). All animals need sulfur in their diet, but manure contains the excess sulfur that farm animals excrete. Bacteria in the soil can oxidize this sulfur into sulfuric acid (H_2SO_4).

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- All plant tissues contain various organic acids. When livestock animals consume them, much of this acid is not absorbed in digestion, and passes into the animal waste. Even without bacterial action, confined livestock waste becomes concentrated, and the accompanying acids also become concentrated.

In the case of natural rubber and some synthetic polymers, exposure to acidic conditions is not a problem. However, certain of the mineral fillers that are frequently blended with rubber are vulnerable to acid attack. The main culprit is “calcium carbonate” (CaCO_3 , ground limestone), which has a basic pH and readily reacts with acids.

Rubber boots using a large PHR of CaCO_3 in the upper rubber compound will experience shrinkage and cracking of the rubber in contact with animal wastes that generate barnyard acid. Therefore, the key to preventing acid damage to rubber farm boots is to minimize the use of ingredients that are vulnerable to acid, especially CaCO_3 . From a marketing standpoint, this technique can be targeted toward styles of boots that are expected to find use in the farm market.

Cold Cracking:

This is not really a problem for vulcanized rubber boots, but I add it here for completeness. Vulcanized rubber is bonded into a stable network of molecules. The molecules are not free to move around in the network, so they can't pull together to form crystals with cold temperatures. Alternatively, vulcanized rubber won't melt with high temperatures, because the molecules are not free to separate from each other and start to flow.

PVC boots and some “thermoplastic rubber” boots are not vulcanized, and they can “freeze” into a stiff form. They can also melt, of course – melting is how PVC products can be injection-molded.

Chapter 7: Quality Assurance/Quality Control

Quality processes like quality assurance (QA) and quality control (QC) are expected by the market, and are a form of financial self-protection for manufacturers and distributors. If QA and QC aren't followed, the result could be that you send out an end product that not only doesn't meet standards but could also have life-threatening consequences.

Both QA and QC processes are important to quality standards, but so is knowing the difference between quality assurance and quality control. They're often used interchangeably, but they are two different processes taking place at different times. Understanding the separate roles these serve can help your organization preserve profits and deliver the best products possible.

Quality Assurance:

QA is a part of your quality management plan. QA encompasses all of the activities within your plan that ensure your product is ready to go through the manufacturing process. In other words, you're verifying that the quality requirements you planned for will be fulfilled as the products are made.

Quality Control:

QC is the inspection phase of QA. It's a series of test procedures used to verify that a product is safe and effective after mass production. Both QA and QC are necessary. You can't "test quality into" a product by relying on QC alone. QC is reactive and exists to identify defects in the quality of products after they have happened.

Proactive (QA) vs. Reactive (QC):

- Effective Quality Assurance is proactive. It aims to prevent defects before they occur through process design. QA involves the design of processes, a typical example being documenting standard operating procedures according to ISO 9000 standards. A safe, effective product should be the result every time processes are followed.
- QC involves the testing of products to ensure they meet standards for safety and efficacy. If QC testing uncovers quality issues, it should result in reactive steps to prevent an unsafe product from being shipped and distributed.

How does QC translate into the field of rubber footwear?

Obviously QC requires testing of rubber boots to any standards required by the market. In Chapter 5, I provided a selection of tests that can be performed on the rubber used in

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manufacturing rubber boots. I also provided information about several tests and standards used in the U.S. for certifying general work-safety footwear.

Rubber industry factories, including rubber boot factories, reach fairly far back into the supply chain. Rubber footwear factories generally produce more of their own components, by purchasing and processing raw materials, in contrast, say, to a sewn leather shoe factory which does not perform its own tanning. Nor do leather footwear factories normally make their own adhesives. The fact that a rubber footwear factory controls both the rubber formulations and the processing of their components internally puts a larger share of responsibility onto their operation, for testing materials and components.

In Chapter 5, I wrote, “It is essential that the factory producing rubber boots have a testing protocol with regular monitoring. It is advisable that their customers understand this testing protocol, regularly receive test result data, and also feel free to question the testing that happens (maybe request different tests), as well as set their own requirements for the test results.” I think that it’s fairly common for Asian factories to have a rather minimal QC program, which includes just the simplest of tests, and maybe even an irrelevant selection of tests. So the foreign customer should be alert to this subject and try to get the factory to correct it, if needed.

Customer-side testing –

Obviously, it is easy for the customer to obtain whole boots and send them out for “whole boot” testing in-country. But also there is nothing to stop the customer from requiring pre-vulcanized rubber testing samples from the factory and testing the samples at a commercial test lab in their own country. Testing the same sample materials at 2 different labs is a great idea anyway – we can sometimes find large differences between test results between labs. Such dual testing can sometimes lead us to find QC discrepancies at a testing lab, which is very helpful.

How does QA translate into the field of rubber footwear?

It is important that the factory should have ISO 9000 certification and a comprehensive testing protocol for its products. If they have their own testing lab, it should be certified by the appropriate authorities. The customers for a factory are well advised to have the same arrangements, although many importers/distributors simply relay on the factory to carry this alone. Beyond these obvious elements, there is one responsibility that a foreign manufacturer is not in a position to take on: A feedback loop with the market for monitoring performance.

Quoting from my Preface to this handbook, “Mainly, U.S.-based personnel understand the product from the cosmetic standpoint, and where the product should fit into a marketing plan – and little else.” Too often a customer has a vague idea of what they want, in relation to the

question “how do you define quality for this product”. They will give a factory samples of a competitor’s products that already exist, and ask the factory to largely copy it, possibly with some cosmetic changes. If the factory is lucky, they will identify the important aspects of the product and get the quality right. Relying on luck is dangerous.

The foreign customer is on-location in their own country, where the end-users can be monitored in several ways that are not available to a factory in Asia, where most rubber boots are made. **The feedback loop has to be the distributor’s responsibility in order to build quality into the design of the product – the heart of the QA mission.** This would take into consideration the elements of:

- Cosmetic design elements, if the market requires that.
- Proper fit of the boots. Will the boots “don and doff” (go on and off of the foot) easily? Do the sizes conform to normal sizing expectations, so that the wearers can reliably purchase the right size? (Especially important for online purchases.) Do the boots stay on in a firm, stable way when walking?
- The wearer’s comfort. For example, does a pair of hip boots provide enough insulation for stream fishing? Does a pair of work boots provide enough cushion and impact absorption for an 8-hour work shift in industry? Does a pair of gardening boots flex enough to be comfortable working in a squatting position?
- Adherence of the boots to any certifications that are required by the market for each style. For example, ASTM F 2413 for work/safety or NFPA 1971 for firefighting, and others.
- Service life after the boots are in the end-user’s hands. For example, a pair of hunting or fishing boots might typically be worn for a few hours per day, and worn perhaps 10-50 days in a year. Work/safety boots might be worn 6-8 hours per day, under hard wear conditions for maybe 250 days per year, or more. The service life expectations will be different for those two different applications. One of my customers came to me to design and source a mining boot that would perform better than 2 months in hard-rock mining. 2 months was the market expectation that we had to beat!

How does the distributor establish the feedback loop? Here are several possibilities:

- Focus groups – These are especially valuable for confirming or modifying the cosmetic appearance and fit. They can be composed of a selection of “elite” end-users (often the case for hunting and fishing boots), or even just people within your own company. The important idea is that people meet together to discuss pros and cons.
- Wear tests – Wear testing should be considered essential for the introduction of any new product. It is also very worthwhile as a real-life check on how your current products are performing in various wear environments.

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- Returned goods monitoring – In my opinion, this is the “acid test” of feedback from the market. The term “acid test” comes from the traditional method to assay an item made of gold, to find its true gold content. Returned goods monitoring really tells you the real value of your products – you see how your boots are performing in the field, because it uses a large statistical sample space – 100% of your sales! The reference to acid is also appropriate because if you have not done enough QA work, made bad guesses or bad choices, your company will definitely get burned!

When I first was hired into the laboratory at LaCrosse Footwear, my boss assigned me to the job of monitoring returned goods during part of every day – the first time anyone there did this on a regular basis. I was able to start seeing patterns in how products failed, failing in similar ways and also different ways, depending on the styles. I developed a report format for that information, and it eventually resulted in large reductions in prematurely failed boots. Of course, this also improved our customer satisfaction and reputation in the market. However, examining returned goods is time-consuming, and can also be space consuming – if your sales are large, even modest numbers of returned boots can consume a lot of space.

And a cautionary note: If you’re relying on failed returned goods to help QA build quality into the product, you may already have a serious problem! Although wear testing and returned goods monitoring are both highly beneficial, it’s clearly better to avoid failed product by running a comprehensive wear test program.

Wear testing during the prototype phase of boot development is the best way to make sure you are building-in quality. For any new style of boot (not referring to simple color changes) it’s a good practice to thoroughly wear-test. Depending on the style, you may need only a few pairs to confirm that there are no surprises. Or, in more innovative or mission-critical boot styles (safety boots, for example), the risk of getting surprised with bad consequences is higher – wear test quantities should probably be higher. Wear testing is always conducted at no expense to the testers (or their employers).

It can be challenging to find enough wear testers to really give you boots a serious trial. For safety boots, local manufacturing facilities may provide a good sample space of workers, if the employer is willing to help. Choosing several different work environments is always good. If you are trying to wear test safety boots, make sure that the style(s) involved have already been tested and approved according to an appropriate safety standard – for example, ASTM F 2413. Do not distribute safety boots for wear testing without certifying them first!

Monitoring wear test boots is very important – you can not count on wear testers to report on the boot condition by themselves. When working at LaCrosse Footwear, I gave a lot of wear test boots to farmers. I learned quickly that farmers will really beat up boots for you – a sort of

accelerated test. I checked their condition about every 2 months, sometimes more often, and that program yielded a lot of good information. Occasionally things will surprise you, however:

- I gave wear test boots to some Amish farmers, once. I checked back in a couple of months, and the boots were like new – the Amish in our area frequently worked barefoot in the summer! (Something I didn't know beforehand.) My testers were so grateful for the boots, they didn't want to ruin them by wearing them! Clearly I was not communicating effectively.
- On the other hand, some of my wear testers were so grateful for the boots that I gave them that they wore them until they were nearly just rubberized rags, impossible to analyze. These testers were too polite to complain about how worn out they became! Again, I needed to QA my communication skills.

Seriously monitoring your footwear products from real-life environments (whether returned goods or wear tests) is the only way to get the feedback that you need for improving your current products. When developing new products, wear testing is essential if you really want to build-in quality.

Do not rely on your footwear manufacturer to understand your quality needs better than you do, or to seek feedback from the market that you serve. They are likely to be too far away for either task, and definitely too far removed from an understanding of your target markets .

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