

Exxon™ butyl and halobutyl rubber

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Model vulcanization systems for butyl rubber and halobutyl rubber manual

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Abstract

The vulcanization of isobutylene-co-isoprene rubber (IIR), brominated isobutylene-co-isoprene rubber (BIIR), chlorinated isobutylene-co-isoprene rubber (CIIR), and brominated isobutylene-co-para-methylstyrene elastomer (BIMSM) differs from that of general-purpose rubbers (GPR). Butyl rubber has approximately 2% unsaturation in the backbone. Halobutyl rubber (BIIR and CIIR) incorporates the butyl backbone with either bromine or chlorine, which significantly increases the chemical reactivity of the isoprenyl units located in the butyl backbone. Similarly, in BIMSM the bromine atom is bonded to the para-methylstyrene (PMS) group, thus affording the completely saturated polymer backbone a site of chemical reactivity. Utilization of the unique attributes of butyl rubber and halobutyl rubbers with their minimal backbone unsaturation and of BIMSM elastomers with no backbone unsaturation is found in many areas of industry. These properties are excellent vapor impermeation, resistance to heat degradation, and improved chemical resistance as compared to general-purpose rubbers. However, this low amount of reactivity requires special consideration to vulcanize these isobutylene-based polymers. The type of vulcanization system selected is a function of the composite structure in which it is used, and the cured product performance requirements. Therefore, vulcanization systems vary and may include an accelerator package along with resins, zinc oxide, zinc oxide and sulfur, and quinoid systems. This review will discuss the types and selection of appropriate vulcanization systems for isobutylene-based elastomers.

1. Introduction.....	4
2. Composition of isobutylene polymers.....	5
3. General trends in vulcanization chemistry.....	7
4. Overview of the vulcanization of isobutylene-based elastomers.....	10
5. Vulcanization of butyl rubber.....	11
6. Halobutyl rubber.....	14
7. Vulcanization of brominated isobutylene-co-para-methylstyrene (BIMSM).....	18
8. Model cure system formulary.....	20
9. Summary.....	24
Appendix 1.....	25
10. References.....	26

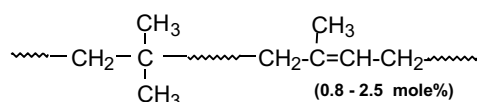
1. Introduction

Isobutylene-based elastomers include butyl rubber, halogenated butyl rubber, star-branched versions of these polymers and brominated isobutylene-co-para-methylstyrene (BIMSM). Due to their impermeability and resistance to heat and oxidation, these polymers find application in tire innerliners, innertubes, curing bladders and envelopes, and other specialty applications where air retention and resistance to heat and oxidation are desired. Butyl rubbers are produced via a cationic polymerization in a methyl chloride diluent at temperatures less than -90°C . These unique attributes and difficult manufacturing requirements place butyl rubbers in the special purpose elastomers category distinct from general-purpose rubbers (GPR) such as polybutadiene rubber (BR), natural rubber (NR), and styrene-butadiene rubbers (SBR)¹.

2. Composition of isobutylene polymers

Butyl rubber (IIR) is the copolymer of isobutylene and a small amount of isoprene, typically in the order of 2%. Figure 1 is a schematic of butyl rubber.

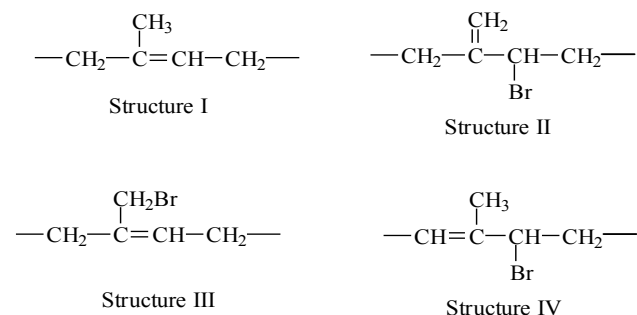
Figure 1
Structure of butyl rubber



Chlorobutyl (CIIR) and bromobutyl (BIIR) rubbers are manufactured similarly to butyl rubber, but with an added subsequent halogenation step. Due to the nearly equivalent reactivity ratios of the monomers and low concentration of isoprene, the isoprenyl units in these polymers are randomly distributed along the polymer chain.

Figure 2 illustrates the structures of the functional halogen containing groups found in bromobutyl rubber^{2,3}. The majority of the isoprenyl units are in the trans-configuration. Structure II, the predominant structure in halobutyl rubber, represents 50%-60%, followed by Structure I representing from 30%-40%. Approximately 5%-15% is Structure III; Structure IV is typically only 1%-3%.

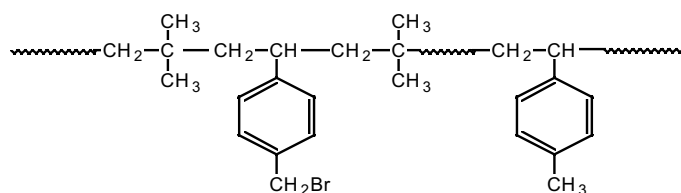
Figure 2
Structure of isoprenyl units in bromobutyl rubber



Copolymers of isobutylene and para-methylstyrene have a random structure, again due to the monomer reactivity ratios being nearly equivalent. After polymerization and subsequent bromination some of the para-methylstyrene groups are converted to reactive bromomethylstyryl groups. These saturated backbone polymers contain isobutylene, 1 to 5 mole-% of para-methylstyrene, and 0.5 to 1.3 mole-% of brominated para-methylstyrene (Figure 3)². Their glass transition or second order transition temperature increases with increasing para-methylstyrene content and is nominally around -57°C. This compares to a nominal -59°C to -60°C for halobutyl polymers.

Figure 3
Structure of brominated isobutylene-co-para-methylstyrene, BIMSM²

Table I illustrates the commercial grades of isobutylene-based



elastomers and their typical compositions that are currently available from ExxonMobil Chemical company.

Table I

Commercial grades of ExxonMobil isobutylene-based elastomers

Elastomer	Grade	Mooney Viscosity (ML1+8 at 125°C)	Isoprene (mol%)	para-Methylstyrene (wt%)	Halogen	Halogen (wt%)	Halogen (mol%) ¹	Typical Applications
Butyl (low viscosity)	065	32	1.05					Tubes, Baldders
	165	32	1.50					Tubes, Baldders
	365	33	2.30					Tubes, Baldders
Butyl (medium viscosity)	068	51	1.15					Tubes, Baldders
	268	51	1.70					Tubes, Baldders
Butyl (high viscosity)	269	57	1.70					Tubes, Baldders
Chorobutyl	1066	38	1.95		Cl	1.26		Tire Innerliners White Sidewalls
Bromobutyl	2222	32	1.70		Br	2.00		Automobile Tires
	2235	39	1.70		Br	2.00		Automobile Tires
	2255	46	1.70		Br	2.00		Truck Tire Innerliners
	2211	32	1.70		Br	2.10		Fast Cure Applications
	2244	46	1.70		Br	2.10		Fast Cure Applications
Exxpro	3035	45		5.00	Br		0.47	Curing Bladders
	3433	35		5.00	Br		0.75	Pharmaceuticals
	3745	45		7.50	Br		1.20	Tires, Engineerd Products

Note: 1. Benzylic bromine content

2. Butyl, chlorobutyl rubber, bromobutyl rubber, and Exxpro polymers are used in pharmaceutical applications

This paper is an overview of the vulcanization of this group of special purpose elastomers and identifies opportunities for further improvement in final compound mechanical properties and final product performance.

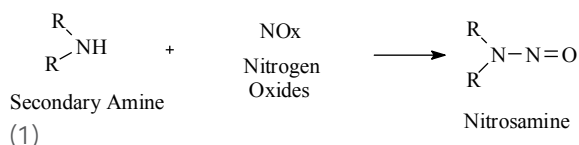
3. General trends in vulcanization chemistry

Five factors influence the development of vulcanization system technology:

- Elimination of accelerators that may generate nitrosamines
- Accelerators for improved scorch resistance and improved ease of compound processing during final product assembly, e.g. a tire
- Vulcanization systems suitable for high-temperature curing with associated benefits in productivity
- Improved reversion resistance
- Improvement in cured compound attributes such as mechanical or dynamic properties

Nitrosamines

Nitrosamines are nitrogen-based compounds with attached carbon-containing groups. Using ammonia as a reference, replacing one of the hydrogen atoms produces a primary amine. Substitution of two or three hydrogen atoms produces secondary or tertiary amines, respectively. As shown in equation 1, secondary amines found in accelerators such as thiurams, dithiocarbamates, and some sulfenamides can react with nitrogen oxides in the air to produce a nitrosamine.



During the vulcanization process accelerators such as tetramethylthiuram disulfide (TMTD) are partly decomposed to their parent secondary amines. Reaction with atmospheric nitrogen oxide can lead to N-nitrosamine generation. In Germany, N-nitrosamine levels in the work place atmosphere are controlled under factory regulation TRGS 552. This directive permits a maximum atmospheric concentration of only $1 \mu\text{g}/\text{m}^3$ of regulated N-nitrosamines. The cabin space of automotive vehicles now falls under the regulations that have implications for rubber parts in this area, which includes the door and window seals. Automotive vehicle manufactures have also placed increasing emphasis on the removal of N-nitrosamines from all parts of their vehicles including rubber components such as gaskets, engine mounts, and hoses⁴. Maximum nitrosamine levels are listed in Table II.

Table II

Nitrosamine limits in pharmaceutical, food utensils⁴

Location	Nitrosamine ppb maximum	Nitrosables ppb maximum
Australia	20	400
Denmark	5	100
Netherlands	1	100
Canada	60	N/A
Switzerland	10	200
Germany	10	200
UK	30	100
USA	60	N/A

European Union directive 93/11/EEC concerns extractable N-nitrosamines for certain food applications. Accelerators that are considered to give rise to N-nitrosamines are listed below (see Appendix 1 for explanation of abbreviations):

TMTD, TMTM, TETD, TBTD, DPTT, DTDM, ZDMC, ZDEC, ZDBC

Tetrabenzylthiuramdisulfide (TBzTD) and zinc dibenzylthiocarbamate (ZBEC) accelerators, though in some instances might give rise to N-nitrosamines, are considered to be outside the scope of regulatory attention⁵. The effect of steric factors on thiuram and dithiocarbamate nitrosamine formation has also been studied. Thiurams and dithiocarbamates made from sterically bulky amines such as diisobutylamine produce orders of magnitude lower levels of nitrosamine than does tetramethylthiuram disulfide (TMTD). At the same time, when used as a secondary accelerator for cyclobenzothiazole sulfenamides, tetraisobutylthiuram disulfide has better scorch safety, but vulcanizes at the same rate as TMTD. Uniquely, tetraisobutylthiuram monosulfide could act as a retarder as well as a secondary accelerator⁶. Accelerators that cannot produce N-nitrosamines since they are based on primary amines or do not contain nitrogen include:

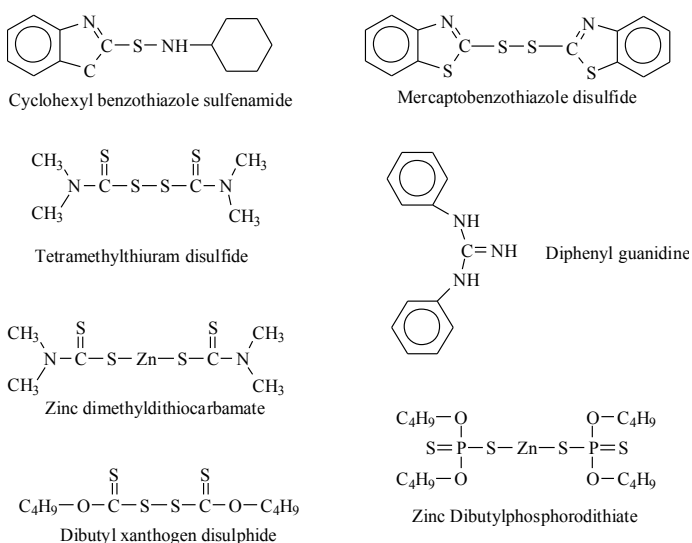
CBS, TBBS, DOTG, DPG, MBT, MBTS, ZMBT, Xanthates

Accelerators for isobutylene-based elastomers

A broad range of accelerators can be found in formulas for isobutylene-based elastomers. Some of the accelerators found are illustrated in Figure 4⁷. These include cyclohexylbenzothiazole sulfenamide (CBS), mercaptobenzothiazole disulfide (MBTS), tetramethylthiuram disulfide (TMTD), diphenyl guanidine (DPG), and zinc dimethyldithiocarbamate (ZDMC).

Figure 4

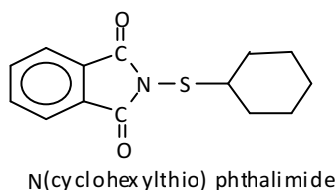
Structure of selected accelerators⁷



Improved scorch resistance is currently achieved by addition of magnesium oxide (MgO). In some instances, with a sulfenamide-based cure system, N-(cyclohexylthio) phthalimide (PVI), whose structure can be found in Figure 5, is used. MBTS can also serve as a pre-vulcanization inhibitor. Calcium oxide and magnesium oxide can be used in zinc oxide-cured halobutyl rubber. However, they will serve as an activator in amine accelerated systems. Calcium stearate and zinc stearate can act as retarders in chlorobutyl rubber compounds. Unlike their use in general-purpose elastomers, benzoic acid and salicylic acid are not effective as scorch retarders.

Figure 5

Structure of PVI



N-(cyclohexylthio) phthalimide

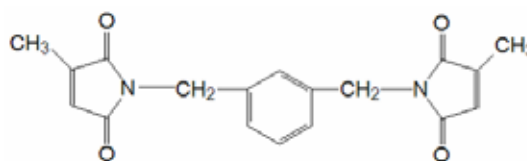
High temperature curing and reversion resistance

As cure temperature increases, care must be taken to avoid reversion while achieving the desired mechanical properties of the product. This infers no marching modulus and the preservation of a stable crosslink network. Cure systems with primary accelerators such as MBTS, or sulfenamides such as TBBS, tend to meet such requirements. Depending on the cure system thiurams, dithiocarbamates, and xanthates tend to have poorer reversion resistance.

Two reversion resistors have been of particular note. These are bis(citraconimido-methyl) benzene (BCI-MX) and sodium hexamethylene-1,6-bisthiosulfide dehydrate. Both function exclusively as reversion resistors. BCI-MX (Figure 6) is understood to react with the polymer chain to form stable flexible carbon-carbon crosslinks which substitutes for and replaces sulfur crosslinks that disappear during reversion⁸.

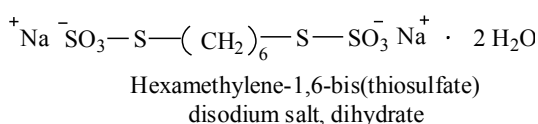
Figure 6

Structure of 1,3-bis(citraconimidomethyl)benzene (BCI-MX)



Alternatively, for resistance to high-temperature reversion, sodium hexamethylene-1,6-bisthiosulfide dihydrate (Figure 7) may be evaluated since it breaks down and inserts a hexamethylene-1,6-dithiyl group within a disulfide or polysulfide crosslink providing a hybrid crosslink. During extended vulcanization periods or accumulated heat history due to product service, polysulfidic-hexamethylene crosslinks rearrange to produce thermally stable elastic monosulfidic crosslinks. At levels up to 2.0 phr, there is little effect on compound induction, scorch times, or other compound mechanical properties.

Figure 7

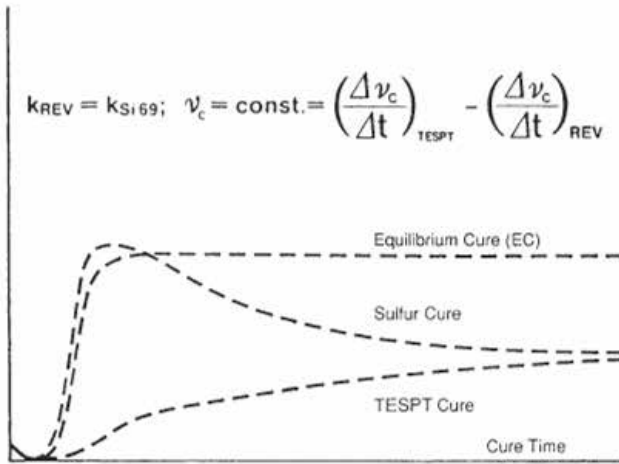


The bifunctional silane-coupling agent, bis-(3-triethoxysilylpropyl) tetrasulfane has dual functions as both a sulfur donor and a reversion resistor⁹. This ability to maintain the polysulfidic or other stable network throughout the curing process and subsequent product service life while offering reversion

resistance can be beneficial (Figure 8)⁹. Natural rubber compounds containing such systems are believed to display improved abrasion resistance and wear properties.

Figure 8

EC cure system rheometer profile⁹



4. Overview of the vulcanization of isobutylene-based elastomers

In butyl rubber, the hydrogen atoms positioned alpha (α) to the carbon-carbon double bond of the isoprenyl unit permits vulcanization into a crosslinked network with sulfur and organic accelerators. The low degree of unsaturation has traditionally required the use of ultra-fast accelerators, such as thiurams and thiocarbamates in order to cure under acceptable conditions of time and temperature. Phenolic resins, bisazidoformates, and quinone derivatives can also be employed. Vulcanization introduces a chemical crosslink approximately every 250 carbon atoms along the polymer chain producing a covalently bonded molecular network. Polysulfidic crosslinks have limited stability at elevated temperature and in many instances can rearrange to form monosulfidic and disulfidic crosslinks. This rearrangement results in permanent set of vulcanizates exposed to high temperatures for long periods of time. Resin cure systems such as alkyl phenol-formaldehyde derivatives can provide carbon-carbon crosslinks resulting in heat-stable vulcanizates^{1,2}.

Halobutyl rubber can be crosslinked by some of the same curatives used for butyl rubber such as zinc oxide, bismaleimides and dithiols. Halogens are good leaving groups in nucleophilic substitution reactions due to the low carbon-halogen bond energy (Table III). When zinc oxide is used to crosslink halobutyl rubber, carbon-carbon bonds are formed through dehydrohalogenation which results in a compound with a very stable crosslink system affording a compound having good retention of aged properties and low compression set.

Table III

Carbon-halogen bond energies and bond lengths¹⁰

Bond	Energy J/mol	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

The bromine-carbon bond in bromobutyl rubber has a lower disassociation energy than does the chlorine-carbon bond in chlorobutyl rubber (Table III). Epoxidized soybean oil (ESBO) can be added to suppress isomerization reactions and HBr formation. Butylated hydroxytoluene (BHT) can be used to stabilize the polymer by serving as an antioxidant. Calcium stearate is added to CIIR, BIIR, and BIMSM as an acid trap to diminish dehydrohalogenation catalyzed by HCl or HBr. Calcium stearate can also act as a cure retarder.

Brominated isobutylene-co-para-methylstyrene (BIMSM) crosslinking involves the formation of carbon-carbon bonds, generally through Friedel-Crafts alkylation chemistry. Diamines, phenolic resins and thiosulfates can also be used to crosslink BIMSM elastomers. The stability of these carbon-carbon bonds combined with the chemically saturated backbone of BIMSM yields excellent resistance to heat and oxidative aging, and to ozone attack.

5. Vulcanization of butyl rubber

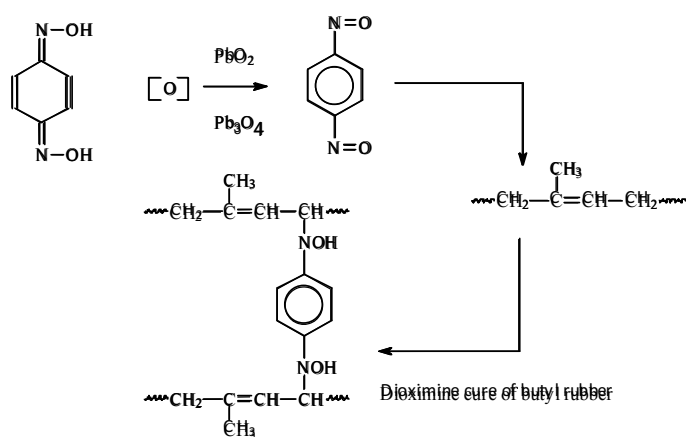
The major applications utilizing butyl rubber are tire innertubes, curing bladders, pharmaceutical closures, and a variety of engineered products such as mounts, sheeting, automotive flaps, and damping pads. These applications require good compound aging resistance, oxidative resistance and heat stability. Depending on the application of the final product, one of the following three cure systems have been used^{11,12}.

- Quinone dioxime
- Resin cure
- Thiuram (i.e. TMTD) accelerated

Quinone cure systems

The crosslinking of butyl rubber with para-quinone dioxime (QDO) or para-quinone dioxime dibenzoate (DBQDO) proceeds through an oxidation step that forms the active crosslinking agent para-dinitrosobenzene. The use of metal oxides (such as PbO₂, Pb₃O₄, MnO₂) or MBTS as an oxidizing agent, increases the vulcanization rate allowing use in room temperature cures such as in cements³. Figure 9 is a schematic illustrating the reaction of a dioxime in the vulcanization of butyl rubber. The dioxime vulcanization system can be used for dry rubber applications. One example is electrical insulation systems, which contain butyl rubber for improved ozone resistance.

Figure 9
Dioxime cure of butyl rubber³



Resin cure systems

Phenol formaldehyde curing resins are classified as resols, i.e. three-dimensional resin systems forming crosslink networks which can serve as reinforcing resins versus novolac resins which are linear. Resin curing of butyl rubber is a function of the reactivity of the phenolmethylo groups in the reactive

phenol formaldehyde resin. Curing resins such as a heat reactive octylphenol formaldehyde resin, which contains methylo groups, can be used³. Table IV contains a model formula illustrating the resin cure system. For a faster cure, addition of a halogen donor such as polychloroprene or stannous chloride is required¹³. In this instance, polychloroprene has not been considered as part of the total compound polymer content.

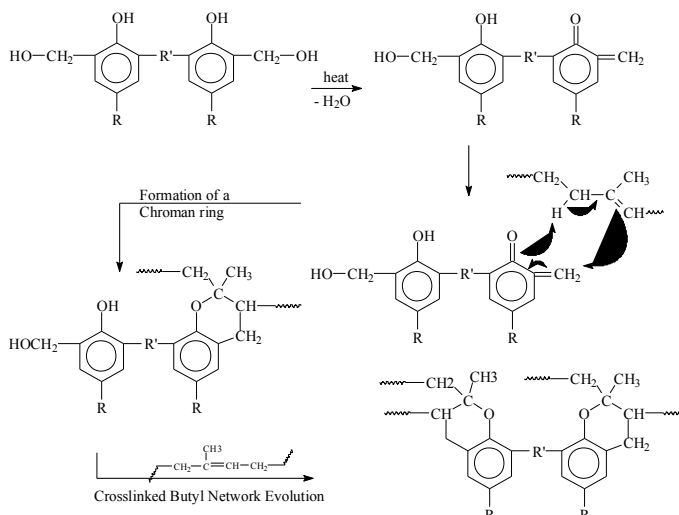
Table IV
Model curing bladder formulation¹³

Material	phr
Butyl 268	100.0
Polychloroprene	5.0
Carbon black N330	50.0
Castor oil	5.0
Zinc oxide	5.0
Octylphenol formaldehyde resin	10.0

A more reactive resin cure system not requiring an activator is obtained when a portion of the methylo groups are replaced by bromine. An example of this resin is brominated octylphenol formaldehyde resin³.

Figure 10 is a schematic illustrating the reaction of a curing resin (heat reactive octylphenol formaldehyde) in the vulcanization of butyl rubber. Following the elimination of water in the reaction sequence, the exomethylene group and carbonyl oxygen react with an isoprenyl unit in butyl rubber to form a chroman ring. Chromanone ring structures are very stable and are frequently found in natural product biosynthesis.

Figure 10
Resin curing of butyl rubber¹³

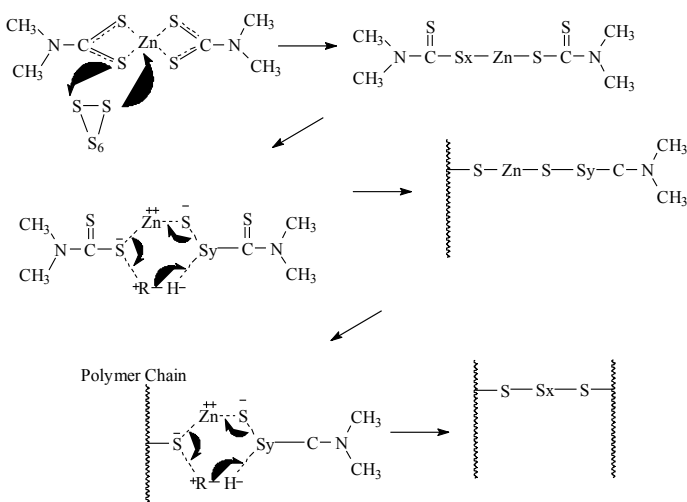


Thiuram accelerated vulcanization

Although thiuram and dithiocarbamate accelerators form nitrosamines, a number of published formulas use these components as vulcanization agents. For completeness, we include the mechanism by which this class of materials is thought to function¹⁴; however, again we recommend the use of alternative non-nitrosamine-generating accelerators. Thiuram accelerated systems participate in the vulcanization process through formation of a zinc complex as shown in figure 11. The sulfur rich complexes are formed by insertion of the sulfur into the zinc dimethyldithiocarbamate molecule, which in turn is an active sulfurating complex. Rubber bounded intermediates are subsequently produced followed by crosslinking to form polysulfidic crosslinks. These polysulfidic crosslinks evolve into monosulfide and disulfidic crosslinks.

Figure 11

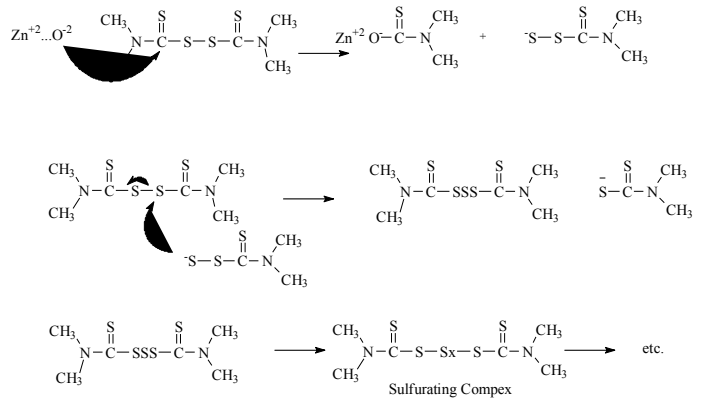
Possible mechanism of thiuram accelerated vulcanization¹⁴



In the absence of sulfur, TMTD can function as a sulfur donor (Figure 12). Increasing the rate of cure without a significant loss of other properties can be obtained with the addition of thiurams or thioureas and zinc oxide at around 5 phr. Substitution of nitrosamine generating thiurams such as TMTD with MBTS or higher molecular weight thiurams such as TBzTD or dithiocarbamates such as ZBEC can be explored to eliminate the future use of these accelerators. TBzTD is a high molecular weight accelerator and functions as a sulfur donor. Due to its molecular weight and steric hindrance these accelerators can have improved scorch resistance hence improving compound processing. When used in combination with sulfenamides such as TBBS, the nitrosamine concentration becomes negligible¹⁵. The high molecular weight of the secondary amine, dibenzylamine (DBA), produced by TBzTD is not as volatile as those generated from lower molecular weight thiurams such as TMTD, TMTM, or TBTD. DBA has a boiling point of 300°C and in the presence of oxygen may decompose below this temperature.

Figure 12

Thiurams as sulfur donors¹⁴

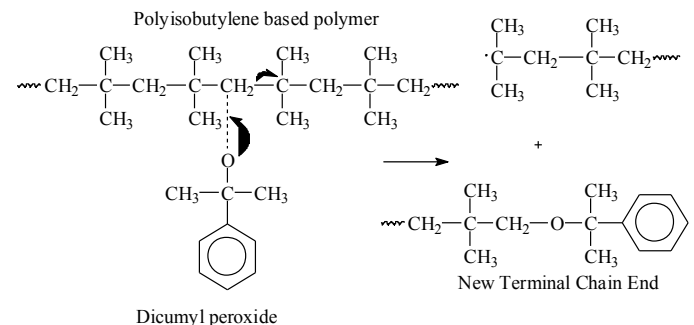


Peroxides and butyl rubber

Polyisobutylene and butyl rubber undergo degradation rather than crosslinking when treated with peroxides. It is believed that scission occurs via a radical substitution mechanism (Figure 13).

Figure 13

Peroxide degradation of polyisobutylene¹⁴



Other vulcanization systems for butyl rubber

Due to the inherent low reactivity of the nearly saturated butyl backbone, there are instances when a secondary accelerator is required in the vulcanization system. Table V¹⁶ contains examples of an amyphenol disulfide polymer secondary accelerator (Vultac series) that can be used.

Table V¹⁶

Vultac series of accelerators

Commercial Name	Chemical Name & Function	Formula	Sulfur Wt%	Softening Point (°C)
Vultac 2	Amylphenol disulfide polymer Sulfur donor. Phenol, 4(1,1-dimethyl propyl)-polymer with sulfur chloride	$(C_{11}H_{16}O.Cl_2S_2)_x$	23	55
Vultac 3	Amylphenol disulfide polymer Sulfur donor. Phenol, 4(1,1-dimethyl propyl)-polymer with sulfur chloride	$(C_{11}H_{16}O.Cl_2S_2)_x$	28	85
Vultac 5	Amylphenol disulfide polymer Sulfur donor.	$(C_{11}H_{16}O.Cl_2S_2)_x$	18	85
Vultac 7	Amylphenol disulfide polymer Sulfur donor. Phenol, 4(1,1-dimethyl propyl)-polymer with sulfur chloride	$(C_{11}H_{16}O.Cl_2S_2)_x$	30	120
Vultac 710	Amylphenol disulfide polymer Sulfur donor. Phenol, 4(1,1-dimethyl propyl)-polymer with sulfur chloride plus 10% stearic acid	$(C_{11}H_{16}O.Cl_2S_2)_x$	27	85

The general structure and crosslink formed by polymeric amyphenol disulfide accelerators is believed to be illustrated in Figure 14. Though these accelerators contain sulfur, the disulfidic group may not be readily assessable due to steric hindrance of the phenol groups. The sulfur linkage is predominantly a disulfide, but trisulfide and tetrasulfide crosslinks have also been reported.

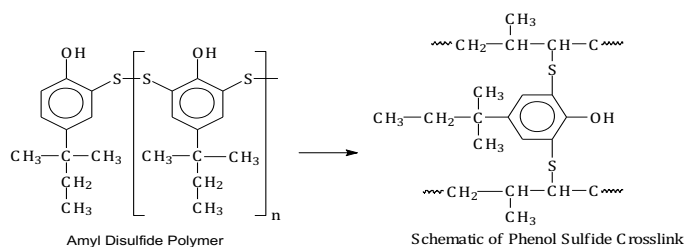
Figure 14^{16,17,18}

Table VI shows that even though the apparent activation energies of the amyphenol disulfide polymer accelerators can be higher than that of TMTD, the rheometer delta torque, DT, or state of cure which relates to tensile strength, elongation, and modulus is higher particularly for Vultac 3. Note that these accelerators improve interfacial bonding in some cure system blends¹⁹. For example, use of amyphenol disulfide polymers in a NR/NBR blend has been investigated. It is suggested that to have good activity the system may require use of up to 4.5 phr of Vultac 3²⁰. Although the mechanism of amyphenol disulfide polymer activity in vulcanization remains uncertain, it has been shown that there was a lower degree of preferential vulcanization in polymer blends when amyphenol disulfide polymer replaced free sulfur. It has been concluded that the amyphenol disulfide polymer moiety played a role in increasing the solubility of the vulcanization intermediates in natural rubber and that a monosulfidic crosslink is created resulting in better reversion resistance.

Table VI

Vulcanization Systems Containing Vultac Accelerators

Accelerator	MDR Rheometer ΔT (dNm) at 160°C	Apparent Activation Energy, E_a (KJ/mol)	Form
TMTD	4.64	81.77	-
Vultac 2	4.79	79.52	Glass
Vultac 3	7.23	99.96	Glass
Vultac 5	6.66	100.97	Powder
Vultac 7	7.23	92.84	Pellets
Vultac 710	7.22	96.41	Pellets

6. Halobutyl rubber

Commercially, chlorobutyl rubber (CIIR) and bromobutyl rubber (BIIR) are the most important derivatives of butyl rubber. Their predominant application is in tire innerliners with the performance of the modern radial tire being impacted by the amount of halobutyl rubber used in the innerliner compound. Typical performance requirements of the tire innerliner are:

- Air retention
- Adhesion to tire carcass compound
- Resistance to fatigue and cracking
- Heat resistance
- High tensile and tear strength

Chlorobutyl rubber has an added application in white sidewall compounds. When blended with NR, SBR or BR, halobutyl rubber may be used in tread compounds. The addition of isobutylene-based polymers increases the dynamic loss modulus leading to improvements in wet and dry traction performance, braking performance, and vehicle stopping distance.

Vulcanization of halobutyl rubber

The primary difference between chlorobutyl rubber and bromobutyl rubber is due to the higher reactivity of the carbon-bromine bond compared to that of carbon-chlorine bond. The carbon-bromine bond has the lowest energy and the longest length (Table III). Bromobutyl rubber has faster cure rates and a shorter scorch or cure induction period (with productivity benefits), requires lower levels of curatives, and enables one to use a wider range of accelerators than could be possible for chlorobutyl rubber. A number of cure systems are suitable for halobutyl rubber and halobutyl rubber/general-purpose rubber (GPR) blends. Cure system selection will be a function of service conditions and the end use of the rubber product. Typical cure systems for halobutyl rubbers include:

Metal oxides

- Zinc oxide will react with the halogen in polymers such as halobutyl rubber and polychloroprene. Magnesium oxide is effective as a retarder.

Sulfur cure systems

- Sulfur cure systems can be used in tire innerliners where a high state of cure, fatigue resistance, high tensile and tear strength, and adhesion to GPR in components adjacent to the innerliner is important. A typical tire innerliner sulfur cure system may include sulfur (0.5-1.0 phr), zinc oxide (1.0-3.0 phr), and MBTS (1.0-1.5 phr).

Amines

- Zinc free compounds may be required in, for example, pharmaceutical applications. Curing of bromobutyl rubber with diamines such as hexamethylene diamine carbamate may be one solution.

Peroxide cure systems

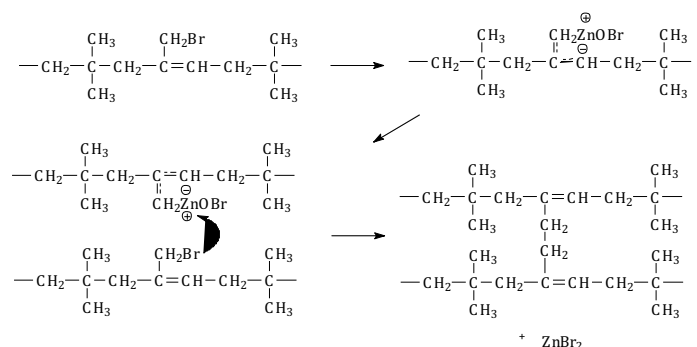
- Halobutyl rubber can be crosslinked with peroxide cure systems. A dicumyl peroxide with a coagent, such as bismaleimide, yields a low compression set, high heat resistant vulcanizate³. Butyl rubber, however, will depolymerize in the presence of peroxide.

Metal oxide curing

Metal oxides such as zinc oxide will react with the halogen in chlorobutyl and bromobutyl polymers. The most active halogen is in the allylic position. Zinc stearate or zinc octoate is required as a solubilizing agent and the mechanism is believed to be a nucleophilic substitution. Structure II (Figure 2) is the kinetically favored bromination product in bromobutyl rubber. However, at curing temperatures, rearrangement leads to an increase in the amount of Structure III. Structure III then dominates the equilibrium state that is achieved²¹. Figure 15 presents a possible scheme for the role of zinc oxide in crosslinking. In the presence of magnesium oxide, the halogen on the polymer can react with ZnBr₂ and reform ZnO and MgBr₂ as seen in the vulcanization of polychloroprene.

Figure 15

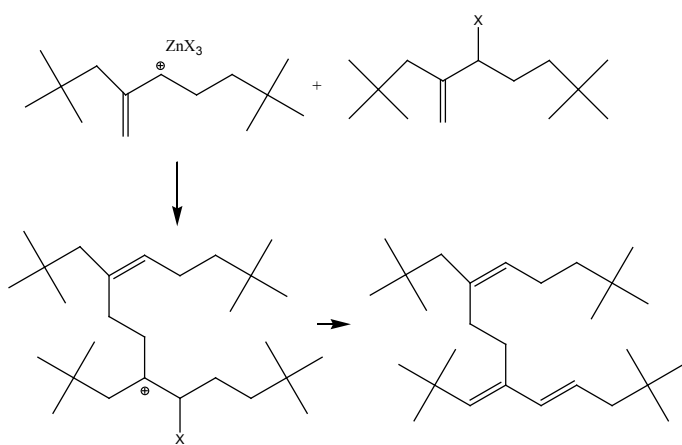
Zinc oxide in the vulcanization of bromobutyl rubber^{21,22,23}



This scheme was initially proposed based on model compound studies such as 2,2,4,8,8-pentamethyl-4-nonene. The final crosslink structure is thought to be as illustrated in Figure 16. There would be less steric hindrance around the methylene group than at the α -carbon rendering this interpretation more likely. Lowering sulfur or thiuram levels can control the greater reactivity of bromobutyl rubber. Mooney scorch and induction periods can also be extended by:

- Increasing the MBTS level (since MBTS can also serve as a retarder)
- Replacing phenolic resins such as octylphenol tackifying resins with hydrocarbon resins
- Lowering the stearic acid level or carboxylic acid content
- Avoiding amine type antioxidants
- Adding magnesium oxide (retarder in bromobutyl rubber)
- Adding polyethylene glycol since the ether functionality can serve as an efficient retarder for bromobutyl rubber.

Figure 16

 Possible mechanism for crosslinking of halobutyl rubber²⁴


Magnesium oxide dual effects on halobutyl rubber systems

Table VII illustrates the effect of magnesium oxide (MgO) on cure rate for a TMTD/zinc oxide cure system⁶. Addition of 0.25 phr of MgO increases the Mooney scorch time by ten minutes without significantly effecting chlorobutyl rubber compound properties such as tensile strength. If the level of magnesium oxide is increased to 0.5 phr, there will be a detrimental effect on cure rate, with magnesium oxide acting as a retarder. As a retarder, magnesium oxide is effective with all vulcanization systems except amine-based cures. In that case magnesium oxide will react with chlorine formed during crosslinking preventing the appropriate vulcanization reaction with the curing agent.

Table VII

 Vulcanization retardation with magnesium oxide (MgO)^{3, 6}

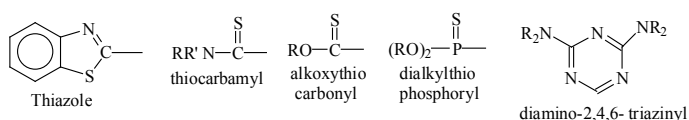
Compound	1 (phr)	2 (phr)	3 (phr)	4 (phr)
TMTD	1.00	1.00	1.00	1.00
MgO	0.00	0.25	0.50	0.00
Mooney Scorch at 126.5°C				
t-5	5.0	15.0	30.0	8.0
Cured at 153.0°C, 45 minutes				
Tensile Strength (MPa)	17.9	18.8	16.6	17.8
Elongation (%)	315	335	380	320
300% Modulus (MPa)	17.2	16.4	12.8	16.3

Formulation (phr): chlorobutyl 100, antioxidant 2246 1.0, HAF 50, stearic acid 1.0, ZnO 5.0, cure system as above.

MBTS accelerated curing

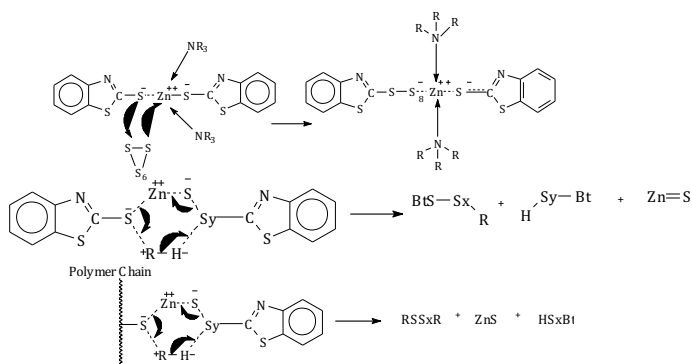
Accelerators tend to be based on one of five structures shown in Figure 17¹⁴, a thiazole, thiocarbamyl, alkoxythio carbonyl, dialkylthio phosphoryl, or a diamino-2,4,6-triazinyl.

Figure 17

 Fundamental structures of organic accelerators¹⁴


As a thiazole, MBTS has a dual function in the vulcanization reaction. First is as a retarder and then as an accelerator in sulfur crosslink formation where MBTS will react with ZnO to form a sulfuring agent. This intermediate can then react with the polymer to form crosslinks (Figure 18)¹⁴.

Figure 18

 Illustration of sulfuring agent and crosslink formation¹⁴


Although the final state of cure or crosslink density may be low, in the absence of zinc oxide MBTS may vulcanize rubber as shown in Figure 19¹⁴. Depletion of MBTS due to the initial reaction with bromine could account for the delayed response observed. Again, at higher levels MBTS can serve as a retarder.

Figure 19
MBTS accelerated crosslinking¹⁴

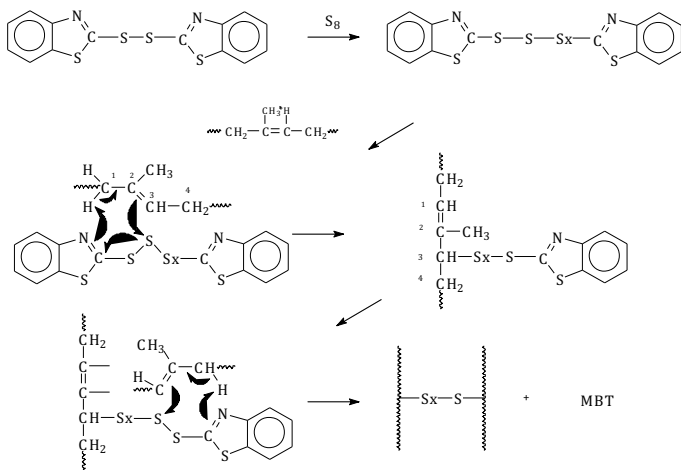


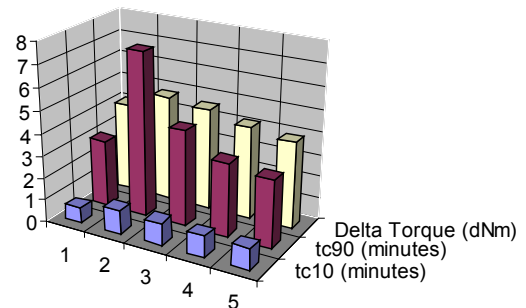
Table VIII illustrates the effect of MBTS concentration on rheometer induction time, cure state, and rate of vulcanization.

Table VIII
Retarding effect of MBTS

Compound	1 (phr)	2 (phr)	3 (phr)	4 (phr)	5 (phr)
Zinc oxide	2.0	2.0	2.0	2.0	2.0
Sulfur	0.5	0.5	0.50	0.50	0.50
MBTS	0.0	0.5	1.0	1.2	2.0
Rheometer (MDR), 180°C, 0.5° arc					
Mh - MI (dNm)	4.04	4.78	4.58	4.16	3.92
tc10 (minutes)	0.68	1.04	0.99	0.96	0.95
tc90 (minutes)	3.02	7.38	4.33	3.31	3.05
Rate (dNm/min)	1.83	2.34	2.38	2.62	2.84

Figure 20 shows that the use of 0.5 phr of MBTS increases the rheometer induction time (tc10 at 180°C) from 0.68 minutes to about one minute. The rheometer tc90 cure times increased to 7.3 minutes then fell to 3.1 minutes as MBTS increased from 0.5 phr to 2.0 phr. This further illustrates the dual role for MBTS as a retarder and as primary accelerator in the halobutyl rubber vulcanization process.

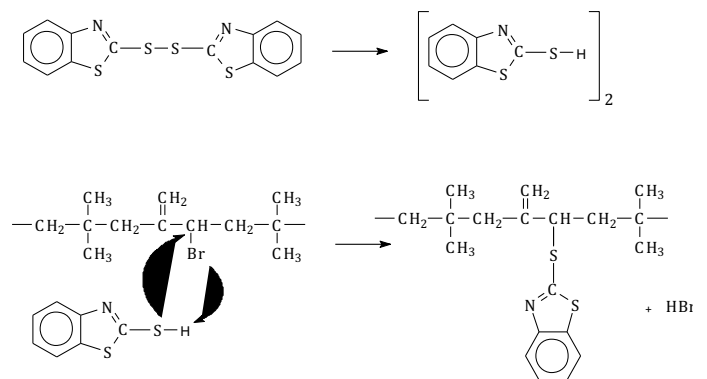
Figure 20
MBTS (phr) and MDR rheometer at 180°C, 0.5° arc



	1	2	3	4	5
tc10 (minutes)	0.68	1.04	0.99	0.96	0.95
tc90 (minutes)	3.02	7.38	4.33	3.31	3.05
Delta Torque (dNm)	4.04	4.78	4.58	4.16	3.92

The proposed retarding mechanism of MBTS is illustrated in Figure 21. Depletion of MBTS due to an initial reaction with bromine would account for the delayed response observed.

Figure 21
Retarding action of MBTS



Other halobutyl rubber cure systems

- Alternatives to TMTD accelerated curing in halobutyl rubber: Nitrosamines result when curing with TMTD and its use is not recommended. However, tetrabenzylthiuram disulfide (TBzTD) or its zinc derivative, zinc dibenzylidithiocarbamate (ZBEC) with a sulfenamide accelerator such as CBS can readily match the compound properties of TMTD. Magnesium oxide may be added to assist in controlling scorch and cure rate.
- Vultac, amylphenol disulfide accelerators: the Vultac group of sulfur donors can be used in chlorobutyl rubber-based tire compounds where good adhesion to natural rubber or NR/SBR blends is required. These compounds tend to show high cure states, which can be controlled with MBTS

and MgO. However, magnesium oxide use can also increase tack to calender rolls and increase mold fouling. With bromobutyl rubber, the use of amylphenol disulfide polymer results in reduction in scorch times thereby limiting their application.

- Diamines and thioureas: diamines and thioureas are very effective accelerators in curing of halobutyl rubbers.
- Peroxides: bromobutyl rubber may be crosslinked with peroxides. For optimal cure, a co-agent is required such as phenyl bismaleimide (HVA-2). Typically, 1.0 to 2.0 phr of dicumyl peroxide and 0.5 to 1.5 phr of HVA-2 will provide an adequate state of cure for both carbon black and clay filled bromobutyl rubber compounds.

Table IXEffect of zinc oxide level on vulcanization of BIMSM ²⁶

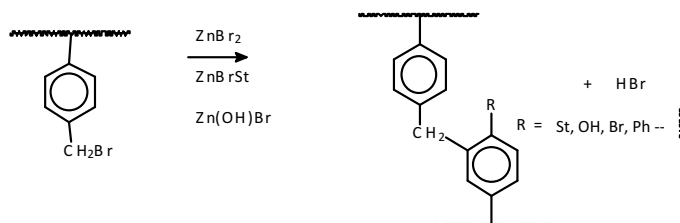
Compound	1	2	3	4	5	6
ZnO	0.25	0.50	1.00	2.00	3.00	4.00
Stearic Acid	2.00	2.00	2.00	2.00	2.00	2.00
Induction Time (ODR Rheometer at 160°C)						
t ₂ (minutes)	13.97	11.30	9.77	8.22	6.15	5.85
Cure Rate (dNm/min)	3.09	5.85	9.83	11.18	11.26	9.12
Mh (dNm)	27.70	43.25	48.22	49.85	49.75	49.80

Table X shows that stearic acid has a significant effect on induction times and cure rates. Although zinc stearate can vulcanize BIMSM, such compounds tend to display short scorch times. In the absence of zinc oxide, hydrogen bromide, which is a strong acid and is formed in the alkylation reaction, can react with zinc stearate to form the more stable ZnBr₂.

Table XEffect of stearic acid on curing of BIMSM ²⁶

Compound	1	2	3	4	5	6
Stearic Acid	0.5	1.0	2.0	3.0	4.0	5.0
ZnO	1.0	1.0	1.0	1.0	1.0	1.0
Induction Time (ODR Rheometer at 160°C)						
t ₂ (minutes)	60.9	31.7	9.5	7.1	6.2	5.2
Cure Rate (dNm/min)	1.6	3.4	9.8	9.5	7.3	4.4
Mh (dNm)	52.2	54.2	49.2	47.2	52.5	29.1

Stearic acid is then reformed as shown in equation 5. (5)



An increase in stearic acid levels can cause lubricating effects with a drop in apparent viscosity and compound stiffness as measured using an oscillating disc rheometer. However, reversion may also occur due to the increase in bromine released via a free radical cleavage from the polymer chain. This may be adjusted by increasing the zinc oxide level in the compound.

8. Model cure system formulary

Isobutylene-based polymers will employ a variety of cure systems depending on the requirements of the final cured product. For example, tire innerliners require good resistance to fatigue, tear strength, and adhesion to adjacent components in the tire. Therefore, sulfur-based systems with their co-curing ability, adequate fatigue and flex life are preferred for liner compounds. Curing bladders, which operate in high temperature environments and undergo many cycles, must have stable crosslinks and not be susceptible to reversion or other oxidative processes. In such instances, resin based cure systems are preferred.

Butyl rubber

Table XI illustrates quinone, resin, and sulfur-accelerator based model cure systems for butyl rubber. These cure systems may provide a starting point for further development.

Table XI

Model cure systems for butyl rubber ^{1,2}

Cure System	Quinone	Resin	Resin	Sulfur Accelerator
Units	phr	phr	phr	phr
Application	Electrical Cable Cover	Curing Bladder	Curing Bladder	Tube
ZnO	5.0	5.0	5.0	5.0
MgO	2.0	-	-	-
Stearic Acid	-	-	1.0	2.0
Sulfur	-	-	-	2.0
MBTS	-	-	-	0.5
TMTD	-	-	-	1.0
Polychloroprene	-	5.0	-	-
Resin (a)	-	10.0	-	-
Resin (b)	-	-	12.0	-
Benzoquinone Dioxime	2.0	-	-	-
Total phr	9.0	20.0	18.0	10.5

Note: Resin (a) is a heat reactive octylphenol-formaldehyde resin
Resin (b) is a brominated octylphenol-formaldehyde heat reactive resin

Halobutyl rubber

Table XII displays a set of model cure systems for halobutyl elastomers. These include a resin, sulfur-accelerator based system for a bromobutyl rubber radial tire innerliner, and a low temperature cure system possibly suitable for pipe seals in inaccessible locations. Again, these cure systems may provide a starting point for further development.

Table XIIModel cure systems for halobutyl rubber^{2,3}

Cure System	Sulfur Accelerator ²	Sulfur Sulfenamide ²	Zinc Oxide & Resin ³	Room Temperature Cure ³	Peroxide ³
Units	phr	phr	phr	phr	
Application	Innerliner	Polymer Blends	Pharmaceutical	Sheeting	Steam Hose
ZnO	3.0	2.0	3.0	5.0	-
ZnCl ₂	-	-	-	2.0	-
Stearic Acid	1.0	1.0	1.0	-	-
Sulfur	0.5	1.0	-	-	-
MBTS	1.5	-	-	-	-
TBBS	-	1.5	-	-	-
Resin (a)	-	-	2.0	-	-
Stannous Chloride (SnCl ₂)	-	-	-	2.0	-
Dicumyl peroxide (DiCup)	-	-	-	-	2.0
HVA-2	-	-	-	-	1.0
Total phr	6.0	5.5	6.0	9.0	3.0

Note: Resin (a) is a heat reactive octylphenol-formaldehyde resin

BIMSM elastomers

Table XIII presents a set of five cure systems for BIMSM.

Table XIIIModel cure systems for BIMSM elastomer²

Cure System	Metal Oxide	Sulfur Accelerator	Ultra Fast Accelerator System	Resin	Amine
Units	phr	phr	phr	phr	
Application	Damping Device	Innerliner	Engineerd Products	Curing Bladder	Engineerd Products
ZnO	2.0	1.0	1.0	1.0	1.0
Zinc Stearate	3.0	-	-	-	-
Stearic Acid	-	2.0	2.0	2.0	2.0
Sulfur	-	1.0	-	1.5	-
MBTS	-	2.0	-	1.5	-
ZDEDC	-	-	1.0	-	-
Triethylene Glycol	-	-	2.0	1.0	-
Resin (a)	-	-	-	5.0	-
DPPD	-	-	-	-	0.5
Total phr	5.0	6.0	6.0	12.0	3.5

Note: Resin (a) is a heat reactive octylphenol-formaldehyde resin

Table XIV illustrates a selection of five model compound formulas one each for butyl rubber, chlorobutyl rubber, bromobutyl rubber, and two for BIMSM elastomers. These model compound formulas illustrate typical properties obtained by utilizing experimental sulfur-accelerator vulcanization systems.

Table XIV

Effect of cure system type on fundamental properties of isobutylene based elastomers

	1 Model BIMSM Compound	2 BIMSM with Zinc Stearate	3 Model Butyl Compound	4 Model Chlorobutyl Compound	5 Model Bromobutyl compound
Master Batch	(phr)	(phr)	(phr)	(phr)	(phr)
BIMSM	100.0	100.0	-	-	-
Butyl 268	-	-	100.0	-	-
CIIR 1066	-	-	-	100.0	-
BIIR 2222	-	-	-	-	100.0
Carbon Black N660	60.0	60.0	70.0	60.0	60.0
Naphthenic Oil	8.0	8.0	-	8.0	8.0
Paraffinic Oil	-	-	25.	-	-
Aromatic & Aliphatic Hydrocarbon Resin Blend	7.0	7.0	-	7.0	7.0
Phenolic Tackifying Resin	4.0	4.0	-	4.0	4.0
Hydrocarbon Resin	-	-	3.0	-	-
Stearic Acid	1.0	1.0	1.0	1.0	1.0
MgO	-	-	-	0.2	0.2
Final Batch	(phr)	(phr)	(phr)	(phr)	(phr)
Sulfur	0.5	0.5	2.0	0.5	0.5
MBTS	1.5	1.5	2.0	1.5	1.2
Zinc Oxide	1.0	-	5.0	1.0	1.0
Zinc Stearate	-	2.0	-	-	-
Zinc dibutylphosphorofi- thiate (ZBPD)	-	-	2.0	-	-
Total (phr)	183.0	184.0	210.0	183.2	182.9
Typical Results	(phr)	(phr)	(phr)	(phr)	(phr)
Mooney viscosity (ML1+4 at 100°C)	69.0	65.0	45.0	55.0	56.0
Rheometer (MDR) at 160°C, 0.5° arc					
Delta torque (dNm)	7.3	2.3	7.3	3.1	3.5
tc10 minutes	2.5	4.4	-	0.9	2.2
tc90 minutes	6.1	4.4	25.0	3.3	12.8
Cure Rate Index	27.8	33.3	4.0	41.7	9.4
Tensile Strenght (MPa)	10.6	9.1	11.1	9.2	9.6
Elongation (%)	565	817	665	868	837

300% Modulus (MPa)	10.6	9.1	11.1	9.2	9.6
Hardness (Shore A)	61	58	49	51	47
Tear Strength (KN/m)	58.0	60.0	39.0	56.0	54.0

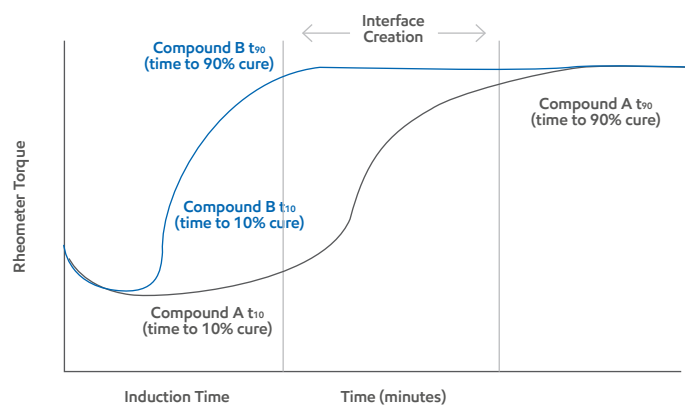
ExxonMobil Chemical Company Data

Isobutylene-based elastomers are highly saturated and therefore have traditionally required ultra-fast accelerators such as thiurams (TMTD) and dithiocarbamates (ZDMC) for effective cure. Though a variety of replacements for accelerators such as TMTD and ZDMC used in general-purpose rubbers have been evaluated, no direct replacement candidates have emerged.

Regardless of the cure system being used in a composite such as a tire, vulcanization rates between adjacent components at the cure temperature of the tire must be similar. Figure 23 illustrates two incompatible cure rates and while the individual components have good mechanical properties, the composite could separate since good interfacial adhesion is not created during cure.

Figure 23

Cure rate compatibility²⁷



In conclusion, a new cure system must display the following requirements:

- Adequate induction times
- High temperature reversion resistance (i.e., temperatures above 160°C)
- Allow adequate adhesion between adjacent components in a composite product

The model cure systems, which provide starting points in new development programs, when used in experimental compounds should be evaluated against the mission profile for which the end-product is intended.

9. Summary

The cure chemistry of isobutylene-based elastomers appears more complex than that for general-purpose rubbers. The backbone of isobutylene-based elastomers are highly saturated, thus ultra-fast accelerators are required for efficient vulcanization. Many of those accelerators are nitrosamine generators, and therefore their use is not recommended. Cure systems typically used for isobutylene-based elastomers tend to be based on

- Resins cures
- Sulfur based accelerated curing
- Use of metal oxides such as zinc oxide
- Dioxime based systems

The selection of a specific system is a function of the polymer type and the specific in-service requirements of the final cured product.

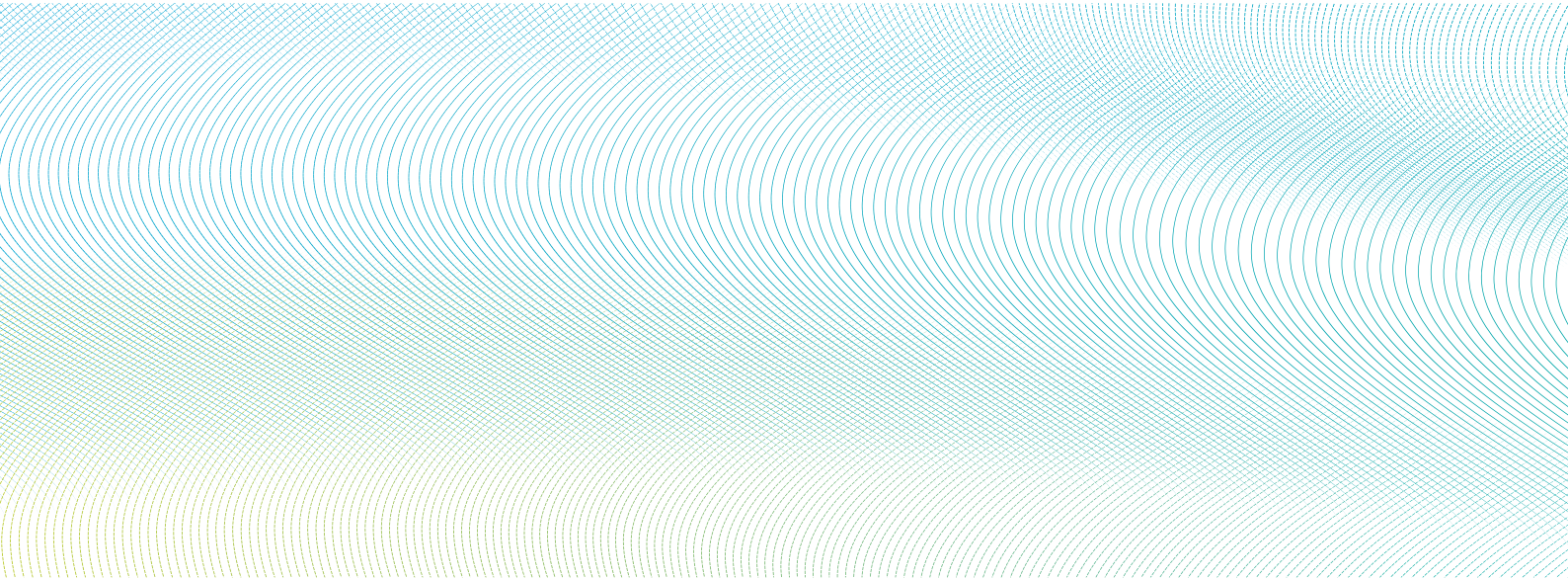
APPENDIX 1

Recognized industry abbreviations for accelerators

Abbreviations or commercial Descriptions	Chemical Name	Function
CBS	N-Cyclohexyl-2-benzothiazolesulfenamide	Accelerator
BCI-MX	1,3-Bis (citraconimidomethyl) benzene	Reversion Resistance
CTP, PVI	N-(Cyclohexylthio) phthalamide	Retarder
DBQDO	Dibenzyl-p-quinone dioxime	Quinone Cure
DCBS	Dicyclohexylbenzothiazole sulfenamide	Accelerator
DETU	Diethylthiourea	Accelerator
DBTU	Dibutylthiourea	Accelerator
DOTG	Di-o-tolylguanidine	Accelerator
DPG	Diphenyl guanidine	Accelerator
DPPD	N,N'-Diphenyl-p-phenylenediamine	Anti-Oxidant
DPTU	N,N'-Diphenylthiourea	Accelerator
DTDM	4,4-Dithiodimorpholine	Vulcanizing Agent
ETU	Ethylenethiourea	Accelerator
HTS	Hexamethylene-1,6-bis (thiosulfate) Disodium Salt, Dihydrate	Reversion Resistance
MBS	2-(4-Morpholiniothio- benzothiazole	Accelerator
MBT	Mercaptobenzothiazole	Accelerator
MBTS	Mercaptobenzothiazole sulfenamide	Accelerator
QDO	p-Quinone dioxime	Quinone Cure
TBBS	tert-Butyl-2-benzothiazole sulfenamide	Accelerator
TBSI	N-t-Butyl-2-benzothiazole sulfenamide	Accelerator
TBzTD	Tetrabenzylthiuram disulfide	Accelerator
TMTD	Tetramethylthiuram disulfide	Accelerator
TMTM	Tetramethylthiuram monosulfide	Accelerator
Vultac 2	Amylphenol disulfide polymer (23% Sulfur)	Sulfur Donor
Vultac 3	Amylphenol disulfide polymer (28% Sulfur)	Sulfur Donor
Vultac 5	Amylphenol disulfide polymer (18% Sulfur)	Sulfur Donor
Vultac 7	Amylphenol disulfide polymer (30% Sulfur)	Sulfur Donor
Vultac 710	Amylphenol disulfide polymer (27% Sulfur, 10% HSt)	Sulfur Donor
ZDMC	Zinc dimethyldithiocarbamate	Accelerator
ZDEC	Zinc diethyldithiocarbamate	Accelerator
ZBDC	Zinc dibutyldithiocarbamate	Accelerator
ZBEC	Zinc dibenzylidithiocarbamate	Accelerator
ZIX	Zinc isopropyl xanthate	Accelerator (low temp.)
ZBPD	Zinc dibutylphosphorodithioate	Accelerator

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