

Exxon™ chlorobutyl rubber

ExxonMobil

Exxon™ chlorobutyl rubber compounding and applications manual

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Abstract

Chlorobutyl rubber (CIIR) is a terpolymer of isobutylene, isoprene and chlorinated Isoprene. Chlorobutyl rubber has many attributes of butyl polymer molecule because of its saturated polyisobutylene backbone. These include physical strength, vibration dampening, low permeability, and resistance to aging and weathering from environmental exposure.

The vulcanization chemistry of chlorobutyl rubber can be more complex than that of general-purpose elastomers such as natural rubber or polybutadiene rubber because of the highly saturated nature of the chlorobutyl rubber backbone. The stereochemistry of the halogenated isoprenyl units is important along with the basicity of the accelerators that are typically used. An understanding of the chemistry of chlorobutyl rubber and chlorobutyl rubber compounding therefore becomes very important. When properly compounded, chlorobutyl rubber displays excellent performance in many other applications besides tire innerliners such as tire inner tubes, tire sidewalls, automotive engine mounts, special purpose conveyor belt covers and pharmaceutical applications.

The modern radial tire in many respects is made possible through the introduction and use of chlorobutyl/bromobutyl rubber innerliners. Use of this polymer in the tire innerliner compound has allowed improvements in air retention performance and improved fuel efficiency. Improvements in tire durability, longer tire life also have been achieved by using chlorobutyl/bromobutyl rubber based tire innerliner.

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1. Introduction

Chlorobutyl rubber (CIIR) is an elastomeric isobutylene-isoprene copolymer containing reactive chlorine atoms. This rubber was the first commercialized halogenated butyl rubber by Exxon in the year 1961. Chlorobutyl rubber has many attributes of butyl polymer molecule because of its saturated poly-isobutylene backbone. These include physical strength, vibration damping, low glass transition temperature, low permeability, and resistance to aging and weathering from atmospheric exposure.

Structurally, chlorobutyl rubber is similar to bromobutyl rubber and like bromobutyl rubber; it has broader vulcanization characteristics than butyl rubber due to the reactivity of chlorine. Compared to butyl rubber, the chlorobutyl rubber display better co-vulcanization properties with unsaturated

general-purpose elastomers such as natural rubber (NR), polybutadiene rubber (BR), and styrene butadiene rubber (SBR), while maintaining other properties of the mostly saturated backbone.

In comparison to bromobutyl rubber, chlorobutyl rubber shows a low level of crosslinking reactivity based upon the higher carbon-chlorine bond energy when compared to the carbon-bromine bond energy of bromobutyl rubber. This results in compounds with slower cure rates that can utilize a wider range of vulcanization systems. Chlorobutyl rubber thus possesses a more predictive curing profile with additional scorch and processing safety, and less sensitivity to mixing, processing and storage conditions. Table I gives the summary of chlorobutyl grades marketed by ExxonMobil Chemical.

Table I

Grades of EXXON™ chlorobutyl rubber¹

Grades			1066	1068
	Test method	Unit		
Mooney viscosity ML 1+8 at 125 °C	ASTM D 1646(Modified)	MU	38 ± 5	50 ± 5
Antioxidant (non-staining)	ExxonMobil test method	wt%	0.02 min	0.02 min
Chlorine	ExxonMobil test method	wt%	1.26 ± 0.08	1.26 ± 0.08
Water	ExxonMobil test method	wt%	0.3 max	0.3 max
Product specifications				
Cure characteristics*	ASTM D 2084 (Modified)			
Maximum torque (M _H)		dN.m	41.0 ± 7.0	45.0 ± 7.0
Minimum torque (M _L)		dN.m	14.0 ± 4.5	17.0 ± 4.5
ts2		mins	2.0 ± 1.5	2.0 ± 1.5
t' 50		mins	5.0 ± 3.0	5.0 ± 3.0
t' 90		mins	13.0 ± 4.0	13.0 ± 4.0

*Rheometer ODR 2000, chlorobutyl standard compound as per ASTM D 3958 modified

The grades primarily differ in Mooney viscosity. The cure characteristics are determined using the reference compound formulation presented in ASTM D3958².

Guide to applications

The major applications for Exxon™ chlorobutyl rubber is in tire innerliners, tire white sidewalls and heavy-duty automobile truck tire innertube applications. In innerliner application,

chlorobutyl rubber is preferred to general purpose rubbers due to its

- Low permeability
- High heat resistance
- Excellent flex resistance
- Ability to co-vulcanize with unsaturated rubber
- Processing ease and safety

When properly compounded, a tire innerliner compound formulation containing 100 phr chlorobutyl rubber provides lower tire inflation pressure loss rate (IPLR) by minimizing air diffusion into the body of the tire, thereby maximizing tire tread life, tire durability, and vehicle fuel economy. For less demanding air barrier applications, blends of chlorobutyl rubber with general-purpose elastomers such as natural rubber, styrene butadiene rubber are used.

Tire sidewalls are another application for chlorobutyl rubber. When used in blends with other elastomers, it improves ozone, fatigue resistance and non-staining properties. In black sidewall compounds, co-curing with Vistalon™ EPDM elastomers combine ozone resistant qualities with high levels of adhesion to adjacent components of the tire³.

The co-curing versatility of chlorobutyl rubber and its ability to form heat-stable crosslinks make it suitable for conveyor belting covers, especially for high temperature service. Conveyor belts are constructed from a variety of layers requiring high levels of adhesion⁴.

2. Chlorobutyl polymers

Chlorobutyl rubber is produced by reacting a solution of butyl rubber in hexane with chlorine.

Crawford, Morrissey and coworkers at the BF Goodrich company first reported the modification of butyl with small amounts of halogen⁵. At ExxonMobil, researchers pursued the chlorination of butyl rubber using elemental chlorine by reacting a solution of butyl rubber in hexane with chlorine⁶. Both chlorination and bromination were described in a paper presented at London in 19606. The chemistry of halogenation was also described, as well as the early work on crosslinking mechanisms and the resulting chemical and physical properties of the vulcanizates^{7,8}. The introduction of chlorine in to the butyl rubber takes place at the unsaturated chemical bond location. This yields increased crosslinking activity and new crosslinking chemistry while maintaining the performance properties of the chemically highly saturated polyisobutylene structure.

Commercial production of chlorobutyl rubber started in 1961. The properties and cost effectiveness of chlorobutyl rubber made it attractive for major industrial applications such as tire innerliners.

The ability of chlorobutyl rubber to cure rapidly using vulcanization systems yielding very low extractable residues makes it a preferred elastomer for pharmaceutical applications. The moisture permeation resistance of chlorobutyl rubber is an added advantage. Chlorobutyl rubber exhibits high damping properties with fast, reversion resistant cures, making it suitable for automotive and other vibration control applications.

Toxicology

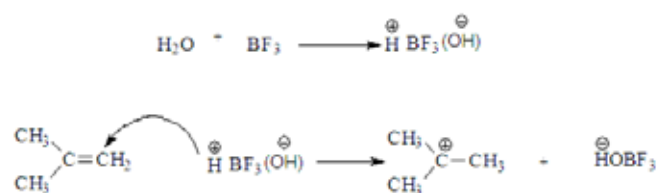
Chlorobutyl rubber is safe to process, fabricate and use under normal conditions where good industrial hygiene is practiced. Complete information regarding product description, health aspects and handling of chlorobutyl rubber are covered in the material safety data sheets (MSDS) for the product.

Process Overview

Butyl rubber (IIR) is first prepared from high purity isobutylene and isoprene. The mechanism of polymerization consists of complex cationic reactions. The catalyst system is a Lewis acid co-initiator with an initiator. Typical Lewis acids co-initiators include aluminum trichloride, alkyl aluminum dichloride, boron trifluoride, tin tetrachloride, and titanium tetrachloride. The initiators used are Brønsted acids such as water, hydrochloric acid, organic acids, or alkyl halides. The isobutylene monomer reacts with the Lewis acid catalyst to produce a positively charged carbocation called a carbenium ion in the initiation step. Figure 1 is a simplified schematic of the initiation step for illustrative purposes.

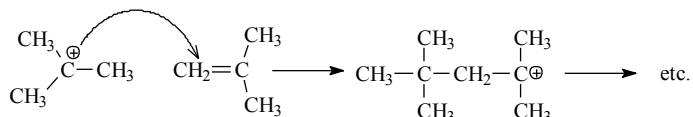
Figure 1

Simplified illustration of a cationic polymerization initiation step⁹



Monomer units continue to be added in the propagation step until chain transfer or termination reactions occur (figure 2). Temperature, solvent polarity, and the presence of counter ions can affect the propagation of this exothermic reaction.

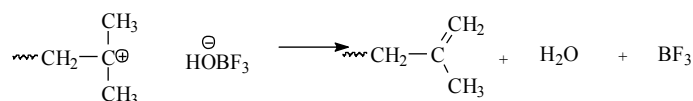
Figure 2
Simplified schematic of a propagation step



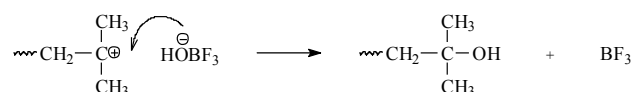
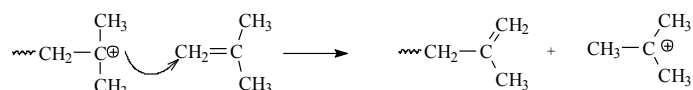
In the chain transfer step that terminates propagation of the macromolecule, the carbenium ion of the polymer chain-reacts with the isobutylene or isoprene monomers, or with other species such as solvents or counter ions, to halt the growth of this macromolecule and form a new propagating polymer chain (figure 3). Lowering the polymerization temperature retards this chain transfer and leads to higher molecular weight butyl polymers. Isoprene is co-polymerized mainly by trans-1,4-addition.

Termination results from the irreversible destruction of the propagating carbenium ion either by the collapse of the ion pair, by hydrogen abstraction from the co-monomer or by formation of stable allylic carbenium ions, or by reaction with nucleophilic species such as alcohols or amines. Termination is imposed after polymerization to control the molecular weight of the butyl rubber and to provide inactive polymer for further halogenation.

Figure 3
Simplified illustration of a termination step



In addition, two minor processes can occur as follows:



In the most widely used butyl rubber manufacturing process, a slurry of fine particles of butyl rubber dispersed in methyl chloride is formed in the reactor after Lewis acid initiation. The reaction is highly exothermic, and a high molecular weight can be achieved by controlling the polymerization temperature, typically from -100°C to -90°C . The most common

polymerization process uses methyl chloride as the reaction diluent and boiling liquid ethylene to remove the heat of reaction and maintain the required low temperature.

The final molecular weight of the butyl rubber is determined by controlling the initiation and chain transfer reaction rates. Water and oxygenated organic compounds that can terminate the propagation step are minimized by purifying the feed systems. The methyl chloride and unreacted monomers are flashed off with steam and hot water, dried and purified, and then recycled back to the reactor. Stabilizers (calcium stearate) and an antioxidant (BHT) are introduced to the hot water/polymer slurry to stabilize the polymer and prevent agglomeration.

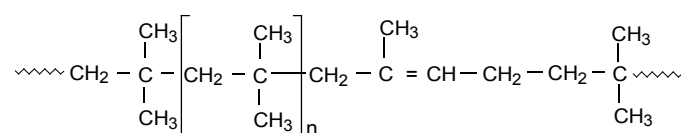
Limited chemical functionality of isoprene isobutylene rubbers.

The commercialization of butyl rubber by ExxonMobil Chemical in 1943 introduced the concept of a highly saturated, more inert polymer containing a limited level of chemical reactive functionality^{10,14}. However, the level of functionality is sufficient to provide crosslinked networks with high strength and elastic physical properties after vulcanization. Butyl rubbers have typical viscosity average molecular weights of 350,000–450,000, and mole percent unsaturation (isoprene) levels of 0.8 to 2.0.

The term “mole percent unsaturation” refers to the number of isoprene molecules in 100 monomer molecules in the polymer. Thus, a one-mole percent unsaturated butyl would contain one molecule of isoprene and ninety-nine molecules of isobutylene. In a single butyl macromolecule made up of thousands of monomer units, the isoprene units are randomly distributed.

Figure 4 shows the structure of butyl rubber³. Commercial butyl rubber (IIR) is the copolymer of isobutylene and a small amount of isoprene, typically in the order of 2-mole percentage. The introduction of chlorine into the butyl polymer takes place at the carbon-carbon double bond location of the isoprenyl unit followed by rearrangement to different stereochemistry. This yields higher levels of crosslinking activity and new crosslinking chemistry, while maintaining the properties of the highly saturated, chemically inert structure.

Figure 4
Butyl rubber structure³

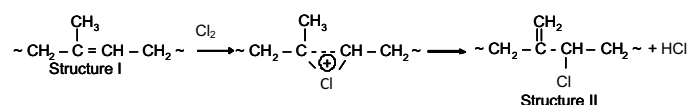


Chemistry of chlorination of butyl rubber

The chlorination of butyl rubber proceeds by a substitution type chemistry in which one molecule of hydrogen chloride is produced for every chlorine atom introduced into the rubber. The result is the formation of a reactive, allylic chloride structure. The primary chlorination reaction proceeds by the well-established substitution mechanism as given in figure 5. Limited allylic rearrangement and migration of the double bond can then follow^{11,12,13,14}.

Figure 5

Chlorination chemistry of isoprene isobutylene rubber



Chlorobutyl rubber is prepared in a continuous process by introducing elemental chlorine to a hexane solution of butyl rubber. The amount of chlorine is controlled so that, one chlorine atom is introduced at the location of each enchainment isoprene unit in the rubber. During the substitution reaction, one molecule of hydrogen chloride is released. A slurry aid, calcium stearate, and an antioxidant Butylated hydroxytoluene (BHT) are added before the elastomer product is recovered from the hexane solution in a flash drum with steam and water. The calcium stearate also prevents de-hydrohalogenation and neutralizes any traces of acid formed in the degradation reactions. Calcium stearate also contributes to scorch safety in most chlorobutyl rubber cure systems.

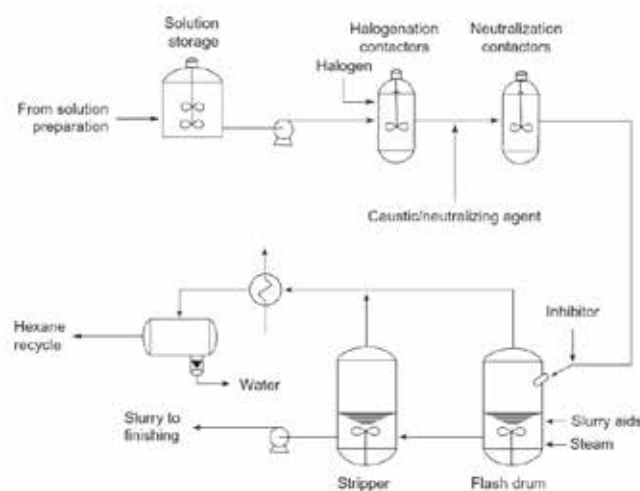
The chlorination process begins with the preparation of a hexane solution of butyl rubber with desired molecular weight and unsaturation. Slurry from a butyl polymerization reactor is dissolved by transferring it into a drum containing hot liquid hexane that rapidly dissolves the fine slurry particles. Hexane vapor is added to flash off methyl chloride and unreacted monomers. The solution of butyl rubber in hexane passes to a stripping column where the final traces of methyl chloride and monomers are removed. The hot solution is brought to the desired concentration for halogenation, typically 20–25 wt % in an adiabatic flash step¹⁴.

Chlorination is the second major chemical reaction in the production of chlorobutyl polymers. It is usually carried out by adding chlorine vapor to a solution of rubber in hydrocarbon solvent. The halogenation of butyl backbone is an ionic substitution reaction; halogen is added to the solution of butyl rubber in hydrocarbon solvent in a well-mixed reactor. Insufficient mixing will lead to poor distribution of the halogen on the polymer, which can cause the product cure characteristics to be unsatisfactory. The byproduct hydrogen

chloride is normally reacted with aqueous sodium hydroxide solution. A schematic diagram of halogenation of butyl rubber is given in figure 6.

Figure 6

Block diagram for halogenation of isoprene isobutylene rubber¹⁴



The chlorinated rubber solution then passes into a vertical drum where the solvent is flashed and stripped by steam and hot water. To prevent polymer agglomeration, calcium stearate is added to the slurry in this drum. The resultant polymer/water slurry is kept agitated and then screened to separate the bulk water from the rubber. The polymer is then dried in a series of extrusion, dewatering and drying steps to get the final moisture content less than 0.3 wt%. Antioxidants (BHT) are added in the final extrusion step¹⁴. Fluid bed conveyors and/or airway systems are used to cool the product to an acceptable packaging temperature. The resulting dried product is in the form of small crumbs, which are subsequently compressed and weighed into 75 lbs. bales before wrapping in ethyl vinyl acetate (EVA).

Overview of chlorobutyl rubber properties

Chlorobutyl rubber has many properties similar to butyl rubber, like low permeability to the passage of gases and moisture due to the closed packing of saturated polyisobutylene backbone. In the vulcanized state, both butyl and chlorobutyl exhibit similar elastic properties, better dampening, resistance to aging, and weathering when compared to general-purpose elastomers.

With many vulcanization systems, chlorobutyl and bromobutyl will exhibit similar vulcanizate properties, which can be superior to sulfur-vulcanized regular butyl compounds. The main differences between chlorobutyl and bromobutyl arise from the different bond dissociation energies of the carbon-halogen bonds⁹. The carbon-chlorine bond energy is 327 kJ/

mole while the carbon-bromine bond energy is 209 kJ/mole (table II).

Chlorobutyl has longer scorch times and less sensitivity to processing conditions because of higher carbon-halogen bond energy. On the other hand, the lower carbon-bromine bond energy of bromobutyl makes it more reactive than chlorobutyl. Thus, bromobutyl provides faster vulcanization rate and better co-vulcanization with general purpose rubbers.

Table II

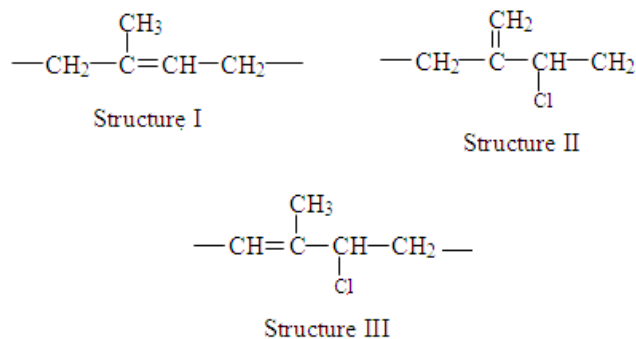
Carbon halogen bond energies and bond length ⁹

Bond type	Bond energy (kJ/mole)	Bond length (nm)
- C -C-	346	0.154
- C -H-	413	0.109
- C -F-	452	0.138
- C -Cl-	327	0.177
- C -Br-	209	0.194

Chlorine content of chlorobutyl rubber is expressed in weight percent (wt %). Figure 7 shows the structures of the chlorine containing groups found in chlorobutyl rubber^{9,10,11}. Structure II is the predominant structure in chlorobutyl rubber¹⁵. Structure I represents about 30% of the isoprenyl units, Structure II is about 60%, Structure III can be up to 10% of the isoprene in the polymer^{15,16}.

Figure 7

Structure of isoprenyl units in chlorobutyl rubber ^{15,16,17}



3. Vulcanization of chlorobutyl rubber

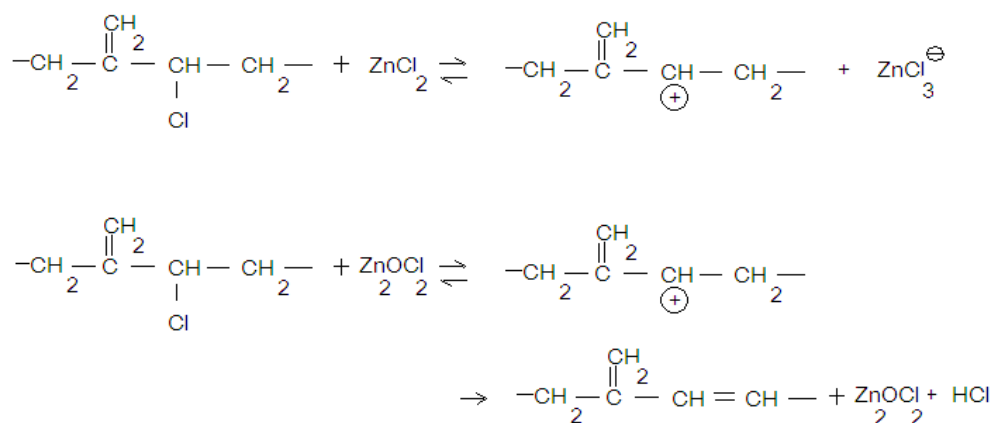
The crosslinking of chlorobutyl rubber with zinc oxide (ZnO) involves the formation of carbon-carbon bonds through alkylation chemistry¹⁴. The de-hydrohalogenation of chlorobutyl to form a zinc halogen catalyst is a key feature of this crosslinking chemistry¹⁶. In the presence of ZnO, hydrogen chloride will be trapped as zinc chloride and the reaction would become auto catalytic²⁰. The initial step in the

zinc oxide crosslinking is the formation of allylic carbocation. The carbocation is the reaction product of allylic halide moiety and zinc species. The carbonium ion alkylates another olefinic center to form carbon-carbon bonds^{20,21}. The ease of halogen elimination is the main difference in the crosslinking behavior of chlorobutyl rubber and bromobutyl rubber¹⁴.

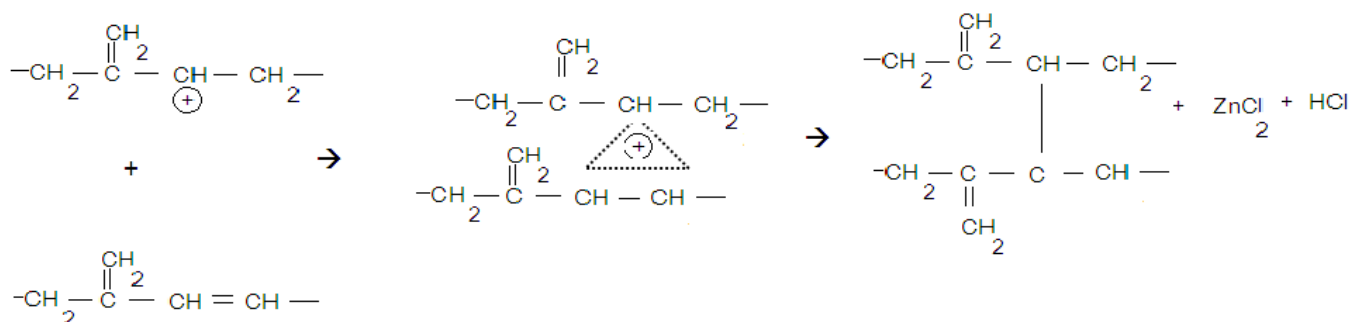
Figure 8

Vulcanization chemistry of chlorobutyl rubber^{7,20,21}

Step 1



Step 2



In the unstabilized state, both the crosslinking rate (expressed as first order rate constant) and the halogen-elimination rate (expressed as second order rate constant) are many times slower for chlorobutyl than for bromobutyl rubber. In presence of stabilizers, the difference in rate constants between the two halobutyl is reduced. The apparent cure rate difference between the halobutyl rubbers can be decreased further by adding retarders and by suitable modification of formulations.

Zinc oxide cure

The zinc oxide vulcanization system is a simple one, frequently used to monitor product quality and specialty applications requiring low extractable. The following principles are to be considered, when zinc oxide cure system is used for curing chlorobutyl compounds¹⁶.

- The zinc oxide cure is sensitive to acidic and basic compounding materials. In general, acids will accelerate cure rate while bases will retard. Water is a strong retarder because it complexes with the reactive intermediates. The acidity, basicity, and moisture content of all compounding ingredients may be considered; acidic clays may accelerate while calcium silicates and silica could retard cures.
- Carboxylate substitution occurs at the chlorine site during zinc oxide vulcanization promoted with stearic acid. As a result, stearic acid accelerates cure rate, reduces scorch safety, and lowers the ultimate extent of cure as measured by change in rheometer torque ($M_H - M_L$, or ΔT). In contrast, calcium stearate depresses both the extent of cure and the rate of cure.

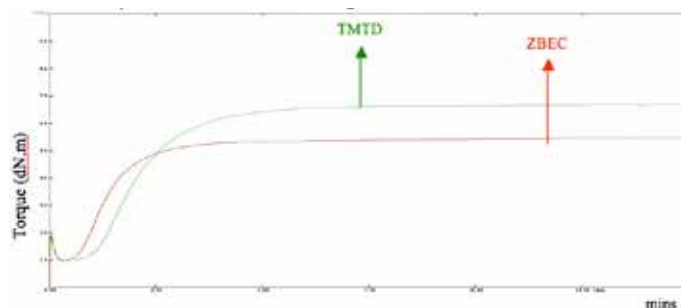
The carbon-carbon bond crosslink formed with zinc oxide cure systems can yield a more heat stable network in chlorobutyl rubber when compared to crosslinks of sulfur-cured general-purpose elastomer such as natural rubber (NR) and styrene butadiene rubber (SBR). Appendix 1 & 2 gives recognized abbreviations for rubber chemicals used in this manual.

Zinc oxide cure modified with thiurams and dithiocarbamates²²

In the absence of sulphur, addition of thiurams or dithiocarbamates increases the state of cure of chlorobutyl rubber. The rheometer curve obtained with two parts of Tetramethylthiuram disulfide (TMTD) and Zinc dibenzylidithio carbamate (ZBEC) is shown in figure 9. Formulation with TMTD show faster cure rates and produce tightly crosslinked networks. The cure plateau tends to be very flat with TMTD and ZBEC.

Figure 9

Comparison of CB 1066 curing with TMTD and ZBEC at 160°C²²

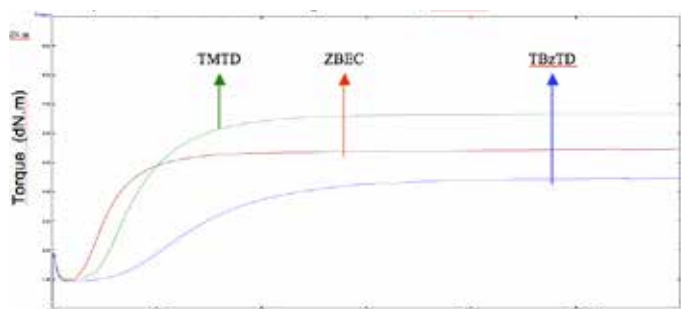


CB 1066 -100, N 660- 60, Naphthenic oil -22, MgO -0.2, Stearic Acid-1.0, Escorez 1102- 3, ZnO-5, ZBEC- 2.0 or TMTD -2.0

Use of accelerators like Tetra benzylthiuram disulphide (TBzTD) improves the processing safety. Figure 10 gives the rheometric property comparison of TMTD, ZBEC and TBzTD.

Figure 10

Comparison of CB 1066 curing with TMTD, TBzTD and ZBEC at 160°C²²



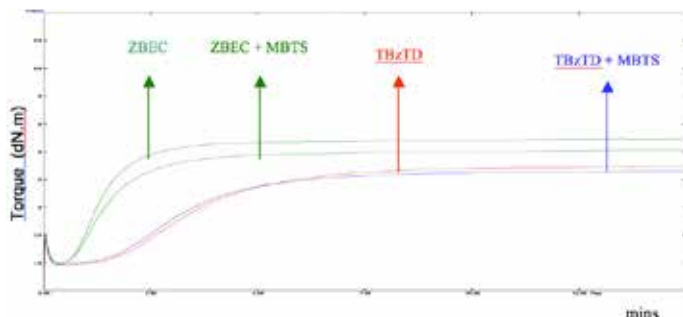
CB 1066 -100, N 660-60, Naphthenic oil- 22, MgO- 0.2, Stearic Acid -1.0, Escorez 1102-3.0, ZnO-5.0, TBzTD -2 or ZBEC- 2 or TMTD -2.0

Zinc oxide cure modified with thiurams, dithiocarbamates and thiazoles.

Addition of thiurams or dithiocarbamates can increase the state of cure and produce very stable networks with low compression set, making them useful for mechanical goods. Adding Dibenzothiazyl disulfide (MBTS) to thiurams or dithiocarbamate-accelerated formulation reduces delta torque as shown in figure 11.

Figure 11

Effect of MBTS on CB 1066 curing based on ZBEC and TBzTd at 160°C²²



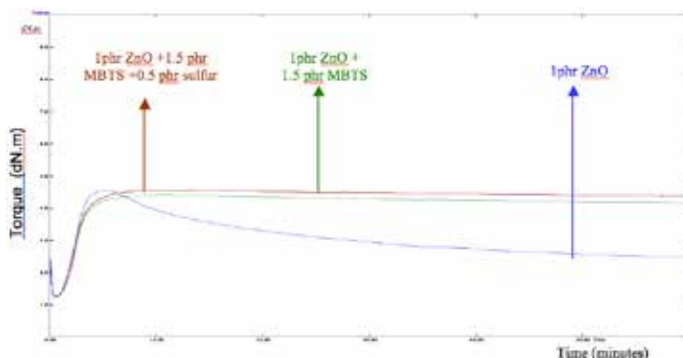
CB 1066-100, N 660-60, Process oil -22, MgO- 0.2, Stearic Acid - 1.0, Escorez 1102--3.0, ZnO-5.0 ZBEC/TBzTD -2.0 phr

Zinc oxide cure modified with thiazoles, and sulphur^{16,22}.

The addition of free sulphur to thiurams or thiuram-thiazole cure systems gives faster, tighter cures with good processing characteristics. Sulphur containing formulations are suggested when good physical properties are desired and where moderate heat and ozone resistance will suffice. Adding sulphur to the MBTS-ZnO system increases the state of cure ($M_H - M_L$) as shown in figure 12.

Figure 12

Effect of MBTS & sulphur on zinc oxide based CB 1066 curing at 160°C²²



CB 1066 -100, N 660- 60, Process oil- 8.0, Aliphatic & Aromatic hydro-carbon blend- 7.0, Stearic Acid-1.0, Escorez 1102- 4.0, ZnO- , MBTS & Sulphur as mentioned in the figure.

Zinc oxide cure modified with thiazoles and sulfenamides^{16, 27}

Dibenzothiazyl disulphides and sulfenamides are the most widely used primary accelerators in highly unsaturated, general purpose rubber curing. In combination with zinc oxide and sulfur, they are also well suited for curing 100 phr content chlorobutyl rubber formulations and chlorobutyl blends with unsaturated elastomers. Appendix 2 & 3 gives the industry abbreviations of the range of accelerators used in vulcanization system.

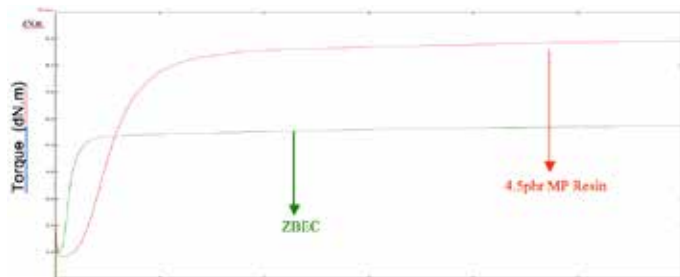
The thiazole/sulfur/zinc oxide cure system is one of the most effective systems for 100 phr chlorobutyl compounds and blends of chlorobutyl-general purpose rubber blends in composite systems such as tire innerliner. It yields heat and fatigue resistant vulcanizates with good cured adhesion to most tire casing compounds.

Zinc oxide cure modified with octylphenol formaldehyde resin.

Polymethylol phenol resins (MP Resins) are effective crosslinking agents for chlorobutyl rubber. Resin-cured chlorobutyl vulcanizates have excellent ozone resistance, compression set and flexing properties. Modulus is high, elongation and tear strength low as would be expected with this type of highly crosslinked structure. Tensile strength retention is good after heat ageing. The brominated resins react at lower curing temperature to give fast tight cures. The un-halogenated resins require no promoters when used with chlorobutyl, and give good cure rates and processing safety at 180°C. The usual cure system consists of 3 to 6 phr of resin with 5 phr of zinc oxide. In contrast to the use of these resins in regular butyl rubber where 6 to 10 phr are required, good cure states can be obtained with only 0.5 to 2.5 phr of resin. No halogen-donating catalyst is required for cure activation in compounds with chlorobutyl rubber. Vulcanization with octylphenol formaldehyde resins probably proceeds by alkylation so that cure rates and the onset of crosslinking are affected by factors similar to that for zinc oxide curing¹⁰. The octylphenol formaldehyde resin cure provides another vulcanization route free of sulfur, and may be suitable for some applications where low levels extractable materials are required.

Figure 13

Comparison of ZBEC and octylphenol formaldehyde resin cure curves at 160°C²²



CB 1066 -100, N 660-60, Process oil -22, MgO -0.2, Stearic Acid -1.0, Escorez 1102-3, ZnO-5., ZBEC -2. phr/M P Resin -4.5 phr.

Scorch control is an important factor in the effective use of resin cures in chlorobutyl. Magnesium oxide is the most effective retarder but affects properties significantly, giving lower tensile, modulus value and higher elongations. MBTS is also a capable modifier for the resin cure system.

Zinc oxide cure modified with alkylphenol disulfide polymer^{22, 24}

Alkylphenol disulfide polymer can be used to adjust scorch times or induction times in chlorobutyl compounds, even when retarders are employed. The alkylphenol disulfide polymer containing cure systems, though not generally required in chlorobutyl to promote co-curing, may help in optimizing adhesion and heat resistance properties depending on the final end-product requirements. As an empirical guide, alkylphenol disulfide polymer accelerators may also be used to adjust halobutyl compound scorch and cure induction times.

Figure 14

Effect of ZBEC and alkylphenol disulfide on CB 1066 curing at 160°C 22.



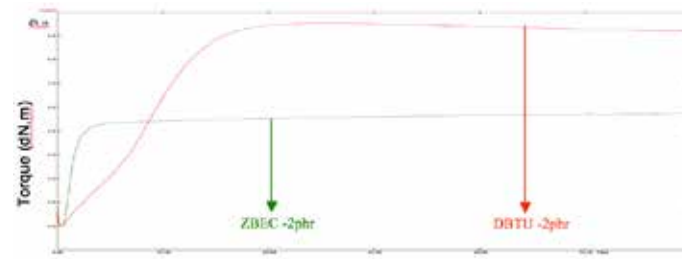
CB 1066 -100, N 660- 60, Process oil- 22, MgO -0.2, Stearic Acid- 1.0, Escorez 1102- 3.0, ZnO-5.0 ZBEC- 2.0 phr/Vultac TB 710- 2.0 phr.

Zinc oxide cure modified with thiourea

Thioureas react through the active chlorine sites in chlorobutyl to crosslink the polymer. Cure is improved when acid acceptors like magnesium oxide are present along with thiourea cure system. These cures provide outstanding ozone resistance.

Figure 15

Effect of ZBEC and DBTU on CB 1066 curing at 160°C 22



CB 1066 -100, N 660- 60, Process oil -22, MgO- 0.2, Stearic Acid -1.0, Escorez 1102- 3.0, ZnO-5.0 ZBEC -2.0 phr/DBTU -2.0

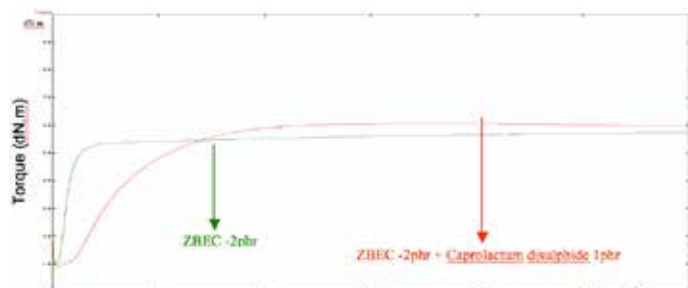
N-nitrosamine free sulphur donor vulcanization system for chlorobutyl rubber⁹

Nitrosamine formation requires the presence of curatives containing secondary amines. Such groups are found in common accelerator including dithiocarbamates (e.g., zinc diethyldithiocarbamate, ZDEC), thiurams (e.g., tetramethylthiuram disulfide TMTD), and sulfenamides (e.g., morpholiniothio sulfenamide, MBS), and some specialized accelerators such as dithiodimorpholine (DTDM). Many commercial compounds and some of the formulations shown in these manual use curatives, which may oxidize, to N-nitrosamines. There are four techniques by which to eliminate or suppress N-nitrosamines, these are:

- Accelerators, which do not contain secondary amine groups, primary amine sulfenamides can replace sulfenamides containing secondary amines. Due to differences in cure activity, these are unlikely to be 'drop-in' replacements and some adjustments to the accelerator system may be required. Other cure systems containing ingredients, which do not have secondary amine functionality, include MBT, MBTS, alkylphenol disulfides, caprolactum disulphide (figure 16) and p-quinone dioxime.

Figure 16

Effect of ZBEC and ZBEC + caprolactum disulphide
On CB1066 curing at 160°C²²

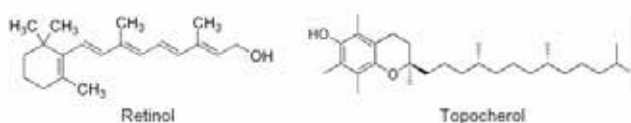


CB 1066 - 100, N 660- 60, Process oil -22, MgO- 0.2, Stearic Acid - 1.0, Escorez 1102- 3.0, ZnO-5.0 ZBEC- 2.0 phr

- Curatives containing non-volatile secondary amines groups: tetrabenzylthiuram disulfide (TBzTD) and its thiocarbamate salt can be used as a replacement for lower molecular weight thiurams and dithiocarbamates. Adjustment of the cure system will be required because of the higher molecular weight and lower vulcanization rate of these accelerator molecules.
- Chemically block N-nitrosamine formation: retinol (vitamin A) and tocopherol (vitamin E), hydroquinone, and calcium hydroxide are known chemical suppressants of N-nitrosamine formation⁹ (figure 17).

Figure 17

Retinal and topochoerol



- Filler modification: the oxidizing agents that convert accelerators to N-nitrosamines are found on the surface of the carbon black filler. Proper choice of black type and level can partially suppress N-nitrosamine formation. The industry-wide problem of N-nitrosamines has gained the attention of accelerator suppliers are continually searching for effective substitutes for the current popular accelerators.

Vulcanization in the presence of mineral fillers

When using clay, talc, or calcium carbonate fillers, the same types of cure systems can be used as carbon black filled compounds. However, because of the large variations in chemical composition and physical structure of mineral fillers, the cure system ingredients may have to be adjusted for each type of filler. Many types of clay are acidic and may therefore require a cure retarder in the cure system. Alternatively, cure systems for compounds containing basic fillers such as calcium silicate, or calcium carbonate coated with calcium stearate may require secondary accelerators or higher levels of accelerator and vulcanizing agent.

Scorch control

Many compounding ingredients alter scorch time and cure rate of chlorobutyl rubber-zinc oxide-based formulations.

Generally, alkaline substances can increase scorch time. The most commonly used material to increase scorch time is magnesium oxide. Typical levels of MgO are 0.1 to 0.5 phr. Calcium oxide, magnesium and calcium stearates, and other alkaline salts of fatty acids also function as retarders. However, use of these materials may reduce cure rate.

- Incorporation of a polyethylene glycol (at approximately 1.0 phr) improves scorch safety or scorch time. This material must be used with care in compounds requiring good building tack.
- Scorch time can be increased by reducing stearic acid, zinc oxide, and/or sulfur levels.
- Addition of secondary accelerators to a chlorobutyl/natural rubber blend may tend to show less effect on scorch time compared to a 100% chlorobutyl compound.
- Phenolic tackifying resins tend to reduce scorch safety, and to be minimized.
- Amine-type antidegradants such as quinolines and phenylene diamines are curing agents for chlorobutyl.
- Retarders used in high unsaturation elastomers to retard the sulfur cure generally have the opposite effect in chlorobutyl by activating zinc oxide and induce a faster, less scorch resistant response.

4. Blends of chlorobutyl rubber with other elastomers

Chlorobutyl rubber can be blended with other elastomers to broaden the range of vulcanization properties. Chlorobutyl rubber is completely compatible with regular butyl rubber, ethylene-propylene diene rubbers (EPDM) and butyl reclaim. It can also be blended with high unsaturation general-purpose rubbers, most commonly natural rubber and styrene butadiene rubber (SBR). Blending with high unsaturation rubber is done for the following purposes:

- To impart better impermeability (butyl like properties) to high unsaturation rubber compound. Heat degradation resistance, weather degradation resistance and flex fatigue properties are improved along with reduced gas permeability.
- To improve cured adhesion of chlorobutyl compound to general-purpose rubbers in composite systems such as tires, belting and hoses. When structurally different high molecular weight polymers are blended, they disperse in one another but remain in distinct phases on microscopic scale. Once adequate dispersion is achieved, the main problem is to select a cure system to provide good crosslinking in both phases and across phase boundaries.

Polymer blending allows attainment of many properties not possible with compounds containing only one polymer. For example, chlorobutyl rubber will impart lower gas permeability, improved heat resistance, flex life, and weather resistance to non-isobutylene based elastomers. Natural rubber blended with chlorobutyl rubber improves building tack, green strength, elasticity, and cure compatibility with highly unsaturated rubber substrates.

Many types of compounds contain blends of elastomers. Elastomer blending can allow improvement in fatigue resistance, reduction in hysteresis, improved crack resistance, and adhesion. It may also improve processing such as extrusion and molding of the final tire construction. For example, addition of natural rubber to a largely synthetic rubber compound will improve end-product buildability, component-to-component adhesion, and tear strength.

Compatibility of two elastomers is defined as when the polymers are immiscible but if in combination show characteristics that are more useful than the properties of the original polymers. Incompatible polymers when blended will show a dual glass transition temperature (T_g) with deterioration of many compound properties. Miscible blends are obtained when at the molecular level, the two polymers are compatible. Polymer compatibility and compounded

properties is governed by three parameters:

- Thermodynamics: micro domain formation is achieved by surface energy reduction (i.e. use of processing aids), and vulcanization.
- Viscosity: oil/filler levels in dissimilar elastomers can be adjusted in mixing to enhance compatibility.
- Cure Rate: NR/EPDM and NR/IIR or NR/HIIR systems where the respective polymers are significantly different.

Polymer compatibilization can therefore be achieved either by reduction of interfacial energy, by improvement of dispersion during mixing, stabilization of the polymers to prevent phase separation after mixing, or improvement of interfacial or interdomain adhesion. For two elastomers of different composition to be miscible, the Gibbs free energy of mixing, ΔG must be negative. Gibbs free energy is a function of the enthalpy of mixing (ΔH), entropy of mixing (ΔS), and temperature (T) in °K, i.e.,

$$\Delta G = \Delta H - T \Delta S \quad (1)$$

Miscible elastomers will tend to show hydrogen bonding or van der Waals forces between chains. However, phase separation may occur if the temperature rises above the critical solution temperature. Miscible elastomers will show single T_g .

The solubility parameter (δ) for a material is related to the enthalpy of mixing. It is defined as the square root of the cohesive energy density, or attractive strength between molecules, i.e.,

$$\delta = (\Delta E / V)^{1/2} \quad (2)$$

where ΔE is the energy of vaporization and V is the molar volume of the polymer. Solubility parameter is expressed in $(\text{MPa})^{1/2}$. As an empirical guide, the solubility parameter difference between two polymers must be less than 1.0 to be compatible, though there are many exceptions. There must also be no change in volume or reaction between the two elastomers. Solubility parameters can only be determined indirectly by methods such as solvency in a solvent such as hexane, toluene, dibutyl phthalate or ethanol. Other methods used have included swelling, refractive index, dipole moment measurements, or intrinsic viscosity.

The solubility parameter of isobutylene based rubbers are in the range 15.7 to 16.6 $(\text{MPa})^{1/2}$ depending on the test and calculation methods. This compares to the solubility parameter

of polybutadiene which is in the range 16.2 to 17.6 (MPa)^{1/2}. Nitrile elastomers range from 18.4 to 21.1 depending on the acrylonitrile content. Solution SBR solubility parameters range from 17.1 to 17.4 depending on the styrene level. These solubility parameters can be used to estimate the miscibility of the elastomers. For illustrative purposes, natural rubber with a solubility parameter of 16.6 when mixed with a NBR with a solubility parameter of 19.4 gives a solubility parameter differential of 2.8. As this is greater than 1.0, the two elastomers would be considered to be immiscible.

Chlorobutyl-bromobutyl rubber blends.

Chlorobutyl and bromobutyl have the same polyisobutylene backbone and very similar functionalities, so they co vulcanize well. In most formulations, they can be blended in any proportion without significant effects on ultimate cure state as measured by extension modulus, tensile strength and rheometer torque development. Incorporation of the more reactive bromobutyl into a chlorobutyl compound increases its cure rate and reduces scorch time.

When bromobutyl rubber is the major component, the presence of chlorobutyl rubber does not reduce scorch tendencies from those of bromobutyl. Blends containing up to 40% chlorobutyl rubber with bromobutyl rubber exhibit nearly equivalent cure activity to the corresponding 100% bromobutyl compounds. For example, a halobutyl blend with 40% chlorobutyl rubber with bromobutyl exhibits co-vulcanization to natural rubber compounds similar to its 100% bromobutyl counterpart^{9,29} (as evidenced by cured adhesion to a natural rubber tire carcass compound).

Chlorobutyl-natural rubber blends

Although chlorobutyl rubber and natural rubber have different backbone structures, different degrees of functionality, and different vulcanization chemistry, they can be blended in various amounts to attain a desired combination of properties. This is due to the versatility of the chlorobutyl vulcanization. Not only can chlorobutyl vulcanize independently from the natural rubber-sulfur cure system by merely crosslinking with zinc oxide, but it also uses sulfur efficiently in the presence of natural rubber to promote co-vulcanization.

The addition of chlorobutyl rubber to a predominantly natural rubber compound reduces the permeability to gases and water vapor, increases the heat and flex crack resistance, and increases vibration damping. Blending natural rubber into chlorobutyl rubber increases cured adhesion to general-purpose rubber compounds as well as increasing building tack and green strength. In blends of two rubbers, the physical properties, in particular tensile strength, usually show a significant change compared to the properties of the separate

rubber compounds. This infers either that one rubber disturbs the cured network of the other, or that the two immiscible phases are curing separately. With chlorobutyl rubber-natural rubber blends, tensile strength values can be equal to or greater than the average of the two homopolymers, which implies crosslinking between the elastomer phases. A thiazole-sulfur cure system generally exhibits the best balance of properties with blends containing 50% (>80 phr) or more of chlorobutyl. Below 40% (<70 phr), an alkylphenol disulfide polymer (VULTAC (R) TB710) cure system is suggested to enhance the co curing between the chlorobutyl and natural rubber phase⁹. Table III shows chlorobutyl and chlorobutyl rubber/natural rubber compound properties using the zinc oxide-sulfur-MBTS cure system. Additional model starting point formulations for a variety of applications can be found at www.butylrubber.com¹.

It is difficult to alter the scorch properties of chlorobutyl/general-purpose rubber blends with classical retarders. For instance, salicylic acid is a retarder for general-purpose rubbers (GPR), but an accelerator for chlorobutyl rubber. Alkaline retarders used with chlorobutyl are often accelerators for general-purpose rubber. Therefore, the scorch time of blends is best set by appropriately choosing the cure system and the compound viscosity (as it influences the heat history of the compound during processing). One possible scorch inhibitor for a 100 phr content chlorobutyl and chlorobutyl-natural rubber blend compounds is magnesium oxide used at between 0.1 to 0.5 phr.

Table IIIModel formulations for an automobile tire innerliner^{1,22}

Material	Units	1	2	3
Exxon™ chlorobutyl 1066	PHR	100.00	80.00	60.00
Natural rubber		-	20.00	40.00
N660		60.00	60.00	60.00
Naphthenic oil		8.00	8.00	8.00
Processing aid		7.00	7.00	7.00
Phenol formaldehyde resin		4.00	4.00	4.00
Magnesium oxide		0.15	0.15	0.15
Stearic acid		2.00	2.00	2.00
Zinc oxide		1.00	1.00	1.00
MBTS		1.50	1.50	1.50
Sulfur		0.50	0.50	0.50

Typical properties: Mooney viscosity	Test method ASTM	Units	100 CIIR	80:20 CIIR:NR	60:40 CIIR:NR
Mooney viscosity ML 1+4, at 100°C	D 1646	MU	53.8	51.2	45.3

Typical properties: Mooney scorch at 125°C					
Time to 5-point rise	D 1646	minutes	30.8	27.1	21.3

Typical properties: MDR rheometer, 160°, 60 minutes, arc ± 0.5°					
Minimum torque (ML)	D 5289	dN.m	1.3	1.3	1.2
Maximum torque (MH)	D 5289	dN.m	4.7	6.5	5.7
Delta torque (MH-ML)	D 5289	dN.m	3.4	5.3	4.4
Time for two-point rise in torque. (ts ₂)	D 5289	minutes	4.6	6.4	3.4
Time to 50% rise in torque. (tc ₅₀)	D 5289	minutes	4.1	7.7	3.6
Time to 90% rise in torque. (tc ₉₀)	D 5289	minutes	11.7	14.3	12.3

Typical stress strain properties-original					
Cure time, Min. (tc 90+2) at 160°C					
Hardness	D 2240	Shore A	44	48	46
100 % modulus	D 412	MPa	0.9	1.2	1.0
300 % modulus	D 412	MPa	2.4	3.3	2.9
Tensile strength	D 412	MPa	8.2	9.3	7.0
Elongation at break	D 412	%	895	770	655
Tear strength (Die B)	D 624	kN/m	37.8	42.0	32.6

Typical stress strain properties-aged at 125°C 72 hrs					
Hardness	D 2240	Shore A	52	66	60
100 % modulus	D 412	MPa	1.4	2.6	3.0
300 % modulus	D 412	MPa	3.7	4.7	--
Tensile strength	D 412	MPa	5.4	5.2	3.9
Elongation at break	D 412	%	540	380	210
Air permeability at 65°C	ml [STP]. mm/mm ² .760 mm Hg. Hour		12.6	21.4	33.2
Oxygen permeation rate by MOCON at 40°C-oxygen conc.: 21%	mm-cc/[m ² -day]		243.2	416.7	686.0

Chlorobutyl-butyl rubber blends

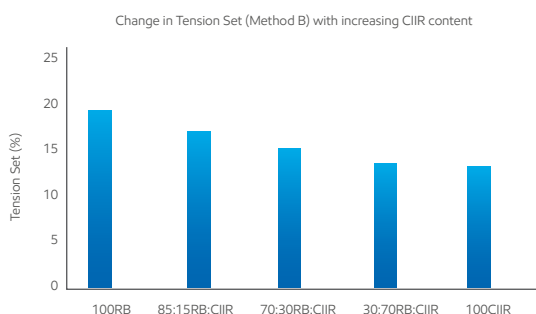
With chlorobutyl-butyl rubber blends, elastomer structures are essentially the same, but the different reactive functionalities provide different vulcanization chemistry. Since chlorobutyl rubber has greater cure reactivity, accelerators that will overcure the chlorobutyl phase may be avoided. Briefly:

- Low level blending of butyl rubber into chlorobutyl rubber increases the scorch time and improves the heat resistance of the compound.
- Blends with up to 20 phr of butyl rubber exhibit chlorobutyl-like adhesion.
- Butyl rubber levels in excess of 20 phr sharply reduce adhesion to general-purpose rubber compound substrates³. Blending up to 30% butyl into chlorobutyl slows the cure rate and provides a small benefit in lower modulus increase and higher retained elongation after heat aging.

As butyl rubber has the same permeability as chlorobutyl rubber, blending it into a chlorobutyl compound does not alter the compound permeability (as natural rubber would, for example, incorporating small amount of chlorobutyl rubber into butyl compounds has the benefit of reducing tension set as shown in the figure 18.

Figure 18

Effect of CIIR rubber on tension set properties on Exxon™ chlorobutyl 1066/Exxon™ butyl 1066 rubber blends (50% Extension at 105°C for 5 hours)



Chlorobutyl-styrene butadiene rubber blends

Like natural rubber, styrene butadiene rubber (SBR) can be blended in all proportions with chlorobutyl. SBR is less desirable for blending than natural rubber due to its low tack and green strength properties. In addition, heat, flex fatigue resistance, and weathering resistance are poorer with SBR blends than with natural rubber blends. Vulcanization systems can be similar as natural rubber blends.

Chlorobutyl-GPR-EPDM rubber triblends

Ethylene propylene diene terpolymers (EPDM) can be used to improve the ozone resistance of chlorobutyl rubber-natural rubber binary polymer blends, eliminating the need for chemical antiozonants. An addition of 10 phr of Vistalon™ 6505 (with a high ethylidene norbornene (ENB) content of 9%) to a 50/50 Exxon™ chlorobutyl 1066/natural rubber blend results in a compound with excellent static and dynamic ozone resistance. A typical chlorobutyl based tri-blend formulation for sidewall application is given in table IV.

In these blends, natural rubber contributes adhesion to adjacent components and lower energy loss, EPDM imparts static ozone resistance, and chlorobutyl rubber provides flex and dynamic ozone resistance.

The highest unsaturation EPDM rubber is preferred for good vulcanization in the presence of general-purpose rubbers. Addition of wood rosin dramatically improves the scorch resistance properties of alkylphenol disulfide polymer cures in chlorobutyl compounds. Starting point model formulas for various applications utilizing chlorobutyl blends can be found at www.butylrubber.com¹.

Chlorobutyl and EP or EPDM rubber can be blended in all proportions and can be co-vulcanized using either zinc oxide/sulfur cure systems or peroxide based cure systems. More information on compounded blends of various elastomers with chlorobutyl can be found at www.butylrubber.com.

Table IVCIIR-GPR- EPDM tri-blend formulation for white sidewall and cover strip ²²

Material	Units	White sidewall compound	Cover strip
Exxon™ chlorobutyl 1066	PHR	50.00	50.00
Vistalon™ 6505		20.00	20.00
Natural rubber		30.00	30.00
Stearic acid		1.00	1.00
Treated clay		35.00	---
Calcined clay		25.00	---
TiO ₂		25.00	---
MC wax		3.00	3.00
Phenolic resin (Tackifier)		5.00	5.00
Ultramarine blue		0.05	0.00
Carbon black (N 550)		---	50.00
Naphthenic oil		---	10.00
Sulphur		0.70	0.70
MBTS		1.00	1.00
Alkylphenol disulfide polymer (VULTAC (R) TB710)		1.35	1.35
Zinc oxide		5.00	5.00

Typical properties: Mooney viscosity	Test Method	Units		
Mooney viscosity ML 1+4, at 100 °C	ASTM D 1646	MU	42.9	48.4

Rheometric properties at 160° C, 60 minutes, arc ± 0.5°				
Minimum torque (ML)	ASTM D 5289	dN.m	1.1	1.3
Maximum torque (MH)	ASTM D 5289	dN.m	7.4	9.3
Delta torque (MH-ML)	ASTM D 5289	dN.m	6.3	8.0
Time for two-point rise in torque. (ts ₂)	ASTM D 5289	minutes	3.4	2.0
Time to 50% rise in torque. (tc ₅₀)	ASTM D 5289	minutes	4.8	3.6
Time to 90% rise in torque. (tc ₉₀)	ASTM D 5289	minutes	10.7	10.6

Stress strain properties, samples cured at 160°C, tc ₉₀ + 2 minutes.				
Hardness	ASTM D 2240	Shore A	49	55
50 % modulus	ASTM D 412	MPa	1.0	1.2
100 % modulus	ASTM D 412	MPa	1.5	2.1
300 % modulus	ASTM D 412	MPa	3.7	7.8
Tensile strength	ASTM D 412	MPa	8.6	11.0
Elongation at break	ASTM D 412	%	570	450
Tear strength (Die C)	ASTM D 624	kN/m	23.2	29.6

Typical stress strain properties-aged at 100°C 72 hrs				
Hardness	ASTM D 2240	Shore A	54	61
50 % modulus	ASTM D 412	MPa	1.4	1.7
100 % modulus	ASTM D 412	MPa	2.3	3.4
300 % modulus	ASTM D 412	MPa	4.2	---
Tensile strength	ASTM D 412	MPa	6.2	9.0
Elongation at break	ASTM D 412	%	460	260
Static ozone testing 40°C. 50pphm O ₃	ExxonMobil Method	No cracks up to 150 hours.		
De-Mattia crack initiation	ExxonMobil Method	No cracks up to 200 kilocycles.		
De-Mattia crack growth at 200 kilocycles	ExxonMobil Method	mm	6.7	9.5

ExxonMobil Chemical data

Comparison of bromobutyl and chlorobutyl rubber in tire innerliner applications

Chlorobutyl as well as bromobutyl rubber can be used in tire innerliner applications. Comparison between a typical chlorobutyl and bromobutyl rubber in tire innerliner formulations are given in table V.

Table VComparison of CIIR & BIIR innerliner formulations ²²

Material	Units	BB 2222	CB 1066
Exxon™ bromobutyl 2222	PHR	100.00	---
Exxon™ chlorobutyl 1066		---	100.00
N660		60.00	60.00
Naphthenic oil		8.00	8.00
Processing aid		7.00	7.00
Escorez™ 1102		4.00	4.00
MgO		0.15	0.15
Stearic acid		2.00	2.00
Zinc oxide		1.00	1.00
MBTS		1.50	1.50
Sulfur		0.50	0.50

Typical properties: Mooney viscosity	Test method	Units		
Mooney viscosity ML 1+4, at 100°C	ASTM D 1646	MU	52.9	53.8
Mooney scorch (5-point rise at 125°C)	ASTM D 1646	minutes	28.2	30.8

Rheometric properties at 160° C, 60 minutes, arc ± 0.5°				
Minimum Torque (ML)	ASTM D 5289	dN.m	1.3	1.3
Maximum Torque (MH)	ASTM D 5289	dN.m	4.8	4.7
Delta Torque (MH-ML)	ASTM D 5289	dN.m	3.5	3.4
Time for two-point rise in torque. (ts ₂)	ASTM D 5289	minutes	6.5	4.6
Time to 50% rise in torque. (tc ₅₀)	ASTM D 5289	minutes	5.8	4.1

Time to 90% rise in torque. (tc ₉₀)	ASTM D 5289	minutes	12.1	11.7
Stress strain properties, samples cured at 160°C tc ₉₀ + 2 minutes.				
Hardness	ASTM D 2240	Shore A	46	44
50 % Modulus	ASTM D 412	MPa	0.6	0.6
100 % Modulus	ASTM D 412	MPa	0.9	0.9
300 % Modulus	ASTM D 412	MPa	2.6	2.4
Tensile Strength	ASTM D 412	MPa	8.6	8.2
Elongation at break	ASTM D 412	%	825	895
Tear Strength (Die B)	ASTM D 624	kN/m	38.8	37.8

Typical Stress Strain Properties- Aged at 125°C 72 hrs				
Hardness	ASTM D 2240	Shore A	54	52
100 % Modulus	ASTM D 412	MPa	1.6	1.4
300 % Modulus	ASTM D 412	MPa	4.1	3.7
Tensile Strength	ASTM D 412	MPa	6.9	5.4
Elongation at break	ASTM D 412	%	655	540
Air Permeability at 65°C	ml [STP]. mm/mm ² .760 mm Hg. Hour (EM Method)		12.6	12.6
Oxygen Permeation rate by MOCON at 40°C - Oxygen conc.: 21%	mm-cc/[m ² -day] (EM Method)		243.2	233.4

1. Scorch resistance

Chlorobutyl compounds have a better scorch resistance than bromobutyl compounds.

2. Reversion resistance

Chlorobutyl compounds have a better reversion resistance than bromobutyl compounds. Cure curves at 160°C is given in figure19.

3. Thermal stability of green compounds

Chlorobutyl compounds have a better thermal stability than bromobutyl compounds. Masterbatches of chlorobutyl compounds are mixed to a dump temperature of 145°C while the dump temperatures of bromobutyl compounds are limited to 135°C.

4. Permeability

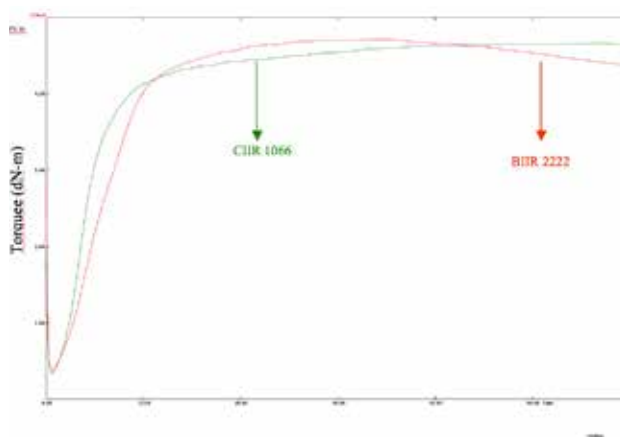
Chlorobutyl rubber and bromobutyl rubber compounds show similar permeability as the polymer backbone remain the same. Permeability varies with other compounding ingredients.

5. Cure system type

Bromobutyl rubber is versatile than chlorobutyl with respect to cure systems. Bromobutyl can be cured with a wide variety of cure systems including zinc free amine cure systems as used in pharmaceutical closures.

Figure 19

Cure curve comparison of Exxon™ chlorobutyl 1066 compound with Exxon™ bromobutyl 2222 (rheo at 160°C/60 minutes)



ExxonMobil Chemical data: Refer table V for formulations.

5. Compounding guidelines

Like other elastomeric compounds, the final properties of chlorobutyl vulcanizate depend upon the nature and the degree of crosslinking, as well as the type and the concentration of the other compound ingredients. Fillers (carbon black and mineral fillers), plasticizers, processing aids, tackifying resins, and antidegradants influence the properties of chlorobutyl compounds to various extents, and their proper selection is important to obtain optimum performance.

Plasticizers

Petroleum-based processing oils, added at between 8 to 20 phr, are the most commonly used plasticizers for carbon black filled chlorobutyl compounds. The amount of plasticizer will depend on the required compound properties such as for example to processing and low temperature flexibility requirements. Aliphatic and particularly naphthenic oils are preferred because they solvate chlorobutyl more effectively and the rubber industry is reducing the use of aromatic oils¹⁸. Aromatic oils can generally be adequate, but they lead to discoloration, staining, show shorter compound scorch times, or affect low temperature flexibility due to poorer solvation of the chlorobutyl compound. Regardless of the oil type, higher oil levels in a compound reduce viscosity, hardness, and modulus, while increasing permeability. Improvements in low temperature flexibility can be achieved by utilizing ester type plasticizers such as adipates and sebacates. Paraffin waxes and low molecular weight polyethylene, although not considered solvating agents, could also be used to improve processing.

An aromatic & aliphatic hydrocarbon resin blend is commonly used in high-chlorobutyl innerliner at loadings between 4 and 10 phr. It functions partly as a plasticizer (replacing about 4 phr of oil) and, more importantly, it enhances cured adhesion to substrates consisting of highly unsaturated rubbers. Materials such as mineral rubber and asphaltic pitch have also been used for this dual function.

Carbon black

The response of chlorobutyl rubber to carbon blacks is generally similar to that of synthetic elastomers. Smaller particle size carbon blacks (SAF, ISAF, HAF) provide additional reinforcement while the carbon blacks with larger particle size (FEF, GPF, SRF) are less reinforcing. A good balance of compound processing, reinforcement, and physical properties can be obtained by using general purpose furnace grades (GPF), such as N660 carbon black at loadings of 50 to 70 phr. Typically, viscosity, hardness, and modulus increase as more carbon black is added to the compound. Tensile strength generally increases, then decreases, often passing through a maximum between 50 to 60 phr. For higher reinforcement and abrasion resistance, high abrasion furnace (HAF) carbon blacks can be used. However, they require more intensive mixing to insure good dispersion. Comparison of different carbon black is given in table VI.

The particle size of the carbon black is of major importance. The smaller particle size carbon blacks increase viscosity, hardness, and modulus. HAF carbon black yields higher tensile strength than the larger particle carbon black. Generally, the tensile strength of a compound with HAF filler may be higher at the 60-phr level than a compound with GPF filler at the 60-phr level²⁵.

Table VI

Effect of different carbon black on the properties of CIIR compounds²²

Compounds	Unit	1 N 220	2 N 326	3 N 339	4 N 330	5 N 660
Exxon™ chlorobutyl 1066	PHR	100.00	100.00	100.00	100.00	100.00
N 220		50.00	---	---	---	---
N 326		---	50.00	---	---	---
N 339		---	---	50.00	---	---
N 330		---	---	---	50.00	---
N 660		---	---	---	---	50.00
Naphthenic oil		3.00	3.00	3.00	3.00	3.00
Stearic acid		1.00	1.00	1.00	1.00	1.00
MgO		0.15	0.15	0.15	0.15	0.15
Escorez™ 1102		3.00	3.00	3.00	3.00	3.00
Antioxidant		1.50	1.50	1.50	1.50	1.50
Zinc oxide		5.00	5.00	5.00	5.00	5.00
Alkylphenol disulfide polymer		1.00	1.00	1.00	1.00	1.00
MBTS		1.00	1.00	1.00	1.00	1.00
Total		165.65	165.65	165.65	165.65	165.65

Typical properties: Mooney viscosity

ML 1+4, at 100°C	MU	78.5	64.9	79.3	71.1	65.1
ML 1+8, at 100°C	MU	78.3	64.7	78.9	71.2	64.7

Typical properties: MDR rheometer, 160°C, 60 minutes, arc ± 0.5°

Minimum torque (ML)	dN.m	3.2	2.4	2.8	2.6	1.9
Maximum torque (MH)	dN.m	13.9	11.0	13.8	12.0	8.6
Delta torque (MH-ML)	dN.m	10.8	8.6	10.9	9.4	6.8
Time for two-point rise in torque. (ts ₂)	minutes	1.8	1.9	1.8	1.9	1.9
Time to 50% rise in torque. (tc ₅₀)	minutes	5.0	3.8	4.7	4.2	2.6
Time to 90% rise in torque. (tc ₉₀)	minutes	20.8	12.9	19.2	16.0	5.0

Table VI

Effect of different carbon black on the properties of CIIR compounds (Continued from previous page)

Typical stress strain properties-unaged (formulations are available in previous page)						
	Unit	N 220	N 326	N 339	N 330	N 660
Hardness	Sh. A	59	54	61	56	50
50 % modulus	MPa	1.5	1.2	1.6	1.3	1.1
100 % modulus	MPa	2.8	2.3	3.2	2.5	2.0
300 % modulus	MPa	12.4	10.3	13.5	10.8	8.0
Tensile strength	MPa	18.2	15.2	16.4	16.9	11.7
Elongation at break	%	430	430	360	460	490
Tear strength (Die B)	N/mm	45.6	33.9	30.8	35.6	28.5

Typical stress strain properties-aged at 125°C 72 hrs						
Hardness	Sh. A	67	60	69	64	53
100 % modulus	MPa	4.4	3.3	4.7	3.8	2.8
Tensile strength	MPa	15.1	12.8	14.4	14.4	11.0
Elongation at break	%	280	300	240	290	350

Static ozone testing						
Cure time, Min. (tc 90+2) at 160°C, tested at 40°C, Ozone concentration 50 pphm, Extension 20%						
Observation at 8 hrs		NC	NC	NC	NC	NC
Observation at 24 hrs		NC	NC	NC	NC	NC
Observation at 50 hrs		NC	NC	NC	NC	NC
Observation at 72 hrs		NC	NC	NC	NC	NC
Observation at 100 hrs		NC	NC	NC	NC	NC
NC: No Cracks						
Tension Set at 105°C	%	13.0	12.3	10.9	11.7	7.6
Oxygen permeation rate at 40°C, Oxygen concentration:21% [mm-cc/[m ² -day] (ExxonMobil Test Method)		176.8	180.2	175.6	187.5	177.8
Oxygen permeability coefficient at 40°C, Oxygen concentration :21% [mm-cc/[m ² -day] *mmHg (ExxonMobil Test Method)		0.264	0.269	0.262	0.280	0.266

ExxonMobil Chemical data

Mineral fillers

Common mineral fillers may be used in chlorobutyl compounds. Fillers vary significantly in both particle size and chemical nature, and they may have the potential to alter vulcanization characteristics. Alkaline fillers, such as calcium silicates, and hygroscopic fillers can strongly retard cure, while acid clays can accelerate cure rates. Depending upon the particle size, mineral fillers may be semi-reinforcing or non-reinforcing. Fillers such as talc or clay are less reinforcing, providing mainly increased stiffness or hardness. Filler selection also affects other properties such as adhesion, flex resistance, and gas barrier properties.

Silica provides the highest amount of reinforcement among mineral fillers²⁶. However, they can be used at moderate levels since they promote compound stiffness and strongly affect cure rates because of their tendency to absorb accelerators such as sulfenamides and thiazoles. Cure rate retardation can be corrected by increasing the levels of curatives. Typically, the smaller particle size (i.e. greater surface area) silica provides higher tensile strength and 300% modulus.

Polyethylene glycols (PEG) are often used with silicates, and sometimes silicas, to improve dispersion of the compounding ingredients. Cure retarding effects of PEG can be overcome by adjusting curative levels. Higher molecular weight thiourea based accelerators are excellent accelerators for silica-filled chlorobutyl compounds but use of thioureas can be limited depending on their conditions of use.

Clay (aluminum silicate) is less reinforcing than silica, and since they vary in surface acidity, they may affect vulcanization. Additional curatives or the use of scorch retarders may be needed to compensate for the effect of the clays. Calcined clay is particularly suited for pharmaceutical stopper applications due to its purity, low water content, and particle uniformity. Very high levels of clay (100 phr) may cause mill sticking, requiring the use of release aids.

Talc (magnesium silicate) is semi-reinforcing when compounded with chlorobutyl and has no major effect on cure. Talc enhances resistance to fragmentation during needle penetration and withdrawal in pharmaceutical closures.

Whiting (calcium carbonate) is mainly used as an inert filler for adjusting compound cost. It is near neutral in curing of chlorobutyl compounds unless the particles are coated with calcium stearate (a retarder) or stearic acid (an accelerator). Starting point model formulations using a variety of fillers in various applications can be found at www.butylrubber.com¹.

Combination of mineral fillers

A combination of two or three mineral fillers can lead to a balance of mechanical properties and cure rates. The cure retarding effect of silicas can be reduced by partial replacement with calcined clay, while the lower tear resistance produced by clays can be improved by the addition of silica. When using combinations of silica and calcined clay at a constant 60 phr total filler loading, the following may be observed:

- Hot tear (160°C) strength and hardness increase with larger proportions of silica.
- Clay and silica have about the same effect on hardness, compression set and hot 160°C tear strength.
- Compression set can be adjusted with change in the level of silica.

Design of experiments can be used as an effective technique to illustrate the effect of blends of inorganic fillers on compound properties. In a resin cured chlorobutyl compound, satisfactory physical properties could be obtained, for example, by using a 50/50 combination of a silica and talc.

Silane-treated mineral fillers

Polymer-pigment interactions with mineral fillers can be enhanced by using chemical coupling agents. Organosilanes such as trimethoxysilyls (MTMO) or amino propyl trimethoxysilanes (AMEO) are particularly useful for chlorobutyl compounds, when added at 0.5 to 1.0 phr. The alkoxy groups of the silane hydrolyze and react with the silicate or carbonate of the filler, while the mercapto or amino groups react with the chlorinated isoprenyl of the chlorobutyl polymer. This results in a substantial increase in reinforcement²⁶.

It is important to allow the polymer, filler, and coupling agent to mix thoroughly before adding other ingredients²⁷. Zinc oxide interferes with the coupling action and can be added late in the first stage or in the second stage of the mix cycle. The use of the coupling agents can result in higher modulus, with the amino derivative of these coupling agents being the most effective. Silane pretreated mineral filler that are useful in chlorobutyl are commercially available and when compared to GPF N660 carbon black, the silane-pretreated mineral filler provides longer scorch times, shorter times to optimum cure, and more resistance to cut growth. The GPF carbon black is superior for adhesion to a natural rubber compound.

Tackifying resins

Tackifying resins are used in chlorobutyl compounds such as innerliner where splicing and assembly to adjacent tire components take place in building operations. In formulating a compound, the level of tack must be carefully balanced with the tendency to stick to metal and other surfaces contacted during processing and building. Non-reactive phenolic or phenol formaldehyde resins are effective tackifying resins for chlorobutyl compounds. Phenol-acetylene resins are also effective. Generally, adequate self-tack is attained with 2 to 4 phr of the above resins. Phenol formaldehyde resins affect the vulcanization of chlorobutyl by reducing scorch time.

Hydrocarbon resins such as Escorez™ 1102 at 2 to 6 phr can also be used to obtain good self-tack and tack to other rubber compounds²⁷. While they are less effective tackifying resins than the phenolic types, they are less likely to reduce compound scorch safety. Phenolic and hydrocarbon resins are generally interchangeable and this can provide an additional tool to the factory rubber technologist in setting tack levels as tack may change due to seasonal effects, factory environmental conditions, and compound compositions. Higher amounts of tackifying resins may be needed to attain good tack to non-chlorobutyl compounds.

Antidegradants

Chlorobutyl compounds, with the low polymer functionality and almost completely saturated polymer backbone, generally do not require extra antioxidant or antiozonants. If antidegradants are added for severe exposure conditions or for use in blends with high-unsaturated rubbers, care should be exercised in their selection. Amine type antidegradants readily react with the allylic chlorine in the polymer chain and can lead to scorch time reduction. Amines may also cause an increase in Mooney viscosity of uncured compounds during storage. Table VIIa & table VIIb gives a comparative evaluation of different antidegradants in chlorobutyl and chlorobutyl-natural rubber blend

Table VIIaEffect of antidegradants on the properties of chlorobutyl compounds²²

Compounds	Unit	1	2	3	4	5	6
Exxon™ chlorobutyl 1066	PHR	100.0	100.0	100.0	100.0	100.0	100.0
N 660		60.0	60.0	60.0	60.0	60.0	60.0
Naphthenic oil		15.0	15.0	15.0	15.0	15.0	15.0
Stearic acid		1.0	1.0	1.0	1.0	1.0	1.0
MgO		0.15	0.15	0.15	0.15	0.15	0.15
Zinc oxide		5.0	5.0	5.0	5.0	5.0	5.0
ZBEC		2.0	2.0	2.0	2.0	2.0	2.0
Sulfur		0.50	0.50	0.50	0.50	0.50	0.50
2,2'-Methylene-bis (4-methyl-6-tert-butylphenol)		1.50	-	-	-	-	-
2-Mercapto benzimidazole		-	1.50	-	-	-	-
Styrenated phenol		-	-	1.50	-	-	-
TMQ		-	-	-	1.50	-	-
6 PPD		-	-	-	-	1.50	-

Typical properties: Mooney viscosity							
ML 1+4, at 100°C	MU	47.5	51.5	48.7	50.0	45.8	50.4
ML 1+8, at 100°C	MU	46.8	51.2	48.0	49.2	45.2	49.5

Mooney viscosity after one week							
ML 1+4, at 100°C	MU	47.5	50.9	48.0	49.1	45.0	48.8
ML 1+8, at 100°C	MU	46.7	50.6	47.0	48.2	44.3	48.0

Mooney viscosity after two weeks							
ML 1+4, at 100°C	MU	48.2	52.7	48.8	49.0	45.8	49.3
ML 1+8, at 100°C	MU	47.2	52.2	47.9	48.2	44.9	48.5

Mooney viscosity after three weeks							
ML 1+4, at 100°C	MU	49.4	52.9	49.7	50.0	47.3	50.5
ML 1+8, at 100°C	MU	48.5	52.5	48.8	49.4	46.4	49.6

Typical properties: MDR rheometer, 160°C, 60 minutes, arc ± 0.5°							
	Unit	1	2	3	4	5	6
Minimum torque (ML)	dN.m	1.4	1.6	1.4	1.4	1.3	1.5
Maximum torque (MH)	dN.m	6.5	7.6	6.5	6.4	9.1	6.8
Delta torque (MH-ML)	dN.m	5.1	6.0	5.0	5.0	7.8	5.3
Time for two-point rise in torque. (ts ₂)	mins.	1.8	1.7	1.8	1.4	1.5	1.9
Time to 50% rise in torque. (tc ₅₀)	mins	2.2	2.4	2.25	1.5	2.3	2.3
Time to 90% rise in torque. (tc ₉₀)	mins.	16.9	17.6	11.8	9.8	6.5	10.0

Static ozone testing						
Cure time, Min. (tc 90+2) at 160°C, Tested at 40°C, ozone concentration 50 pphm, Extension 20%						
Observation at 8 hrs	NC	NC	NC	NC	NC	NC
Observation at 24 hrs	A1	NC	A1	NC	NC	NC
Observation at 50 hrs	B3	NC	B2	NC	NC	NC
Observation at 72 hrs	B4	NC	B3	A1	NC	A1
Observation at 100 hrs	B5	NC	B4	B2	NC	B2
NC: No Cracks A: Small number of cracks B: Large number of cracks C: Numberless cracks		1: Cracks, which cannot be seen with naked eye but can be confirmed with 10 times magnifying glass. 2: Cracks that can be confirmed with naked eye. 3: Cracks those are deep and comparatively large. 4: Cracks those are deep and large.				

Typical stress strain properties-unaged							
Cure time, Min. (tc 90+2) at 160°C							
Hardness	Sh. A	40	48	41	42	50	43
50% modulus	MPa	0.6	0.8	0.6	0.7	0.9	0.7
100% modulus	MPa	1.1	1.5	1.0	1.1	1.7	1.2
300% modulus	MPa	5.3	6.2	4.8	4.9	7.2	5.6
Tensile strength	MPa	9.9	10.4	9.6	9.5	9.3	10.1
Elongation at break	%	550	530	570	590	410	530
Tear strength (Die B)	N/mm	33.7	32.3	32.4	35.1	25.7	33.9

Typical stress strain properties-aged at 125°C for 72 hrs							
Hardness	Sh. A	45	56	47	50	58	49
50% modulus	MPa	0.8	1.33	1.07	1.19	2.10	0.86
100% modulus	MPa	1.5	2.73	2.11	2.36	4.53	1.66
300% modulus	MPa	6.8	8.72	7.71	8.13	---	6.91
Tensile strength	MPa	8.9	9.75	9.26	8.97	8.69	9.32
Elongation at break	%	420	350	380	350	190	410

Typical stress strain properties-aged at 125°C for 168 hrs							
Hardness	Sh. A	47	55	50	52	59	51
50% modulus	MPa	0.8	1.1	0.9	1.0	1.5	1.0
100% modulus	MPa	1.7	2.3	1.7	2.0	3.5	1.8
300% modulus	MPa	7.0	7.9	6.7	7.3	--	7.0
Tensile Strength	MPa	8.4	8.8	8.2	8.4	8.0	8.5
Elongation at break	%	390	360	390	360	200	380
Tension set at 105°C	%	6.1	8.9	5.6	6.8	7.9	4.9
Oxygen permeation rate at 40°C, Oxygen conc.:21% [mm-cc/[m ² -day]		366.7	364.8	373.6	355.9	375.3	351.8

Table VIIb

Effect of antidegradants on chlorobutyl/natural rubber blends

Compounds	Unit	1	2	3	4	5	6
Exxon™ chlorobutyl 1066	PHR	80.00	80.00	80.00	80.00	80.00	80.00
Natural rubber		20.00	20.00	20.00	20.00	20.00	20.00
N 660		60.00	60.00	60.00	60.00	60.00	60.00
Naphthenic oil		15.00	15.00	15.00	15.00	15.00	15.00
Stearic acid		1.00	1.00	1.00	1.00	1.00	1.00
MgO		0.15	0.15	0.15	0.15	0.15	0.15
Zinc oxide		5.00	5.00	5.00	5.00	5.00	5.00
ZBEC		2.00	2.00	2.00	2.00	2.00	2.00
Sulfur		0.50	0.50	0.50	0.50	0.50	0.50
2,2'-methylene-bis(4-methyl-6-tert-butylphenol)		-	1.50	-	-	-	-
2-mercapto benzimidazole		-	-	1.50	-	-	-
Styrenated phenol		-	-	-	1.50	-	-
TMQ		-	-	-	-	1.50	-
6 PPD		-	-	-	-	-	1.50

Typical properties: Mooney viscosity							
ML 1+4, at 100°C	MU	48.0	46.6	49.4	46.5	47.1	46.9
ML 1+8, at 100°C	MU	47.3	46.1	48.9	45.8	46.2	45.9
Mooney viscosity after one week							
ML 1+4, at 100°C	MU	47.8	45.5	48.3	46.1	46.5	47.4
ML 1+8, at 100°C	MU	46.8	44.6	47.6	45.0	45.4	46.0
Mooney viscosity after two weeks							
ML 1+4, at 100°C	MU	49.5	46.5	49.1	46.9	47.0	48.0
ML 1+8, at 100°C	MU	48.0	45.6	48.3	45.7	45.9	46.4
Mooney viscosity after three weeks							
ML 1+4, at 100°C	MU	49.9	47.0	50.3	48.0	48.2	49.1
ML 1+8, at 100°C	MU	48.7	46.0	49.5	46.6	47.0	47.5

Typical properties: MDR rheometer, 160°C, 60 minutes, arc ± 0.5°							
Minimum torque (ML)	dN.m	1.5	1.4	1.6	1.4	1.4	1.5
Maximum torque (MH)	dN.m	7.3	6.9	11.1	7.0	7.4	8.7
Delta torque (MH-ML)	dN.m	5.8	5.5	9.5	5.6	5.9	7.2
Time for two-point rise in torque. (ts ₂)	mins	2.7	3.0	1.8	2.9	2.4	2.5
Time to 50% rise in torque. (tc ₅₀)	mins	6.1	6.2	3.7	6.2	4.8	8.1
Time to 90% rise in torque. (tc ₉₀)	mins	25.2	26.5	12.8	25.6	15.7	18.1

Static ozone testing							
Cure time, Min. (tc 90+2) at 160°C, Tested at 40°C, ozone concentration 50 pphm, extension 20%							
	Unit	Comp1	Comp2	Comp 3	Comp 4	Comp 5	Comp 6
Observation at 8 hrs		NC	NC	NC	NC	NC	NC
Observation at 24 hrs		NC	B2	NC	B2	NC	NC
Observation at 50 hrs		A2	C4	NC	B3	A1	NC
Observation at 72 hrs		B3	C5	NC	B4	A2	A1
Observation at 100 hrs		B4	CR	NC	B5	B2	A1
NC: No Cracks A: Small number of cracks B: Large number of cracks C: Numberless cracks CR: Complete Rupture			1: Cracks which cannot be seen with naked eye but can be confirmed with 10 times magnifying glass. 2: Cracks that can be confirmed with naked eye. 3: Cracks those are deep and comparatively large. 4: Cracks those are deep and large. 5: Cracks that are 3mm or more.				

Typical stress strain properties-unaged							
Cure time, Min. (tc 90+2) at 160°C							
Hardness	Sh. A	43	43	59	43	43	44
50% modulus	MPa	0.8	0.8	1.4	0.7	0.7	0.9
100% modulus	MPa	1.4	1.3	2.8	1.3	1.4	1.7
300% modulus	MPa	5.5	5.0	10.1	5.0	5.6	7.4
Tensile strength	MPa	9.5	8.2	11.2	8.5	9.3	10.1
Elongation at break	%	470	480	340	460	490	400
Tear Strength (Die B)	N/mm	27.5	28.5	26.7	27.8	31.2	26.4

Typical stress strain properties-aged at 125°C for 72 hrs							
Hardness	Sh. A	57	55	64	56	57	59
50% modulus	MPa	1.3	1.3	1.7	1.3	1.3	1.5
100% modulus	MPa	2.4	2.3	3.5	2.5	2.4	3.0
Tensile strength	MPa	8.2	7.7	8.7	8.7	8.5	8.1
Elongation at break	%	290	310	220	300	310	240

Typical stress strain properties-aged at 125°C for 168 hrs							
Hardness	Sh. A	66	62	69	62	64	67
50% modulus	MPa	2.5	2.5	3.1	2.4	2.5	2.6
100% modulus	MPa	3.6	3.6	4.9	3.6	3.7	4.3
Tensile strength	MPa	6.1	6.6	7.8	7.0	7.0	7.3
Elongation at break	%	230	250	190	250	250	190
Tension set at 105°C	%	15.6	13.0	12.2	16.5	14.3	16.9
Oxygen permeation rate at 40°C, Oxygen concentration: 21% [mm-cc/[m ² -day]		648.0	626.4	628.6	678.4	641.7	661.7

Release agents

Alkaline earth metal stearates are used as release agents in rubber product production. They are cure retarders for chlorobutyl and cure system composition adjustments may be necessary. In contrast, stearic acid and zinc stearate tend to accelerate most chlorobutyl cures.

6. Optimizing key properties of chlorobutyl compounds.

Chlorobutyl compounds have a number of important properties that enable their use in many demanding applications where general-purpose elastomers are not effective. These qualities can be summarized as follows:

Heat resistance

Chlorobutyl rubber offers cost effective high temperature performance, particularly for applications where low permeability is necessary. An inherent characteristic of the chlorobutyl rubber is the ability to withstand prolonged service at elevated temperature with relatively little degradation in properties due to its low functionality and its ability to form carbon-carbon and monosulfidic crosslinks¹⁶. For very high service temperatures over prolonged periods, thiuram based cure systems may be avoided. Reversion resistance of chlorobutyl compounds can be improved by use of phosphate accelerators such as zinc salt of dibutyl dithio phosphate, alkylphenol disulfides.

Reinforcing carbon blacks, give better high temperature performance than other non-reinforcing/semi reinforcing carbon blacks. Chlorobutyl demonstrates much better retention of properties than many other highly unsaturation elastomers. Additional starting point model formulations using Exxon™ chlorobutyl 1066 elastomers can be found on the web site, www.butylrubber.com¹.

Permeability

The low permeability of chlorobutyl rubber and its ability to co-vulcanize with highly unsaturated rubbers makes it a polymer of choice for air and moisture barrier applications, like tire innerliner and pharmaceutical closures. At room temperature, for example, compounds based on 100 phr content chlorobutyl are more than tenfold less permeable than 100 phr content natural rubber compounds³.

General guidelines for formulating low permeability chlorobutyl compounds are as follows:

- Chlorobutyl and bromobutyl rubbers are equivalent regarding their effect on compound permeability.
- Compound permeability is predominantly a function of the chlorobutyl/GPR polymer ratios, and secondarily affected by the remainder of the ingredients (e.g. oils, fillers, and plasticizers). 100 phr content chlorobutyl compounds provides the lowest permeability to air and moisture. Blends of chlorobutyl and GPR rubbers exhibit a near-average permeability value based on the fraction of the polymers.
- Gas permeability can also be decreased by doing the following⁹

- Increase filler content up to about 50% by volume. Above this level, permeability increases sharply due to discontinuities in the rubber phase.
- Decrease process oil or other plasticizer levels.
- Using fillers with a larger particle size.
- Use platy fillers such as talc or ground oyster shells.

All elastomers show an increase in permeability with temperature.

Adhesion to other elastomers

Several of the major applications for chlorobutyl rubber are in composite constructions where serviceability requires long term adhesion to general purpose rubber compounds. Chlorobutyl compounds ranging from blends to 100 phr chlorobutyl provide good cured adhesion to these compounds. Guidelines on factors that influence adhesion are outlined below:

1. Chlorobutyl grade

The two grades of chlorobutyl (1066 and 1068) are equivalent in their chemical ability to co-cure with general-purpose elastomers. However, their molecular weight difference and related rheological responses affect the compliance of the compound in laminated and shaped constructions. The ability of the stock to stress relaxes after extension during radial tire building depends on molecular weight.

2. Substrate types

The level of adhesion depends strongly upon the composition of the adjoining substrate or compound. As a guideline, chlorobutyl adheres to general-purpose rubber in the following descending order of adhesive strength:

natural rubber > styrene-butadiene rubber > polybutadiene rubber.

3. Blending elastomers

Chlorobutyl rubber does not require blending with general-purpose elastomers to achieve good co-cured adhesion. However, if blending is required, the preferred material to use is natural rubber due to its ability to enhance interfacial crosslinking and its ease of processing. In cases where the substrate has a high percentage of styrene-butadiene rubber, incorporation of styrene-butadiene rubber into the chlorobutyl compound enhances adhesion. If chlorobutyl compound adhesion is inadequate, blending with bromobutyl may be considered. This offers maximum impermeability with enhanced adhesion.

4. Filler systems

Higher adhesion is obtained with larger particle, less reinforcing carbon blacks, or mineral fillers. The best furnace black is SRF, followed closely by GPF. In 100 phr chlorobutyl content innerliner, carbon blacks more reinforcing than GPF are detrimental to adhesion. Most mineral fillers provide acceptable adhesion levels, but they may have a detrimental effect on flex crack resistance.

5. Plasticizers and process aids²⁸

Chlorobutyl compounds typically contain between 5 and 10 phr of oil. Within this range, laminate adhesion is generally independent of the oil content. In compounds containing more than 40% (>70 phr) chlorobutyl rubber, 5 to 10phr of certain processing aids such as aromatic and aliphatic hydrocarbon resin blends and mineral rubber improve adhesion to other rubber compounds.

6. Curing system

Sulfur-based cure systems containing for example sulfur, MBTS, ZnO, and stearic acid, provide good adhesion of chlorobutyl compounds to general purpose rubber compounds such as found in tire casing compounds. A suggested vulcanization system could thus be designed and optimized from 3.0 phr zinc oxide, 0.50 phr sulfur, and 1.5 phr MBTS. Magnesium oxide, if it is used as a scorch inhibitor, can be kept to a minimum (e.g., 0.05 phr to 0.15 phr) because it may have a negative effect on adhesion.

For a tire, the innerliner component flexes through a high frequency, constant strain cycle as the tire deflects through the footprint. Due to the plied-up thickness of the tire, the liner is exposed to conditions that could cause flex cracking. To obtain optimum flex and fatigue resistance performance, low modulus compounds tend to be used thereby producing lower stresses during the operation of the tire²¹. In commercial tire innerliner compound, a heat resistant network is also required, in order to withstand degradation when operating at high temperatures. Therefore, when compounding chlorobutyl innerliner compound some additional guidelines might include:

- Use medium reinforcing carbon blacks (e.g., GPF, FEF, or SRF) with little or no non-black fillers (i.e., CaCO₃, clays, talc).
- Design low modulus compound (suggested target for 300% modulus to be in the range 3.00 MPa to 5.00 MPa)²².
- Maximize dispersion of the ingredients to avoid flaws that might initiate cracks.
- Use about 1.0 phr to 3.0 phr of zinc oxide for a balance of crack growth resistance and adhesion.

Abietic acid derivatives, like wood rosin, have been shown to promote flex resistance, cut growth resistance, and fatigue

resistance. In some instances, a lower cure temperature for a longer time can provide better flex resistance versus short cure times at high temperatures due to the reduced volatilization of lower molecular weight compounding additives and better crosslink distribution.

Resistance to chemicals

Chlorobutyl rubber is a non-polar, saturated hydrocarbon elastomer. In non-polar hydrocarbon solvents, uncured chlorobutyl rubber will readily dissolve. When cured, chlorobutyl rubber will swell substantially in nonpolar hydrocarbon solvents. In contrast, they are insoluble or resistant to swelling in polar solvents.

Chlorobutyl rubber is soluble in or will swell in the following materials:

- Aliphatic hydrocarbons: hexane, heptane, decane.
- Cyclic hydrocarbons: cyclohexane.
- Chlorinated hydrocarbons: carbon tetrachloride.
- Alkylated substituted aromatics: toluene or xylene.

Chlorobutyl rubber is insoluble in or will not swell in the following materials:

- Ketones: acetone, methyl ethyl ketone.
- Alcohols: ethanol, ethylene glycol.
- Ester-type solvents.

A high state of cure is important for maximizing service life in liquid media. The selection of fillers and plasticizers also has a significant effect. Carbon blacks are preferred since they generally allow higher cure states. Silica, talc, and whiting are attacked by mineral acids, but have good resistance to animal and vegetable oils and phosphate ester hydraulic fluids. Chlorobutyl rubber is resistant to mineral acids, bases except when highly concentrated nitric, sulfuric, and chlorosulfonic acids are employed. For acid resistant compounds, barium sulfate filler is suggested. Silicas and calcium carbonate fillers are not recommended in such applications.

Compression set

The most important variable for compression set with chlorobutyl compounds is the curative system. It may be selected to give carbon-carbon or monosulfidic crosslinks (i.e. short, stable crosslinks). This requirement can be easily met with chlorobutyl rubber because of its versatile vulcanization chemistry. A post cure of two hours at 175°C produces markedly lower compression set values, which approach those of specially formulated, peroxide cured EPM/EPDM compounds. Carbon black fillers impart lower compression set properties to chlorobutyl compounds than do mineral fillers. Mineral fillers may be limited to clays and talc. High levels of silica pigments produce compounds with high compression set values.

Ozone resistance

Chlorobutyl compounds show good resistance to attack by ozone due to its high saturation. It is superior to general-purpose rubbers^{3, 29}. High loadings of fillers and plasticizers are detrimental to ozone resistance, especially high aromatic oils even at moderate levels. Chlorobutyl compound vulcanization systems containing curing resins, higher molecular weight thioureas (e.g., DBTU), and alkylphenol disulfide polymer can yield vulcanizate with better ozone resistance.

Weather resistance

Carbon black filled chlorobutyl compounds have good resistance to weathering³³. Light colored compounds can be compounded to minimize degradation due to ultraviolet light. The following suggested techniques can be considered when developing improved weather resistance of mineral-filled compounds^{16, 30}.

- Obtain a high state of cure.
- Use low levels of a high quality paraffinic plasticizer.
- Include ultraviolet light absorbers such as titanium dioxide.
- Depending upon the application, use up to 10 phr of paraffin wax to protect the surface.
- Avoid use of clays, to the extent that is possible, especially hard clays. Calcium carbonate, talc, and silicas may generally perform better.
- Blends of chlorobutyl with EPDM can yield compounds with superior weather resistance under dynamic conditions as in the case of passenger radial tire white sidewall compounds.

7. Chlorobutyl compound processing

This section on processing describes steps and techniques that are important for fabricating chlorobutyl rubber products. Though tubeless tire innerliner represent the largest application for chlorobutyl, the following suggestions may apply equally to other applications. Figure 20 presents a stepwise view of tire innerliner compound processing. Tire innerliner compounds are usually mixed in a two-stage process and then calendered or extruded into thin sheets for tire building. The various processing steps are discussed below in detail.

The following mixing recommendations apply to 100 phr chlorobutyl innerliner compounds, chlorobutyl-general-purpose rubber blend innerliner containing mostly chlorobutyl, and many chlorobutyl compounds for other applications.

General guidelines

- It is suggested that chlorobutyl compounds are mixed in two stages. The first non-productive stage (masterbatch) can have all the ingredients except zinc oxide, other curatives, and accelerators.
- The batch weight may be approximately 5 to 10% greater than that used for a comparable compound based on general-purpose rubbers. It is important to use a sufficiently high batch weight to avoid air entrapment in the compound and to ensure good shear for dispersion of compounding ingredients.
- It is essential that the polymer does not become excessively cold while in storage. Use of cold polymer can lead to poor dispersion of ingredients and polymer lumps in the batch. As a minimum requirement, the polymer may be at room temperature prior to use, and preferably pre-warmed (e.g. 24 hours at 40°C). Care to be exercised while using hot housing of halobutyl as degradation of the polymer occurs³¹.

³³.

Mixing guidelines ³¹

A recommended mix cycle for chlorobutyl innerliner is shown in table VIII. Actual times are dependent upon specific equipment design and rotor speed²⁷. For Banbury mixing:

- Zinc oxide is a curative for chlorobutyl rubber and may be added in the final mixing stage.
- Scorch inhibitors (magnesium oxide) are added early in the first stage for maximum effect.
- Plasticizers are held back to allow maximum shear development early cycle.
- Masterbatch or non-productive dump temperatures above 145°C may result in polymer dehydrohalogenation, causing loss of performance of the vulcanizate.

- Batch weight for the second step can be the standard weight for the mixer.
- For enhanced polymer and carbon black dispersion, masticate the polymer(s) in the mixer for approximately 30 seconds prior to adding any of the other ingredients. This improves the rate of incorporation of the fillers into the polymer and often results in shorter overall mixing times.
- Higher drop temperature can lead to reduced compound scorch, loss of tack, and loss of adhesion properties.
- Chlorobutyl compounds usually stay on the cooler rolls of the batch off mill. To minimize bagging and back roll tendency, a cooler front roll may be maintained (5°C to 10°C differential)
- In common with mixing of general-purpose elastomers, plasticizers and oils can be delayed to facilitate carbon black incorporation, and a small amount of carbon black can be added along with oil to prevent slippage of rotors.

If variable drive speed is available, select high speed for mastication and carbon black incorporation and then lower speed at the end of the mixing cycle to maintain low drop temperatures. With a constant mixing time, degree of dispersion increases as mixer speed increases. Comparison between Tangential & Intermeshing type mixing is given in table IX.

Table VIIISuggested mix cycle for chlorobutyl innerliner compounds^{31,32}

Time (minutes)	Temperature (°C)	First pass (non-productive)
0.0		Load polymers, resins, MgO
0.5-0.7		Add carbon black
~ 1.5-2.0	110-115	Add oil, resin, stearic acid
~ 3.0-4.0	125-140	Dump (maximum temperature for CIIR masterbatch is 145°C)
		Second pass (productive)
0.0		Load first pass mix, zinc oxide, sulfur, and MBTS
2.0	105	Dump at 105°C maximum

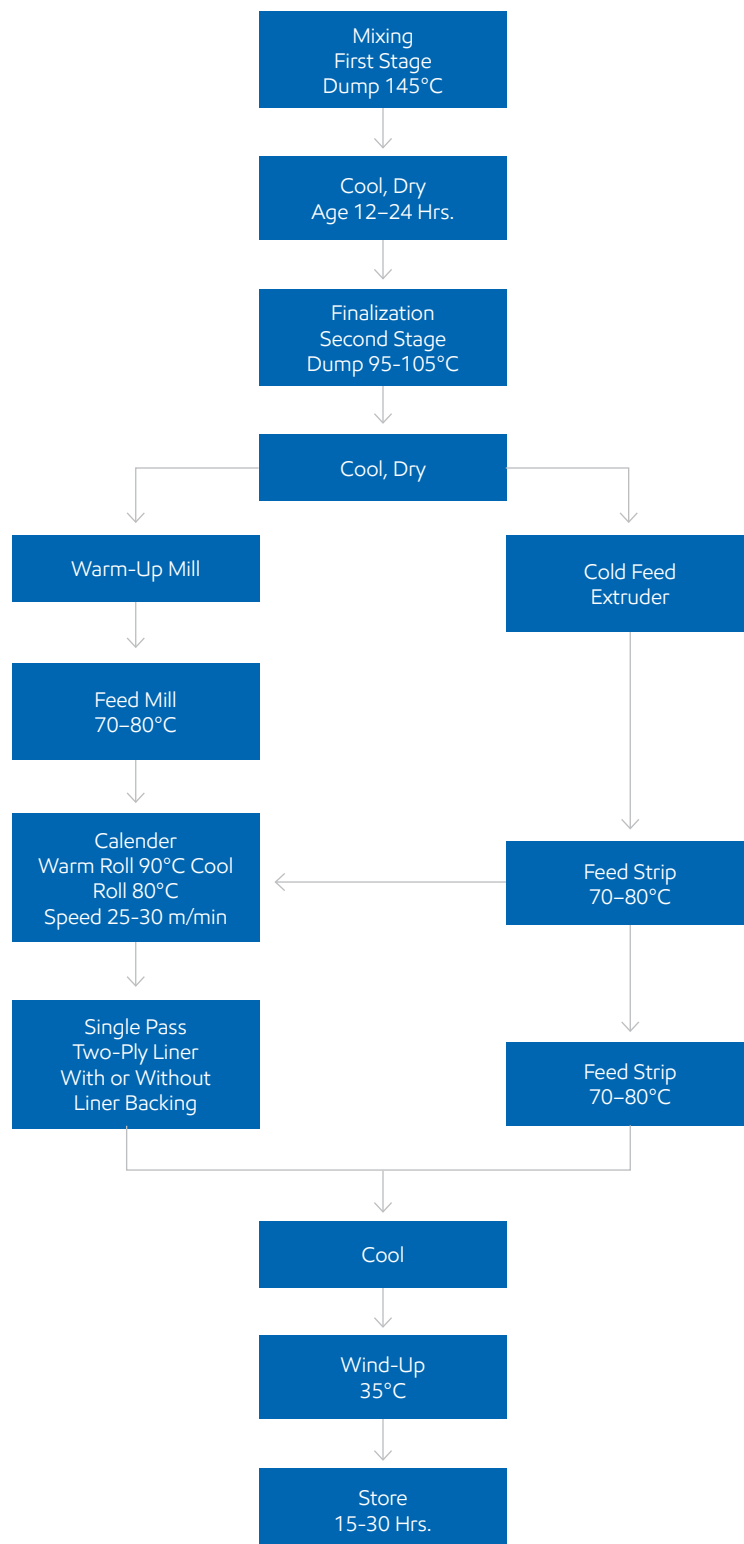
Table IXTangential vs interlocking mixing of chlorobutyl innerliner compounds^{22,31}

	Tangential	Interlocking
Energy efficiency	+	++
Thermal performance	+	+++
Mixing efficiency	+	+++
Co-mastication at partial fill	-	+
Plastisizer blending capacity	-	+
Machine utilization	++	+
Feed intake and Discharge performance	++	+

+++ Excellent ++ Good + Satisfactory - Unsatisfactory

Figure 20

Chlorobutyl rubber compound processing



1. Mill mixing

In some cases, mixing must be done on a two-roll mill. This is best accomplished with a roll friction ratio of 1.25:1 and roll temperatures of 40°C on the slow (front) roll and 55°C on the fast roll. A suggested mill mix procedure is as follows:

- Band part of the polymer in a smooth, continuous band with a small rolling bank. Preferably, leave a small amount of the previous chlorobutyl batch on the mill to serve as a "leader" and assist in adding the new polymer and subsequent compounding ingredients.
- Add scorch inhibitor, acid acceptors, stearic acid, and one-quarter of the fillers in small increments.
- Add the remainder of the polymer, opening the mill to maintain a small rolling bank.
- Add fillers in small increments, opening the mill to maintain a small bank as batch weight increases. Reinforcing fillers may be added first without plasticizers. Plasticizers may be added incrementally with non-reinforcing pigments.
- Add the curatives last, provided the batch temperature is below 105°C. Above 105°C, scorch of the compound may occur.

2. Calendering guidelines^{27, 31, 32}

Calender feed preparation by milling

- A two-mill operation (warm-up mill followed by a feed mill) is preferred to ensure constant quality and temperature of the compound.
- Rolling banks on both mills may be kept as small as possible to minimize trapped air.
- Chlorobutyl follows the cooler roll. Therefore, the take-off roll may be 10° to 15°C cooler than the other roll.
- The temperature of the calender feedstock can be kept between 70° to 80°C.
- A mill friction ratio of 1.1:1 is suggested.

Calender feed preparation by extruder

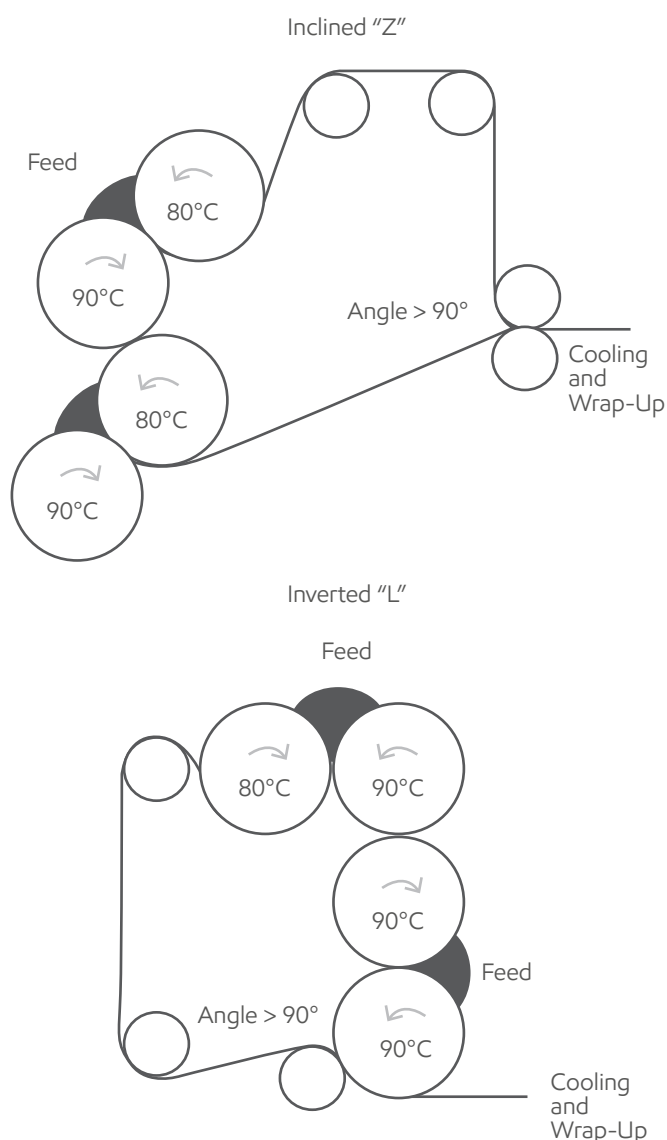
- Force-feeding of the extruder is suggested to prevent starvation and trapped air.
- Extruder barrel and screw temperature zones can be regulated to give a feed temperature to the calender of 70° to 80°C.
- This method is generally used to provide a continuous strip of feed to the calender. It is, therefore, essential to synchronize the extruder and calender speeds to minimize the rolling bank on the calender and to prevent scorch of the compound in the extruder barrel.

3. Configuration for calendering of innerliner

Wide varieties of three and four roll configurations are used to calender innerliner. Of the four roll configurations, the inclined "S", "Z" type and the inverted "L" are most common. An example of configurations as well as recommended roll temperatures is shown in figure 21.

Figure 21

Calender configurations



Note: ExxonMobil Chemical Company data. See 'www.butyrrubber.com' for a more comprehensive review of tire innerliner compound processing.

Liner production

Liners are generally produced from a calendered sheet, or two or sometimes three calendered sheets plied together to minimize air trapping and pinhole effects. Plyed-up sheets can be prepared via multiple turns of the building drum as the liner is supplied from the server on the tire building machine.

Calender conditions

Further reference can be made to the web site, www.butylrubber.com, for an extensive discussion on calendaring setups and conditions for processing chlorobutyl compounds. However, as a guide there are some points, which can be highlighted here:

- As in milling operations, chlorobutyl compounds tend to follow the cooler roll. The take-off roll may be kept 10° to 15°C cooler than the other roll.
- Roll temperatures can be maintained between 75° to 85°C for the cool (take-off) roll, 85° to 95°C for the warm roll.
- It is important to maintain small, rolling banks in the calender nips to avoid trapping air.
- Ensure that the speeds of the calender rolls, cooling drums, and wind-up roll are synchronized. The speed differential over the system should be no more than 2% in favor of the wind-up roll. Excessive stretch can cause splice opening in the uncured tire due to high shrinkage of the liner.
- When the two liner plies are consolidated, keep the sheets apart until the point of positive squeeze roll pressure. A wide approach angle (greater than ninety degrees) if possible, is preferred. Contact of the sheets prior to the squeeze rolls can trap air between the plies.
- A large diameter squeeze roll with thick fabric wrap can help to reduce blisters by prolonging consolidation pressure.
- Maximum cooling of the calendered liner is beneficial for retention of tack and green strength. Stock temperature at the wind-up should be no higher than 35°C.
- Treated cotton or polypropylene sheets can be used to store the calendered liner.
- Typical calendaring speeds for chlorobutyl compounds are twenty-five to thirty meters per minute.
- The liner may be aged 12 to 24 hours in order to ensure complete cooling of the compound, allow stress relaxation to occur, and to minimize subsequent liner flow in the unvulcanized tire.

Extrusion of innerliner

Overall, the extrusion of innerliner is simpler than calendaring. However, a disadvantage of this method is the possible scorching of the compound in the extruder barrel. For this reason, compounds with very good scorch safety are suggested. Briefly:

- A two-roll mill or other suitable procedure may be used to supply the extruder.
- Compound temperature at the feed box may be 70°C to 80°C, while the temperature of the extruded liner could be up to 100°C.
- Positive feed to the extruder is suggested to prevent extruder starvation and subsequent trapped air.

Worn extruder screws or poorly fitted screws allowing excessive flight clearance between the screw and barrel can lead to air entrapment and, later, blisters in the final product.

Defect prevention in innerliner-blisters ^{31, 32}

There are several sources of potential defects. Due of the low permeability of chlorobutyl innerliner, blisters can occur during liner fabrication and tire building. In general, blisters can be seen in three areas:

- Within the innerliner ply.
- The interface between the two plies or between the liner and the liner backing.
- At the interface between the liner and the first carcass ply.

Preventive action for blisters within the ply

- Ensure that the innerliner compound is mixed well (good dispersion of ingredients) to prevent porosity.
- Allow the compound to thoroughly dry during cooling through the calendar or extruder festoon system.
- Ensure that any rework is dry and thoroughly dispersed.

Preventive action for blisters between plies

- Avoid using highly volatile compound process oils.
- When plying up the innerliner, the sheets may come together at a wide approach angle to prevent contact until the point of initial squeeze roll pressure.
- Use a large diameter squeeze roll with a cushioned surface.
- Avoid excessively high calender roll temperatures to minimize scorching of the stock and to retain tack.
- Ensure adequate cooling to retain tack.
- Avoid using compounds that have excessively low viscosities.

Preventive action for blisters between the liner and the tire carcass

- Optimize the use of the stitching rollers on the building equipment. Stitching rollers may be set to touch at the center of the drum and move toward the bead area to expel trapped air.
- Check the moisture level in the carcass cord. The cord may be stored at low humidity if possible.

Extrusion of inner tubes and sidewall compounds

Force-feeding of the extruder is recommended to prevent stock starvation and subsequent air entrapment. Feed temperature for a hot feed extruder can be kept between 80-90°C. Separate warm-up and feed mills are suggested for best uniformity of extrusion.

Suggested extrusion temperatures are:

- Die 100-125°C
- Barrel 75-95°C
- Screw 75-80°C

Extruded stock temperature can be kept between 100-110°C for good surface texture. The extrudate may be cooled as quickly as possible for minimal heat history. Extruder tack off belt and wind up speeds to be synchronized to prevent stretching of green tubes. Excessive stretching causes difficulty in splicing innertubes due to uneven tube width, and in assembling sidewall components using rolled stock due to splice opening as the stock relaxes.

4. Guidelines for molded goods

Chlorobutyl compounds can be molded into highly intricate designs using compression, transfer, and injection molding techniques. Compounds containing chlorobutyl rubber can be developed showing the following features:

1. High thermal stability with no reversion or degradation at molding temperature.
2. Good flow properties for fast mold fill, and good mold release.
3. Rapid cure rates for fast molding cycles at molding temperatures.
4. Adequate compound scorch times.
5. High resistance to environmental attack by ozone, weather, and sunlight.
6. Very low permeability to gases and moisture.

Injection molding requires more attention to scorch resistance compared to compression or transfer molding due to the higher heat history. Suggested cure systems for injection molding are (i) zinc oxide-zinc dithiocarbamate and (ii) zinc oxide-phenol formaldehyde curing resin. Some additional suggestions are given below to optimize the manufacturing of molded goods using chlorobutyl compounds.

5. Mold flow

For best mold flow, use lower viscosity grade of chlorobutyl 1066. Using higher levels of plasticizers may also increase mold flow, as well as using processing aids, or low molecular weight polyethylene. Soft clay like Whitetex Clay or Mistron Vapor Talc provides good mold flow characteristics. Mold flow is also related to scorch resistance, especially in injection molding.

6. Blisters

Chlorobutyl compounds may require special attention to prevent the formation of blisters due to its low permeability.

Blisters can often be removed by bumping the press (quick relief of the molding pressure followed by immediate reapplication of pressure) during the early part of the molding cycle.

7. Hot tear

Carbon black is preferred for hot tear resistance. In mineral filled compounds, the addition of silica will help improve the hot tear resistance for demolding. Use of mineral fillers clay, talc, and silica for optimization of hot tear has been discussed earlier.

8. Mold fouling and sticking³³

Some chlorobutyl compounds may foul the curing mold, possibly leading to the deterioration in appearance of the finished article, difficulties in demolding, and lower heat transfer. The following points are therefore suggested:

- Use silicone mold release sprays. However, use them moderately since they tend to interfere with good knitting.
- Use internal release agents such as;
 - Low molecular weight polyethylene,
 - Paraffin wax,
 - Stearates, but it is suggested that their potential effect on vulcanization may be considered.
 - Chrome plating.

Some mold fouling problems have been related to the use of resin cures.

9. Mold corrosion³³

Some steel or aluminum molds may be affected by the vulcanization of chlorobutyl compounds. Zinc chloride, formed as an intermediary in most chlorobutyl cures at very low levels, may react with certain mold metals. The following remedies are suggested²³:

- Use large particle fillers in the compound.
- Use fillers with a pH greater than 5.
- Use acid scavengers like magnesium oxide or zinc chloride complexing agents (though these may retard cure).
- Use internal release agents (as listed under 'mold fouling and sticking')
- Use high quality mold materials that are resistant to corrosion. Coating
- Molds with Teflon™ or another thermosetting polymer is also effective.

8. Chlorobutyl rubber applications

Chlorobutyl rubbers find a broad range of applications from tires and automotive parts to pharmaceuticals and industrial products because of its saturated nature, safety and environmental attributes. Some examples of these products are as follows:

Tire innerliner

The modern pneumatic tire is a highly engineered product consisting of many specialized components. The innerliner is one such component. Its function is to act as an air and moisture vapor barrier to minimize any diffusion through the tire. In doing so, it helps maintain proper inflation pressure, thereby minimizing the negative effects of under inflation, higher rolling resistance (lower vehicle fuel economy), lower tire durability, and poorer handling and performance. Thus, it helps minimize the detrimental effects of oxidative corrosion of other tire components³⁴.

Table X

100 phr content chlorobutyl and chlorobutyl/natural rubber blends-impact on an EMCC innerliner permeation coefficient⁽²²⁾

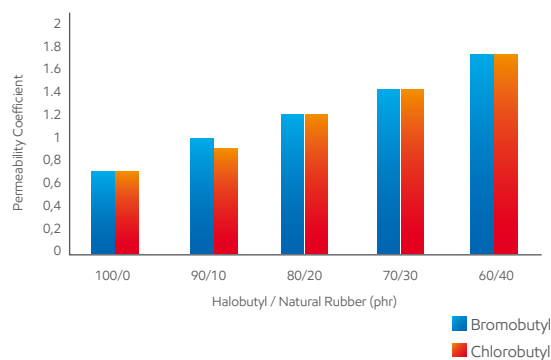
Material	Units	1	2	3
CIIR 1066	PHR	100.00	80.00	60.00
Natural rubber (SMR 20)	PHR	---	20.00	40.00
Air permeability at 65°C	ml [STP]. mm/mm ² .760 mm Hg. Hour	12.6	21.4	33.2
Oxygen permeation at 40°C-oxygen conc.: 21%	mm-cc/[m ² -day]	243.2	416.7	686.0

Chlorobutyl innerliners exhibit very low moisture vapor transmission, relative to general-purpose rubber innerliner. For example, moisture from condensation in air compressor lines can be introduced into the air chamber of tires during inflation. A high content chlorobutyl innerliner minimizes the diffusion of moisture from the air chamber into the body and belt cords of radial tires, reducing the possibility of steel cord corrosion. This is important in all-steel commercial radial truck tires.

The combination of low permeability to gas and to moisture vapor, high heat resistance, high flex resistance, and the ability to co-vulcanize with high unsaturation rubbers makes chlorobutyl uniquely suited for use in innerliner. 100% chlorobutyl innerliner provides lower tire inflation pressure loss rate (IPLR) by virtue of its extremely low permeability. Only when a tire is properly inflated can it perform as designed, providing the vehicle driver with adequate traction, vehicle handling, steering control and rolling resistance. Table X and figure 22 show oxygen permeation coefficients for a range of innerliner compounds¹. Generally, increasing the natural rubber content of an innerliner, allows more air to escape through the liner and into the tire interior.

Figure 22

100 phr content halobutyl and halobutyl/natural rubber blends impact on an EMCC innerliner permeability coefficient^{1,9}



ExxonMobil Chemical data

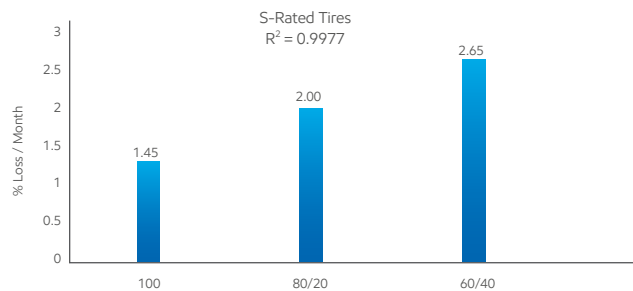
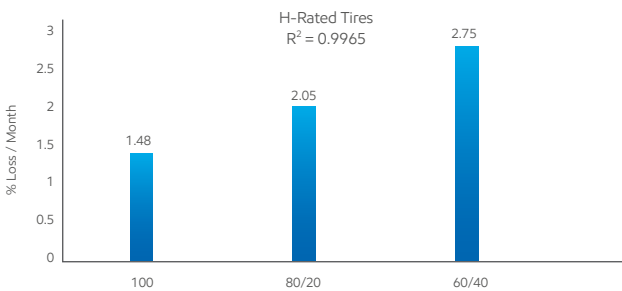
Inflation pressure loss rate (IPLR)

Figure 23 shows Inflation pressure loss rate values as they correlate with halobutyl content. Due to low permeability, bromobutyl and chlorobutyl provides a better air barrier and lowers the intracarcass pressure within the body of the tire than a halobutyl/natural rubber blend. Therefore, increasing halobutyl content in a tire innerliner reduces the tire inflation

pressure loss rate. Figure 24 gives the effect of halobutyl content and innerliner gauge on tire inflation pressure loss rate. IPLR is critical to tire performance; lower the IPLR better will be the performance of tire with regard to operating temperature, rolling resistance, handling and ride characteristics, durability, and wear rates.

Figure 23

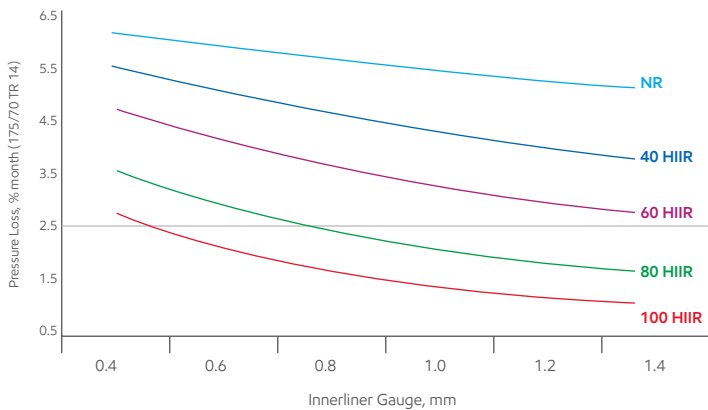
Effect of halobutyl content on inflation pressure loss rate²²



Halobutyl/natural rubber blends (phr), ExxonMobil Chemical data

Figure 24

Effect of halobutyl content and innerliner gauges on tire inflation pressure loss rate.²²



ExxonMobil Chemical data

Figure 25

Effect of halobutyl content on air permeability & moisture permeability²²

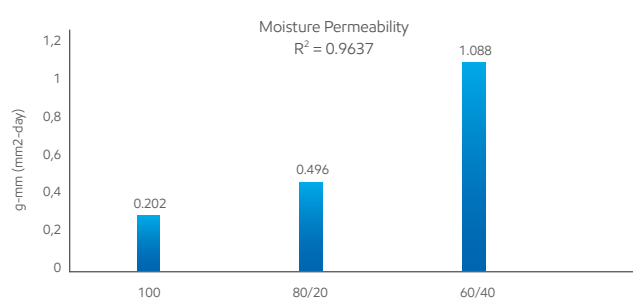
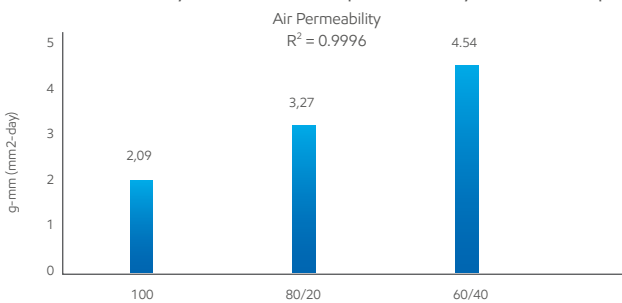


Figure 25 gives the effect of halobutyl content on air permeability & moisture permeability of innerliner compound. Increasing the halobutyl content desirably decreases both air and moisture permeability

Intracarcass pressure (ICP)

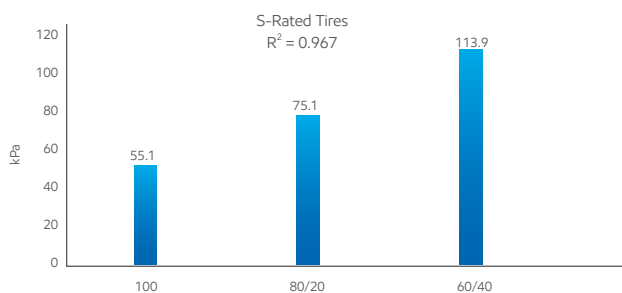
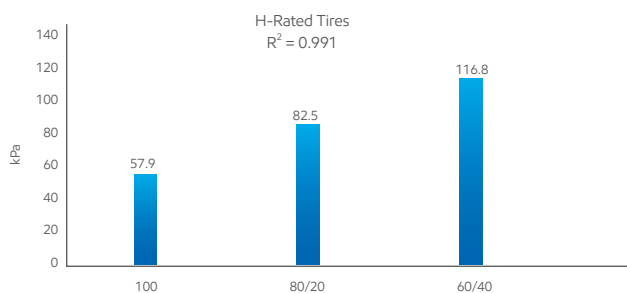
High chlorobutyl content innerliner minimize gas pressure buildup within the body of the tire. The tubeless tire is a pressure vessel with a somewhat permeable wall of laminated components. The pressure difference between the air chamber and the atmosphere causes a pressure gradient to form across the various tire components and can result in air pressure to build up within the body of the tire. This intra-tire pressure is most often measured in the cord area of the sidewall and is thus called Intracarcass Pressure (ICP). Figure 26 gives the

effect of increasing the halobutyl rubber content in a tire innerliner on Intra carcass pressure (ICP) ²²

Finite element modeling of air diffusion through the tire can be used to demonstrate the capability of 100 phr content chlorobutyl innerliner to markedly reduce intracarcass pressure. High ICP can cause plies to weaken and separate and may result in increased oxidation of components such as the tire wire coat compound or skim compound. Increasing the halobutyl content significantly decreases tire Intracarcass pressure figure 27 gives the effect of halobutyl content and innerliner gauge on tire Intra carcass pressure. High gauge and higher halobutyl content desirably reduces the tire intra carcass pressure enhancing tire performance.

Figure 26

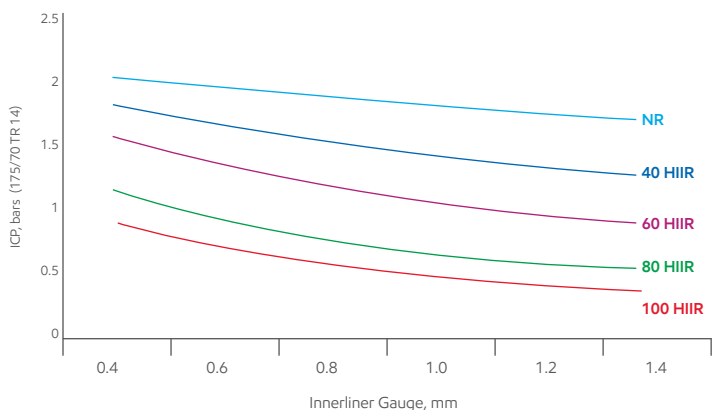
Effect of increasing halobutyl rubber content on tire intra carcass pressure (ICP) ²⁷



ExxonMobil Chemical data

Figure 27

Effect of halobutyl rubber content and innerliner gauge on tire intra carcass pressure ²²



ExxonMobil Chemical data

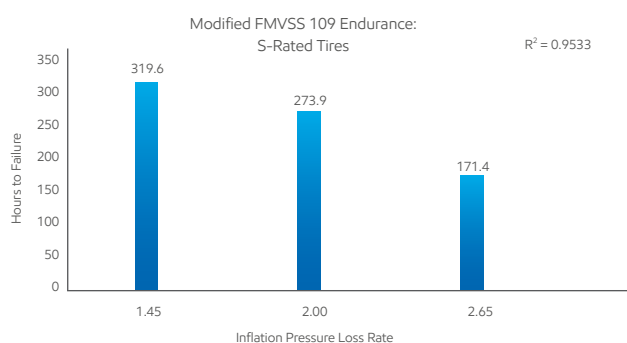
As has already been noted, chlorobutyl rubber has the same air barrier properties as bromobutyl. Low permeability innerliner improve tire durability, in this case by reducing the tendency for belt edge separation. The flow of air out of the tire includes oxygen, which can cause oxidation of the internal components of the tire. The reduction of air pressure in the ply and other internal components of the tire by using high chlorobutyl content innerliner serve to lessen the oxidative degradation of these components. Inflation pressure retention is one of the major factors that contribute to tire rolling resistance. Figure 28 gives the effect of inflation pressure retention on tire endurance life. Higher the inflation pressure retention, better is the tire endurance life. Figure 29 gives the effect of inflation pressure retention on tire rolling resistance. Rolling resistance increases more for tires with high inflation pressure retention (IPR) values.

In summary, chlorobutyl rich innerliner compounds enhances the tire performance by:

- Enhancing the durability of tubeless tires;
- Reducing rolling resistance by maximizing pressure retention,
- Minimizing oxidative degradation in the interior of the tire
- Minimizing intra-carcass pressure build up

Figure 28

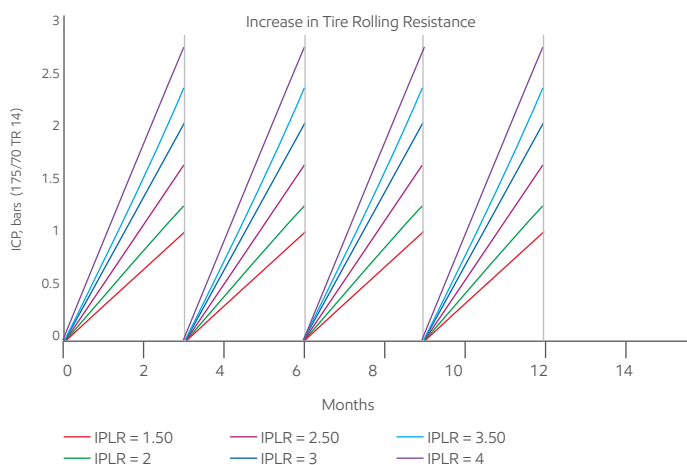
Effect of tire inflation pressure loss rate on tire endurance ²²



ExxonMobil Chemical data

Figure 29

Effect of tire inflation pressure retention on tire rolling resistance ²²



ExxonMobil Chemical data

9. Tire innerliner compounding

Due to its ability to better adhere to compounds based on high unsaturation rubbers, bromobutyl is preferred over chlorobutyl for 100 phr content halobutyl innerliner for truck tires and other severe service applications requiring maximum cured adhesion. More information on the development of chlorobutyl innerliner compounds can be found in earlier sections of this manual. Furthermore, the web site, “www.butylrubber.com”, has additional information with ExxonMobil Chemical model starting point formulations that can be used to initiate development programs for tire innerliner or other applications¹.

Chlorobutyl grade

Chlorobutyl is available in two grades of differing viscosity. Table XI, presents a laboratory-conducted comparison of standard chlorobutyl rubber grades in a 100 phr chlorobutyl simplified formulation. These simplified formulations help to illustrate the direct impact the different Mooney viscosity grades have on compound viscosity and cure properties.

Fillers and oils

Typically, the carbon black grade used for one hundred phr chlorobutyl or high-chlorobutyl innerliner compound is N660, or similar medium reinforcing furnace blacks, at 50 to 60 phr with approximately 8 to 10 phr of plasticizer. This composition shows good adhesion to other tire compounds, with good fatigue resistance and splice integrity in long term tire testing.

The use of non-black fillers may be less effective as they may cause processing difficulties (sticking) and may adversely affect flex performance and splice durability. Clay, whiting, and other low or semi reinforcing fillers may be used at moderate levels (20 to 30 phr) in combination with N660 carbon black. The use of mineral fillers may lower air permeability. Chlorobutyl compounds with lower levels of plasticizers (including oil) show lower permeability values. Higher carbon black levels (i.e., greater than 65 phr) or more reinforcing blacks (e.g., HAF grades) tend to reduce adhesion to other tire compounds. Chlorobutyl-natural rubber innerliner blends are more suitable to use with higher reinforcing carbon blacks and moderate levels of mineral fillers.

Paraffinic and naphthenic process oils are preferred because of

their solubility in chlorobutyl rubber. Aromatic oils may be used, but they can decrease compound scorch safety, requiring adjustments to the cure system. Furthermore, use of aromatic oils is declining due to other industrial & environmental concerns.

Compound scorch time

Magnesium oxide (MgO) and polyethylene glycol (PEG) can be used to improve scorch safety in chlorobutyl compounds containing zinc oxide based cure systems. Typically, by using 0.10 to 0.50 phr of the retarder (depending on manufacturing conditions and compound formulation) provides adequate scorch times. However, the addition of PEG may reduce aged tack, while MgO, could result in a decrease in adhesion. Therefore, care must be taken when using PEG or MgO as retarders. Table XII gives the effect of MgO and polyethylene glycol in typical chlorobutyl tire innerliner formulations.

Table XIComparison of different CIIR grades in typical tire innerliner formulations²²

Compound		Units	CB1068	CB1066
Exxon™ chlorobutyl 1068		PHR	100.00	---
Exxon™ chlorobutyl 1066			---	100.00
N660			60.00	60.00
Naphthenic oil			8.00	8.00
Processing aid			7.00	7.00
PF resin			4.00	4.00
MgO			0.15	0.15
Stearic acid			2.00	2.00
Zinc oxide			1.00	1.00
MBTS			1.50	1.50
Sulfur			0.50	0.50
Typical properties: Mooney viscosity		Test method	Units	
Mooney viscosity ML 1+4, at 100°C		ASTM D 1646	MU	58.7
Mooney scorch time to 5-point rise at 125°C		ASTM D 1646	minutes	27.0
MDR, rheometric properties at 160° C, 60 minutes, arc ± 0.5°				
Minimum torque (ML)		ASTM D 5289	dN.m	1.6
Maximum torque (MH)		ASTM D 5289	dN.m	5.0
Delta torque (MH-ML)		ASTM D 5289	dN.m	3.4
Time for two minutes rise in torque. (ts ₂)		ASTM D 5289	minutes	4.2
Time to 50% rise in torque. (tc ₅₀)		ASTM D 5289	minutes	3.7
Time to 90% rise in torque. (tc ₉₀)		ASTM D 5289	minutes	10.2
Typical stress strain properties-original				
Hardness		ASTM D 2240	Shore A	44
50% modulus		ASTM D 412	MPa	0.6
100% modulus		ASTM D 412	MPa	0.9
300% modulus		ASTM D 412	MPa	2.5
Tensile strength		ASTM D 412	MPa	8.9
Elongation at break		ASTM D 412	%	885
Tear strength (Die B)		ASTM D 624	kN/m	37.1
Typical stress strain properties-aged at 125°C for 72 hrs				
Hardness		ASTMD 2240	Shore A	49
50% modulus		ASTM D 412	MPa	0.7
100% modulus		ASTM D 412	MPa	1.1
300% modulus		ASTM D 412	MPa	3.3
Tensile strength		ASTM D 412	MPa	5.5
Elongation at break		ASTM D 412	%	560
Air Permeability at 65°C		ml [STP]. mm/mm ² .760 mm Hg. Hour		11.9
Oxygen Permeation rate at 40°C, Oxygen concentration.: 21%		mm-cc/[m ² -day]		257.3

ExxonMobil Chemical data. See 'www.butylobutyl.com' for a more comprehensive list of properties.

Table XIIEffect of MgO and PEG on the properties of ClIR compounds ²²

Material	Units	1	2	3	4	5
Exxon™ chlorobutyl 1066	PHR	100.00	100.00	100.00	100.00	100.00
N 660		60.00	60.00	60.00	60.00	60.00
Naphthenic oil		8.00	8.00	8.00	8.00	8.00
Processing Aid		7.00	7.00	7.00	7.00	7.00
Escorez™ 1102		4.00	4.00	4.00	4.00	4.00
Stearic acid		2.00	2.00	2.00	2.00	2.00
MgO		---	0.30	0.60	---	---
PEG		---	---	---	0.30	0.60
Zinc oxide		1.00	1.00	1.00	1.00	1.00
MBTS		1.50	1.50	1.50	1.50	1.50
Sulfur		0.50	0.50	0.50	0.50	0.50

Typical properties: Mooney viscosity

ML 1+4, at 100 °C	D1646	MU	50.0	53.5	54.7	50.5	50.8
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Typical properties: MDR rheometer, 160°C, 60 minutes, arc ±0.5°

Minimum torque (ML)	D 5289	dN.m	1.3	1.3	1.3	1.3	1.3
Maximum torque (MH)	D 5289	dN.m	4.6	5.6	6.3	4.9	5.0
Delta torque (MH-ML)	D 5289	dN.m	3.3	4.3	5.0	3.6	3.8
Time for two-point rise in torque. (ts ₂)	D 5289	minutes	2.7	7.9	11.3	4.1	5.8
Time to 50% rise in torque. (tc ₅₀)	D 5289	minutes	2.5	8.2	12.9	3.9	5.6
Time to 90% rise in torque. (tc ₉₀)	D 5289	minutes	4.4	15.2	26.5	7.4	10.5

Typical stress strain properties-unaged

Cure time, Min. (tc 90+2) at 160°C							
Hardness	D 2240	Shore A	39	43	45	39	39
50% modulus	D 412	MPa	0.6	0.7	0.7	0.6	0.6
100% modulus	D 412	MPa	0.9	1.0	1.1	0.9	0.9
300% modulus	D 412	MPa	2.7	3.1	3.5	2.8	2.8
Tensile Strength	D 412	MPa	8.1	8.7	9.1	8.3	8.7
Elongation at break	D 412	%	810	770	730	820	820
Tear strength (Die B)	D 624	kN/m	39.6	41.3	40.8	40	37.5

Typical stress strain properties-aged at 125°C 72 hrs

Hardness	D 2240	Shore A	44	49	52	40	40
50% modulus	D 412	MPa	0.7	0.8	1.0	0.6	0.6
100% modulus	D 412	MPa	1.0	1.3	1.6	0.9	0.9
300% modulus	D 412	MPa	2.9	3.8	4.7	2.8	2.6

Tensile Strength	D 412	MPa	5.5	6.4	7.4	5.1	4.8
Elongation at break	D 412	%	610	580	550	580	590
Oxygen permeation rate at 40°C, oxygen concentration: 21%		mm-cc/[m ² -day]	274.2	268.6	252.1	283.3	279.6

Process aids

Process aids are not necessary in chlorobutyl innerliner for satisfactory processability. However, aromatic aliphatic resin blends or mineral rubber can be used in high chlorobutyl content innerliner because they improve cured adhesion to natural rubber based compounds. The cure rate and cure state will be only slightly affected. These materials are understood to improve compatibility due to the aliphatic and aromatic character in their resinous compositions.

Vulcanization systems

Cure systems for innerliner consisting of 80 phr or more chlorobutyl is typically based on zinc oxide, sulfur and MBTS, with magnesium oxide as a scorch inhibitor or resistor. This system provides a good balance of important liner properties such as scorch resistance, cure rate properties, tensile strength, adhesion to other compounds, and heat and flex crack resistance. To obtain good balance of properties using, Exxon™ Chlorobutyl 1066 in a model innerliner formulation, suggested levels of compounding ingredients are illustrated in table XIII.

Table XIII

Chlorobutyl rubber cure system components ^{16,17}

Ingredient	Level (PHR)	Reason
ZnO	1-3	Fatigue cut growth resistance, scorch safety, cure rate and modulus.
MBTS	0.8-1.5	Adhesion to GPR substrate.
Sulfur	0.3-0.5	Modulus development, cure rate, tensile strength.
MgO	< 0.15	Scorch safety, balanced with minimum adverse effects on adhesion, cure rate, and cure time.

To obtain a comparable balance of properties when using less than 70 phr-chlorobutyl rubber in the compound, use of a cure system based on polymeric alkylphenol disulfide accelerators can be considered.

Optimization of MBTS, ZnO & MgO in chlorobutyl tire innerliner formulation.

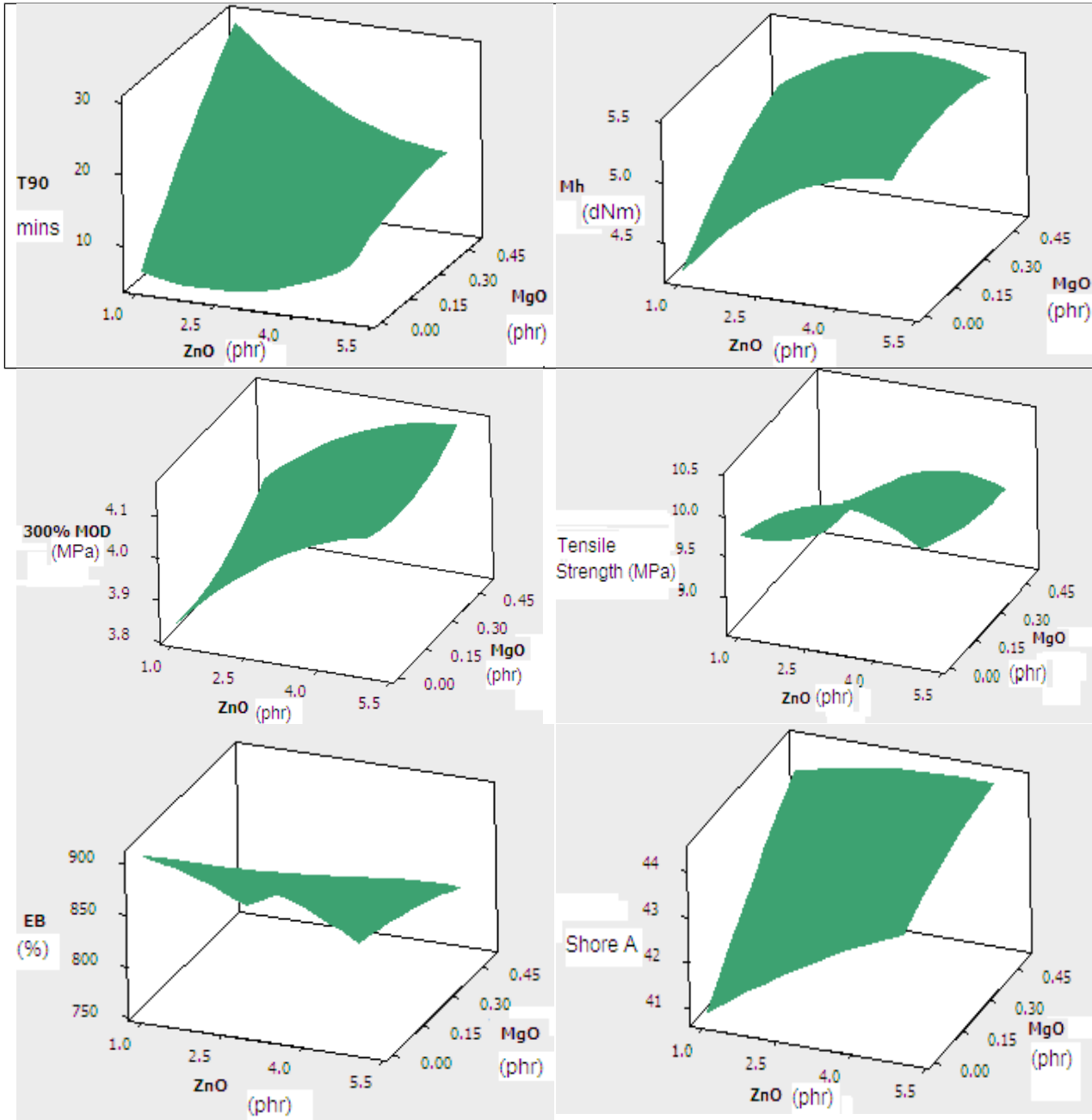
A model chlorobutyl rubber based innerliner compound as described in table XI is used for the study. MBTS, ZnO and MgO levels were evaluated using a designed experiment where independent variables were varied within the range shown in table XIV. The responses are given in figure 30 & figure 31.

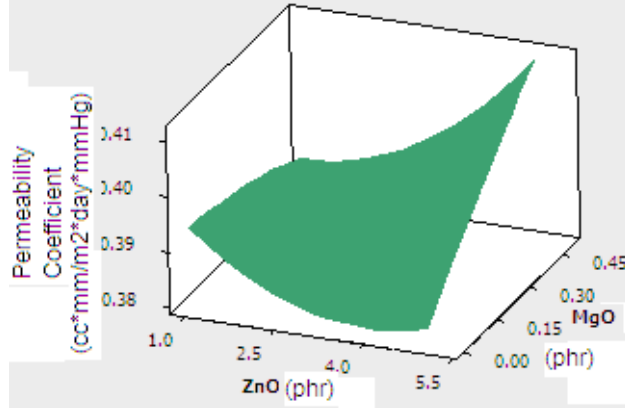
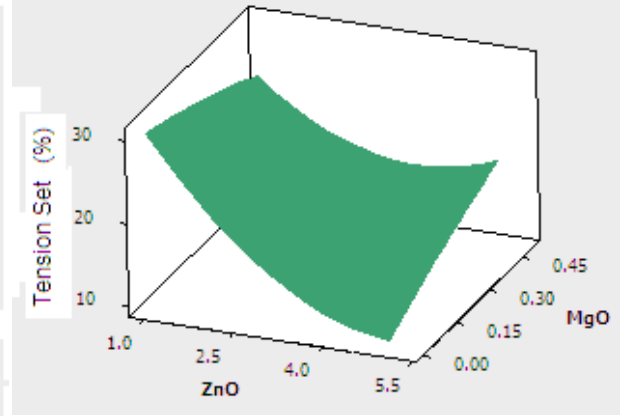
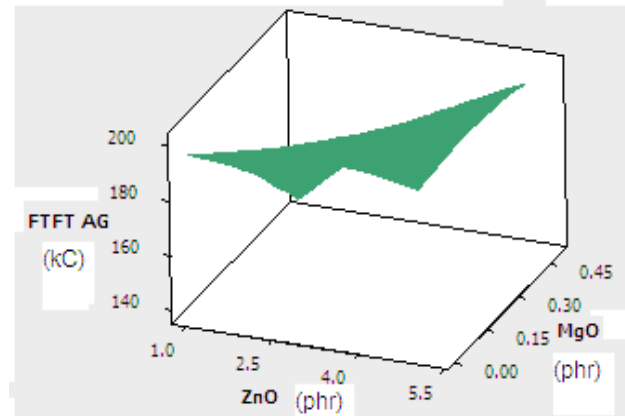
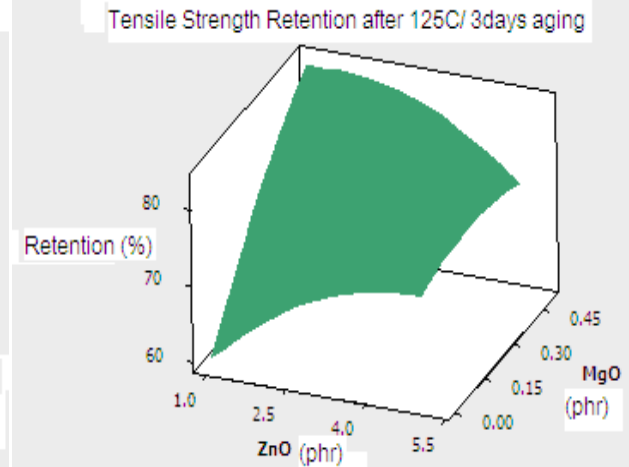
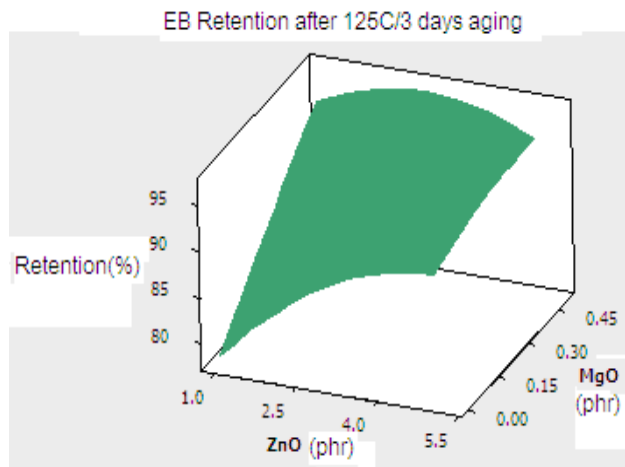
Table XIV

Designed experiment: independent variables ²²

Variable	Minimum (phr)	Maximum (phr)
MBTS	1.0	2.0
ZnO	1.0	5.0
MgO	0.0	0.5

Figure 30
Response optimization: relationship ZnO & MgO (MBTS fixed at 1.0 phr)

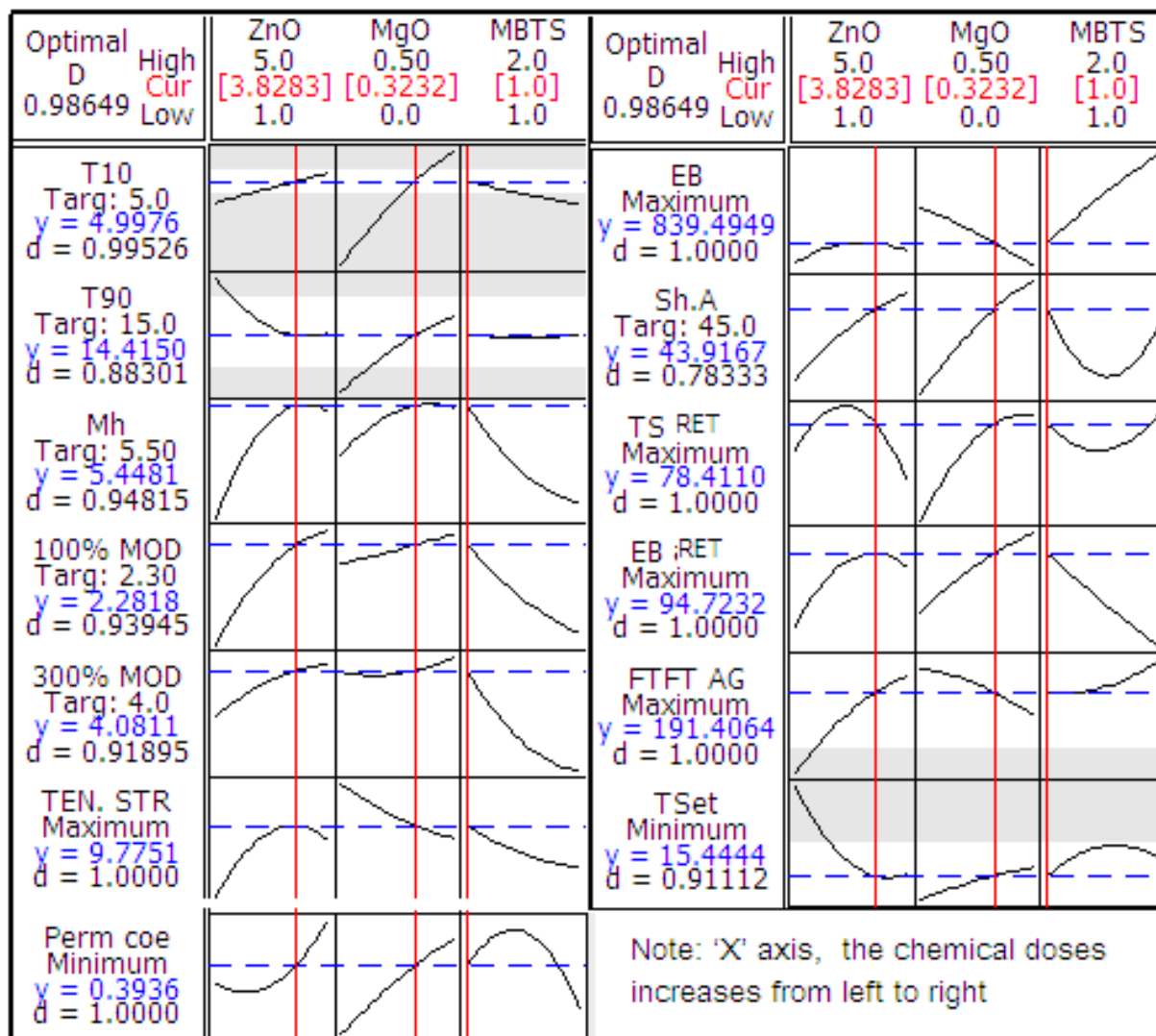




Source: ExxonMobil Chemical data

Figure 31

Minitab response optimization curves.



Source: ExxonMobil Chemical data

Improvement of specific innerliner characteristics

A number of other important compound properties can be improved by optimizing the use of compounding materials. Some examples would include:

- Tack: rapid innerliner cooling after calendering or extruding, combined with use of a tackifying resin in the formulation improves tack. Phenolic tackifying resins are often used at 2.0 to 4.0 phr. Hydrocarbon resins such as Escorez™ 1102, at 2.0 to 6.0 phr may also be used. Compared to phenolic resins, hydrocarbon resins are preferred for scorch resistance and optimum cost. Generally, compounds using phenolic resins retain higher levels of tack after aging versus compounds with hydrocarbon resins. In warm factory environments, hydrocarbon resins would be preferred while in cooler factory conditions, phenolic resins may perform better.
- Flex-crack resistance: this property of chlorobutyl innerliner can be further improved by the compounding approaches listed below:
 - Use medium reinforcing carbon black filler systems, at 50 to 65 phr.
 - Avoid the use of mineral or other non-black fillers.
 - Use 1.0 to 3.0 phr of zinc oxide in the cure system.
 - Compound for low modulus (300% Modulus of 3.0 to 6.0 MPa) and high elongation (700% or greater).
 - Use paraffinic or preferably naphthenic oils rather than aromatic oil.
 - Add small amounts of wood resin (abietic acid) to the compound. This may reduce scorch safety, requiring formulation adjustments to compensate.
 - Adhesion to GPR compounds: cured adhesion can be improved by using a phenolic tackifying resin or mineral rubber. Other compounding approaches are suggested as follows:
 - Use medium reinforcing carbon black fillers (GPF N660) at 50 to 60 phr.
 - Use at least 0.8 phr of MBTS in the cure system and minimize the use of magnesium oxide (MgO) or polyethylene glycol (PEG).
 - Use of alkylphenol disulfide polymer accelerators.

Tire inner tubes.

Inner tubes are used inside the tire to retain the inflation pressure. Correct inflation pressure retention is now more than ever recognized as a key factor in maintaining operating safety, low rolling resistance, minimum fuel consumption and long life for all classes of tire. Blends of EPDM and butyl rubber have long been established as a heat resistant inner tube. The main drawback in using EPDM is poor splice strength, higher growth of the tubes in service because of the higher set properties, & higher permeability. These defensive properties of butyl/EPDM blends led to the development of chlorobutyl rubber based heat resistant inner tubes. The advantages of chlorobutyl tubes are:

- Low permeability.
- High heat resistance.
- Excellent flex resistance.
- Lower Tension Set.
- Resistance to chemicals.

In the manufacturing of tire inner tubes with chlorobutyl rubber, the internal curing media has to be hot air. Steam if used as the internal curing media, leads to the degradation of green compound by the process de-hydrohalogenation. Typical chlorobutyl based innertube formulations are given in table XV.

Table XVAutomobile innertubes based on chlorobutyl rubber: typical formulations ²²

Compound	Units	1	2
Exxon™ chlorobutyl 1066	PHR	100.00	100.0
N660		75.00	60.00
Naphthenic oil		28.00	15.00
MgO		0.50	0.15
Stearic acid		1.00	1.00
Zinc oxide		5.00	5.00
ZBEC		2.00	2.00
Sulfur		0.50	0.50

Typical properties: Mooney viscosity	Test method	Units		
Mooney viscosity ML 1+4, at 100°C	ASTM D 1646	MU	35.2	50.4
Mooney scorch at 125°C	ASTM D 1646	minutes	26.1	18.2

MDR, rheometric properties at 160°C, 60 minutes, arc ± 0.5°				
Minimum torque (ML)	ASTM D 5289	dN.m	1.0	1.5
Maximum torque (MH)	ASTM D 5289	dN.m	6.1	6.8
Delta torque (MH-ML)	ASTM D 5289	dN.m	5.1	5.3
Time for two minutes rise in torque. (ts ₂)	ASTM D 5289	minutes	2.8	1.9
Time to 50% rise in torque. (tc ₅₀)	ASTM D 5289	minutes	3.5	2.3
Time to 90% rise in torque. (tc ₉₀)	ASTM D 5289	minutes	15.0	10.0

Typical stress strain properties-original				
Hardness	ASTM D 2240	Shore A	42	43
100% modulus	ASTM D 412	MPa	1.1	1.2
300% modulus	ASTM D 412	MPa	4.8	5.6
Tensile strength	ASTM D 412	MPa	8.2	10.1
Elongation at break	ASTM D 412	%	480	530
Tear strength (Die B)	ASTM D 624	kN/m	28.8	33.9

Typical stress strain properties-aged at 125°C for 72 hrs				
Hardness	ASTMD 2240	Shore A	50	49
100% modulus	ASTM D 412	MPa	2.0	1.7
300% modulus	ASTM D 412	MPa	6.8	6.9
Tensile strength	ASTM D 412	MPa	7.5	9.3
Elongation at break	ASTM D 412	%	340	410

Typical stress strain properties-aged at 125°C for 7 days		Common NR/BR black sidewall compounds can contain		
Hardness	ASTMD 2240	Shore A	53	51
100% modulus	ASTM D 412	MPa	2.3	1.8
300% modulus	ASTM D 412	MPa	---	7.0
Tensile strength	ASTM D 412	MPa	6.7	8.5
Elongation at break	ASTM D 412	%	290	380
Tension set method B	ASTM D 412	%	8.4	4.9
Fatigue to failure (kC)	ASTMD 4482	kC	56	100
Oxygen permeation rate at 40°C	mm-cc/[m ² -day]		505.3	351.8
Oxygen concentration.: 21%				

Radial tire sidewalls

The design features of the radial tires impart superior wear, handling, fuel efficiency and traction. It also creates severe dynamic flex and weathering of the compounds in the sidewall region. Regular sidewall compounds with highly unsaturated, rubbers are added with antioxidants, antiozonants and waxes to provide flex, fatigue, and ozone crack protection. These materials diffuse to the surface of the sidewall during service. They are consumed in reactions with atmospheric ozone and oxygen and in turn, the sidewall compound is prevented from degradation. The more effective antiozonants such as p-phenylenediamines discolor black sidewalls and stain adjacent white sidewalls. Consequently, their use must be carefully controlled with respect to concentration in the sidewall.

Tire development trends such as using thinner components, development of weight reduction technologies, and attainment of longer tire life, has led to new technology chemical protectant systems. Polymeric protectant sidewall compounds based on chlorobutyl-EPDM-GPR blends are of considerable interest in the tire industry because of their permanent protection effectiveness and non-discoloring/non-staining features.

Black sidewalls

Important properties of a black tire sidewall for radial passenger vehicle tires are as follows:

- Dynamic ozone and flex crack resistance for the life of the tire.
- Low heat buildup (i.e., low hysteresis).
- Retention of the black color (i.e., compounding ingredients to be non-blooming and no-discoloring).
- Serviceable adhesion to adjacent general-purpose rubber components in the tire.
- Resistance to abrasion and curb scuffing.

antiozonants such as para-phenylenediamines (e.g., 6PPD) which continually diffuse to the tire surface, and dihydroquinolines (e.g., TMQ). The sidewall compound can function as the reservoir for these chemical protectants. As the sidewall volume is reduced, its capacity to hold the antioxidants and anti-ozonants is reduced. Use of higher chemical protectant concentrations can increase the intensity of the discoloration and white sidewall staining problems, and cause undesirable changes in vulcanizate properties.

Significant quantities of some common chemical protectants can also be lost through volatilization during component processing, tire curing, and tire use. Compounds based on blends of chlorobutyl (approximately 30 parts) with EPDM (approximately 10 parts), natural rubber (approximately 35 parts) and butadiene (approximately 25 parts) are well suited for use in black sidewall construction because of the following reasons:

- They exhibit permanent ozone and flex resistance not subject to depletion of low molecular weight compounding ingredients.
- They are non-staining and non-discoloring since the protection is inherent in the polymer system.

Chlorobutyl/EPDM/NR/BR polymer systems, which also exhibit the above advantages, are well established as radial passenger tire white sidewall and cover strip compounds. Table XVI contains a typical sidewall formulation, which utilizes Exxon™ chlorobutyl in place of general-purpose rubbers. Please refer www.butylrubber.com¹ for additional formulations.

Table XVIModel formulation for automobile tire sidewall ²²

EXXON™ chlorobutyl 1066-vistalon™ EPDM grade 7000-natural rubber-polybutadiene rubber blend

Material	Units	Amount
Exxon™ chlorobutyl 1066	PHR	30.00
Vistalon™ EPDM Grade 7000		10.00
Natural rubber (TSR 20)		35.00
Polybutadiene grade Budene™ 1207		25.00
Carbon black N660		50.00
Naphthenic oil		12.00
Phenolic tackifying resin		5.00
Stearic acid		1.00
Zinc oxide		5.00
Sulfur		0.20
Mercaptobenzothiazyl disulfide (MBTS)		1.00
Alkylphenol disulfide polymer		0.50

Chlorobutyl/EPDM/NR/BR compounds have been the subject of much development to exploit their potential for fast cure and broader adhesion latitude, the latter being particularly important in tread over sidewall (TOS) tire constructions.

Proper mixing of chlorobutyl/EPDM/NR/BR compounds is critical to their success. A model mixing cycle for black sidewalls is shown in table XVII. Phenol formaldehyde tackifying resins may be minimized to ensure adequate scorch time for sidewall compounds with chlorobutyl rubber. Escorez™ 1102 hydrocarbon resin can provide good tack and scorch safety.

Table XVII

Banbury mix cycle for black sidewall compounds

Time (minutes)	First pass (non-productive)
0.0	Load polymers
0.5	Add black, ram down
1.7	Add oil, stearic acid, resin
3.5	Dump at 145°C
Second pass	
0.0	Load first pass masterbatch and curatives including zinc oxide
2.0	Dump at 110°C maximum
	Alternatively, add curatives on mill; blend at 70°C

Optimum levels of alkylphenol disulfide accelerators may be used with chlorobutyl compounds, again because these accelerators can allow modification of scorch and vulcanization induction times. Properly formulated chlorobutyl blended black sidewall compounds exhibit excellent dynamic ozone resistance.

Chlorobutyl blend black sidewall stocks also possess excellent flex fatigue resistance, and retain this performance after aging. This has been demonstrated in the laboratory using the fatigue cut growth test²². This test measures crack growth as a function of tearing energy in a pure shear specimen. The specimen is cycled under condition of low strain amplitude, high strain rate, and high frequency that closely models sidewall strain conditions of radial passenger tires. These features give the fatigue cut growth test significant advantages over conventional laboratory flex tests in relating to long-term tire component fatigue resistance performance.

White sidewalls

Important properties of white sidewall compounds for radial passenger car tires include the following:

- Long term resistance to flex fatigue, weathering, ozone cracking resistance, and UV crazing resistance.
- Resistance to stain and discoloration caused by migrating chemicals.
- Good original and aged whiteness.
- Adhesion to adjacent components in the tire.
- Smoothness of the buffed surface.

While EPDM/NR/SBR white compounds frequently failed to meet the dynamic requirements of the radial tire construction, it was found that the addition of chlorobutyl to the EPDM-containing white compound greatly improved dynamic ozone and fatigue crack resistance. Use of such compounds has been well established for radial passenger car tires for many years. Typical formulation is given in table IV.

A suggested mix cycle for a white sidewall compound containing chlorobutyl rubber is shown in table XVIII.

Table XVIII

Banbury mix cycle-white sidewall compounds

Time (minutes)	First pass (non-productive)
0.0	Load polymers
1.0	Add 2/3 fillers,
3.0	Add 1/3 fillers, wax, resin, stearic acid
4.0	Sweep
5.0	Dump at 140°C
Second pass (productive)	
0.0	Load first pass masterbatch and curatives including zinc oxide
2.0	Dump at 100°C maximum
Alternatively, add curatives on mill; blend at 70°C	

Tire tread compounds

Improvements in some tire attributes have been observed when chlorobutyl rubber is blended with other tire tread rubbers. One such attribute is winter (mud-snow) tire performance. These tires use aggressive lug patterns with a lower net pavement contact area to penetrate and grip snow and wet surfaces. Inclusion of halobutyl polymers in the tread compound formulation will increase the compound hysteresis and $\tan \delta$ resulting in better tire traction performance. Typical formulation is given in table XIX.

Belting for high temperature resistance

Large scale conveyor belts systems are highly complex with a typical system consisting of 6 components, the conveyor belt, drive system, support assemblies, tightening system, feeding system, and discharge system. The most common form of conveyor belt consists of a core reinforcement system, sometimes a friction or barrier component between plies, the outside cover compound, which carries the load, and the inside cover exposed to the pulley wheels. Fabric reinforced conveyor belts are typically made from either polyester or nylon. Steel cord reinforced belts can use brass coated wire or cables, galvanized steel cables, or brass wire mesh. Brass wire and fabric reinforcement is covered with a layer of rubber whose formulations are similar in composition to those found in wire coat and fabric coat compounds in tires. Galvanized wire reinforcement coat compounds are typically formulated differently. The strength requirements to which the belt has been designed dictate the number of layers of reinforcement⁷.

The power consumed by conveyor belts systems can be viewed in several components:

- Power necessary to move a load.
- Power necessary to move the belt or overcome resistance to motion.
- Power necessary to overcome friction in the idlers.
- Power necessary to operate tippers.
- Power required to elevate the materials or loads when the belt is on an incline.

Conveyor belts operating in special service environments such as in high temperature conditions or food processing facilities could use belts with cover compounds based on EPDM or halobutyl rubber formulations.

Halobutyl rubber compounds have been used for many years in conveyor belts where heat and chemical resistance is required. Table XX, shows a model formulation for a premium conveyor belt cover using Exxon™ chlorobutyl 1066 suitable for the parts of a fabricated conveyor belt needing resistance to elevated temperatures. The formulation shown in the table exhibits good heat aging resistance at temperatures up to 150°C, good tear strength, and abrasion resistance. Additionally, high quality conveyor belt covers can be made with CB 1066. Model formulations, which can be used as starting points in a development program, can be found at www.butylobutyl.com¹.

Table XIX

Model formulation for a winter tire tread 40/40/20 Exxon™ chlorobutyl 1066, polybutadiene rubber and natural rubber blend

Material	Units	Winter tire tread
Exxon™ chlorobutyl 1066	PHR	40.00
Polybutadiene rubber		40.00
Natural rubber		20.00
Precipitated silica (highly dispersible)		75.00
Bis-(triethoxysilylpropyl) polysulfide (50%)		7.80
Aromatic process oil		30.00
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6 PPD)		1.50
Diphenyl guanidine (DPG)		2.00
Stearic acid		1.00
1,2-dihydro-2,2,4-trimethylquinoline (TMQ)		1.00
Zinc oxide		2.00
Sulfur		0.80
N-tert-butyl-2-benzothiazole-sulfenamide (TBBS)		1.50
Total		222.60

Properties	Test method based on	Units and conditions	Typical values
Rheometer (MDR)	ASTM D5289	160°C, 30 minutes, $\pm 0.5^\circ$ arc	
MI (minimum torque)	ASTM D5289	dNm	3.8
Mh (maximum torque)	ASTM D5289	dNm	17.1
Mh-MI (delta torque)	ASTM D5289	dNm	13.3
tc ₅₀ (time to 50% torque increase)	ASTM D5289	minutes	4.0
tc ₉₀ (time to 90% torque increase)	ASTM D5289	minutes	7.0

Cured 10 minutes at 160°C			
Tensile strength	ASTM D412	MPa	12.6
Elongation at Break	ASTM D412	%	796
Modulus 300%	ASTM D412	MPa	4.3
Hardness	ASTM D 2240	Shore A	60
Din abrasion	ASTM D 5963	ARI	109
ARES dynamic properties	ExxonMobil method	2% strain, 1Hz, 0°C	
G'		MPa	12.4
G''		MPa	3.0
Tan delta			0.20
ARES dynamic properties		2% strain, 1Hz, 60°C	
G'		MPa	7.1
G''		MPa	0.97
Tan delta			0.14

ExxonMobil Chemical data. Refer 'www.butyrrubber.com' for a more comprehensive list of properties.

Table XXModel formulation for conveyor belt covers ²² Exxon™ chlorobutyl 1066 premium conveyor belt cover

Material	Units	Compound
Exxon™ chlorobutyl 1066	PHR	100.00
Carbon black grade N220		50.00
Naphthenic oil		3.00
2,2'-methylene-bis (4-methyl-6-tert-butylphenol		1.50
Magnesium oxide		0.15
Stearic acid		1.00
Escorez™ 1102		3.00
Zinc oxide		5.00
Mercaptobenzothiazyl disulfide (MBTS)		1.00
Alkylphenol disulfide polymer		1.00
Total (PHR)		165.65

Properties	Test method	Units and conditions	Typical values
Rheometer (MDR)		160°C; 30 minutes; ± 0.5 deg. arc	
MI (minimum torque)	ASTM D5289	dNm	3.2
Mh (maximum torque)	ASTM D5289	dNm	13.9
Mh-MI (delta torque)	ASTM D5289	dNm	10.8
Tc10 (time to 10% torque increase)	ASTM D5289	minutes	1.2
Tc50 (time to 50% torque increase)	ASTM D5289	minutes	5.0
Tc90 (time to 90% torque increase)	ASTM D5289	minutes	20.8
Stress strain properties:		Cured at Tc 90+2 mins at 160°C	
Tensile strength	ASTM D412	MPa	18.2
Elongation at break	ASTM D412	%	430
Modulus 100%	ASTM D412	MPa	2.8
Modulus 200%	ASTM D412	MPa	7.2
Modulus 300%	ASTM D412	MPa	12.4
Tear strength (Die B)	ASTM D624	KN/m	45.6
Hardness	ASTM D2240	Shore A	59
Rebound	DIN 53512	%, 23°C	13.0

Aged stress strain properties: aging condition 125°C/3 Days			
Tensile strength	ASTM D412	MPa	15.1
Elongation at break	ASTM D412	%	280
Modulus 100%	ASTM D412	MPa	4.4
Modulus 200%	ASTM D412	MPa	10.6
Tear strength (Die B) mean	ASTM D624	kN/m	33.6
Hardness	ASTM D2240	Shore A	67

Aged stress strain properties: aging condition 125°C/7 Days			
Tensile strength	ASTM D412	MPa	12.7
Elongation at break	ASTM D412	%	230
Hardness	ASTM D2240	Shore A	70

ExxonMobil Chemical data. Refer 'www.butylrubber.com' for a more comprehensive list of properties.

Chemical resistant tank lining compounds

The inherent resistance of isobutylene based elastomers toward contact with normal concentrations of acids and bases is well known. Chlorobutyl rubber can offer greater cure versatility over regular butyl polymers. Mineral fillers like Barytes are preferred in such applications. These elastomers will not be resistant to concentrated nitric, sulfuric, or chlorosulfonic acids.

Pharmaceuticals

Halobutyl rubber compounds are used extensively in pharmaceutical closures due to the following properties:

- Low permeability to gases and moisture vapor.
- Chemical and biological inertness.
- Low extractable levels, due to cure system.
- Resistance to heat, ozone, and ultraviolet light.
- Self-sealing and low fragmentation during needle penetration.
- Cure versatility of Halobutyl rubber

The spectrum of pharmaceutical closure types for which chlorobutyl rubber is used includes stoppers for antibiotics containers, blood transfusion equipment, and blood sampling equipment. Low viscosity chlorobutyl grades are available, which allow the formulating of closure compounds with reduced, or no plasticizer. This approach lowers the potential for low molecular weight hydrocarbon extractable compounding ingredients. Lower amounts of plasticizers also lower the permeability of the closure. Table XXI offers a model starting point formulation for a pharmaceutical closure using Exxon™ chlorobutyl 1066.

Chlorobutyl closure formulations usually employ calcined clay or talc as the base filler. Moderate levels (up to 30 phr) of silica can be included to enhance hot tear resistance. Higher silica levels tend to retard cure. Silane treated talc can also be considered. In compounding for closure formulations, the other ingredients may be as pure as possible. Zinc oxide may be of pharmaceutical grade, and free of lead and sulfur. Plasticizers can be inert materials such as low molecular weight polyethylene or paraffin wax. Small amounts of saturated white oils may be acceptable depending on the particular specifications to which the closure is produced.

Processing of pharmaceutical closures

The elastomer is added first to internal mixers, followed by the clay and other white fillers in three steps, with the plasticizers added during the last filler addition. Suggested drop or dump temperatures are 145°C max. If the stock temperature can be kept below 105°C, the zinc oxide and other curatives can be added in a one-step mixing procedure. Otherwise, curatives can be introduced in a second mix cycle stage, or on a cold mill. Vulcanization is commonly completed by compression molding, although injection molding is also used. Production schedules employ short curing times of 4 to 8 minutes.

Table XXIModel formulation for a pharmaceutical closure¹ Exxon™ chlorobutyl 1066

Material	Units	Amount
Exxon™ chlorobutyl 1066	PHR	100.00
Calcined kaolin clay		50.00
Talcum		40.00
Titanium dioxide		4.00
n-butene isobutylene copolymer		5.00
Zinc oxide		2.00
Octylphenol formaldehyde resin		2.00
Stearic acid		1.00
Total (PHR)		204

Properties	Test method based on	Units and conditions	Typical values
Mooney viscosity ML1+4	ASTM D1646	MU at 100°C	65.0
Rheometer (MDR)	ASTM D5289	180°C, 40 minutes, 0.5° arc	
MI (minimum torque)	ASTM D5289	dNm	1.5
Mh (maximum torque)	ASTM D5289	dNm	7.4
Mh-MI (delta torque)	ASTM D5289	dNm	5.9
Tc50 (time to 50% torque increase)	ASTM D5289	minutes	1.4
Tc90 (time to 90% torque increase)	ASTM D5289	minutes	3.4

Stress strain properties Cured 5 minutes at 180°C			
Tensile strength	ASTM D412	MPa	5.6
Elongation at break	ASTM D412	%	700
Modulus 100%	ASTM D412	MPa	1.8
Modulus 200%	ASTM D412	MPa	3.0
Modulus 300%	ASTM D412	MPa	3.6
Tear resistance (Die C)	ASTM D 624	kN/m	21.2
Hardness	ASTM D2240	Shore A	46
Compression set	ASTM D 395 Method B	% 22 hrs, 120°C, 25%	37.0

ExxonMobil Chemical data. Refer 'www.butylrubber.com' for a more comprehensive list of properties.

Ball bladders

Maximum air retention is essential for bladders used in sporting goods. Butyl and halobutyl are widely used in the industry for this reason. Chlorobutyl rubber can be blended with natural rubber to obtain improved splice strength and faster cure rate, while retaining good air retention properties. Typically, a balance between processability and tack for splicing is critical for production factory handling.

Adhesives

The inherent tack, aging resistance, and low permeability of butyl type polymers account for their use in various adhesive applications. Valve cement based on chlorobutyl rubber will exhibit good adhesive performance for butyl and chlorobutyl innertube compounds and on either CIIR or butyl based precured valves. Model adhesive & sealants formulations are available in ExxonMobil Chemical website www.butylrubber.com.

Automotive parts

Chlorobutyl rubber is finding acceptance in a wide variety of vibration control applications because of its high damping properties, fast reversion resistant cures, and excellent aging properties, especially with respect to hot flex fatigue. In contrast to regular butyl polymers, chlorobutyl rubber can be formulated to have an intermediate level of oil resistance. Chlorobutyl is recommended for a variety of automotive

dynamics applications including automotive transmission mounts & exhaust hangers. Model formulations are available in ExxonMobil Chemical website www.butylrubber.com.

Recommended formulations

ExxonMobil Chemical model starting point formulations for a variety of applications including innerliner can be found at www.butylrubber.com. These models starting point formulations can be an excellent way to help initial development studies.

Global supply and support

ExxonMobil Chemical produces chlorobutyl at Baton Rouge, Louisiana (USA), Fawley in the United Kingdom, and Kashima, Japan. Over the years, ExxonMobil Chemical has made significant improvements in product quality through a wide variety of raw material and process control programs.

Research and development laboratories in Baytown, Texas, Clinton, New Jersey (USA), Machelen, Belgium (near Brussels), and Bangalore, India provide technical support for manufacturing and marketing operations. Worldwide offices for chemical products provide trained personnel for sales and customer service activities. Please visit "www.butylrubber.com" for information of grades, datasheets, MSDS, applications, formulary, and other news items and useful links.

10. Summary

Chlorobutyl rubber is one of the dominant isobutylene based polymer in production. This is due to its impermeability properties and its versatility regarding cure systems. Chlorobutyl rubber is one of the preferred elastomer used in tire innerliner. Chlorobutyl rubber has also found use in special purpose applications such as pharmaceutical stoppers, tire inner tubes, tire sidewalls, tire curing envelopes, tread compounds, special purpose conveyor belt covers and automotive dynamic parts. This review has presented some basic information on two different grades of chlorobutyl rubbers that are manufactured by ExxonMobil Chemical and available commercially. This review also gives some insight on how chlorobutyl rubbers are manufactured, and the stereochemistry of the reactive isoprenoid and chlorinated isoprenyl groups.

Compounding guidelines of chlorobutyl rubber along with processing of the final rubber formulations through a production facility has been discussed in this review. Precautions such as maximum compound mixing non-

productive drop temperatures, productive stage drop temperatures, and optimized calendaring conditions has been outlined. The review also discusses the impact of different compounding ingredients on important compound properties like impermeability, heat resistance, adhesion, compound viscosity, green strength, and shrinkage resistance.

The review also gives an overview of the chlorobutyl applications with special reference to tire inner liners. Statistical tools like design of experiments have been used for optimizing the properties of tire innerliner. The advantage of using halobutyl inner liners in tire and its effects on tire performance, tire durability and rolling resistance is also discussed.

This review focus on grades, manufacturing, processing and applications of different grades of chlorobutyl.

APPENDIX 1

Recognized industry abbreviations for polymers

AU	Polyester urethane
BR	Polybutadiene
BIIR	Brominated isobutylene-isoprene rubber (chlorobutyl rubber)
BIMS	Brominated Isobutylene-co-para-methylstyrene rubber
BHT	Antioxidant. Protects against degradation.
CIIR	Chlorinated isobutylene-isoprene rubber (chlorobutyl rubber)
CPE	Chlorinated polyethylene
CR	Chloroprene rubber
CSM	Chlorosulfonyl polyethylene
EAM	Ethylene-vinyl acetate copolymer
EPDM	Terpolymer of ethylene, propylene and a diene with a residual unsaturated portion in the chain
EPM	Ethylene propylene copolymer
EU	Polyether urethane
ESBO	Epoxidized soybean oil. Epoxy groups capture any acids, including excess stearic acid. Level is approx 1.3%
GPR	General Purpose Rubber
HNBR	Hydrogenated acrylonitrile butadiene rubber
IIR	Isobutylene isoprene rubber
IR	Synthetic polyisoprene
NBR	Acrylonitrile butadiene rubber
SBR	Styrene butadiene rubber
E-SBR	Emulsion styrene butadiene rubber
S-SBR	Solution styrene butadiene rubber
X-NBR	Carboxylated acrylonitrile butadiene rubber
X-SBR	Carboxylated styrene butadiene rubber
Y-SBR	Block copolymer of styrene and butadiene

APPENDIX 3

List of common terms for miscellaneous compounding ingredients

Altax	Benzothiazyl disulfide
Barytes	Barium sulfate
BHT antioxidant	Butylated hydroxytoluene
DEG	Diethyleneglycol
DIAC No. I	Hexamethylene diamine carbamate
Di-Cup 40C	Dicumyl peroxide (409 active)
Escorez™ 1102	Petroleum based resin
Flexon 876	Paraffinic mineral oil
Flexon 641	Naphthenic mineral oil
Flexon 580	Naphthenic mineral oil
Flexon 391	Aromatic mineral oil
MBI	Mercaptobenzimidazole
MBT	Mercaptobenzothiazole
MBTS	Benzothiazyl disulfide
Mineral rubber	Blends of maltenes, asphaltenes
Morfax	4-morpholinyl-2 benzothiazole disulfide
Parapol 2225	Low molecular weight isobutylene-butane copolymer
Retarder W	Salicylic acid
Ultramarine blue	Blue pigment
Wood rosin	Derivatives of abietic acid
MP resin	Octylphenol formaldehyde resins

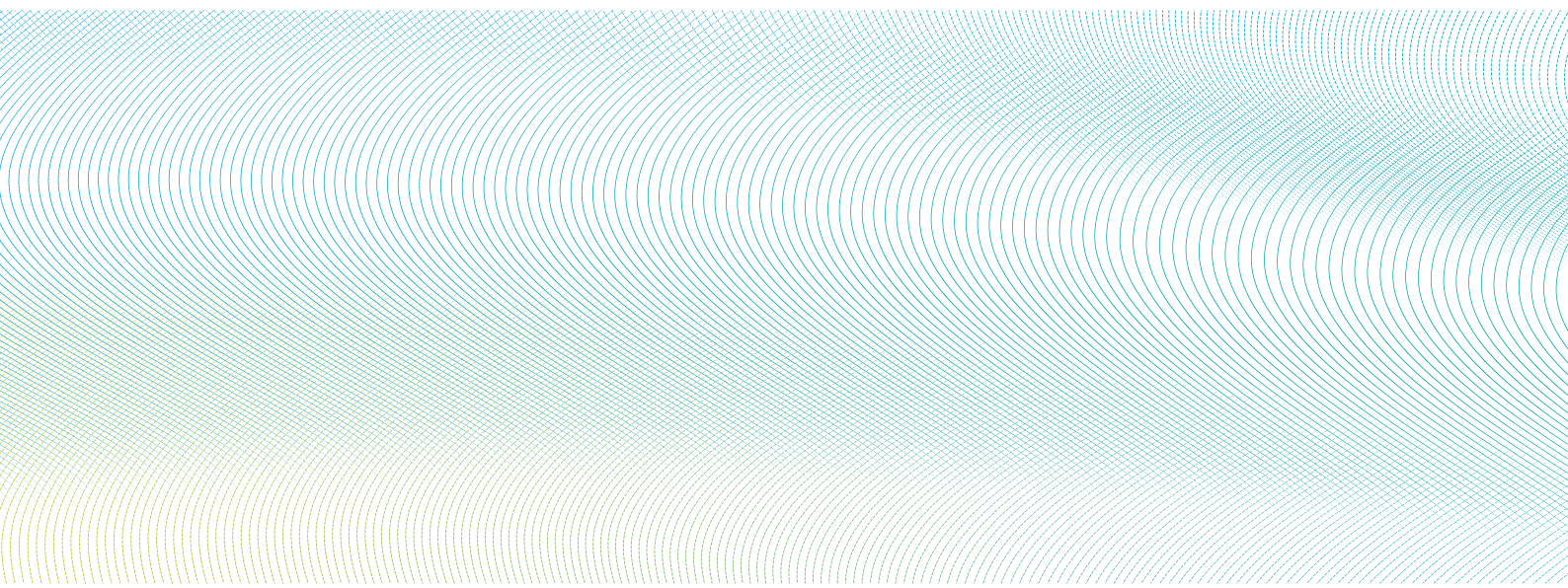
APPENDIX 2

Recognized industry abbreviations for accelerators

Abbreviation & commercial descriptions	Chemical name	Function
CBS	N-cyclohexyl-2-benzothiazolesulfenamide	Primary Acc.
BCI-MX	1,3-bis(citraconimidomethyl) benzene	Reversion Res.
CTP	N-(cyclohexylthio) phthalimide	Retarder
DBQDO	<i>p</i> -quinone dioxime dibenzoate	Quinone Cure
DCBS	Dicyclohexylbenzothiazole sulfenamide	Primary Acc.
DETU	Diethylthiourea	
DBTU	Dibutylthiourea	
DOTG	Di- <i>o</i> -tolylguanidine	Secondary Acc.
DPG	Diphenyl guanidine	Secondary Acc.
DPPD	Diphenyl- <i>p</i> -phenylenediamine	Accelerator
DPTU	N, N'-diphenylthiourea	
DTDM	4,4-Dithiodimorpholine	Vulcanizing Agent
ETU	Ethylthiourea	Accelerator
HTS	Hexamethylene-1,6-bis(thiosulfate) Disodium salt, dihydrate	Reversion Res.
MBS	Oxydiethylene benzothiazole-2 -sulfenamide	Primary Acc.
MBT	Mercaptobenzothiazole	Accelerator
MBTS	Mercaptobenzothiazole disulfide	Primary Acc.
QDO	<i>p</i> -quinone dioxime	Quinone Cure
TBBS	<i>tert</i> -Butyl-2-benzothiazole sulfenamide	Primary Acc.
TBSI	N- <i>t</i> -butyl-2-benzothiazole sulfenimide	Primary Acc.
TBzTD	Tetrabenzylthiuram disulfide	Secondary Acc.
TMTD	Tetramethylthiuram disulfide	Secondary Acc.
TMTM	Tetramethylthiuram monosulfide	Secondary Acc.
Amylphenol disulfide 1	Amyl disulfide polymer (23% S)	Sulfur Donor
Amylphenol disulfide 2	Amyl disulfide polymer (28% S)	Sulfur Donor
Amylphenol disulfide 3	Amyl disulfide polymer (18% S)	Sulfur Donor
Amylphenol disulfide 4	Amyl disulfide polymer (30% S)	Sulfur Donor
Amylphenol disulfide 5	Amyl disulfide polymer (27% S, 10% HSt)	Sulfur Donor
Vultac® TB 710	Alkylphenol disulfide polymer	Accelerator
ZDMC	Zinc dimethyldithiocarbamate	Secondary Acc.
ZDEC	Zinc diethyldithiocarbamate	Secondary Acc.
ZDBC	Zinc dibutyldithiocarbamate	Secondary Acc.
ZBEC	Zinc dibenzoyldithiocarbamate	Secondary Acc.
ZIX	Zinc isopropyl xanthate	Low temp. Acc.
ZBPD	Zinc dibutylphosphorodithiate	Accelerator
MBMTBP	2,2'-Methylene-bis (4-methyl-6- <i>tert</i> -butylphenol	Antioxodant
6 PPD	N-(1,3-dimethylbutyl)-N'-Phenyl- <i>p</i> -Phenylenediamine	Antiozonant
TMQ	Polymerised 1.2 dihydro-2, 4 trimethyl quinoline	Antioxodant

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