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PRESENT STATUS
OF
DESULFURIZATION TECHNOLOGY

(INTERNAL REPORT)

Abbreviations and Acronyms

BR	Butadiene rubber
C-C	Carbon-carbon
C-S	Carbon-sulfur
EPDM	Ethylene propylene diene monomer
GRT	Ground rubber tire, or ground tire rubber
NR	Natural rubber
PPH	Parts per hundred
RRM	Renewable resource material
SBR	Styrene-butadiene rubber
S-S	Sulfur-sulfur
DD-CR	Dynamic Desulfurization of Crumb Rubber
HTDD-CR	High Temperature Dynamic Desulfurization of Crumb Rubber
POTW	Publicly Owned Treatment Works

Chapter 1 - Introduction

Approximately 25 potential devulcanization technology researchers and developers were identified throughout the world, however, only a very small number of devulcanization systems are now operating. These are primarily small-capacity systems, which are devulcanizing natural or synthetic rubbers (as opposed to devulcanizing the mixture of rubbers recovered from waste tires).

The general types of devulcanization technologies identified and analyzed in the study are shown below.

Technology	Basis of Processing	Zone of Reaction
Chemical	Chemicals/chemical reactions	Surface of particles
Ultrasonic	Ultrasonic waves	Throughout particles
Microwave	Microwaves	Throughout particles
Biological	Microorganisms	Surface of particles
Other	Mechanical Steam	Surface of particles

Key findings

- Reliable information and data on devulcanization of waste tire rubber are difficult to obtain due to proprietary claims, efforts to hide poor or infeasible process performance and product quality, and the limited number of technology researchers and developers and of peer-reviewed data. Reliable data relating waste tire characteristics, devulcanized rubber quality, end product performance, and production costs is scarce.
- Only a very small number of low-capacity devulcanization systems are operating in the United States (at approximately 50 Kg /hr, all R&D scale, mechanical, or ultrasonic). No proven commercial capacity units could be found that are currently devulcanizing waste tires, for example, at 500 Kg/hr or greater. The likely reasons include insufficient product quality and high costs of production.
- **In terms of the potential of producing high-quality devulcanized rubbers (for example, high strength), the best technology appears to be ultrasonic, based on the current state of the art.**
- Devulcanization of single rubbers has much more history than that of multi-rubber mixtures such as waste tires. Only a few companies devulcanize single formulation rubber as a result of captive conversion or merchant scrap recovery from manufacturing. The production of devulcanized rubber from home manufacturing scrap in the U.S represents about 1 to 2 percent of total U.S. rubber consumption.
- The quality of devulcanized single rubbers is higher than that of devulcanized multiple rubbers.
- Devulcanization that depends on surface devulcanization technologies (for example, chemical and mechanical) appears destined in the near term to produce low- or medium-quality devulcanized rubber material.
- The estimated cost for producing devulcanized materials from waste tires is \$0.3 to \$0.6/Kg ± 30 percent, **if including the cost of crumb rubber feedstock**. This range of production costs is significantly greater than that of virgin rubbers.

A typical tire compound contains the following constituents:

Table 1. Composition of Tires

Passenger Tire	Constituents	Common Materials
Natural rubber	14%	Natural rubber
Synthetic rubber	27%	SBR, butadiene rubber
Carbon black	28%	Carbon black
Steel	14%–15%	Steel
Fabric, fillers, accelerators, antiozonants, etc.	16%–17%	Polyester, nylon, aromatic oil, coumarine resin, silica, bonding agent, stearic acid, antioxidant, processing chemicals, sulfur, zinc oxide
Truck Tire		
Natural rubber	27%	Natural rubber
Synthetic rubber	14%	Synthetic rubber
Carbon black	28%	Carbon black
Steel	14%–15%	Steel
Fabric, fillers, accelerators, antiozonants, etc.	16%–17%	Polyester, nylon, aromatic oil, stearic acid, antioxidant, wax, processing chemicals, sulfur, zinc oxide

Source: Rubber Manufacturers Association, 2004.

- *Reclaiming* is a procedure in which scrap tire rubber or vulcanized rubber waste is converted—using mechanical and thermal energy and chemicals—into a state in which it can be mixed, processed, and vulcanized again. The principle of the process is devulcanization (Franta, 1989). Historically and practically, in the concept of rubber reclaiming, devulcanization consists of the cleavage of intermolecular bonds of the chemical network, such as carbon-sulfur (C-S) and/or sulfur-sulfur (S-S) bonds, with further shortening of the chains also occurring (Rader, 1995). This description of devulcanization is different than that given below, which is limited to chemical interactions involving sulfur atoms.

- **Reclaim is an interesting raw material as it reduces the production costs of new rubber articles, due to shorter mixing times and lower power consumption. The processing temperature is lower, and the material has a higher dimensional stability during calandering and extrusion due to the remaining three-dimensional network. The most important advantage of cured articles containing reclaim in terms of properties is an improvement of aging resistance.**

- Devulcanization is the process of cleaving the monosulfidic, disulfidic, and polysulfidic crosslinks (carbon-sulfur or sulfur-sulfur bonds) of vulcanized rubber. Ideally, devulcanized rubber can be revulcanized with or without the use of other compounds. The different types of devulcanization processes also modify other properties of the rubbers. These processes cause diminution of some properties over those of the parent rubber. Ideally, devulcanization would yield a product that could serve as a substitute for virgin rubber, both in terms of properties and in terms of cost of manufacture.

Polymers can be divided into two groups: thermoplastics and thermosetting materials. Thermoplastics soften when heated, making it possible to (re-)shape them at higher temperatures. Thermosetting materials, like rubbers, are crosslinked on heating and therefore cannot be softened or remodeled by raising the temperature. Therefore, thermosets are more difficult to recycle compared to thermoplastics. The three-dimensional network has to be broken in order to make the material (re-)processable: the so-called reclaiming process. In this process, either sulfur crosslinks connecting the polymer chains or carbon-carbon bonds in the polymer backbone are broken. The first mechanism is preferred, as the backbone of the polymer remains intact. Scission can be obtained by heat, shear or chemical reactions. Basically, processes of rupturing the rubber network by crosslink or main-chain scission can be classified into five main groups.

- Thermal reclaiming;
- Thermo-mechanical reclaiming;
- Mechano-chemical reclaiming;
- Reclaiming by radiation, and
- Microbial reclaiming.

In actual practice, combinations of thermal and mechanical reclaiming are mostly used, with in some cases the addition of a devulcanization aid for chemical reclaiming.

1.1-Thermal Reclaiming

For this kind of processes, heat (often combined with addition of chemicals) is used to break the sulfur bonds and thus to plasticize the rubber. Hall patented in 1858 one of the oldest and most simple processes in the rubber reclaiming industry, *the Heater* or *Pan process (Oil law)*. In this process, finely ground natural rubber powder is mixed with oils and reclaiming agents and treated with high or medium pressure steam at temperatures varying from 170°C to 200°C. The reclaiming time is long and the homogeneity of the reclaim is low, but this process is able to reclaim a large number of polymers: natural rubber (NR), styrene-butadiene rubber (SBR), chloroprene rubber (CR), acrylonitrile-butadiene rubber (NBR) and butyl rubber (IIR) and the equipment is rather inexpensive.

The use of the heater or pan process became less popular after Marks patented the *Digester* or *Alkali process* in 1899. The fibers of the rubber scrap, remnants of the tire carcass, were first removed by mixing it with alkali, water, plasticizing oils and, if needed, chemical peptizers. The mixture was heated in a jacketed, agitator equipped autoclave to 180-210°C. The most important disadvantage of this process is the pollution generated by the chemicals. Modifications of this process minimized the pollution, but increased the reaction times. Processes with short reaction times are for example the *High Pressure Steam processes* or the *Engelke process*. In the first process, a fiber-free, coarse ground rubber is mixed with reclaiming agents, and reclaiming is done in a high-pressure autoclave at approximately 280°C. In the latter process, coarse ground rubber scrap is mixed with plasticizing oils and peptizers and is put into small autoclaves. The material is heated to very high temperatures for a short period of 15 minutes, after which it is lead through refiners (mills with very narrow gaps) and strainers.

1.1.1 - Steam With or Without Chemicals (Digester, DD-CR, HTDD-CR)

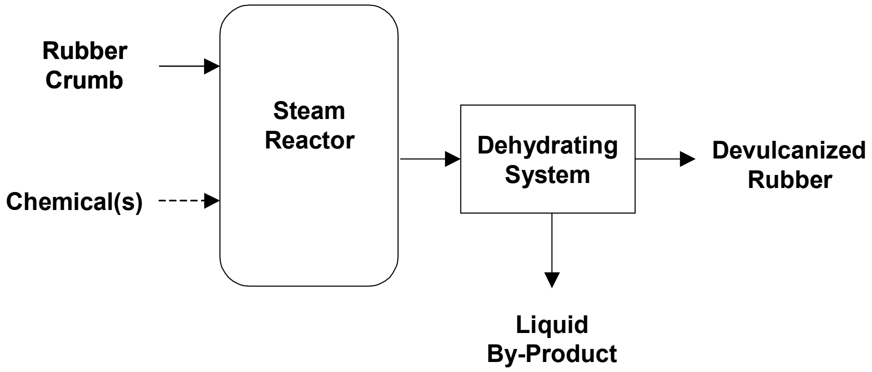
Steam devulcanization of crumb rubber uses a steam vessel equipped with an agitator for continuous stirring of the crumb rubber while steam is being applied. There are two variants of the basis steam process, namely, “wet” and “dry.” The wet process uses caustic and water mixed with the rubber crumb, while the dry process uses only steam.

If necessary, various reclaiming oils may be added to the mixture in the reaction vessel. In one case, a wet process using diaryl disulfide and reclaiming oils with saturated steam at 190°C

(374°F) was fed finely ground NR and synthetic rubber scraps. A charge of about 440 lbs. was partially devulcanized after 15 to 17 hours of processing. This process required 12 hours at ambient temperature for pre-treatment and 3 to 5 hours for steam or high temperature treatment (Adhikari, et al., 2000).

The dry process digester has the advantage of generating less pollution than the wet process. Scrap rubber containing natural and synthetic rubbers can be reclaimed by the steam digestion process. Reclaiming oil used for this process has molecular weights between 200 and 1000, consisting of benzene, alkyl benzene, and alkylate indanes. A generic processing diagram for steam devulcanization is shown in Figure A.

Figure A. Schematic Diagram of a Steam Devulcanization System



1.2 - Thermo-Mechanical Reclaiming

The thermo-mechanical reclaiming processes make use of shearing forces to plasticize the rubber. Energy is introduced into the materials, resulting in a significant temperature increase, high enough to cause thermal degradation. The *Lancaster-Banbury process* is one of the oldest processes. Fiber-free coarse ground rubber scrap is mixed with reclaiming agents and sheared in a high speed, high-pressure internal mixer. When a continuously working, multiscrew devulcanizer is used instead of the internal mixer, the process is called the *Ficker reclaiming process*.

One of the first continuous reclaiming processes is the so-called *reclaimator process*. This is basically a single screw extruder that has been adapted to reclaim fibre-free rubber scrap in very short extrusion times. The short extrusion times make this method suitable for SBR, that tends to harden when longer recycling times are applied.

Another mechanical reclaiming process is the ***De-Link process***. In this process finely ground rubber powder is mixed with the De-Link masterbatch (**DeVulc**) : a zinc salt of dimethyldithiocarbamate and mercaptobenzothiazole in a molar ratio of 1:1 to 1:12, dispersed in thiols and activated by stearic acid, zinc oxide and sulfur. Advantages of the process are its simplicity and the fact that standard rubber equipment is used. No evidence is available to demonstrate that the De-Link process is used beyond laboratory or pilot scale.

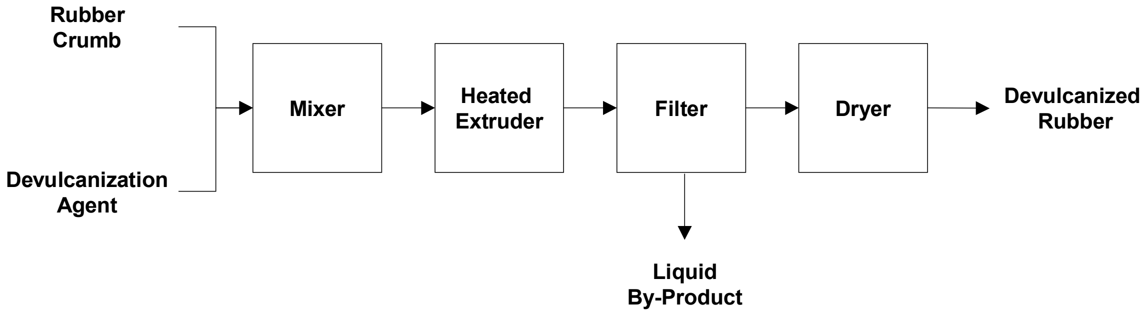
The Toyota process is another development of mechanical reclaiming. In this process a mixture of ground rubber, virgin rubber, oils and a devulcanization aid is masticated on a two-roll mill or in an extruder. Mechanical devulcanization is achieved through the repeated deformation of rubber particles under specific conditions of temperature and pressure.The result is a devulcanized rubber, ready for further processing.

Toyota developed another continuous process, Toyota Gosei (TG) combining pulverization, reclaiming and deodorization. The rubber waste has to be ground to a particle size of 5-10 mm before it can be fed into a “modular screw-type reactor” with a pulverization zone and a reaction zone. The operating temperature is in the range of 100-300°C and 100-900 rpm screw speeds are applied, the process requires about 100 Kw (kilowatts) to process 200 to 300 kg (kilograms)/hr of rubber, or approximately 0.4 kW/kg. By manipulating screw configuration and rotational speed, and processing temperature, researchers are able to control the duration of the treatment. In this way they can, to some extent, control the properties of the devulcanizate.The TG process has been primarily, if not exclusively, used to devulcanize specific types of rubber compounds, such as NR and SBR.

1.3 - Mechano-Chemical Reclaiming

Mixing of the rubber powder with a peptizer (chemicals used to reduce the viscosity of NR) and a reclaiming agent prior to the mechanical breakdown of the material improves the reclaiming process. The devulcanization aid is supposed to selectively break the sulfur crosslinks in the rubber network. This chemical breakdown is combined with input of thermal and/or mechanical energy, as the rate of this process is sufficiently high only at higher temperatures. The most common devulcanization aids are disulfides, e.g. aryl disulfides or diphenyl sulfides, thiophenols and their zinc salts and mercaptanes. These chemical compounds are radical scavengers: they react with the radicals generated by chain- or crosslink scission and prevent recombination of the molecules. Typical concentrations for the reclaiming agents are 0.5 to 4 wt%. Suitable peptizers are aromatic and naphthenic oils with a high boiling point.

Figure B. Schematic Diagram of a Chemical Devulcanization System



Unfortunately, a detailed accounting of test materials, performance parameters, and conditions is lacking, thus inhibiting the extent of interpretation of the data. Comparisons of data are primarily limited to comparing the properties of virgin rubbers with compounds containing the virgin and devulcanized material at concentrations of about 30 percent devulcanized material. As shown by the data in the table, the properties of the mixtures containing devulcanized material are in general moderately lower than those of their virgin counterparts.The reported data reflect two different types of chemical devulcanization technologies.

Table 2. Properties of Waste Tire Rubber Devulcanized Using Chemical or Chemical/Mechanical Technology

Generic Technology	Technology Surrogate	Test Rubber Compounds	% Devulc (or Ground) Mat'l	Mooney Viscosity (ML-4 @ 212°F)	Tensile Strength (lbs/in^2)	300% Modulus (lbs/in^2)	Elongation to Break (%)
Chemical	STI-K Polymers DeLink[a]	NR	0	61.9	4,270	1,987	534
		NR w/devulc NR	30	72.3	4,020	2,151	489
		Virgin SBR (1520)	0	96.6	3,880	3,059	358
		SBR (1520) w/devulc SBR	30	109.2	3,580	2,923	345
Chemical/ Mechanical	LandStar/ Guangzhou Research Institute[b]	NR	100	28.4			680
		SR	100	17.2			514
		AMR[c] Powder (devulc. additive)	100	23.9			640
		Tread Tire Compound[d]	0	20.3			772
			28.6	19.7			628
		Light Duty Truck Tire Compound[e]	0	23.8			536
			28.6	20.5			500

1.4 - Reclaiming by Irradiation

Bond type	Dissociation energy (KJ/mol)
C-C	349
C-S	302
S-S	273
Polysulfidic	253

Table 3. Typical bond energies

1.4.1 - Ultrasonic

Rubber devulcanization by using ultrasonic energy was first discussed in Okuda and Hatano (1987). It was a batch process in which a small piece of vulcanized rubber was devulcanized using 50 kHz ultrasonic waves after treatment for 20 minutes. The process apparently could break down C-S and S-S bonds, but not carbon-carbon (C-C) bonds. The properties of the revulcanized rubber were found to be very similar to those of the original vulcanizates.

One continuous process for devulcanization of rubbers is based on the use of high-power ultrasound electromagnetic radiation. This is a suitable way to recycle waste tires and waste rubbers. The ultrasonic waves, at certain levels, in the presence of pressure and heat, can quickly break up the three-dimensional network in crosslinked, vulcanized rubber. The process of ultrasonic devulcanization is very fast, simple, efficient, and it is free of solvents and chemicals. The rate of devulcanization is approximately one second. This may lead to the preferential breakage of sulfidic crosslinks in vulcanized rubbers. (Isayev, 1993; Yu. Levin, et al., 1996; Isayev, et al., 1997; Yun, et al., 2001; Yun & Isayev, April 2003).

Under a license from the University of Akron for the ultrasonic devulcanization technology, NFM Company of Massillon, Ohio, has built a prototype of the machine for ultrasonic devulcanization of tire and rubber products (Boron, et al., 1996; Boron, et al., 1999). It was reported that retreaded truck tires containing 15 and 30 weight percent (percent by weight) of ultrasonically-devulcanized carbon black-filled SBR had passed the preliminary dynamic endurance test (Boron, et al., 1999).

Extensive studies on the ultrasonic devulcanization of rubbers, and some preliminary studies on ultrasonic decrosslinking of crosslinked plastics, showed that this continuous process allows recycling of various types of rubbers and thermosets (Isayev, 1993; Hong & Isayev, 2002 (pp. 160–168); Shim, et al., 2002; Shim & Isayev, 2003; Gonzalez-de Los Santas, et al., 1999).

As a consequence of the process, ultrasonically-devulcanized rubber becomes soft, therefore enabling this material to be reprocessed, shaped, and revulcanized in very much the same way as virgin rubber. This new technology has been used successfully in the laboratory to devulcanize ground tire rubber (commonly referred to in the industry as GRT) (Isayev, et al., 1995; Yun, et al., 2001; Boron, et al., 1996), unfilled and filled rubbers N (Hong & Isayev, 2001; Yu. Levin, et al., 1996; Isayev, et al., 1997; Diao, et al., 1998; Shim, et al., September 2002; Ghose & Isayev, 2003), guayule rubber (Gonzalez-de Los Santas, et al., 1999), fluoroelastomer, ethylene vinyl acetate foam, and crosslinked polyethylene (Isayev, 1993; Isayev & Chen, 1994). After revulcanization, rubber samples exhibit good mechanical properties, which in some cases are comparable to or exceeding those of virgin vulcanizates.

Structural studies of ultrasonically-treated rubber show that the breakup of chemical crosslinks is accompanied by the partial degradation of the rubber chain; that is, the C-C bonds (Isayev, et al., 1995; Tukachinsky, et al., 1996; Yu. Levin, et al., 1997 (pp. 641–649); Yushanov, et al., 1998). The degree of degradation of C-C bonds can be substantial, depending on conditions. The mechanism of rubber devulcanization under ultrasonic treatment is presently not well understood, unlike the mechanism of the degradation of long-chain polymer in solutions irradiated with ultrasound (Suslick, 1988).

Ultrasonic devulcanization also alters the revulcanization kinetics of rubbers. The revulcanization of devulcanized SBR appeared to be essentially different from those of virgin SBR (Yu. Levin, et al., 1997, pp. 120–128). The induction period is shorter or absent for revulcanization of devulcanized SBR. This is also true for other unfilled and carbon black-filled rubbers such as ground rubber tire (GRT), SBR, natural rubber (NR), ethylene propylene diene monomer (EPDM), and butadiene rubber (BR) cured by sulfur-containing curative systems, but not for silicone rubber cured by peroxide.

Ultrasonically-devulcanized rubbers consist of sol and gel. The gel portion is typically soft and has significantly lower crosslink density than that of the original vulcanizate. Due to the presence of sol and soft gel, the devulcanized rubber can flow and is subject to shaping. Crosslink density and gel fraction of ultrasonically-devulcanized rubbers were found to correlate by a universal master curve (Yushanov, et al., 1996; Diao, et al., 1999; Yushanov, et al., 1998). This curve is unique for every elastomer due to its unique chemical structure.

In a comparative analysis of ultrasonically reclaimed unfilled SBR, NR and EPDM rubbers, it was found that it was more difficult to reclaim EPDM than NR and SBR. Reclaiming of EPDM roof-sheeting resulted in a good quality reclaim, which after revulcanization showed more or less equal mechanical properties compared to the virgin compound. The surface smoothness of the revulcanized compounds could be controlled by the process conditions.

Most companies marketing ultrasonic devulcanization technologies are utilizing very similar technologies involving cold feed extruders and varying physical arrangements of ultrasonic equipment.

Ultrasonic devulcanization technology is actually composed of a “devulcanization system”—namely, extrusion and ultrasonic processing. Two key differences in some cases are the equipment and materials used to generate the ultrasonic energy required for the process, and the positioning of the transducer(s) relative to the extruder.

Two different arrangements of ultrasonic devulcanization systems are shown in Figures C and D. In this type of devulcanization system, size-reduced rubber particles are loaded into a hopper and are subsequently fed into an extruder. The extruder mechanically pushes and pulls the rubber. This mechanical action serves to heat the rubber particles and softens the rubber. As the softened rubber is transported through the extruder cavity, the rubber is exposed to ultrasonic energy.

The resulting combination of heat, pressure, and mechanical mastication is sufficient to achieve varying degrees of devulcanization. The time constant of the devulcanization process takes place in seconds. Essentially all of the rubber entering the process is discharged from the extruder in semi-solid product stream. Process losses would be primarily those due to emissions of fine particulates or of gases, if any, generated due to the mechanical and thermal processes occurring during the devulcanization process. After exiting through the extruder die, the rubber is passed through a cooling bath and then dried.

Figure C. Schematic Diagram of an Ultrasonic Devulcanization System Showing a Mid- Extruder Location for the Ultrasonic Subsystem

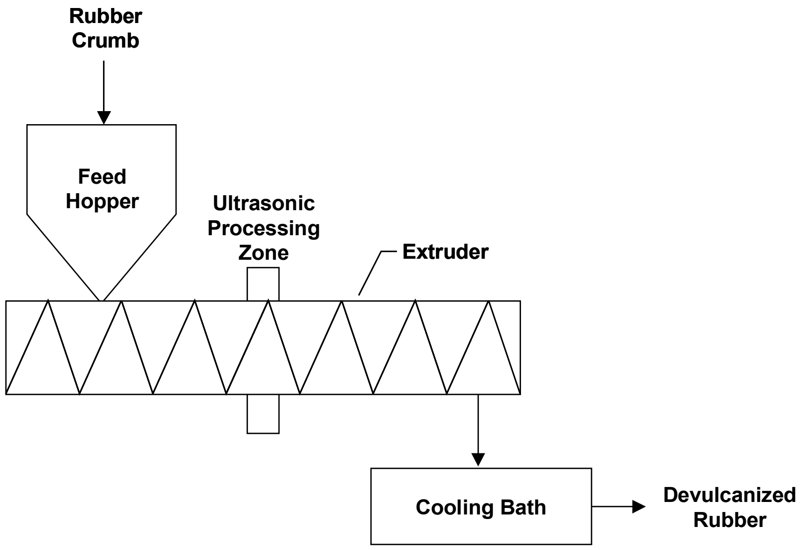


Figure D. Schematic Diagram of an Ultrasonic Devulcanization System Showing the Ultrasonic Subsystem Located at the Discharge End of the Extruder

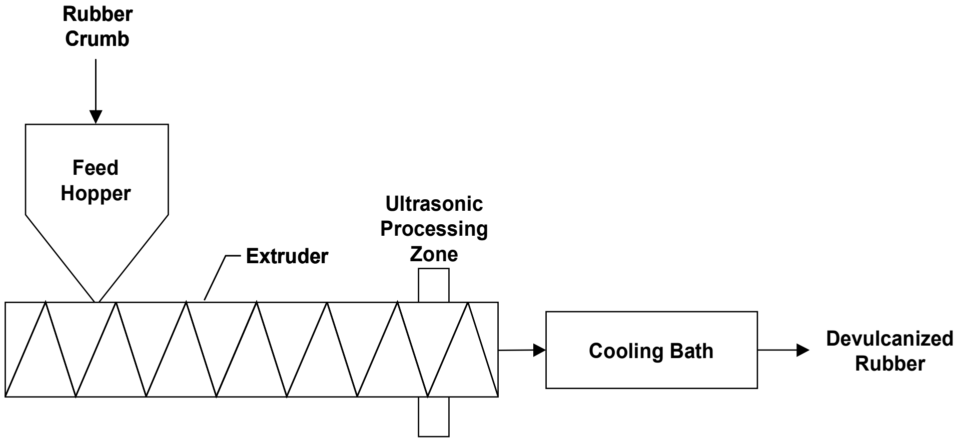


Table 4. Properties of Waste Tire Rubber Devulcanized Using Ultrasonic Technology

Technology Surrogate	Test Rubber Compounds	% Devulc or (Ground) Mat'l	Mooney Viscosity (ML-4 @ 212˚F)	Tensile Strength (lbs/in^2)	100% Modulus (lbs/in^2)	300% Modulus (lbs/in^2)	Elongation to Break (%)
U of Akron	SBR 1848[a]	0		2,415		740	780
	SBR (1848) w/devulc SBR[a]	10		1,075		790	540
	SBR (1848) w/whole train reclaim[a]	(10)		1,940		760	660
	SBR (1848) w/30 mesh buffings[a]	(10)		1,440		780	480
	100% NR (SMR CV60) & 0% SBR (23.5% bound styrene, and Duraden 706)[b]	0		3,263	116		670
	NR (SMR CV60) & 25% SBR (23.5% bound styrene, and Duraden 706)[b]	0		1,885	123		600
	NR (SMR CV60) w/devulc SBR (23.5% bound styrene, and Duraden 706)[b]	25		580	123		380
	NR (SMR CV60) & 50% SBR (23.5% bound styrene, and Duraden 706)[b]	0		406	131		390

Technology Surrogate	Test Rubber Compounds	% Devulc or (Ground) Mat'l	Mooney Viscosity (ML-4 @ 212°F)	Tensile Strength (lbs/in^2)	100% Modulus (lbs/ in^2)	300% Modulus (lbs/ in^2)	Elonga-tion to Break (%)
	NR (SMR CV60) w/devulc SBR (23.5% bound styrene, and Duraden 706)[b]	50		363	123		320
	NR (SMR CV60) & 75% SBR (23.5% bound styrene, and Duraden 706)[b]	0		363	145		295
	NR (SMR CV60) w/devulc SBR (23.5% bound styrene, and Duraden 706)[b]	75		276	131		250
	100% SBR (23.5% bound styrene, and Duraden 706)[b]	0		290	152		200
	100% SBR (23.5% bound styrene, and Duraden 706)[b]	100		290	138		180

Table 5. Percent Change from Virgin with Selected Devulcanization Rubber Formulations

Test Rubber Compounds (grade) Parts or %	% Devulc. or (Ground) Mat'l.	Hardness Shore	Tear Strength	Tensile Strength	100% Modulus	300% Modulus	Elongation to Break
Chemical							
STI-K Polymers DeLink[a]							
NR w/devulc NR	30			-5.9%		8.3%	-8.4%
SBR (1520) w/devulc SBR	30			-7.7%		-4.4%	-3.6%
Kyoto University[b]							
Truck tire (93 NR+ 7 BR)							
84 NR+ 6 BR + 20 devulc	18	8.1%		-2.3%	2.6%		0.0%
74 NR+ 6 BR + 40 devulc	33	12.9%		-11.9%	28.2%		-17.4%
65 NR + 5 BR + 60 devulc	46	11.3%		-19.1%	23.1%		-13.0%
LandStar/Guangzhou R I[c]							
100 SIR 10 + 50 devulc							
SIR vs. Case 1	33	4.3%		-23.7%	6.7%		-6.7%
SIR vs. Case 2	33	6.5%		-23.0%	11.5%		-8.6%
Tread Tire Compound							
50 NR + 30 SR + 20 CIS-BR +40 AMR	28.6	6.7%	-17.3%	-3.0%			-18.7%
Light Duty Truck Tire Compound							
30 NR + 70 SR + 0 CIS-BR + 40 AMR	28.6	1.6%	-10.9%	-13.9%			-6.7%
Retread Tire Compound							
[c]65 NR + 35 SR +40 AMR	28.6	6.3%	-8.6%	-10.3%			-16.8%
Ultrasonic							
University of Akron[d]							
Versus Akrochem SBR (1848)							
SBR w/devulc SBR	10			-55.5%		6.8%	-30.8%

Test Rubber Compounds (grade) Parts or %	% Devulc. or (Ground) Mat'l.	Hardness Shore	Tear Strength	Tensile Strength	100% Modulus	300% Modulus	Elongation to Break
SBR w/whole Tire Reclaim	10			-19.7%		2.7%	-15.4%
SBR w/30 Mesh Buffings	10			-40.4%		5.4%	-38.5%
Natural Rubber and SBR versus devulc							
Base 100% NR (SMR CV60) & 0% SBR (23.5% bound styrene, and Firestone Duraden 706)	0						
Add 25% SBR, 75% NR	0			-42.2%	6.3%		-10.4%
Devulc SBR replaces SBR							
25% devulc SBR, 75% NR	25			-69.2%	0.0%		-36.7%
50% devulc SBR, 50% NR	50			-10.7%	-5.6%		-17.9%
75% devulc SBR, 25% NR	75			-24.0%	-10.0%		-15.3%
SBR versus devulc SBR							
100% devulc SBR	100			0.0%	-9.5%		-10.0%

Heavy carbon-blacked rubber is the hardest to devulcanize, and silica, or other mineral-filled EDPM, is the easiest. Reincorporation of the devulcanized rubber is typically in the 20 to 40 percent range.

Devulcanized single-product rubber applications are wide ranging. The reclaimed product may be reintroduced into the same end product or one with more tolerant performance characteristics for the devulcanized rubber.

Devulcanized rubber seems to have advantages in bonding, strength, and tread integrity above the properties of crumb rubber, which acts only as a “rubber”-like filler.

According to one developer of a devulcanization process, about 3 to 10 percent of the final product can be blended into virgin material before performance properties are affected. Variations of a few percent are reported by developers of devulcanization when they vary process run conditions. Run-to-run variations are normally acceptable.

Devulcanized single rubber products have a much lower degree of degradation than multiple rubber mixtures with devulcanized rubber. Virgin single-grade SBR—or natural rubber replacement with devulcanized material shown by the STI-K and the University of Akron datasets—has, at worst, a reduction of 10 percent in tensile strength, modulus, or elongation.

In some cases, the addition of devulcanized rubber causes a major reduction in performance of some properties, along with improvements in one or two properties (hardness and modulus). Because the modulus is the measure of deformation—that is, tension (stretching), compression (crushing), flexing (bending), or torsion (twisting). Similarly, the increase in hardness could be an improvement or detraction, depending on the application.

The devulcanized rubber properties displayed are not necessarily optimized for a specific end use. Formulators will likely be able to incorporate devulcanized rubber along with other formulation components to achieve a higher level of final product performance. Key product performance variables are level of contamination, number of rubber types in the rubber mixtures, and additives used by the formulations. The effect of additives was discussed previously under "Product Characteristics." The number of types of rubber in waste tires is one of the most important factors affecting quality of devulcanized waste tire rubber. Optimizing a devulcanization process is very difficult when more than one type of rubber is involved.

Depending on the process used, process conditions, the material, and the blending level of the devulcanized rubber, most properties will be reduced by a few percent to more than two-thirds of those of the virgin material. In situations where the devulcanized rubber properties are within 10 percent of the original rubber material, blending would seem to be an attractive opportunity that offers the potential of adding a low-cost recycled substitute.

The best operating model for devulcanizers of single rubber formulation is a dedicated devulcanization line (or long run) of specific rubber. Smaller volumes of single formulations require incurring extra costs for downtime and lost product caused by the cleanout between runs.

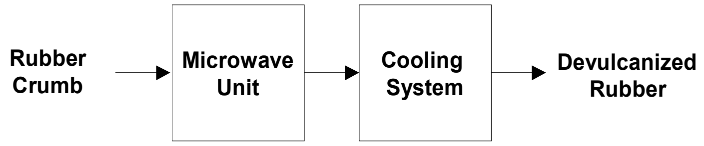
The devulcanized rubber itself and some of its additives and fillers—such as carbon black—presumably add value. These fillers take the place of new additives and fillers that would otherwise be necessary.

1.4.2 - Microwave

Microwave technology has also been proposed to devulcanize waste rubber (Fix, 1980; Novotny, et al., 1978). This process applies the heat very quickly and uniformly on the waste rubber. The method employs the application of a controlled amount of microwave energy to devulcanize a sulfur-vulcanized elastomer—containing polar groups or components—to a state in which it could be compounded and revulcanized into useful products such as hoses.

The process requires extraordinary or substantial physical properties. On the basis of the relative bond energies of C-C, C-S, and S-S bonds, the scission of the S-S and carbon-sulfur crosslinks appeared to take place. However, the material to be used in the microwave process must be polar enough to accept energy at a rate sufficient to generate the heat necessary for devulcanization. This method is a batch process and requires expensive equipment.

Figure E. Schematic Diagram of a Microwave Devulcanization System

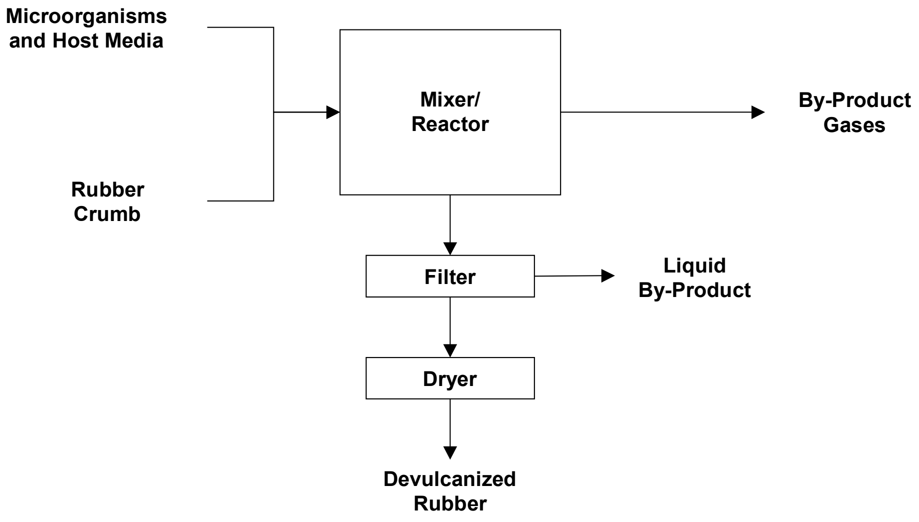


1.5 - Microbial Reclaiming

Thiobacillus-bacteria are able to oxidise the sulfur in polysulfonic bonds to sulphate. This reaction is limited to a surface layer of the rubber with a thickness of less than 1 μm and the oxidation takes several weeks. The thiophilic bacteria Sulfolobus Acidocaldarius is able to split carbon-sulfur bonds in a stepwise oxidation reaction of the carbon-bound sulfur into a sulfoxide, a sulfone and finally to a sulphate[8, 9]. The disadvantage of these processes is the low devulcanization rate.

Apparently, these types of biological devulcanization processes are exclusively or primarily limited to the surface layers of the elastomers (Christiansson, et al., 1998). This circumstance may explain the overall low rates of desulfurization based on total mass processed.

Figure F. Schematic Diagram of Biological Devulcanization System



Chapter2 - Cost Analysis

Given the lack of information in the literature, the cost estimates are based on a synthesis of information and data from multiple sources for a given generic type of technology;

The analysis was generally performed by determining the costs (capital and operating and maintenance) of the processes and equipment described in the available literature. The cost analyses were conducted for three technologies that use different processing approaches: chemical, ultrasonic, and mechanical.[*] The key processing elements of each of these technologies have been previously described in this report, and they serve as the primary basis of estimating capital and operating and maintenance costs.

The data in Table 6 summarize the capital costs and operating and maintenance costs for the technologies analyzed. The data for the capital cost analysis include an allowance for engineering services for the construction of the facility. The information shows that the capital costs for the processes vary from about $92,000 to about $166,000.

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*[*] Insufficient technical information and data were found during the study to enable reliable cost analyses for other devulcanization technologies.

Table 6. Estimated Unit Costs for the Production of Devulcanized Rubber

Item	Mechanical	Chemical	Ultrasonic
Capacity (lb/hr)	100	75	75
Capital Cost ($)	92,000	166,000	163,000
O&M Cost ($)	135,000	172,000	136,000
Amortized Capital and O&M ($)	143,000	186,000	150,000
Amortized Unit Cost ($/lb)	0.7	1.2	1.0

Interest rate: 6% per year; Amortization period: 20 years

Similarly, the data in the table indicate that the operating and maintenance costs for facilities of this type range from about $135,000 to $172,000. **The operating cost estimates include the cost of crumb rubber feedstock for each of the processes**. Based on the relative small size of the facilities, **the costs of the rental of a building for processing in operating and maintenance are included**. This eliminated the cost of building a structure.

As shown in the Table, the estimated amortized costs for producing devulcanized rubber are: $1.0/lb for the ultrasonic process, $1.2/lb for the chemical process, and $0.7/lb for the mechanical process. The analysis used an interest rate of 6 percent per year and an amortization period of 20 years. Due to uncertainties represented by the lack of detailed technical data and operating history for the technologies, the accuracy of the cost estimates is +/- 30 percent. As mentioned earlier, these costs reflect production at low capacities.

Some reduction in unit cost would likely occur due to economies of larger scale production. However, estimating reduction in unit cost is difficult because of the lack of data relating to production costs to different levels of throughput capacity for particular devulcanization technologies.

For the size of operations considered in this analysis, labor costs are a substantial portion of the production costs. It is very difficult, however, to estimate the magnitude of any potential reductions in unit labor costs that might occur if processing capacities were increased substantially. All circumstances considered, any estimates of commercial production costs for devulcanization of waste tire rubber are highly speculative at best. The best estimate of the study team is that perhaps production costs could be reduced by 25 to 30 percent if processing capacities were increased by a factor of approximately 5 to 10.

The estimates of processing costs developed in this study do not include the costs of pollution control. The chapter lists the types of emissions that could be expected. The difficulty of permitting such a process and the cost of compliance with environmental regulations may comprise a significant barrier to the implementation of this technology.

Conceivably, pollution control costs could add 10 to 30 percent to the cost of devulcanization. The difficulty of permitting—and the cost—would be a function of the type of devulcanization technology, the processing rates, and other factors. In general, the expectation is that the cost of environmental control systems for chemical devulcanization systems would be greater than that for ultrasonic or mechanical processes.

The composition of rubber and additives that are used in rubber compounds in the manufacture of vulcanized rubber can and do have a dramatic effect on the properties of materials manufactured from devulcanized rubber. **Apparently, the inferior properties of some poorly (inadequately) devulcanized rubber can be compensated for by the addition of chemicals and the adjustment of operating conditions, among other remedies.** In many cases in the literature, this situation is not addressed or discussed. Consequently, comparing devulcanization technologies is difficult. From most of the literature descriptions of the processes, what happens to the sulfur and other vulcanization chemicals during the various processes is unclear.

Chapter 3 - Environmental Analysis

Little information is available in the literature on the environmental effects associated with waste tire devulcanization technologies. The lack of information apparently exists because business developers and researchers have concentrated their efforts primarily on technology improvements and achieving satisfactory properties for devulcanized rubber, an estimation of emission rates and a detailed environmental analysis are therefore not possible.

However, using data and information from some other types of tire manufacturing processes (for example, extrusion of rubber) and the characteristics of vehicle tires, a qualitative analysis was performed. The environmental analysis described subsequently is limited to chemical and ultrasonic devulcanization and assumes that control of emissions would be required.

3.1 – Chemical technology

Chemical devulcanization processes are usually batch processes that involve mixing crumb rubber with chemical reactants at a specific temperature and pressure. Once the design reaction time has elapsed, the contents are then rinsed, filtered, and dried to remove any remaining unwanted chemical components. The product can then be bagged or otherwise processed for resale. A block flow diagram of a generic chemical devulcanization process is illustrated in Figure G, showing the raw material feed is crumb rubber.

The crumb rubber is mixed with one or more devulcanization agents. Chemical agents identified as devulcanization agents are listed in Table 8. During processing in the batch reactor, vapors are released that must be collected and treated before release to the ambient atmosphere. Typical types of vapors that might be emitted from a batch reactor are listed in Table 9.

The chemicals that would be vented from the batch reactor are dependent on the characteristics of the waste tire feedstock and on the chemical agent(s) used in devulcanizing the crumb rubber. For example, if disulfides are used in the process, they could result in formation of hydrogen sulfide (H_2S) or methyl or other mercaptans (RSH).

If the chemical agent orthodichlorobenzene is used, chlorinated hydrocarbons could potentially be released in the form of air emissions. Methyl iodide is volatile, and if used as a devulcanization agent, it could be vaporized. Since tire manufacturing utilizes zinc oxide and zinc carbonate, chemical devulcanization might also produce airborne metal particulates.

Once the batch is fully processed, the reactor is vented. The vent gases are treated prior to release to the atmosphere. The vapors cannot be treated by vapor phase carbon because these chemicals will plate out and blind the carbon, making it ineffective. Instead, the vapor from the batch reactor needs to be thermally oxidized. At the high exit temperatures, typically as high as 2000°F (1100°C), the thermal oxidizer vent gases need to be cooled in a quench tower to approximately 300°F (150°C). Then, to remove any metals or other particulate, the vent gases are piped to a baghouse.

Because of the high thermal oxidizer temperatures, methyl mercaptans (RSH) or hydrogen sulfide (H_2S) from the crumb rubber is oxidized to sulfur dioxide (SO_2). Therefore, downstream of the baghouse, a scrubber is required to remove sulfur dioxide (SO_2), as shown in Figure G. Scrubbed vent gases are then released to the atmosphere.

In addition to the scrubber vent gases described above, liquid waste is generated from the scrubber. This liquid stream contains sodium sulfate (Na_2SO_4). This liquid waste can be disposed in receiving waters such as a river, stream, or bay. However, discharging to receiving waters will require a significant amount of treatment equipment and eventually a permit.

As seen in Figure G, the devulcanized rubber is moved from the batch reactor to a separator by a heated extruder. Liquid that drips off the devulcanized rubber is removed in the separator and eliminated by feeding it to the same thermal oxidizer as the vent gases from the batch reactor. After the liquid has dripped off the devulcanized rubber in the separator, any remaining moisture is removed in the dryer. Fired dryers are typically fueled by natural gas burners. Dryer vent gases are piped to the common thermal oxidizer.

Based on the concentration of solids in the scrubber effluent, processing the scrubber effluent through a filter press to dewater the solids may be necessary and cost-effective. Filter-pressed dewatered solids are called “filter cake.” Filter cake might require disposal in a hazardous waste site. Even though the waste disposal site may accept the scrubber effluent water, the economics may favor installation and use of a filter press. This is necessary to dewater the solids due to the high cost of disposal of liquid waste**.**

Figure G. Block Flow Diagram of a Chemical Devulcanization System

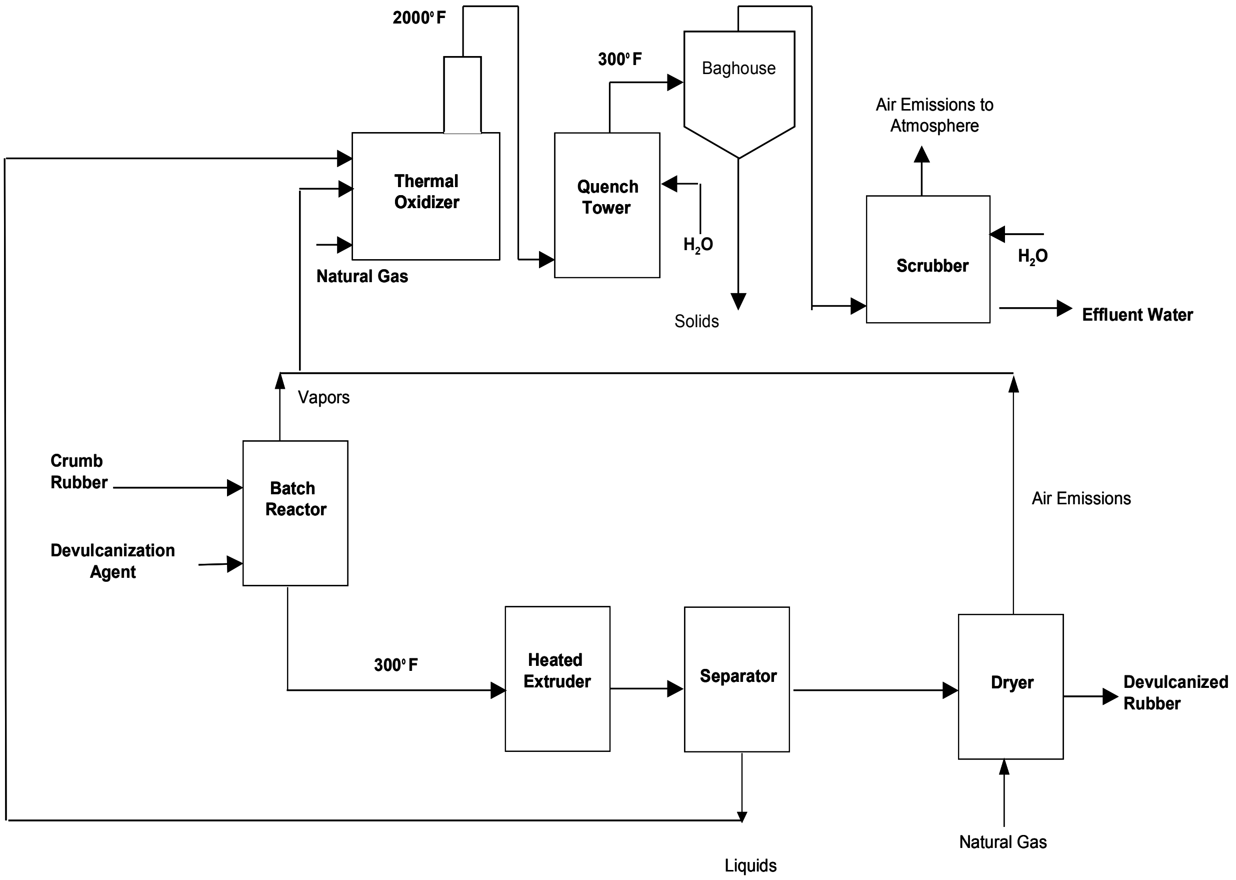

Table 7. Tire Raw Materials

Polymers
Natural Rubber (polyisoprene)
Styrene-Butadiene Rubber (SBR)
cis-Polybutadiene copolymer
Vulcanizing Agents
Sulfur
Tetra-methyl thiurame sulfide
Accelerators
Diphenylguanidine
2-Mercaptobenzothiazole
n-Cyclohexyl-2-benzothiazolylsulfenamide
2-(n-Morpholinyl)-mercaptobenzothiazole
Hexamethylenetetramine
Activators
Zinc oxide
Zinc carbonate
Stearic acid

Antiozonants
2,2,4-trimethyl-1,2-dihydroquinoline (polymer)
n,n-(1,3-dimethylbutyl)-p-phenylenediamine
paraffinic wax
Antioxidants
Alkylphenols
Resorcinol
2,6-Diterbutylhydroquinone
Retarders
n-Cyclohexylthiophthalimide
Plasticizers
Aliphatic oil
Aromatic oil
Naphthenic oil
Di-(2-ethylhexyl)-phthalate
Extenders
Silica gel
Carbon black

Table 8. Chemical Agents Used in Chemical Tire Devulcanization Processes

Triphenyl phosphine
Sodium di-n-butyl phosphite
Thiol-amine reagents (specifically propane-thiol/piperidine, dithiothreitol, and hexane-l-thiol)
Lithium aluminum hydride
Phenyl lithium
Methyl iodide
Hydroxide with quaternary ammonium chloride as a catalyst
Orthodichlorobenzene
Diphenyldisulphide
Diallyl disulfide
Toluene, naphtha, benzene, and/or cyclohexane, etc. in the presence of sodium
Diamly disulfide
Dibenzyl disulfide
Diphenyl disulfide
Bis(alkoxy aryl) disulfides
Butyl mercaptan and thiopenols
Xylene thiols
Phenol sulfides and disulfides
Alkyl phenol sulfides (for SBR)
N,N-dialkyl aryl amine sulfides (for SBR in neutral or alkaline solutions)

3.2 - Ultrasonic technology

Devulcanization by ultrasonic methods may be a continuous process (see Figure H). As the figure illustrates, crumb rubber is loaded into a hopper and is subsequently fed into an extruder. The extruder mechanically pushes and pulls the rubber. This mechanical action serves to heat the rubber particles and soften the rubber.

As the softened rubber is transported through the extruder cavity, the rubber is exposed to ultrasonic energy. The resulting combination of ultrasonic energy, along with the heat, pressure, and mechanical mastication, is sufficient to achieve varying degrees of devulcanization. The exposure time to the ultrasonic energy is only seconds. Essentially all of the rubber entering the process is discharged from the extruder in a semi-solid product stream. Process losses would be primarily emissions of fine particulate or of gases, if any, resulting from the mechanical and thermal applications occurring during devulcanization.

Since the typical operating temperature of an ultrasonic devulcanization reactor is about 230°F (110°C), less vapor emission would be expected than from chemical devulcanization. Furthermore, since no chemicals are added to break the sulfur bonds that caused vulcanization to occur, there would likely be lower air emissions. After exiting through the extruder die, the rubber is passed through a cooling bath and then dried.

Vented vapors would need to be treated by one of two methods. One method would be to use a small thermal oxidizer. The design of the thermal oxidizer, baghouse, and scrubber would be similar to that described previously for chemical devulcanization. However, the physical size of the oxidizer would be smaller, and the baghouse and scrubber would be larger.

A second method to treat the vent gases exiting the ultrasonic devulcanization reactor would be use of vapor phase carbon. In this method, due to the lower operating temperatures of the ultrasonic process, vent gas exiting the ultrasonic zone would have to be heated above the dew point temperature. If this elevation in temperature is not accomplished, the vent gases could condense on the surface of the carbon and thus blind the bed. In other words, adsorption sites on the surface of the carbon would be ineffective, and vent gases would exit the carbon bed untreated.

If vapor phase carbon were to be used, the capital cost would be less than that of a thermal oxidizer. However, carbon is not very efficient. Weight loading can be approximately 10 weight percent—in other words, adsorbing ten pounds of vent gas contaminants for every 100 pounds of carbon used. Use of carbon will have a relatively high operating cost. Also, the disposal of spent carbon can be very expensive. This is especially true if the spent carbon requires disposal at a hazardous waste disposal site. Even if the carbon is regenerated on-site, adsorption efficiency decreases after each regeneration. Typically, carbon can only be regenerated ten times. For illustration purposes, Figure H indicates the use of vapor phase carbon.

Devulcanized rubber exiting the ultrasonic processing zone has to be cooled. A common method of reducing the rubber temperature is a cooling bath. The volume of cooling water used would be significant. Cooling water may become contaminated from the process; this effluent water leaving the cooling bath has to be treated. If an air cooler such as fin fans is used in lieu of water in the cooling bath, the volume of effluent liquid would be reduced.

Another alternative would be to use a closed-loop cooling system, where the cooling water is cooled and returned to the process for reuse. If there is a buildup of contaminants, a small slip-stream could be taken off and treated in a POTW, greatly reducing the amount of effluent that would otherwise require treatment.

Figure H. Block Flow Diagram of an Ultrasonic Devulcanization System

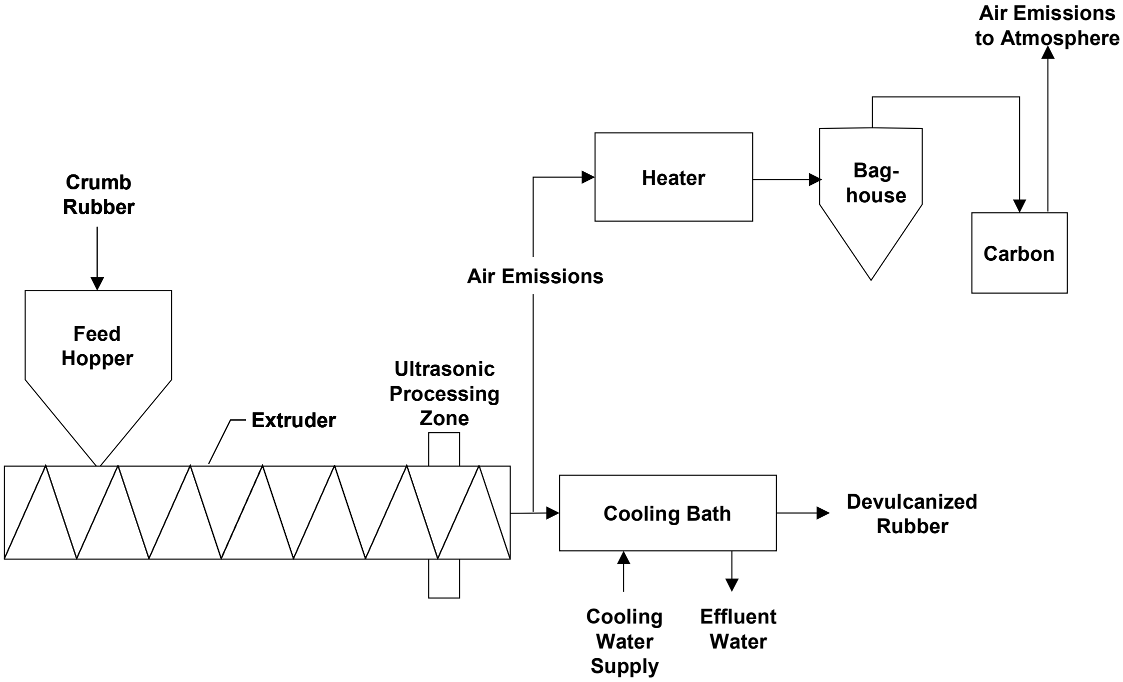

Table 9. Potential Types of Chemical Compounds Emitted by Chemical and Ultrasonic Devulcanization Technologies

Compound	Probable Source
Benzene	Plasticizers: Aromatic oil
Methylcyclohexane	Plasticizers: Na phthemic oil
Toluene	Plasticizers: Aromatic oil
Heptane	Plasticizers: Aliphatic oil
4-Vinylcyclohexene	Polymers: Natural Rubber (polyisoprene), styrene-butadiene rubber (SBR), cis-Polybutadiene
Ethylbenzene	Plasticizers: Aromatic oil
Octane	Plasticizers: Aliphatic oil
p-Xylene	Plasticizers: Aromatic oil
Styrene	Polymers: styrene-butadiene rubber (SBR)
Nonane	Plasticizers: Aliphatic oil
1,4-Cyclohexadiene-1-isopropyl-4-methyl	Polymers: Natural Rubber (polyisoprene)
Isopropylbenzene	Plasticizers: Aromatic oil
Cyclohexene-1-methyl-3-(1-methylvinyl)	Polymers: Natural Rubber (polyisoprene)
Propylbenzene	Plasticizers: Aromatic oil
Benzaldehyde	Polymers: styrene-butadiene rubber (SBR)
1-isopropyl-4-methylcyclohexane (trans)	Plasticizers: Naphthemic oil
1-isopropyl-4-methylcyclohexane (cis)	Plasticizers: Naphthemic oil
1-isopropyl-3-methylcyclohexane	Plasticizers: Naphthemic oil
Decane	Plasticizers: Aliphatic oil
Tri-isobutylene	Polymers: styrene-butadiene rubber (SBR) & cis-Polybutadiene; Plasticizers: Naphthemic oil
Cyclohexene-5-methyl-3-(1-methylvinyl)	Polymers: Natural Rubber (polyisoprene)
Indane	Plasticizers: Naphthemic oil
1-Isopropyl-4-methylbenzene	Plasticizers: Aromatic oil
Cyclohexene-1-methyl-4-(1-methylvinyl)	Polymers: Natural Rubber (polyisoprene)
1-Isopropyl-2-methylbenzene	Plasticizers: Aromatic oil
Dimethylstyrene	Polymers: styrene-butadiene rubber (SBR)
Undecane	Plasticizers: Aliphatic oil
Tetramethylbenzene	Plasticizers: Aromatic oil
1,2,3,4-Tetrahydronaphthalene	Plasticizers: Naphthemic oil
1,3-Di-isopropyl benzene	Plasticizers: Aromatic oil
1,4-Di-isopropyl benzene	Plasticizers: Aromatic oil

Compound	Probable Source
2-Isopropyl-6-methylphenol	Antioxidents: Alkylphenols
Cyclohexylisothiocyanate	Retarders: n-Cyclohexyl-thiophthalimide
Cyclododecatriene	Polymers: cis-Polybutadiene
Dodecane	Plasticizers: Aliphatic oil
Tridecane	Plasticizers: Aliphatic oil
Tetraisobutylene	Polymers: styrene-butadiene rubber (SBR) & cis-Polybutadiene; Plasticizers: Naphthemic oil
p-ter-Butylstyrene	Polymers: styrene-butadiene rubber (SBR)
Dimethylpropylhexahydronaphthalene	Plasticizers: Naphthemic oil
Tetradecane	Plasticizers: Aliphatic oil
Nonylbenzene	Plasticizers: Aromatic oil
2,6-Di-ter-butyl-p-quinone	Antioxidents: 2,6-Diterbutyl-hydroquinone
Pentadecane	Plasticizers: Aliphatic oil
1,6-dimethyl-4-isopropyl-1,2,3,4-tetra-hydronaphthalene	Plasticizers: Naphthemic oil
Decylbenzene	Plasticizers: Aromatic oil
Di-ter-butylthiophene	Plasticizers: Aromatic oil
Diethyl phthalate	Plasticizers: Di-(2-ethylhexyl)-phthalate
Hexadecane	Plasticizers: Aliphatic oil
1,2-Di-tolylethane	Polymers: styrene-butadiene rubber (SBR)
Heptadecane	Plasticizers: Aliphatic oil
2,6-Di-ter-butyl-4-ethylphenol	Antioxidents: Alkylphenols
Octadecane	Plasticizers: Aliphatic oil
1-Phenylnaphthalene	Plasticizers: Aromatic oil
Di-iso-butyl phthalate	Plasticizers: Di-(2-ethylhexyl)-phthalate
Tridecylbenzene	Plasticizers: Aromatic oil
Dibutyl phthalate	Plasticizers: Di-(2-ethylhexyl)-phthalate
Eicosane	Plasticizers: Aliphatic oil
Heneicosane	Plasticizers: Aliphatic oil
Docosane	Plasticizers: Aliphatic oil
Di-(2-ethylhexyl) phthalate	Plasticizers: Di-(2-ethylhexyl)-phthalate

Chapter 4 - Conclusions

Devulcanization of specific types of rubber and/or waste tire rubber has a long history. However, only recently have limited technical data been reported in the available literature. Usually when reported, the tested properties of devulcanized rubber compose an incomplete list. This is especially true in the interpretation of how the devulcanized product would perform during compounding, in the manufactured end product, or both.

Circumstantial and anecdotal evidence indicates significant technical and economic barriers to devulcanization of waste rubber.

Based on the information collected in the study, is believed that **the only method of achieving bulk devulcanization, as opposed to surface devulcanization, rests with ultrasonic or microwave devulcanization methods.** Of these two methods of energy application, ultrasound appears to have substantially more research and development history. An important observation is that **microwave technology is not an effective or efficient way to devulcanize non-polar rubber types, which collectively compose the vast majority of the mass of rubber in waste rubbers.**

Because of the ability to internally devulcanize cured rubber, ultrasonically devulcanized waste tire rubber may have more desirable marketing characteristics than those of surface-devulcanizing processes under similar conditions of cost and yield. The latter processes (surface devulcanizing) include mechanical, chemical, and biological processes. However, test data and applications for ultrasonically devulcanized waste rubber are lacking in the industry, along with process cost documentation.

The devulcanized rubber market is most fully developed for single product materials made from manufacturing scrap that are reclaimed for reuse in the same process or in a broader specification application. The reprocessing of single rubbers depends upon being located near a large-volume rubber products company with enough scrap and enough rubber applications to justify the devulcanization step.

Devulcanization of waste rubber, despite considerable research and developmental effort, is still in an early growth stage. Devulcanization lacks adequate test data and data interpretation, and it has poorly defined end product specifications without adequately justified and defined applications and uses. Research funds appear to be most available for studying devulcanization of single rubber types, as opposed to studying rubber types with complex mixtur.

In applications already using crumb rubber, devulcanized rubber can have advantages if the process combines a vulcanized rubber or other compatible material to create an integrated structure. The structure must have much better properties than those imparted by the filler role that crumb rubber frequently serves.