Rubber Boots – Understanding an Industry

by Jon Nicholson, President
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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 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.

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

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 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.

- 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.

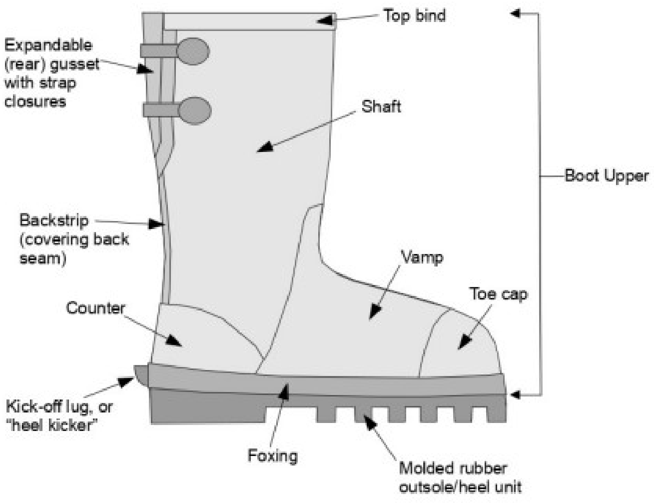

Figure 3: Diagram of typical boot zones and parts

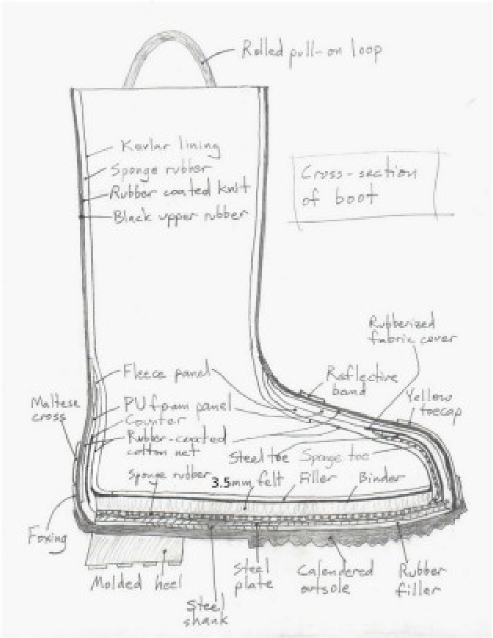

Figure 4: Cross-sectional sketch of high-performance firefighter boot, showing complex engineering that is possible with "hand laid" construction – and impossible to achieve with injection-molded PVC.

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=yGzF9yXPMlU&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".

“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=Bgktc4IpKBY&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=h4oqRSoaG7Q&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 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

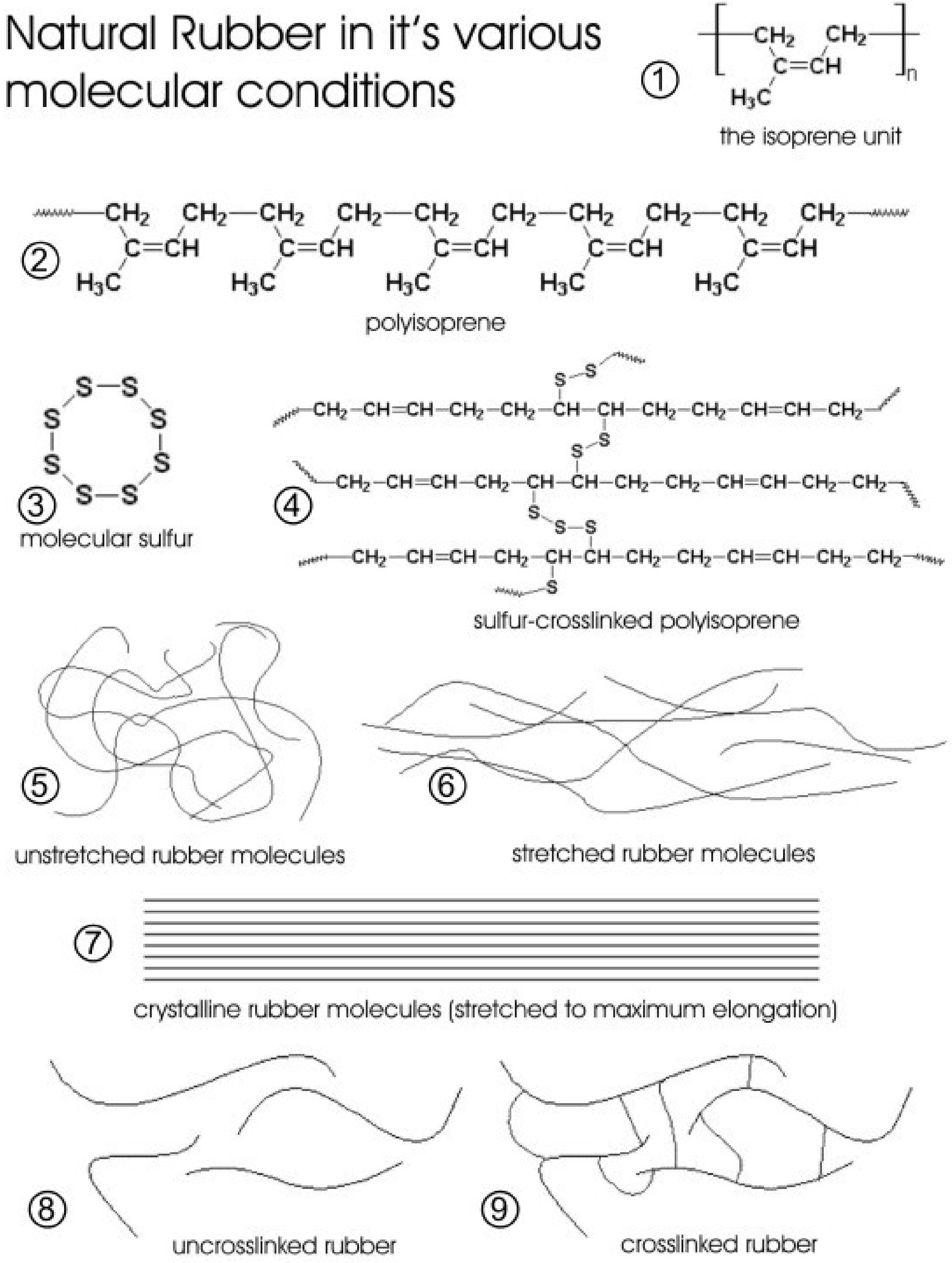

Figure 3: Refer to the following discussion for each diagram.

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.

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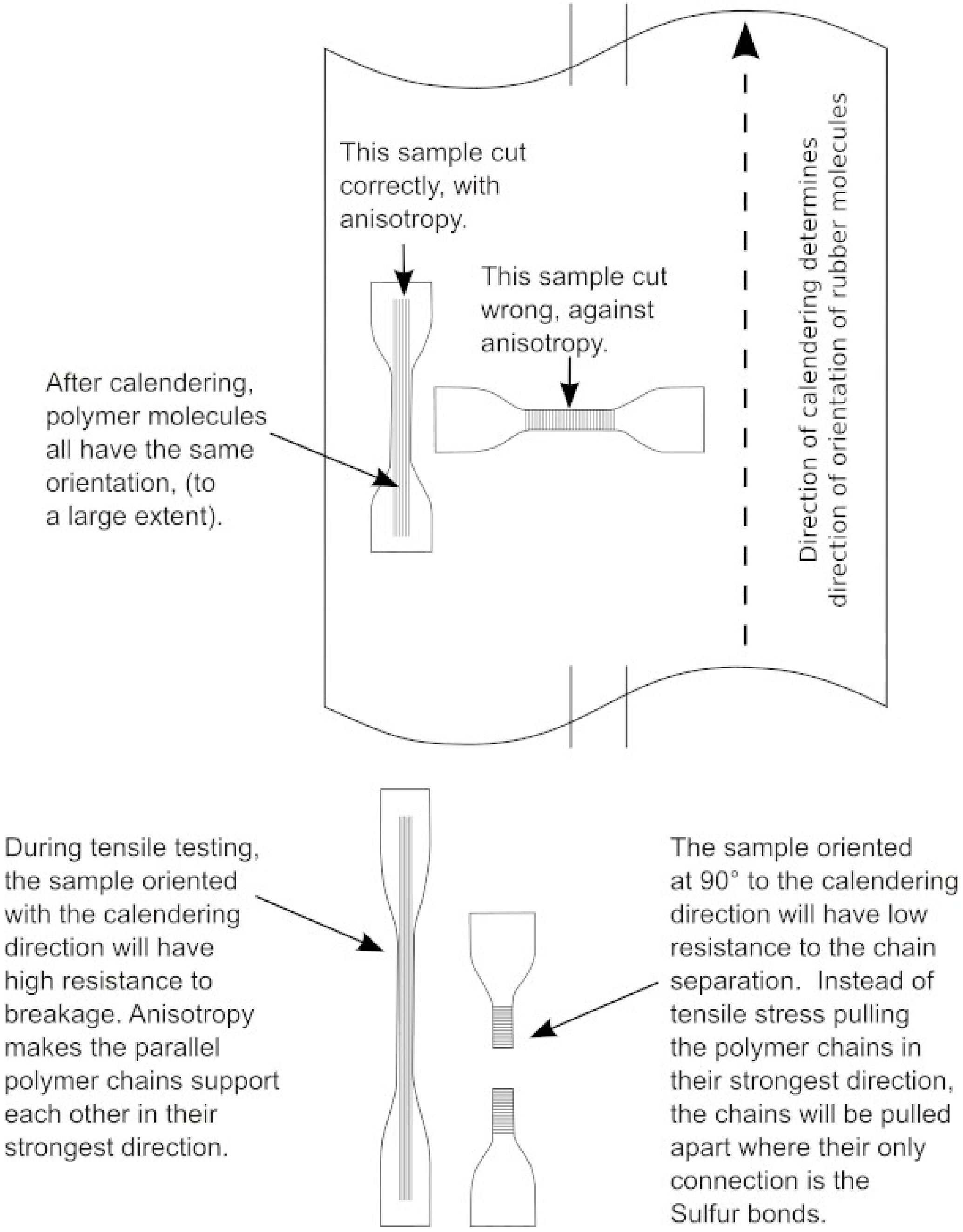
Anisotropy:

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



This sample cut correctly, with anisotropy.

This sample cut wrong, against anisotropy.

After calendering, polymer molecules all have the same orientation, (to a large extent).

During tensile testing, the sample oriented with the calendering direction will have high resistance to breakage. Anisotropy makes the parallel polymer chains support each other in their strongest direction.

The sample oriented at 90° to the calendering direction will have low resistance to the chain separation. Instead of tensile stress pulling the polymer chains in their strongest direction, the chains will be pulled apart where their only connection is the Sulfur bonds.

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

Materials	**PHR**
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 (TiO2)	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.

Antioxidant: Oxygen (O_2) 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

Materials	PHR
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

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

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, expecially 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

Materials	PHR
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

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 ($CaCO_3$, 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); 65g./165 g. = 0.39 or **39% of the mixture total <u>weight</u> 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:

- 100 g. of polymer has a volume of 100g./0.95 g./ml. = 105 ml.
- 65 g. of $CaCO_3$ has a volume of 65g./2.71 g./ml. = 24 ml.
- 105 ml. + 24 ml. = 129 ml. (total volume of batch); 24 ml./129 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)

	Maximum PHR
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)

	Maximum PHR
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.

<u>Suggestions for preventing blooming on rubber boots</u>:

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.

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.

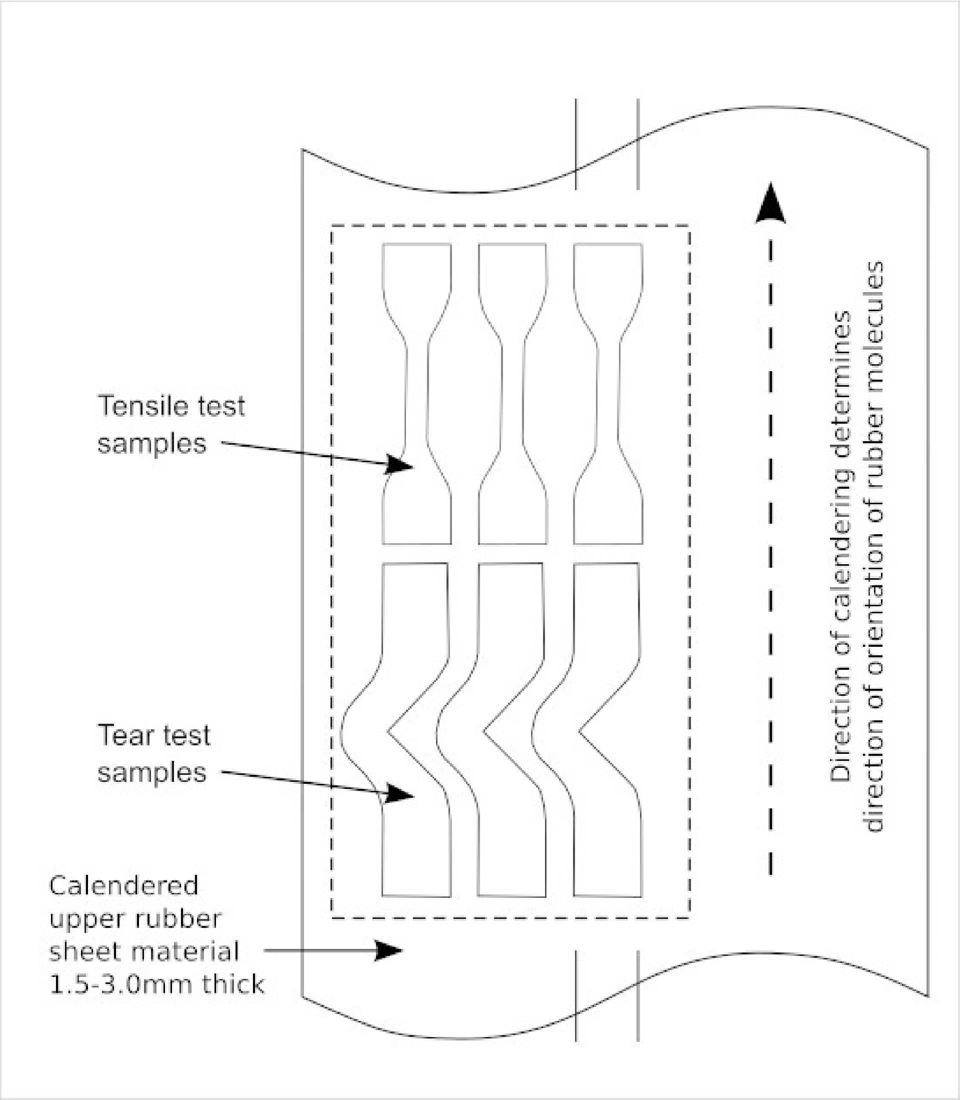
Tear: ASTM D 624 – Test rubber sheeting

- 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".

- 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 a 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 **de**creases (becomes more abrasion-resistant), the NBS test (ASTM D 1630) value **in**creases (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 40ºC 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.

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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.

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

Chapter 6: Failure Modes of Rubber Cracking

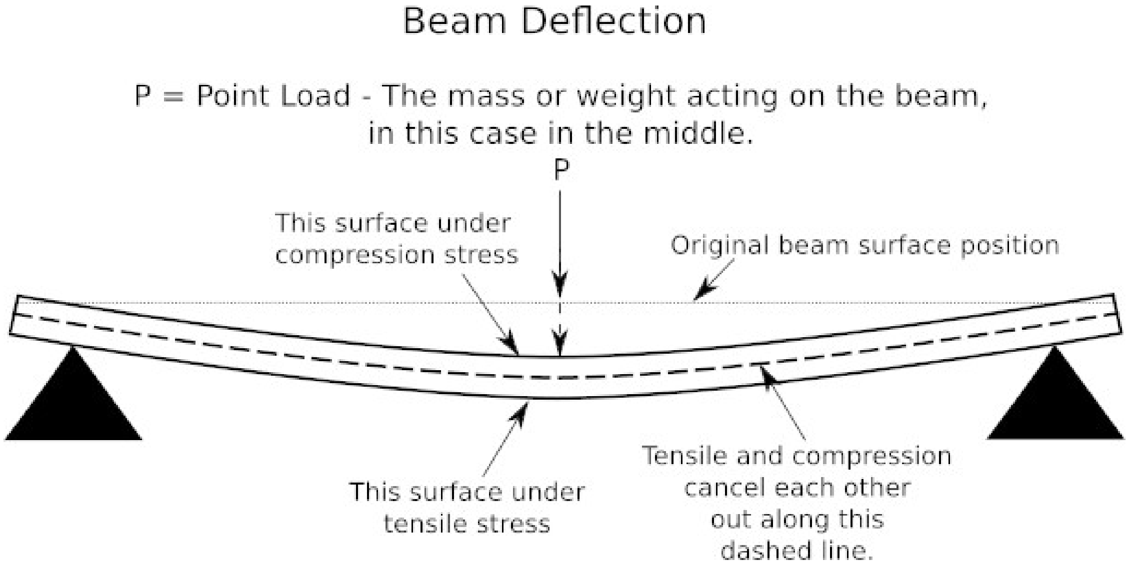
Failure mode: The specific pathway of events leading to failure of a machine, equipment, or system.

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 –

#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.

<u>Here are some important facts about ozone and rubber</u>:

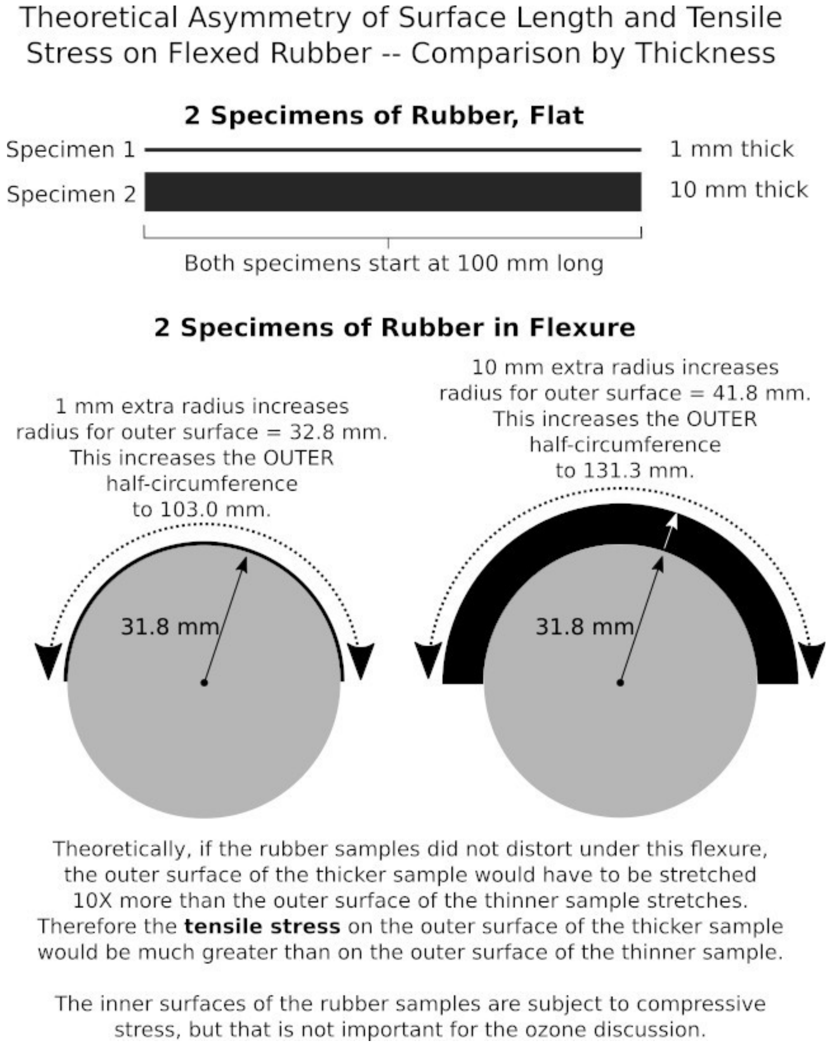
1. The natural ozone in the stratosphere is heavier than air, and it falls over time. Since ozone is a highly reactive chemical, it is <u>mostly destroyed before it reaches the Earth's surface</u>, reacting with volatile gases in the atmosphere, dust particles, bacterial and mold spores, etc. – anything 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, <u>thick cross-sections of rubber will generate more</u>

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 keeping 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

2 Specimens of Rubber, Flat

2 Specimens of Rubber in Flexure

1 mm extra radius increases radius for outer surface = 32.8 mm. This increases the OUTER half-circumference to 103.0 mm.

10 mm extra radius increases radius for outer surface = 41.8 mm. This increases the OUTER half-circumference to 131.3 mm.

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 * **π** * radius, the half-circumference of a semi-circle or half-circle will be **π** * radius. Therefore, to make exactly a half circle of these two samples, the radius of the cylinder should be 31.8 mm (**π** * 31.8 mm = 100 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) * **π** = 103.0 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)* **π** = 131.3 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

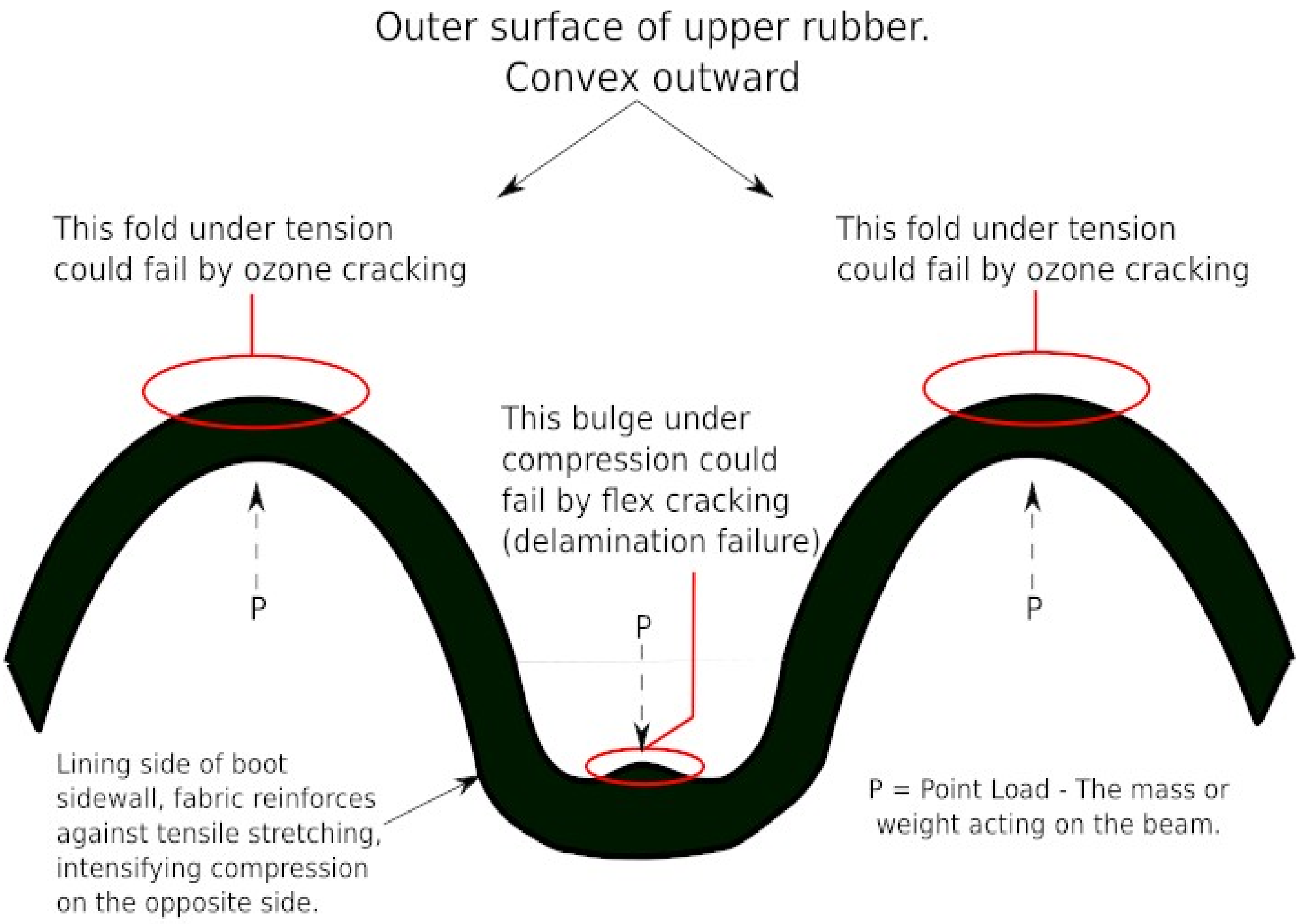
Flex cracking is caused by these kinds of incompatibility, and is also promoted by oxidation, which can cut polymer chains, and initiate a crack. On the previous page are a few photos of flex cracking, which show how its appearance differs from ozone cracking.

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.



Outer surface of upper rubber.
Convex outward

This fold under tension could fail by ozone cracking

This fold under tension could fail by ozone cracking

This bulge under compression could fail by flex cracking (delamination failure)

Lining side of boot sidewall, fabric reinforces against tensile stretching, intensifying compression on the opposite side.

P = Point Load - The mass or weight acting on the beam.

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 (HNO3) 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 (H2SO4).

- 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 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.

<u>Customer-side testing</u> –

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.

- 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 .

As this handbook is expected to be distributed only online, in .PDF format, there is no "Index". Readers can more efficiently use the PDF viewer "Search" function to find terms in the text.

Rubber Hacks and Compromises: Notes from Lab, Field, and Factory Floor

by Jon Nicholson, President

NorthStar Rubber Specialties, L.L.C.

Preface

前言

This booklet, Rubber Hacks and Compromises: Notes from Lab, Field, and Factory Floor is a follow-on volume to my previous release, Rubber Boots – Understanding an Industry.

Rubber Hacks and Compromises… can be considered as a collection of brief case studies of how I've analyzed problems and reached solutions by using my personal expertise, available industry literature, and input from other experts – including my technical colleagues and our factory workers, all experts in their own work. In other words, solutions usually emerge from combining a wide body of experience with a scientific analysis, to understand why a specific solution solves a specific problem. Both are essential to solving a problem permanently.

At this point I'd like to acknowledge my debt to several people. My old boss, Paul Phillips, Senior Chemist at LaCrosse Footwear, combined an understanding of rubber chemistry and factory operations with a wise management style – he expected people to do their jobs without his constant oversight. He is largely responsible for my career. Additionally, our Senior Lab Tech, Gary Beyer, had a special talent for communicating with the factory workers in our preparatory departments (Warehouse, Cement Room, Mixing, Mill Room, etc.) and was alert to anything going wrong – or anything going right, which could provide fresh opportunities for improvement. Bruce Lindseth, Supervisor of our Scheduling Department, had a wealth of insight regarding how "this" affected "that" in our factory setup, and how some proposed change might disrupt or improve the factory operation. Rob Rinehart, my boss after I moved to the Product Development Department, was responsible for my career shift from working at the LaCrosse factory to working directly with Chinese factories. Rob was another boss who expected his people to work competently without micromanagement on his part. Roger and Phoebe Newman provided the opportunity for me to work independently in a deep partnership with Chinese companies. Finally, my colleague and peer Steven Smith, Product Development Manager at Tingley Rubber Company, has generously offered me editorial comment both on both my previous work, Rubber Boots-…, and the current work, Rubber Hacks and Compromises:... Thanks for your valuable help, Steve!

Readership of this booklet will probably be more limited than for the first one – which, in only 4 months, has been downloaded nearly 5,000 times. However, some readers may recognize similar challenges that they've already dealt with. For some of us, it's always interesting to see how other people approach their own challenges. As the title to this booklet suggests, solutions to problems are, perhaps, not always the most elegant solutions possible. Sometimes you settle for solving part of the problem, just enough to keep the affected production line running. Any solution that keeps a production line running is better than no solution at all.

Jon Nicholson

Rubber Hacks and Compromises: Notes from Lab, Field, and Factory Floor

July 23, 2022

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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. Furthermore, the case histories presented herein reflect the author's personal experience, and they are certainly subject to errors of memory and biased opinion.

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". Various synthetic rubber types can be made from petroleum-based feedstocks, including:

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

Latex rubber – This is a liquid produced by plants, normally from the "rubber tree" (Hevea brasiliensis), a native of South America. The Hevea tree sap contains microscopic particles of the natural rubber polymer "polyisoprene". Latexes can also be made from synthetic rubbers.

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 elevated temperature. This raw rubber is formed into solid bales and sheets, which are blended with other materials to prepare dry rubber compounds for manufacturing.

Rubber compound – Solid raw rubber has to be mixed with various other materials in order to make it easily processable on standard rubber machinery, to modify it's 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:

- <u>Polymer rubber</u> – Natural Rubber (NR) and/or a selection from the synthetic types mentioned above.
- <u>Vulcanization chemicals</u> – 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). Other chemical combinations are also possible.
- <u>Antidegradants</u> – These chemicals prevent or slow down the deterioration of rubber by heat, oxygen, ozone, acid attack, fire or other causes of rubber deterioration.
- <u>Fillers</u> – 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, and carbon black (like HAF, derived from incomplete combustion of petroleum-based fuels). There are many others.

1. Rubber “grinds” – What is it, what does it smell like, and how do you fix it?

“Grinds” and plasticity

An understanding of “plasticity” is an important aspect of rubber technology. Generally, the term refers to the ability (or susceptibility) of a solid material to both deform and flow when subjected to some kind of physical force. There are different ways to measure plasticity, and plastic flow is desirable in different degrees when rubber compounds need to be mixed and processed. Raw NR (natural rubber in dry form) has a fairly high resistance to plastic flow. We often add “plasticizer” oils or resins to rubber, to make it soften at a lower temperature and flow more easily. We can also improve plastic flow by cutting the long molecular chains in a mass of rubber into shorter chains that can flow more easily, with fewer entanglements of the molecules. This is called “peptizing”. Peptizing the rubber molecules has an advantage over plasticizers – sometimes we need to improve the rubber flow, but plasticizer oils can have negative effects on the physical properties of the rubber. Therefore, we often prefer to peptize NR molecules so that we can minimize the presence of plasticizers in the finished product.

In “open mill” mixing, the rubber is placed onto a surface composed of 2 “counter-rotating” steel rollers (rotating inward toward each other, when looking down from above). The rollers grab the rubber in the gap between them, squeeze the rubber between the rollers, and a worker loops the rough rubber sheet up into the gap between rollers again, for further working. The tearing action of rollers against the rubber (“shear stress”) rips rubber chains apart, which exposes bare electrons at the torn ends of molecules. These highly reactive torn ends of molecules can immediately rejoin, if nothing prevents that from happening. However, in the presence of oxygen (O_2) molecules from the air, the exposed electrons will react with O_2, so that adjacent torn ends of the rubber chain are sealed off with oxygen atoms. The result is that long molecular chains now have shorter length, improving their plastic flow characteristics.

In the first 44 seconds of the following video, you can see “open mill” grind-making. The only purpose of the operation is to expose the rubber to oxygen while the molecules are being sheared apart.
https://www.youtube.com/watch?v=7Ju7J9zJ1Ow&ab_channel=JonNicholson

In “internal mixer” grinding (typically using a Banbury mixer), the closed nature of the machine prevents ready access of oxygen from the air. In that case, we must add a chemical peptizing chemical to prevent torn rubber chains from reuniting. Adding a peptizer replaces the chemical role of oxygen in open milling.

“Open mill” peptizing is convenient, but if you want to hit a specific plasticity measurement, you are very dependent on the amount of time that the rubber “rides” on the open mill rolls. The more time “grinding”, the more time that the rubber is exposed to O_2 in the air, and the softer/more plastic the rubber becomes. In “internal grind mixing”, you control the degree of plasticity mostly by controlling the amount of added peptizing chemical. The time factor is less critical (no oxygen exposure), and the result is more precisely controllable.

"Grinds" (rolls or slabs of peptized NR) are usually allowed to sit overnight to cool, and for any residual peptizing chemical reaction to finish.

Note: NR is very responsive to reducing the length of molecules (aka"molecular weight") by "grinding". Synthetic rubbers show less response to the shearing action of grinding – especially Neoprene rubber (CR), which normally shows no effect at all.

Zinc Oxide (ZnO) in grinds to suppress odors and smoke

At LaCrosse Footwear, we produced rubber "grinds" at the end of the compound mixing schedule each day. Any hot processing of NR can cause the release of a strong odor -- especially "grind" mixing, which can also produce a smoky haze. Sometimes NR can cause intense odors during the grinding/batch dump/milling stages. Our worst experience involved a shipment of NR from Liberia, which produced a smell like burning sewage during grind production. Relief arrived when our desperate workers randomly tried adding Zinc Oxide (ZnO) to the grinds, and by doing that solved their own problem. This not only improved the situation with the Liberian NR, but for all NR grinds, and we instituted that change permanently.

Our operating theory was that naturally occurring organic chemicals (oils, aldehydes and fatty acids) were volatilizing because of the heat generated by the rubber mixing cycle. When we added ZnO during grinding, it formed "coordination complexes" with these chemicals, and after complexing together the combined weight of the ZnO and the bound organic molecules was sufficient to reduce volatilization. Consequently, the objectionable smells and smoke were much reduced in the Mixing Dept., which made the whole factory more "livable".

Here is a typical formula for a lightly peptized "grind" which contains ZnO:

- RSS-1 Smoked Sheets – 100 PHR
- Struktol A-86/Peptizer PTP – 0.10 PHR
- Zinc Oxide – 5.62 PHR

Compound formulas need a specific amount of ZnO. Therefore, for individual rubber compounds (using grinds that already contain ZnO), we made adjustments of the ZnO dosing to meet the total amount needed by the compound formula (normally a total of 5.0 PHR). (I have discussed "PHR" units in my previous book, Rubber Boots – Understanding an Industry.)

Sappy concluding anecdote: After I made the job change from Development Chemist to Product Development Manager (Work Boots), I no longer worked in the factory every day. One day, my children told me (and my wife agreed), "Dad, we miss your old smell!". Grinds.

2. What is "polarity", and how can you survive (or thrive) with it?

Polarity of molecules – a little problem with compatibility

There are maybe 20-30 (or even more) different kinds of rubber (or "elastomer"), depending on how you classify them. Some of them are easier to mix together in well-dispersed blends, and some combinations of them blend together poorly. The major factor determining their compatibility is "polarity" of the rubber molecules.

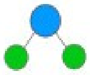
A molecule is 2 or more atoms joined by a shared electron bond, called a "covalent" bond. In this kind of bond, the positively charged atom nuclei share their negatively charged electrons, but if the atoms are of different elements they may not share the electrons equally. The electrons will be denser around one of the atoms. This makes a molecule "polar". If a molecule lacks this kind of electron concentration, it is called "non-polar".

If we mix NR with SBR rubbers, their polarities are very similar, therefore these two polymers do not have strong compatibility problems. In the case of NR with NBR (Nitrile), NR is non-polar and NBR is highly polar, and there are no strong attractions between those different rubber molecules -- they resist evenly blending together.

To be clearer, we can say that the electrostatic attraction of polar NBR molecules to each other is so strong that it excludes (literally "squeezes out") any NR molecules that may be inserted between NBR molecules. A mundane example of this effect is seen by mixing olive oil and water. The electrostatic attraction of water molecules (H_2O) to each other is so strong that the water molecules squeeze out oil molecules that might be inserted between them when they are mixed. For water, this attraction is strong enough to have its own name: "hydrogen bonding". As demonstrated in an oil-and-vinegar salad dressing, it results in an obvious separation of water solution (vinegar) from the oil, resulting in oil droplets being excluded together into a separate layer.

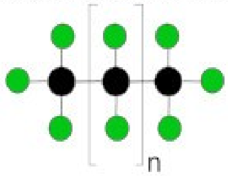
The following diagram shows an example of this separation, in a very simplified representation. It displays the molecules in 2 dimensions, but keep in mind that the actual system is 3 dimensional. It uses water (H_2O) as an example of a polar molecule, and a generalized "alkane" hydrocarbon as an example of a non-polar molecule. Also note that all of the motivating force in this system comes from the attraction of water molecules to each other. The hydrocarbon molecules, in this case, are attracted together by "van der Waals force" which is a weaker attractive force compared to hydrogen bonding. The hydrocarbon molecules have this same weaker attraction to each other and to the water molecules. The hydrocarbon molecules are not actively pulling each other away from the water molecules, instead they are merely pushed out of the way as the more strongly attracted water molecules crowd together and stay together.

Polar molecule: Water
Blue = Oxygen
Green = Hydrogen

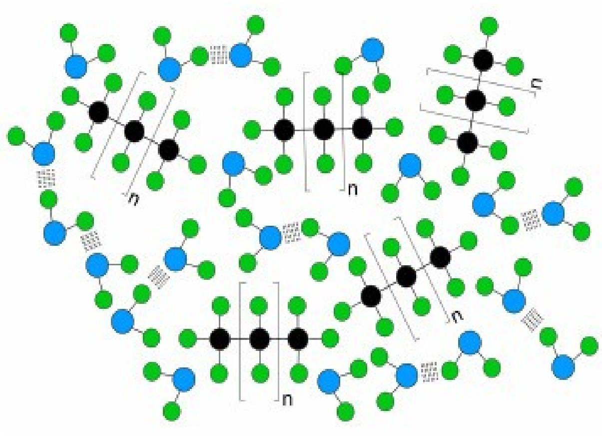


||||| = Hydrogen bond

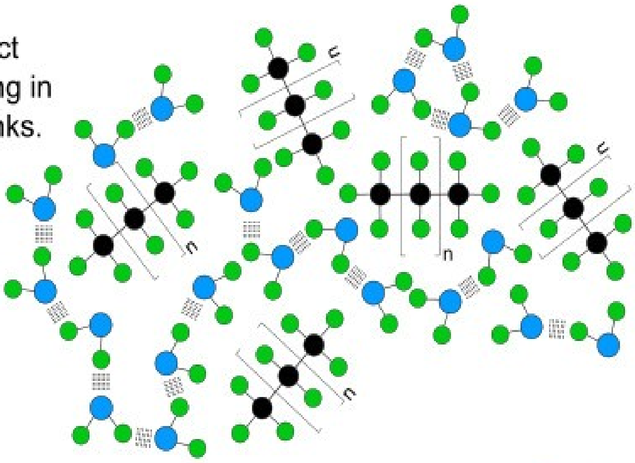
Non-polar molecule: Generalized alkane hydrocarbon
Black = Carbon
Green = Hydrogen



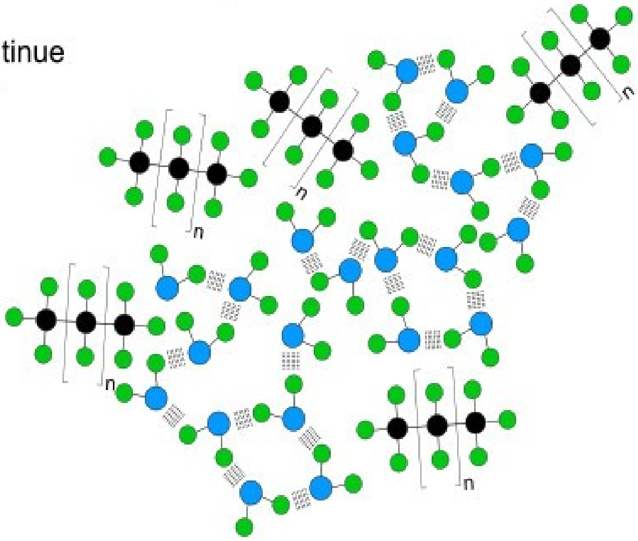
Mixture is well agitated.



Water molecules interact with each other, resulting in more hydrogen bond links.



Water molecules continue intereacting together forming persistent networks, forcing non-polar molecules to the periphery.



For rubber, on a microscopic level, this means that we see regions of each kind of rubber dispersed amid the other rubber -- not a smooth uniform mixture. This is called "phase separation". The lack of completely uniform structure weakens the final rubber product. Despite this, the strength may be good enough if we use certain fillers (especially carbon black and precipitated silica) to bring up the strength to some required level.

Why would we blend incompatible polymers? For certain applications, we might need a combination of chemical properties that is considered more important than a certain loss of physical strength. Examples follow.

Incompatibilities – NR + EPDM have a polarity problem

Every rubber application has its own performance demands, and consequently the rubber formulation has to reflect those in its compound design. For rubber boots, an important rubber application is in the "upper" rubber – everything covering the outer surface of the boot, above the sole layers. Examine the field of use of the boots. Are they work boots that are potentially worn 8-10 hours per day, every workday of the year? Or just protective boots worn in certain circumstances? Are they rain boots used sporadically, or gardening boots used more heavily, but only for 3-6 months in a year? We have to think about the intended usage of the boots, which may require gathering some information from the market.

Let's consider the ozone molecule (O_3). I have discussed ozone formation in my previous book, Rubber Boots – Understanding an Industry. I didn't mention that ozone concentration in the troposphere (lower atmosphere, where we live) changes seasonally. Seasonal variation of ozone in the Northern Hemisphere is stronger than in tropical areas closer to the Equator. Ozone concentration varies with time of year, and weather conditions:

- Higher relative humidity supports less ozone production than drier air.
- Colder air supports less ozone production than warmer air.
- Fewer daylight hours (winter) supports less ozone production than more daylight hours (summer)
- Rural regions support less ozone production than metropolitan regions, which have higher air pollution concentrations.

Consequently, you may think that rubber boots worn only in winter – like insulated pac boots – have less need for ozone protection than rubber boots worn in sunny, warm-weather conditions. You would be correct. I have very rarely seen any ozone damage on insulated pac boots.

For safety/work-related rubber boots (my area of specialty), the need for ozone protection is high, because these boots are worn regularly, in all seasons, and for longer periods. Like most rubber compounders, I use the synthetic rubber EPDM mixed with NR to provide basic ozone protection in the upper rubber. (Rubber outsoles almost never experience enough "angle of flexing" to trigger ozone attack, so we almost never use EPDM in outsoles.) NR is generally considered to be a "non-polar" polymer, but it is more polar than EPDM, so a blend of the two polymers always has "phase separation", as discussed above. This weakens the upper rubber to some extent, because not only is there phase separation, there is also a big problem with vulcanization. Even though EPDM can vulcanize ("cure") with Sulfur and normal "accelerator" chemicals, it never gets an opportunity to cure in a blend with NR. NR's slight polarity allows it to dissolve/absorb much more of the cure chemicals used in vulcanization than EPDM will. Furthermore, it will react with those chemicals in its own vulcanization far faster than EPDM can. In the typical 1 hour vulcanizer cycle used for rubber boots, NR will absorb and react with essentially all of the available cure chemicals, leaving EPDM with barely a trace amount.

Therefore, we have to balance the amount of EPDM used in an upper rubber formula, to obtain the ozone-protection benefit but avoid the worst effects on the cured rubber strength. In my footwear products, I compromise at the EPDM content of 28 PHR. In my experience, less than 26 PHR of EPDM will result in a noticeable increase in ozone cracking, and more than 30 PHR will increase the risk of "flex cracking" (see my previous book, referenced above).

I'll share this story of a rubber boot catastrophe related to "too much EPDM":

By early 2001, the old LaCrosse Footwear company (based in LaCrosse, WI) had mostly transferred production from the U.S.A. to Asia. One Chinese supplier received most of the orders, and they were producing our largest volume of hunting/fishing boots. The owner of the trading company wanted to be sure to produce the best boots possible, so he told his factory to improve quality regardless of cost. The Chemist for that factory knew that EPDM rubber was important to the upper rubber quality, but actually he had no knowledge or experience relevant to using EPDM, and almost no understanding of the demands placed on hunting/fishing boots. To "improve" the upper rubber formula which I had given him, he increased the EPDM content from 28 PHR to 33 PHR. As noted above, EPDM barely vulcanizes in a blend with NR, and it therefore weakens the physical strength properties of the rubber blend. As you increase the PHR content of EPDM, you are also decreasing the NR content, which can leave too little NR for cohesion of the rubber mass.

Both the trading company owner and the Chemist of the Chinese factory were quietly proud of their dedication to quality, and they did not inform anyone at LaCrosse Footwear of their unauthorized change. The result was that LaCrosse Footwear began receiving shipments of these sporting boots that began to fail from flex cracking within days of customers wearing them. You can imagine the initial confusion inside our company, then the panic as hundreds and then thousands of pairs of failed boots began arriving in our Returned Product department. I flew to China immediately to discover the source of the problem, and then learned the sad story above. But for all the boots that had already been produced and shipped – many of them still on ships on the ocean – it was too late to prevent disaster. As those boots arrived at our warehouse, they were immediately dumped into large waste containers. Ultimately (if my memory is correct), LaCrosse Footwear discarded more than 14,000 pairs of boots upon arrival.

The Chinese trading company replaced all of them at no cost to us, so they absorbed most of the consequences of this disaster. But these events also disrupted our shipments to customers and damaged our respected brand. It required some time and effort for us to restore our reputation in the marketplace.

The strength of a rubber compound containing an NR/EPDM blend will also be affected by other ingredients used in the formula – especially (as mentioned above) carbon black and precipitated silica. You can use these, or change the amounts of other ingredients, to partially compensate for the NR/EPDM incompatibility. When have you compensated enough? A good way to verify your strength compensation is by testing for tensile strength. In an ASTM D 412 tensile test, the desirable "tensile strength at break" for upper rubber would be a minimum of 9 Mpa (1,305 psi), with a minimum "elongation at break" of 400%.

Further Incompatibilities – NR + EPDM + NBR

I wrote a formula in which the polymer portion consisted of:
NBR – 40 PHR
NR – 32 PHR
EPDM – 28 PHR

The purpose of adding NBR to NR + EPDM was to produce a rubber knee-boot that was suitable for food service applications, where the upper rubber was required to resist moderate exposure to animal and vegetable fats and oils. This boot was also designed to accept a special 3rd-party outsole that provided excellent traction and slip resistance in environments where a floor could be both wet and greasy.

- NBR was needed in the formula for oil/fat resistance.
- EPDM was needed, because NBR is as vulnerable to ozone as NR is.
- NR was needed for its inherent strength and rubbery feel, and it's ability to be calendered into smooth rubber sheet material.

As far as compatibility is concerned, this blend goes from bad to worse! NBR is very polar, much more than either NR or EPDM. Therefore all 3 polymers are mutually incompatible. Furthermore, neither EPDM nor NBR have the inherent sticky quality of NR, so that it is more difficult to build rubber boots using the "hand-laid" method. It requires more use of solvent-based adhesives. On the other hand, NR will cure competitively alongside NBR, so that part of the situation is better compared to NR + EPDM. Furthermore, I used HAF carbon black and precipitated silica, which form their own bonds to these different polymers, and thereby helped to bridge over some of the incompatibilities. The resulting tensile strength (and other physical properties) were rather low for upper rubber, but still acceptable.

With the addition of an adhesive that I invented for the purpose (containing 50% NR + 50% ENR [Epoxidized Natural Rubber]), the boot upper and special outsole bonded together well.

So many incompatibilities! – NR + EPDM + NBR + PPD

When I wrote the NBR-NR-EPDM formula, I knew that the upper rubber needed some chemical ozone protection, in addition to the EPDM protection. For my chemical antiozonant I chose a chemical in the category “para-phenylene-diamine” (PPD). This class of chemicals is widely used as antioxidants/antiozonants in rubber compounds. Due to their low “ionization energy”, these chemicals can react faster with ozone than ozone can react with rubber. Of the various PPD’s, I’ve used IPPD, 6PPD and CPPD as secondary antiozonants. (EPDM is the primary antiozonant.) For this formula, I originally chose IPPD, because it was easy for the factory to obtain in China. All PPDs discolor light-colored rubber, but these boots were black, so no problem.

The way that PPDs function in a rubber compound is by dissolving into the rubber at mixing time, and then “blooming” (migrating to the surface) over time, so that they can preferentially react with ozone at the surface, preventing damage to the rubber. However, there are differences in the polarity (hence, the solubility) of different PPD’s in different kinds of rubber. This caused a problem with my oil/fat resistant upper rubber, because it became clear (in my examination of returned/failed boots) that I was not getting the ozone protection from IPPD that I had expected.

I consulted with a chemist working for the supplier and was told that IPPD was a very polar molecule, and extremely soluble in NBR rubber. As a result of this extreme solubility, all of the IPPD was being absorbed by the NBR in the formula, leaving the low-polarity NR portion of polymer completely exposed to ozone attack. Following his advice, I replaced the IPPD with CPPD, which was less polar and more balanced in solubility between the NBR and NR. After that change, we no longer had any returns for ozone cracking in that product.

3. How cleaner air makes human life better, but makes factory life more complicated.

Clean Air Act – 1990 Amendments

After the enactment of the 1990 Amendments to the U.S. 1970 Clean Air Act, a new level of regulatory pressure was placed on U.S. factories to reduce toxic air emissions. I'll summarize our main sources of air emissions at the time of enactment:

- We produced most of our liquid adhesives on-site, by mixing solid NR-based adhesive compounds with heptane solvent in large churns. This production permitted solvent to escape into the air. (We also purchased smaller amounts of specialized solvent-based adhesives from outside sources).
- In the preparatory departments and on production lines, these adhesives were applied to rubber and rubberized fabric parts, and the solvent was allowed to evaporate into the air. To reduce worker exposure, most of this solvent was evacuated from the work areas by the use of hood vents.
- Some of the solvents that we used in production were especially problematic. For example, we used a comparatively small amount of toluene (methyl benzene) at certain points, but toluene carries a higher risk for worker exposure, fire/explosion hazard, and regulatory limits.
- Our autoclave vulcanizers generated some oily smoke from plasticizers used in the rubber compounds. The heat of vulcanization caused some plasticizers to off-gas. When the pressurized air was released at the end of each vulcanizer cycle, the smoky off-gas was released directly into both exterior and interior air.

One strategy that we used to become compliant with the new regulations was to find less-polluting substitutes for some of our solvents that volatilized during manufacturing.

- To reduce the toluene emissions from the factory, we adopted a special solvent blend: 2/3 Shell Cypar 7 and 1/3 toluene. (note: Cypar 7 is no longer available.)
- To reduce our vulcanizers off-gassing of plasticizer oils, we switched from our standard plasticizer oil to an oil grade that was less volatile, therefore more resistant to off-gassing.

Our biggest challenge was to reduce the amount of "VOCs" (volatile organic compounds) released from our adhesive applications. We used solvent-based adhesives everywhere in our process, and it was not obvious how we could reduce our usage to a level that would allow compliance with regulations. But there are limited classes of adhesive systems, so – something HAD to work!

The most obvious choice was to use latex-based adhesives, in which the liquid medium is water. We did begin using some latex-based adhesive, but the adaptability of our methods to latex was limited. Switching from a fast-drying liquid (solvent-based) to a slow-drying liquid (water-based) limited several production parameters – especially when you need to pile cut/flat parts together when they have adhesive applied to them, but the adhesive is still wet. Nonetheless, latex-based adhesive did solve part of our problem.

Unexpected – but effective! Vulcanizable hot melt adhesives

Inevitably I considered (and, at first, rejected) the class known as "hot melts". As the name suggests, hot melt adhesives rely on polymeric materials that 1.) will melt and flow when exposed to heat, and; 2.) are sticky enough to have an adhesive bonding effect. For example, the hand-held electric "glue gun" in your utility drawer at home uses a stick of hot melt adhesive. However, rubber boots are built by bonding various layers and parts together, and then vulcanizing them in a large autoclave, at high temperature. Everything glued with hot melt adhesives could be expected to fall apart under that treatment.

My breakthrough came when I reviewed the literature about hot melt adhesives, of which there are many types. I discovered that some hot melts are made using SIS (Styrene-Isoprene-Styrene block copolymer) and SBS (Styrene-Butadiene-Styrene block copolymer). Here is a description of these hot melt polymers.

- Repeating isoprene units or butadiene units are the soft, stretchy backbones of the polymer chains.
- Polystyrene end blocks on the polymer chains provide the thermoplastic component that allows these polymer molecules to melt and flow, then cool off and harden, as is needed in hot melt adhesives.
- In addition to the above polymers, hot melts include various softeners and "tackifying agents" (resins that promote stickiness).

The long polyisoprene and polybutadiene chains (between polystyrene end blocks) are the same as the NR and BR polymers used in rubber compounds. When I discovered this information, I realized that certain hot melt adhesives could be vulcanized. There were 4 complications, with each having an interesting solution:

- Hot melt adhesives never include crosslinking curatives – i.e., vulcanization chemicals. Vulcanization is initiated by heat, and heating the adhesive to apply it in melted form would start to vulcanize the polymer, even before it could be applied as intended. Therefore, I needed to find a way to avoid adding vulcanization chemicals directly to the hot melts. I solved this conflict by only using hot melt adhesive on surfaces that would be <u>assembled to</u> solid rubber surfaces, <u>which already contain curatives</u>. I knew that curative chemicals could migrate through rubber from regions of high concentration to regions of low concentration, especially at higher temperatures. <u>In contact with normal, uncured rubber surfaces, the hot melt would absorb the cure chemicals from the normal</u>

rubber surface and vulcanize itself in contact with that rubber. As far as I am aware, this was a totally innovative usage of hot melt adhesives.

- Rubber boots are assembled from multiple parts and layers. We could easily build boots using hot melt adhesives, but I would need a method to hold parts together during the vulcanizer cycle, when the high heat should melt the adhesive into a liquid which has no "holding power". My solution was to assemble parts onto the boots so that any parts using hot melt adhesive were overlaid by rubber parts that would hold them in place during vulcanization.

- If we applied hot melt adhesive to textile fabric parts (like linings, reinforcing parts, etc.), the porosity of the fabric would allow liquid hot melt to penetrate through the fabric and possibly bond to the aluminum lasts that the boots were built around. This would make it difficult to pull the finished boots off of the lasts. My solution was to specify that hot melt was not to be directly applied to porous fabric surfaces, but only applied to the facing rubber surfaces. That way, the contact between hot melt and the fabric surfaces was delayed – under the hot conditions of the vulcanizers, the hot melt would start to flow into the fabric, but simultaneously begin curing from contact with the rubber surface that it had been applied to. A compromise, but very successful.

- Deciding on application methods for the hot melt adhesive would be essential – our floppy rubber sheet layers and rubberized fabric parts might be difficult to apply hot melt to. Fortunately, the factory representative for our hot melt adhesive supplier was also familiar with hot melt equipment. Together we were able to develop methods and make decisions about application machinery. Training the workers to use the new equipment required the workers to abandon familiar techniques (which is always a challenge), but they succeeded in mastering the new skills.

The experience of becoming compliant with the 1990 Amendments was intimidating, at first. As I worked through the new approaches that were necessary, I was excited to realize that all of the elements of a solution were pre-existing – I just needed to combine them in a way that would work in the factory. This solution required most of a year to develop and implement, but it was similar to my experience with our factory becoming compliant to ISO 9000 – intimidating at first, but the effort was rewarding. Big projects like this – when successful -- can be some of the most satisfying work of a person's career.

Note: Since my old factory closed in 2001, and I began working independently in China, this vulcanized hot melt adhesive technology has been unused. In countries with fewer air pollution regulations, it's just too convenient to use solvent-based adhesives! Should rubber boot production ever return to the U.S., it would be a great choice for applications requiring vulcanizing adhesives.

4. Catalysis by color

At LaCrosse Footwear, we applied colored liquid latexes (or "latices") as narrow stripes on unvulcanized rubber strips. These rubber strips were used as foxing strips on certain boot styles. We did this for many years without any apparent problems. However, it emerged that for some time, a single color of latex (brown) was not "curing" properly. When the vulcanized boots with these strips were piled together after vulcanization, the colored latex was soft and sticky, causing the latex to transfer to any boots that it came into contact with. This caused extra work in our Packing Department, as workers had to scrub off the transferred color with organic solvent on a soft cloth. After Packing, it was also discovered that the sticky colored latex continued to transfer to the packing paper and from one boot to various areas on its mated boot.

Being "color-vision-impaired", I usually had no contact with issues related to color – my boss was responsible for formulating the colored latexes. However, I began hearing about this problem in various meetings, and started to research. I found that not only was the brown latex stripe soft and sticky, but also that the rubber foxing strip underneath the brown stripe was also slightly softer than the rubber foxing strip farther away from the latex. Unintended soft NR usually results from an "undercure" state (our first conclusion), or else by oxidation. Clearly, the stripe contained something affecting the rubber at a chemical level.

On reviewing the ingredients of the latex stripe, I found that the brown color depended on a pigment dispersion called "burnt umber". This pigment contained both manganese oxide (MnO_2) and a trace amount of copper oxide (CuO). Further reading in the industry literature brought me to the realization that both manganese and copper can catalyze the decomposition of NR (natural rubber) molecules. The oxides release their metal ions, which react with fatty acids (like stearic acid) to form soluble fatty acid salts, and these accelerate the thermo-oxidative decomposition of rubber. In other words, starting from the first mixing of the pigment with the latex, through the vulcanization cycle of the boots, and afterward, the burnt umber pigment was actively catalyzing rubber oxidation, cutting the rubber molecules into shorter, softer and stickier lengths.

After I presented this information to my boss, he re-formulated the colored latex stripe compound, using an alternative brown pigment. The problem immediately disappeared.

5. Giving directions to rubber

Anisotropy

As explained in my previous volume, Rubber Boots – Understanding an Industry, the hand-built or "laid-up" method of rubber boot construction requires calendering operations. Calendering draws rubber compound through a gap or "nip" set between 2 or more rollers. This creates a continuous sheet form, also known as a "band". Calendering can laminate rubber to fabric, and also produce rubber sheet – both materials are used for cutting into parts for rubber boot. As I also explained, "anisotropy" is the condition of a material when you have aligned its molecules in specific directions, imposing a parallel orientation to the rubber molecules, which didn't exist before the process occurred.

As calender rolls pull and squeeze the mass of rubber into a thin sheet or band, the long rubber molecules are forced to align. Since the rubber volume can't be changed:

- Passing the "band" of rubber between rollers compresses the rubber into a thinner sheet.
- Pulling the rubber through the narrow gap or "nip" between the rollers stretches the molecules longer, in the direction of calendering.
- This lengthwise stretching also pulls the "band" of rubber into a narrower strip on the exit side of the calender nip. In other words, the volume of the rubber is fixed, so as you stretch the band of rubber longer, the increase in length is compensated for by a narrowing of the band.

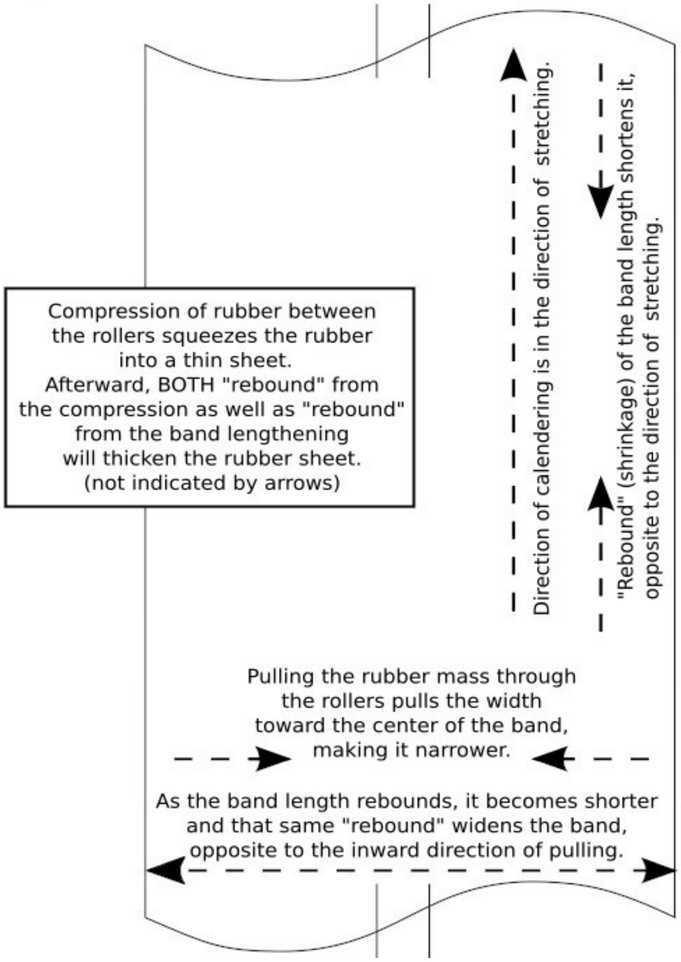
By this action, the disordered state of the rubber mass has been permanently altered by the calender. The heated rubber flows during the calendering process, then cools down and the band of rubber becomes "set" into its new dimensions. However, there are latent stresses that were not completely relieved when the rubber softened and flowed through the calender machinery. These residual stresses or "reaction forces" (Newtonian reaction forces) are "waiting" for a chance for the stresses to be relieved. In other words, the system has been loaded with a certain amount of mechanical "potential energy".

The state of these stresses is:

- The calendered rubber sheet has lengthwise anisotropy (orientation of the rubber molecules).
- The rubber has been compressed into a thinner sheet – this will tend to rebound (reaction force) into a thicker sheet.
- The sheet has been stretched in its length dimension – this will tend to rebound (reaction force) or "shrink" rubber boot parts into a shorter length. Additionally, this rebound will contribute to the rubber sheet becoming thicker.
- The band has been pulled into a narrower sheet width – this will tend to rebound (reaction force) into the band becoming wider.

Partial release of the potential energy will happen when the rubber molecules can become more mobile again, i.e., when the rubber is heated during vulcanization. After vulcanization happens, if any latent stresses remain from the rubber processing stage, they are permanently locked in place. Parallel orientation of the rubber molecules will be largely retained.

Note that the direction of anisotropy is also always the direction of greatest strength of any rubber part.


Compression, stretching and rebound -- the effect on a band of rubber compound.

A fixed volume of rubber will not change due to rubber processing. Any distortion in a certain dimension must be compensated for by changes in other dimensions.

Anisotropy + shrinkage solves a problem

I was assigned the task to reduce fabric usage in our rubber boots at LaCrosse Footwear. Higher quality fabrics are expensive, and they require a lot of processing in the factory, which adds further cost. However, when laminated with a rubber coating, they usually provide much greater tensile and tear strength to the boots, compared to rubber without fabric. As I worked on developing a high-strength rubber compound that could be calendered and replace fabric + rubber, I encountered the "problem" of anisotropy and rubber "shrinkage" (shorthand term for the rebound discussed above). My rubber formula (named "555") gave me excellent tensile and tear strength, but the "% shrinkage" test result was very high, about 40% – greater than we would have normally considered to be usable.

We already had a sporadic problem with anisotropy in our boot constructions. The normal upper rubber that was laminated to rubber-coated lining fabric was oriented toe-to-heel on the boot. Furthermore, the rubber-coated knit lining was also oriented toe-to-heel. There was another piece (rubber-coated fabric) in between those two layers, but it did not prevent the lining and the upper from shrinking in the direction toe-to-heel. Since the "toe spring" of the boot last created a concave surface over the vamp area, the shrinkage of these layers in the toe-to-heel direction occasionally caused <u>the entire vamp construction to lift off of the last and form a rounded ridge</u> along the middle of the vamp.

When we made cut rubber parts from 555 sheet, cut in the same direction that we always did, it only made this situation worse. But when we tried rotating the cutting direction of 555 by 90°, the strong side-to-side shrinkage of the 555 clamped the vamp layers firmly to the boot last, and solved that problem – as well as costing less than rubber-coated textile. The following diagram shows a boot without the outsole – so that the "toe spring" aspect can be clearer.

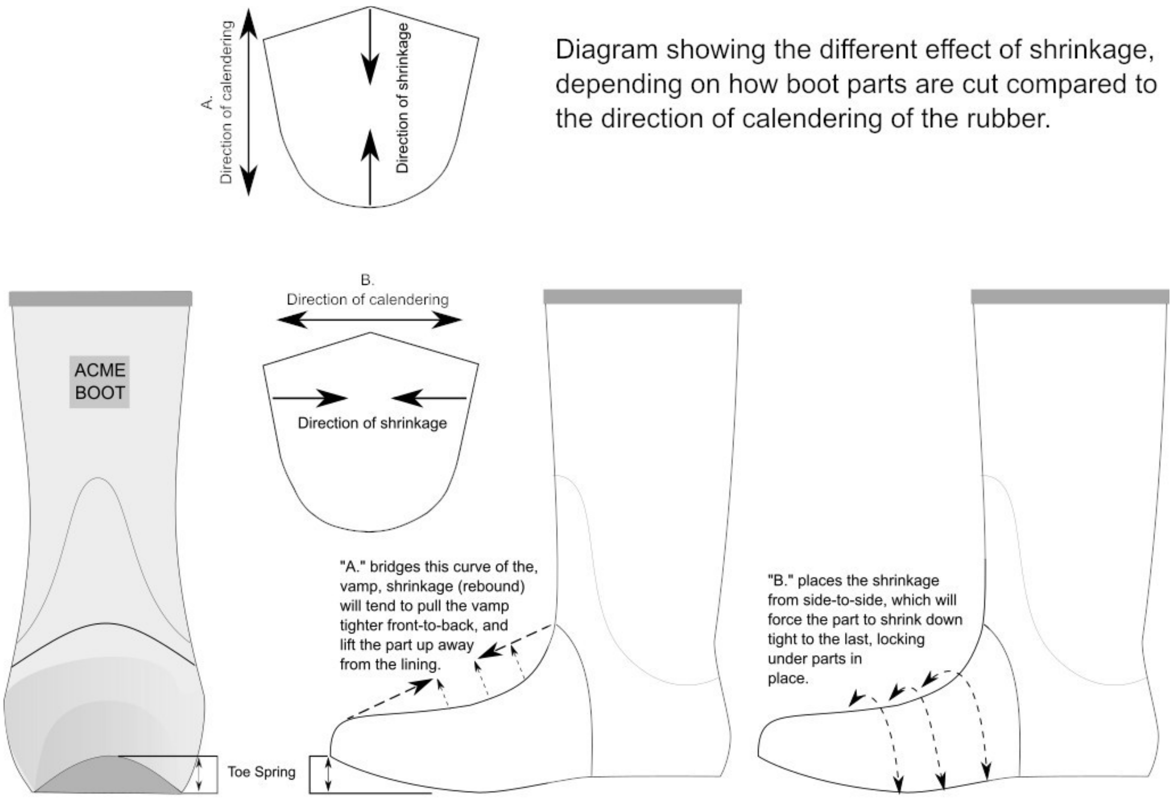


Diagram showing the different effect of shrinkage, depending on how boot parts are cut compared to the direction of calendering of the rubber.

6. A bad case of gas

Ozone – the worst gas in a dairy barn

Among many other responsibilities, I managed the wear test program for LaCrosse Footwear. I had a long list of people (mostly local to West-central Wisconsin and Southeast Minnesota) who were willing to receive and wear our boots for free, with the stipulation that they must wear them in their work environment. These testers were usually reliable people who gave our boots a fair test. The program provided extremely useful feedback about our products, which we used in order to constantly improve product performance.

Dairy farmers were some of my best testers because they're always working, and they very much need rubber boots. I learned most of what I know about "barnyard acid attack" on rubber from evaluating boots worn by dairy farmers (see Rubber Boots – Understanding an Industry). I had one case, however, where the farmer's boots were returned to me with a shocking amount of ozone cracking, a phenomenon I also discussed in my previous book. I made a special trip out to this farmer's location, to try to discover the cause of this ozone cracking.

Ozone (O_3) is, of course, created naturally in the upper atmosphere, and it serves an important purpose -- to protect the Earth from too much ultraviolet light. The ozone that is considered a pollution chemical is mostly the result of sunlight acting on pollution molecules down near the Earth's surface. However, there are other causes of ozone pollution – "corona discharge" from electrical fields in power transmission lines, transformers, motors, or other electrical equipment – including laser printers!. Chronic ozone exposure is considered a health risk, if the ozone formation takes place in closed locations without enough ventilation.

If you want to produce as much ozone as possible, look to anything that has electrical sparks. The biggest source of electrical sparks, of course, is lightning. Before and after a lightning storm, the smell of ozone is often quite evident, if you know what ozone smells like. If you pull a knit sweater over your head in the winter, or if you pull apart hot laundry from a clothes dryer, you'll often create sparks – the resulting "pungent, clean laundry" smell of ozone can be detected then as well.

When I was visiting this farm, I found the source of the ozone that had done such damage to my wear-test boots. Inside his dairy barn, the farmer had installed a very large bug-zapper – one of those devices that attracts flying insects with light, causing their bodies to bridge a gap between 2 electrically charged grids, exploding/killing the insects. If you've visited a farm with livestock, you'll know that flies and other insects are a big problem. When I was there, the sparking (and ozone production) was continuous, and the smell of ozone was quite strong. I informed the farmer about the cause of the boot cracking. I also warned him about the ozone concentration in the barn, and that long-term exposure can cause respiratory damage. However, I suspect that the bug-killing power of the device had more compelling value to him than any potential bad future effect on his health. That's often the way it goes, right?

7. The healing power of cold testing

Our Human Resources office at LaCrosse Footwear loved to give me workers who had been classified as “light duty”, people recovering from some fairly mild injury, or at a late stage of recovery from something more serious. When I had these workers, I would run “cold testing” at a frozen food warehouse across the street from our factory. Their huge freezer room would be set at around -8°F to -10°F. I and/or our Senior Lab Tech would dress up along with the light duty workers in insulated coveralls, and some of our styles of insulated boots. The boots would be wired with several thermocouple leads, in different standard locations in the boots. The leads were connected to small data-logger device, and we would record the temperature drop over time, alternating between walking and standing-still inside the freezer. We also took periodic notes about the comfort level of the test subjects (including ourselves).

When we started this program, we didn’t know how long we should stay in the freezer to get meaningful results. We soon arrived at a limit, however. When a thermocouple at the interior toe surface of our boots reached 52° F (11°C), every one of us always had the same thought: “OK, I’m not freezing yet, but I think that I should leave sometime soon.” It seemed like a universal reaction: 52°F at our toes triggered everyone’s awareness of discomfort, even if we otherwise felt acceptably warm.

To return to the subject of “light duty” workers: There was always a need for this kind of testing, so that we could evaluate our insulation strategies. However, one half-day of this work would usually lead workers to report to HR that they felt well enough to return to normal duties. The HR Department was always grateful for the miraculous healing power of our cold-testing program.

8. Bubble troubles

A vulcanizer is a heated, pressurized “autoclave”, which has an internal air environment (sometimes the air is largely replaced by water steam). If there is some gaseous material within the body of the rubber products, and if the amount of gaseous material is small, this pressurization will prevent the formation of bubbles in the rubber. In this case, the vulcanization of rubber will proceed to completion, and the rubber network is tight and strong. When the pressure is released at the end of the vulcanization cycle, any gases present in the cured rubber will slowly migrate out of the rubber, causing no damage. However, there are several situations that can develop which are not so benign, and which can damage the finished products.

At LaCrosse Footwear, we encountered problems many times with rubber boots that were cosmetically defective or functionally defective, due to gas formation and expansion during the vulcanization cycle. The problems were not easy to solve, due to the difficulty of controlling the causative conditions (mainly, the weather).

Water

Natural rubber is a good barrier to water, which is why it makes great rain boots. In many cases, NR provides all of the barrier needed to shield people or things from undesired conditions. But the material NR is somewhat permeable to gases and many liquids, including (with a sufficiently long exposure period) water. During manufacturing, any absorbed water (or other liquid) can create problems for the factory.

- Hygroscopy – During the compound mixing process some of the ingredients may introduce a small amount of water into the rubber batch. Any ingredient with some "hygroscopic" (water-attracting) property, like precipitated silica, can introduce water into the mixed compound, as well as any ingredient that may have become contaminated with water. Even high humidity can result in rubber absorbing some small amount of water. Raw NR, as a natural agricultural product, contains a variable amount of salt. This salt content can create a hygroscopic effect which aggravates absorption of water from the air into the raw rubber. Often a factory will hold its inventory of raw NR in a heated room – this can reduce the water content, before using it in a rubber compound.
- Humidity + solvent evaporation – Organic solvents (for example, heptane for NR or MEK for CR/Neoprene rubber) will often be used as liquid solvents in adhesives, or to "activate" an uncured rubber surface, so that rubber surfaces are sticky enough to bond together. In warm, humid weather the applied adhesive or solvent will cool the rubber surfaces as it evaporates. If the "dew point" of the ambient air is high enough, this cooling can result in a thin film of water condensation "**ad**sorbed" onto the rubber surfaces. If the water film persists long enough, or if water is trapped between surfaces that are stacked together or assembled together, the water can be absorbed into the rubber compound. Even if not absorbed into the rubber per se, any trapped water film sitting between assembled layers of uncured rubber boots will be a huge problem.

The absorption of water due to contamination with water during mixing or other handling has an unfortunate result. Absorbed water will turn into gaseous steam during the hottest parts of the vulcanizer cycle, and the steam will form bubbles in the rubber material. These bubbles will disrupt the bonding of rubber chains into a strong network during vulcanization, and will also reduce the density of the rubber – thus reducing the strength properties. At the end of a vulcanizer cycle, when the interior air pressure is released, bubbles will expand – creating structural damage to the vulcanized rubber network -- and also cause severe cosmetic defects on the surfaces of finished boots.

Adsorbed water (a film sitting on rubber surfaces) has an equally disruptive effect. If this water is trapped between assembled parts, the resulting steam will literally blow the assembled layers apart at the end of the vulcanization cycle – when the vulcanizer pressure is released. The boots can look like a balloon coming out of the vulcanizer, or actually be blown open.

Gases

Aside from water, absorbed gases in rubber have 2 sources:

1. The gaseous reaction byproducts of the chemical reactions that occur inside the rubber during vulcanization. Rubber formulations typically use a combination of chemically-reactive ingredients in order to achieve the fully-cured state of vulcanization. These reactions will also form some reaction byproducts that are smaller gaseous molecules, which can potentially blow into bubbles upon the release of pressure. Normally, reaction byproducts have a low concentration in the rubber, so that they will only cause a problem if there is incomplete vulcanization: if the vulcanization time, temperature or pressure parameters are not correct. In that case the gases can form bubbles before the rubber network is strong enough to resist them. For example, if an air pressure valve leaks during the vulcanization cycle, or if the heating system fails, you can expect to see bubbles formed on the surfaces of the rubber boots, resulting in cosmetic defects.
2. Absorbed liquid solvents that result from applying solvent-based adhesives (or pure solvent) to improve the "tackiness" (stickiness) of the rubber surface. Typically some amount of solvent will be absorbed by the rubber material. If the rubber parts are not given enough drying time prior to assembly, there can be sufficient absorbed solvent to blow into gas bubbles when the air pressure is released – or even blow apart laminated layers.

Gaseous reaction byproducts can form bubbles in upper rubber if vulcanization is incomplete (see #1 above).

It is theoretically easy to prevent problems with absorbed/adsorbed water or organic solvents.

- Compound ingredients should be thoroughly dry <u>before</u> mixing rubber batches.
- Processed parts that require adhesive or a solvent wash should be given enough drying time so that water or solvent liquids can completely evaporate from the rubber parts and

their surfaces. Drying time can be augmented by additional heating, and/or by dehumidification of the ambient air in the assembly areas.

- Vulcanizer/autoclave equipment should be in good working order, with curing parameters regularly monitored.

<u>In practice</u>, it can sometimes hard to maintain the required conditions to avoid bubble/expanded gas formation.

- Often, factory management will be focused more on production rate rather than the problems that can possibly result. Management may push the factory to speed up the boot-making process to a point that creates marginally acceptable results – good enough to mostly have good production, but sometimes resulting in product that is marginally acceptable or outright defective. Speeding up production can come with a cost.
- Adding dehumidifier equipment to the production area is a good solution to problems caused by excess humidity inside the rubber footwear factory. However, consider that use of solvents in the production process will require good ventilation of work areas, with replacement fresh air. Otherwise, the solvent creates possible worker exposure violations, and can cause an explosion hazard. The cost of dehumidification can be significant, and we also have to accept that there will be a continuous flow of humid air into the work area, which must pass through dehumidification equipment. At LaCrosse Footwear, we eventually used the fairly crude method of placing ordinary room dehumidifiers at each production "jack" to create a local area of lower humidity. We then shut some of the windows in the assembly areas – enough to allow fresh air replacement, but without a high flow of humid air overwhelming the dehumidifiers. Fortunately, our northern climate only made this awkward arrangement necessary during our hot, humid summers.

<u>Warning</u>: Usually managers will not allow cosmetically defective product to ship, but there is a certain case that is more of a functional problem: boots which have layers that were blown apart after the release of vulcanizer pressure. These boots will look like balloons when removed from the vulcanizer – typically in the sole region of the boot – but after cooling, they may contract back to a condition where the internal layer separation is not obvious. This misleading condition sometimes happens when a molded outsole is used, since the outsole part was already vulcanized into its final shape during the earlier molding process.

Assuming that the sole edges were not blown open, the gas filling the void between the outsole and midsole layers contracts upon cooling, and many boots could (visually, at least) be passed as 1st Quality. The "warning" here is that such boots are fatally compromised – any significant use will result in excess flexing around the edges of the outsoles and foxing, and they will probably fail very prematurely. I've negotiated with managements on a number of occasions to declare such boots defective. <u>If a company has any warranty obligation with their product, they need to understand that the return for refund of "cosmetically acceptable but functionally defective" product (including shipping costs) can be much more costly than just discarding the product at the factory</u>.