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

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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

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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.

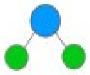
A molecule is 2 or more atoms joined by a shared electron bond, called a "covalent" bond. In this kind of bond, the positively charged atom nuclei share their negatively charged electrons, but if the atoms are of different elements they may not share the electrons equally. The electrons will be denser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

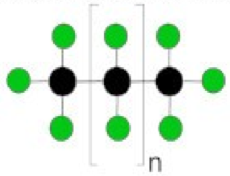
To be clearer, we can say that the electrostatic attraction of polar NBR molecules to each other is so strong that it excludes (literally "squeezes out") any NR molecules that may be inserted between NBR molecules. A mundane example of this effect is seen by mixing olive oil and water. The electrostatic 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

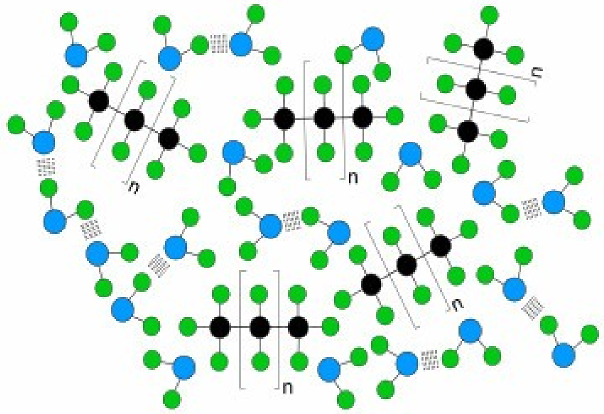


Non-polar molecule: Generalized alkane hydrocarbon
Black = Carbon
Green = Hydrogen

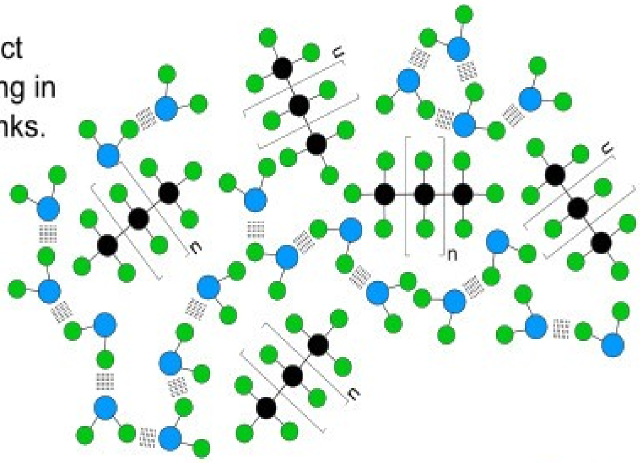


|||||| = Hydrogen bond

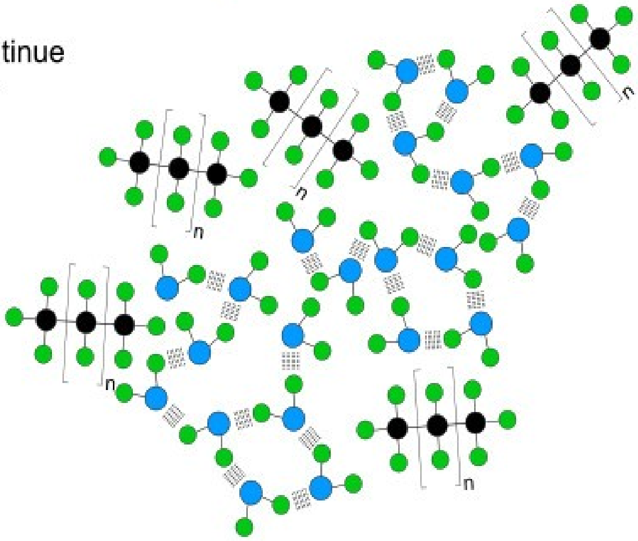
Mixture is well agitated.



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:

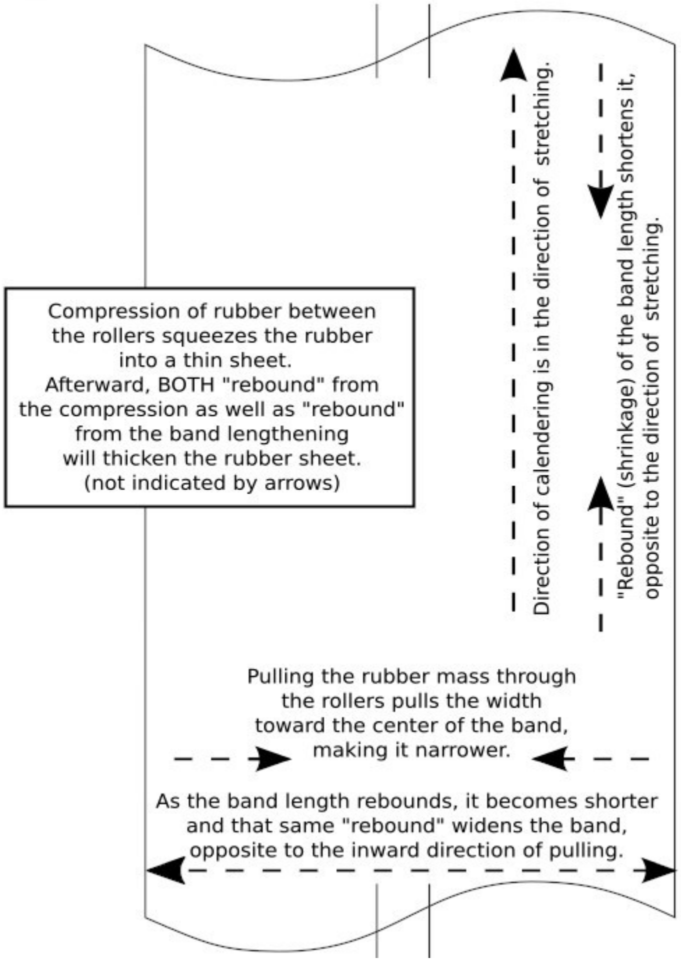
- The calendered rubber sheet has lengthwise anisotropy (orientation of the rubber molecules).
- The rubber has been compressed into a thinner sheet – this will tend to rebound (reaction force) into a thicker sheet.
- The sheet has been stretched in its length dimension – this will tend to rebound (reaction 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 the entire vamp construction to lift off of the last and form a rounded ridge 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.

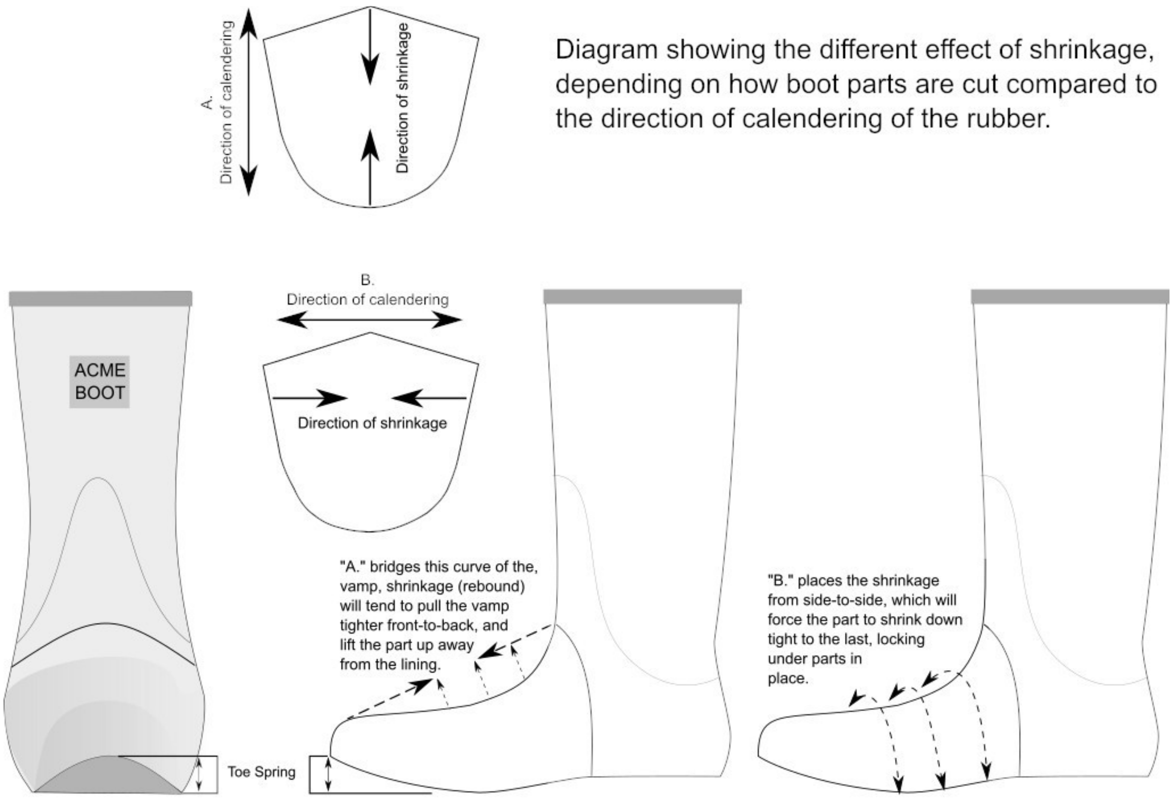


Diagram showing the different effect of shrinkage, depending on how boot parts are cut compared to the direction of calendering of the rubber.

"A." bridges this curve of the, vamp, shrinkage (rebound) will tend to pull the vamp tighter front-to-back, and lift the part up away from the lining.

"B." places the shrinkage from side-to-side, which will force the part to shrink down tight to the last, locking under parts in place.

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>.