Kirk-Othmer Encyclopedia of Chemical Technology.

RUBBER CHEMICALS

Rubber chemicals are materials that are added in minor amounts to rubber formulations in order to improve their properties and make them commercially useful. Raw rubber polymer has very limited practical applications because of tackiness, flow, and other undesirable features. Rubber chemicals are added to assist processing, promote cross-linking, and provide longevity to the part in service. Vulcanizing adjacent polymer chains together by cross-links prevents flow, increases strength, and provides recovery from deformation. The most widely used method of cross-linking polymer chains is by heating with elemental sulfur (vulcanization). Accelerators speed up the reaction of sulfur with polymer to improve the economics of manufacture and prevent degradation that would otherwise occur upon prolonged heating. Peptizers and process aids assist flow during the mixing and shaping operations. Antidegradants protect the part in service from heat, oxygen, ozone, and repeated flexing. Other rubber chemicals function as blowing agents, adhesion promoters, and activators or retarders which modify the onset of cross-linking.

Organic chemicals which are used primarily in the rubber industry contributed $415 million to the United States economy in 1994 (1). The historical sales of the primary classes of organic rubber-processing chemicals are summarized in Table 1. Accelerators and antidegradants are the two main types of rubber chemicals. The U.S. production of accelerators has been declining, due to longer-lasting radial tires and to fewer domestic producers. The production of antidegradants shows the effect of the adoption of radial tires in the 1970s but has been increasing more recently because of the desire for articles with longer service life. Antidegradants are discussed elsewhere (see Antioxidants; Antiozonants). A significant component of the “other” category in Table 1 is alkyl mercaptans, used as polymerization regulators. Total organic rubber chemical use has remained stable at about 6% of synthetic rubber production.

In addition to the materials shown in Table 1, other organic materials find a minor portion of their use in rubber processing, such as waxes and fatty acids. Also, the rubber industry uses modest amounts of inorganic compounds, notably elemental sulfur, zinc oxide, magnesium oxide, and sodium bicarbonate.

1. Accelerators of Vulcanization

Vulcanization was first reported in 1839 with the discovery that heating natural rubber with sulfur and basic lead carbonate produced an improvement in physical properties (2). In 1906, aniline was the first organic compound found to have the ability to accelerate the reaction of sulfur with natural rubber (3). Various derivatives of aniline were soon developed which were less toxic and possessed increased acceleration activity.

1.1. Mercaptobenzothiazoles

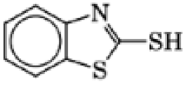
These compounds form the basis for the largest-volume organic accelerators. 2-Mercaptobenzothiazole (MBT) **(1)** is prepared by heating aniline, carbon disulfide, and sulfur in an autoclave at elevated temperature and

Table 1. U.S. Sales of Organic Rubber-Processing Chemicals,[a] 10^6 kg

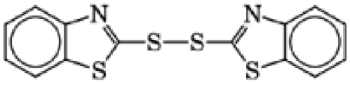
	Year					
Chemicals	1965	1970	1975	1980	1985	1990
accelerators	31.8	38.7	32.1	29.3	21.3	
benzothiazoles and sulfenamides	20.0	26.5	24.5	21.0	16.4	25.4
dithiocarbamates and thiurams	6.3	7.1	4.5	3.9	2.5	
antidegradants	45.1	52.5	44.5	43.3	47.7	72.9
substituted *p*-phenylenediamines	13.4	18.6	17.9	15.4	19.8	26.6
other amines	21.6	19.1	18.2	10.9	12.2	20.0
phenols and phosphites	10.1	14.8	8.4	17.0	15.7	26.3
other chemicals	11.0	12.2	15.9	15.4	11.9	
Total	*87.9*	*103.4*	*92.5*	*88.0*	*79.1*	*136.4*

[a] Ref. 1.

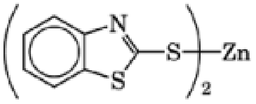
pressure. Tars from the reaction can be removed by taking the crude MBT up in water by making the sodium salt, clarifying the solution, and then precipitating pure MBT with acid. MBT can be oxidized to the disulfide (MBTS) **(2)** or it can react with zinc oxide to form the zinc salt (ZMBT) **(3)**. MBTS is the largest-volume of the three benzothiazole accelerators, selling for under $3/kg. ZMBT is too fast-curing for most dry rubber compounds and is used mainly in latex applications.



(1)



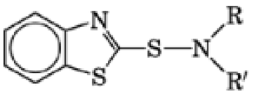
(2)



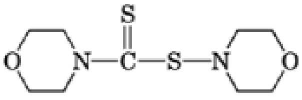
(3)

1.2. Sulfenamides

Sulfenamides **(4)** are often produced by oxidizing an equimolar mixture of MBT and an aliphatic amine. Alternatively, the *N*-chloroamine can react with the sodium salt of MBT. One sulfenamide, OTOS **(5)**, uses a thiocarbamyl functionality in place of the benzothiazole group.



(4)

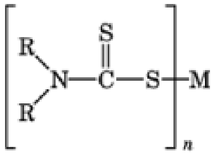


(5)

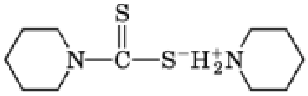
Sulfenamides do not become active accelerators until the sulfur–nitrogen bond thermally dissociates, providing delayed action before cross-linking occurs. Delayed action is useful in applications which require lengthy processing operations such as joining many layers together to make a tire. Sulfenamides are the primary accelerator used in building tires, making them the largest-volume of all accelerator classes. Sulfenamides are priced at over $4/kg. Because of environmental concerns of exposure to stable *N*-nitrosamines, tire makers have switched from sulfenamides based on morpholine or other secondary amines to sulfenamides based on primary amines (R′ = H).

1.3. Dithiocarbamates

These compounds, **(6)** and **(7)**, are prepared by the reaction of dialkyl amines with carbon disulfide in the presence of sodium hydroxide. For use as rubber accelerators, the sodium salts initially prepared are converted to water-insoluble zinc or other metal salts. Dithiocarbamates provide the most rapid cross-linking and, together with the related thiurams, are known as ultra-accelerators. Various metals are used to achieve specific properties. Copper provides low compression set for O-rings and gaskets based on synthetic rubbers. Selenium and tellurium provide good aging and high modulus. Heavy metals such as cadmium and lead do not migrate and have been used in polymer blends although they are being replaced by bismuth. Sodium and piperidine are exceptionally fast-curing and are used in latex operations. Zinc is most frequently used (see Table 2).



(6)



(7)

Table 2. Properties of Selected Commercial Accelerators

Name	Acronym	Color	CAS Registry Number	Mol wt	d, mg/m^3	Melting point, °C	Sol'y, toluene[a]	Acute oral LD$_{50}$, mg/kg[b]
		Benzothiazoles						
2-mercaptobenzothiazole **(1)**	MBT	light yellow–buff	[149-30-4]	167	1.50	175–182	v sol	3, 800
bis(2,2′-benzothiazolyl)disulfide **(2)**	MBTS	cream–light yellow	[120-78-5]	332	1.51	164–179	m sol	7,900
zinc 2-mercaptobenzothiazole **(3)**	ZMBT	pale yellow	[155-04-4]	398	1.63	300 min	sl sol	>5, 000
		Sulfenamides						

Table 2. *Continued*

Name	Acronym	Color	CAS Registry Number	Mol wt	*d,* mg/m^3	Melting point, °C	Sol'y, toluene[a]	Acute oral LD$_{50}$, mg/kg[b]
N-tert-butyl-2-benzothiazolesulfenamide (**4**, $R = H$, $R^1 = t - C_4H_9$)	TBTS	light tan–buff	[95-31-8]	238	1.28	105 min	m sol	>6,300
N-cyclohexyl-2-benzothiazolesulfenamide (**4**, $R = H$, $R^1 = C_6H_{11}$)	CBTS	cream–light tan	[95-33-0]	264	1.28	94–102	v sol	5,300
N-oxydiethylene-2-benzothiazolesulfenamide (**4**, $RR'N = N(CH_2CH_2)_2O$)	OBTS	light tan	[102-77-2]	252	1.37	70–90	v sol	>8,200
4-morpholinyl-2-benzothiazole disulfide (**4**, $RR'N = SN(CH_2CH_2)_2O$)	MBSS	cream–light yellow	[95-32-9]	284	1.51	115–130	sol	11,500
N-dicyclohexyl-2-benzothiazolesulfenamide (**4**, $R = R' = C_6H_{11}$)	DCBS	off-white	[4979-32-2]	347	1.20	90–102	m sol	3,400
N-tert-butyl-2-benzothiazolesulfenimide **(14)**	TBSI	off-white	[3741-80-8]	404	1.35	128 min		>5,000
N-oxydiethylenethiocarbamyl-*N*-oxydiethylenesulfenamide **(5)**	OTOS	white–cream	[13752-51-7]	248	1.34	136–142	sol	~5,000
Dithiocarbamates								
bismuth dimethyldithiocarbamate (**6**, $R = CH_3$, $n = 3$, $M = Bi$)	BiDMC	lemon yellow	[21260-46-8]	570	2.04	230 dec	sl sol	>3,000
cadmium diethyldithiocarbamate (**6**, $R = C_2H_5$, $n = 2$, $M = Cd$)	CdDEC	white–light gray	[14239-68-0]	409	1.39	65 min	m sol	7,100[c]
copper dimethyldithiocarbamate (**6**, $R = CH_3$, $n = 2$, $M = Cu$)	CuDMC	dark brown	[137-29-1]	304	1.75	325 min	m sol	>5,000
lead diamyldithiocarbamate (**6**, $R = C_5H_{11}$, $n = 2$, $M = Pb$)	PbDAC	light amber	[36501-84-5]	672	1.10	liquid	v sol	>10,000
lead dimethyldithiocarbamate (**6**, $R = CH_3$, $n = 2$, $M = Pb$)	PbDMC	gray	[19010-66-3]	448	2.43	300 min	p insol	
piperidinium pentamethylenedithiocarbamate		cream–light yellow	[98-77-1]	246	1.20	163 min	m sol	250
selenium dimethyldithiocarbamate (**6**, $R = CH_3$, $n = 4$, $M = Se$)	SeDMC	yellow	[144-34-3]	560	1.58	140–172	sol	>200
sodium di-*n*-butyldithiocarbamate (**6**, $R = n - C_4H_9$, $M = Na$)	NaDBC	pale amber	[136-30-1]	227	1.09	liquid	v sol	>16,000
tellurium diethyldithiocarbamate (**6**, $R = C_2H_5$, $n = 4$, $M = Te$)	TeDEC	orange-yellow	[20941-65-5]	721	1.44	108–119	sol	>5,000
Zinc dithiocarbamates (**6**, $M = Zn$, $n = 2$)								
zinc diamyldithiocarbamate ($R = C_5H_{11}$)	ZDAC	light amber	[15337-18-5]	530	0.99	liquid	v sol	14,900
zinc dibenzyldithiocarbamate ($R = CH_2C_6H_5$)	ZBEC	white–light cream	[14726-36-4]	610	1.42	180–190		>5,000
zinc di-*n*-butyldithiocarbamate ($R = n - C_4H_9$)	ZDBC	white–cream	[136-23-2]	474	1.21	104–112	sol	>16,000
zinc di-*iso*-butyldithiocarbamate ($R = i - C_4H_9$)	ZDiBC	white–cream	[36190-62-2]	474	1.24	110–120	sol	
zinc diethyldithiocarbamate ($R = C_2H_5$)	ZDEC	white	[14324-55-1]	362	1.48	171–183	m sol	3,500
zinc dimethyldithiocarbamate ($R = CH_3$)	ZDMC	white	[137-30-4]	306	1.71	242–257	m sol	1,400[d]
zinc di-*iso*-nonyldithiocarbamate ($R = i - C_9H_{19}$)	ZDiNC	off-white		754	1.24	~77	sol	>5,000
zinc pentamethyldithiocarbamate (R_2N = piperidine)	ZPDC	off-white	[13878-54-1]	386	1.60	225		1,200 (mice)
Thiurams								
dipentamethylenethiuram disulfide (**9**, $x = 2$)	DPTD	white–cream	[94-37-1]	321	1.40	120		>5,000 (mice)

Table 2. ***Continued***

Name	Acronym	Color	CAS Registry Number	Mol wt	d, mg/m^3	Melting point, °C	Sol'y, toluene[a]	Acute oral LD$_{50}$, mg/kg[b]
dipentamethylenethiuram hexasulfide (**9**, $x = 6$)	DPTH	light yellow–buff	[971-15-3]	449	1.50	115 min	sol	$>200^e$
dipentamethylenethiuram monosulfide (**9**, $x = 1$)	DPTM	yellow	[725-32-6]	289	1.40	110		
tetrabenzylthiuram disulfide (**8**, $R = CH_2C_6H_5$, $x = 2$)	TBzTD	light yellow	[10591-85-2]	545	1.31	127–135		$>5,000$
tetra-*n*-butylthiuram disulfide (**8**, $R = n-C_4H_9$, $x = 2$)	TBTD	dark amber	[1634-02-2]	409	1.06	liquid	v sol	2,300^e
tetra-*iso*-butylthiuram disulfide (**8**, $R = i-C_4H_9$, $x = 2$)	TiBTD	light yellow	[3064-73-1]	409	1.14	65–70		
tetraethylthiuram disulfide (**8**, $R = C_2H_5$, $x = 2$)	TETD	light yellow	[97-77-8]	297	1.27	67 min	sol	1,300
tetramethylthiuram disulfide (**8**, $R = CH_3$, $x = 2$)	TMTD	white–cream	[137-26-8]	240	1.42	146–156	sol	1,800^f
tetramethylthiuram monosulfide (**8**, $R = CH_3$, $x = 1$)	TMTM	yellow	[97-74-5]	208	1.37	103–114	v sol	1,300^g
		Guanidines						
diphenylguanidine (**10**, $R = C_6H_5$)	DPG	white–faint yellow	[102-06-7]	210	1.20	144–149	sl sol	350
di-*ortho*-tolylguanidine (**10**, $R = o-C_6H_4CH_3$)	DOTG	white–pink	[97-39-2]	238	1.20	173–179	sl sol	134–500
DOTG salt of dicatechol borate	PML	tan–light brown	[16971-82-7]	467	1.25	165 min	m sol	570
		Thioureas						
N,N′-di-*n*-butylthiourea (**11**, $R = n-C_4H_9$)	DBTU	white–light tan	[109-46-6]	188	1.03	56–65	v sol	350
N,N′-diethylthiourea (**11**, $R = C_2H_5$)	DETU	white–light yellow	[105-55-5]	132	1.11	68–77	m sol	310
N,N′-diphenylthiourea (thiocarbanilide) (**11**, $R = C_6H_5$)	DPTU	white–light gray	[102-08-9]	228	1.30	148	sl sol	1,500
ethylenethiourea (**11**, $R = CH_2CH_2$)	ETU	white	[96-45-7]	102	1.40	195		1,800^h
trimethylthiourea (**11**, $R = CH_3$)	TMTU	white	[2489-77-2]	118	1.23	80–90	m sol	670^i
		Xanthates						
dibutylxanthogen disulfide (**12**, $R = n-$butyl, M not present)	CPB	amber	[105-77-1]	445	1.15	liquid		
dibutylxanthogen polysulfide (**12**, $R = n-$butyl, $M = S_x$)	XPS	yellow			1.29	liquid		1,800
zinc di-*iso*-propylxanthate (**12**, $R = i-$propyl, $M = Zn$)	ZIX	white–light yellow	[1000-90-4]	336	1.56	140 dec	sl sol	$>2,000$
		Dithiophosphates						
copper *O,O*-di-*iso*-propylphosphorodithioate (**13**, $R = i-C_3H_7$, $M = Cu$)	CUT	yellow-green	[41593-12-8]	490	1.10	69		
zinc *O,O*-di-*n*-butylphosphorodithioate (**13**, $R = n-C_4H_9$, $M = Zn$)	ZBPD	yellow-green	[6990-43-8]	548		liquid		
		Aldehyde–amines						
butyraldehyde–aniline reaction			[34562-31-7]		0.98	liquid	v sol	500–5,000
butyraldehyde–monobutylamine			[68411-19-8]		0.86	liquid	v sol	1,000 (ALD)
heptaldehyde–aniline reaction			[9003-50-3]		0.93	liquid	v sol	
hexamethylenetetramine[100-97-0]			[100-97-0]	140	1.30	200 dec		
		Other accelerators						

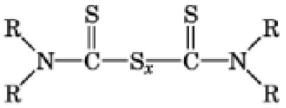
Table 2. *Continued*

Name	Acronym	Color	CAS Registry Number	Mol wt	*d*, mg/m^3	Melting point, °C	Sol'y, toluene[a]	Acute oral LD$_{50}$, mg/kg[b]
dimethylammonium hydrogen isophthalate			[71172-17-3]	211	1.35	190 dec	sl sol	$>15,000$
3-methyl-2-thiazolidinethione			[1908-87-8]	133	1.39	64		1,200
mono- and dibenzyl amine					1.16	liquid	v sol	225
N-ethylcyclohexyl amine			[5459-93-8]	127	0.85	liquid		
dihydrogenated tallow amine			[31789-79-5]	510	0.80	62		$>10,000$

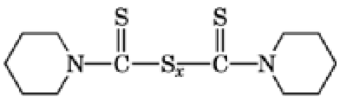
[a] Solubility range: p insol = <0.1 g solute/100 mL solution; sl sol = $0.1 - <1.0$; m sol = $1.0 - <5.0$; sol = $5.0 - <10.0$; and v sol = ≥ 10.0.
[b] Toxicity data are for rats unless otherwise indicated.
[c] TDL$_0$ mice for 78 wks.
[d] 320 mg/kg in second study.
[e] Intraperitoneal for mice.
[f] For females; 3700 mg/kg males.
[g] LD$_{LO}$: 500 mg/kg rats, 100 mg/kg dogs, 100 mg/kg rabbits, and 10 mg/kg guinea pigs.
[h] Classified as IARC carcinogen.
[i] In structure **(11)**, one hydrogen is replaced with a methyl group.

1.4. Thiuram Sulfides

These compounds, **(8)** and **(9)**, are an important class of accelerator. Thiurams are produced by the oxidation of sodium dithiocarbamates. The di- and polysulfides can donate one or more atoms of sulfur from their molecular structure for vulcanization. The use of these compounds at relatively high levels with little or no elemental sulfur provides articles with improved heat resistance. The short-chain (methyl and ethyl) thiurams and dithiocarbamates are priced ∼$2/kg. Producers have introduced ultra-accelerators based on longer-chain and branched-chain amines that are less volatile and less toxic. This development is also motivated by a desire to minimize airborne nitrosamines.



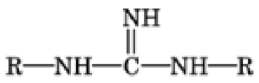
(8)



(9)

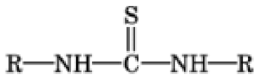
1.5. Guanidines

Guanidines **(10)** were one of the first aniline derivatives used as accelerators. They are formed by reaction of two moles of an aromatic amine with one mole of cyanogen chloride. Diphenylguanidine (DPG) has enjoyed a resurgence in demand as an activator for sulfenamides and a co-accelerator in tire tread compounds which employ silica fillers for low rolling resistance. Guanidines alone show too little activity to be extensively used as primary accelerators. There were no U.S. producers as of mid-1996.



$$\mathrm{R{-}NH{-}}\overset{\overset{\mathrm{NH}}{\|}}{\mathrm{C}}\mathrm{{-}NH{-}R}$$

(10)



$$\mathrm{R{-}NH{-}}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{{-}NH{-}R}$$

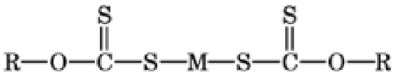
(11)

1.6. Thioureas

Thioureas **(11)** are typically made from primary amines and carbon disulfide. The amine can be ethylamine, butylamine, ethylenediamine, or aniline. The last produces diphenylthiourea which is commonly known as thiocarbanilide. Thioureas are often used as accelerators for polychloroprene (Neoprene) or other rubbers that contain chlorine as reactive cross-linking sites.

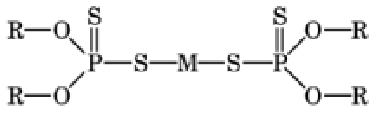
1.7. Xanthates

These compounds **(12)** are relatively fast accelerators which are used at low temperature because most examples decompose without cross-linking at higher temperature. Xanthates (qv) are produced by reaction of equimolar amounts of alcohol and carbon disulfide in the presence of caustic. The sodium salt is then converted to the zinc compound or oxidized to the disulfide.



$$\mathrm{R{-}O{-}}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{{-}S{-}M{-}S{-}}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{{-}O{-}R}$$

(12)



(13)

1.8. Dithiophosphates

These compounds **(13)** are made by reaction of an alcohol with phosphorus pentasulfide, then neutralization of the dithiophosphoric acid with a metal oxide. Like xanthates, dithiophosphates contain no nitrogen and do not generate nitrosamines during vulcanization. Dithiophosphates find use as high temperature accelerators for the sulfur vulcanization of ethylene–propylene–diene (EPDM) terpolymers.

1.9. Aldehyde–Amines

There is a long history of use of the reaction products of aldehydes and amines. Most such reactions yield a dark-colored liquid mixture containing many different structures. Hexamethylenetetramine (Hexa) is a notable exception, giving an adamantane-type structure with nitrogen atoms replacing carbon at the bridgeheads. Hexa reverts to formaldehyde and ammonia in the presence of water, and is a scorchy accelerator sometimes used in adhesion systems. At one time, aldehyde–amines were used in making hard rubber (ebonite), but this use of rubber has largely been replaced by plastics. Aldehyde–amines find use as accelerators for thiadiazole cures of halogenated polymers.

1.10. Other Accelerators

Amine isophthalate and thiazolidine thione, which are used as alternatives to thioureas for cross-linking polychloroprene (Neoprene) and other chlorine-containing polymers, are also used as accelerators. A few free amines are used as accelerators of sulfur vulcanization; these have high molecular weight to minimize volatility and workplace exposure. Several amines and amine salts are used to speed up the dimercapto thiadiazole cure of chlorinated polyethylene and polyacrylates. Phosphonium salts are used as accelerators for the bisphenol cure of fluorocarbon rubbers.

A listing of selected commercial accelerators and their properties is shown in Table 2. Within a family of accelerators, materials of low molecular weight usually provide more cross-links at a given dosage. In general, rubber chemicals with low density are preferred, because rubber chemicals are purchased by the kilogram but rubber articles are sold by the item (volume). Liquid products are often available adsorbed on an inert carrier for easier handling as flowable powders. Solid materials with low melting points ($<100^\circ C$) can be offered as flakes or pastilles; those products with higher melting points must be ground to fine powders to disperse properly in the mixing operation. Most accelerators dissolve in the hot rubber mixture. Upon standing at room temperature, an accelerator can migrate to the surface (bloom) if its solubility limit is exceeded. Toluene provides a good model to estimate solubility limits in highly unsaturated hydrocarbon rubbers. Accelerators have poorer solubility in predominantly saturated hydrocarbon rubbers such as EPDM and isobutylene–isoprene copolymer (butyl rubber), and greater solubility in polar rubbers such as Neoprene and butadiene–acrylonitrile copolymer (nitrile rubber) (see Elastomers, synthetic).

1.11. Health and Safety Factors

To minimize exposure to potentially toxic materials, powders are generally offered with an antidusting agent applied. Many chemicals, including accelerators, can cause skin irritation in sensitive individuals. The availability of pellets, prills, and polymer-encapsulated master batches to minimize worker exposure to chemicals is a service offered by several suppliers. Accelerators based on secondary amines can liberate small quantities (parts per billion) of *N*-nitrosodialkylamines. Most nitrosamines do not have the five-strain Ames test that is accepted in the 1990s. In some test animals, a few nitrosamines are carcinogenic, with the potency ranking being *N*-nitrosodiethylamine (NDEA) = *N*-nitrosodimethylamine (NDMA) > *N*-nitrosomorpholine (NMOR) > *N*-nitrosonornicotine (NNN) > *N*-nitrosodiethanolamine (NDELA) > *N*-nitrosodiphenylamine (NDPhA) (4). Nitrosamine levels in rubber articles for use by infants are regulated in several countries. Manufacturers of these articles have developed nitrosamine-free compounds. However, great care must be taken in manufacturing and packaging to prevent recontamination of the articles with nitrosamines which are ubiquitous in the environment.

The main producers of organic accelerators for rubber vulcanization are shown in Table 3. This table is not meant to be completely comprehensive, but rather to indicate the principal historical suppliers to the rubber industry. Most producers offer chemical equivalents in the largest-volume products. Within the range

Table 3. Producers of Accelerators

Company	Headquarters location
Bann Quimica, Ltd.	Sao Paulo, Brazil
Bayer AG	Leverkusen, Germany
Chemetal GmbH	Frankfurt-am-Main, Germany
Flexsys, NV	Brussels, Belgium
General Química, SA	Burgos, Spain
The B.F. Goodrich Co.	Akron, Ohio
Karbochem	Sloane Park, South Africa
Kawaguchi Chemical Industry Co., Ltd.	Tokyo, Japan
Lestar Quimica, SA	Buenos Aires, Argentina
MLPC International	Rion des Landes, France
Oriental Chemical Industries	Seoul, Korea
Ouchi Shinko Chemical Industrial Co.	Tokyo, Japan
Premier Chemical Co., Ltd.	Taipei, Taiwan
Robinson Brothers, Ltd.	West Midlands, Great Britain
Sanshin Chemical Industry Co., Ltd.	Yamaguchi, Japan
Sumitomo Chemical Co., Ltd.	Tokyo, Japan
UCB, SA	Brussels, Belgium
Uniroyal Chemical Co.	Middlebury, Conn.
R. T. Vanderbilt Co., Inc.	Norwalk, Conn.

of smaller-volume specialty accelerators, chemical equivalents become less common. Each producer may offer different products to achieve the same purpose of rapid cross-linking, resistance to thermal degradation, or other performance characteristics. Many offer proprietary blends of accelerators.

2. Cross-Linking Agents

2.1. Sulfur

The most widely used and economical cross-linking agent is sulfur, selling for about $0.35/kg. It provides rubber articles with high strength and excellent resistance to failure when flexed. Improved resistance to heat can be obtained by reducing the amount of sulfur and increasing the amount of accelerator. This change provides a greater proportion of monosulfide cross-links, which have higher thermal stability than di- and polysulfide cross-links. For optimum dispersion of small amounts of sulfur, some suppliers offer sulfur preblended with magnesium carbonate or in polymeric master batch forms.

2.1.1. Insoluble Sulfur

In natural rubber compounds, insoluble sulfur is used for adhesion to brass-coated wire, a necessary component in steel-belted radial tires. The adhesion of rubber to the brass-plated steel cord during vulcanization improves with high sulfur levels ($\sim 3.5\%$). Ordinary rhombic sulfur blooms at this dose level. Crystals of sulfur on the surface to be bonded destroy building tack and lead to premature failure of the tire. Rubber mixtures containing insoluble sulfur must be kept cool ($< 100^\circ C$) or the amorphous polymeric form converts to rhombic crystals.

2.1.2. Sulfur Donors

MBSS, DPTH, and the thiuram disulfides (see Table 2) are examples. The morpholine disulfide and caprolactam disulfide examples in Table 4 can also donate one atom of sulfur from their molecular structure for cross-linking purposes. Monosulfide cross-links provide better thermal stability than the sulfur–sulfur bonds in di- and polysulfide cross-links, which predominate when elemental sulfur is used.

2.2. Peroxy Compounds

Peroxides give carbon–carbon cross-links, which provide rubber articles with the maximum resistance to heat, oxygen, and compression set. Resistance to compression set is important in applications such as gaskets and O-rings, which must maintain a seal by recovering their initial dimensions after deformation. Peroxides are beneficial in polymer blends or fully saturated polymers that cannot be cross-linked by other methods. Dialkyl peroxides are the principal type of peroxide used in the rubber industry. A prime example is dicumyl peroxide which sells for about $9/kg and is used in wire and cable insulation for good electrical properties in applications requiring water immersion. Peroxyketals find growing use for faster cross-linking and greater productivity. Benzoyl peroxide is used mainly in silicone.

Coagents are often used with peroxides to increase the state of cure. Some coagents, such as polybutadiene or multifunctional methacrylates, are used at high levels to form polymer grafts or interpenetrating networks. Other coagents such as triallyl cyanurate, triallyl trimellitate, and *meta*-phenylene bismaleimide are used at low levels to reduce the tendency of the polymer to degrade by chain scission.

The use of peroxides requires special handling precautions and compounding considerations. Compounds containing peroxides must be protected against exposure to air (oxygen) during the high temperature cross-linking process or chain scission and a tacky surface result. Some branched polymers such as butyl rubber, epichlorohydrin, and polypropylene undergo chain scission with peroxides and cannot be cross-linked by this method. Acidic materials heterolytically decompose peroxides without generating cross-links. Peroxy radical traps such as aromatic process oils (5) and many antidegradants interfere with the cross-linking process, giving a lower state of cure (lower hardness and modulus). The standard antioxidant for peroxide cross-linking is polymerized 1,2-dihydro-2,2,4-trimethylquinoline.

Most peroxides of the appropriate thermal stability for rubber cross-linking are liquids or low melting solids which, in addition to the 100% active product, are offered adsorbed on inert, free-flowing carriers or in polymeric master batches for easy handling. Peroxides (qv) are oxidizing materials and should be stored away from other rubber chemicals and kept away from heat sources.

2.3. Multifunctional Hydroxy, Mercapto, and Amino Compounds

These are used to cross-link halogenated polymers. Depending on the lability of the halogen, the cross-linking agents can be capped to reduce reactivity or used in combination with accelerators to increase the rate of reaction. Benzoyl capping is common with hydroxy and mercapto compounds; forming the carbamate by reaction with one equivalent of carbon dioxide is used with diamines.

Quinone dioximes, alkylphenol disulfides, and phenol–formaldehyde reaction products are used to cross-link halobutyl rubbers. In some cases, nonhalogenated butyl rubber can be cross-linked by these materials if there is some other source of halogen in the formulation. Alkylphenol disulfides are used in halobutyl innerliners for tires. Methylol phenol–formaldehyde resins are used for heat resistance in tire curing bladders. Bisphenols, accelerated by phosphonium salts, are used to cross-link fluorocarbon rubbers.

2,5-Dimercapto-1,3,4-thiadiazole derivatives, accelerated by amines, are used to cross-link chlorinated polyethylene. Polyisobutylene containing brominated *para*-methylstyrene cure functionality can be cross-linked in polymer blends with dimercapto-1,3,4-thiadiazole derivatives accelerated with thiuram disulfides. Trithiocyanuric acid is suggested for use in polyacrylates containing a chlorine cure site and in epichlorohydrin rubbers.

Diamine curatives were the first cross-linking agents for fluorocarbon rubbers. They are corrosive to mild steel molds and have been replaced in many applications by the bisphenol or other more recent cure systems.

Table 4. Properties of Cross-Linking Agents

Agent	CAS Registry Number	Mol wt	Density, Mg/m^3	Melting point, °C	Acute oral LD_{50}, mg/kg[a]
		Vulcanizing agents			
sulfur	[10544-50-0]	256	2.07	~95[b]	
insoluble sulfur	[9035-99-8]	high[c]	1.95	~115	
4,4′-dithiodimorpholine	[103-34-4]	236	1.35	123–131	5,600
N,N′-caprolactam disulfide	[23847-08-7]	288	1.3	>120	3,620
		Peroxides			
dicumyl peroxide	[80-43-3]	270	1.00		4,100
2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane	[78-63-7]	290	0.87	liquid	>32,000
2,5-dimethyl-2,5-di(*t*-butylperoxy)hexyne	[1068-27-5]	286	0.89	liquid	1,850 (ip)
2,5-dimethyl-2,5-di-(benzoylperoxy)hexane	[2618-77-1]	386	1.23		
2,2′-bis(*t*-butylperoxy)-di-*iso*-propylbenzene	[25155-25-3]	338	0.93		>23,000
1,1-bis(*t*-butylperoxy)-3,3,5-trimethyl cyclo-hexane	[6731-36-8]	302	0.91	liquid	>13,000
n-butyl 4,4-bis(*t*-butyl-peroxy)valerate	[995-33-5]	334	0.95	liquid	5,000
t-butyl -perbenzoate	[614-45-9]	194	1.04	liquid	>3,600
benzoyl peroxide	[94-36-0]	242			>5,000
		Hydroxy compounds			
para-quinone dioxime	[105-11-3]	138	1.40	215 dec	679
alkylphenol disulfide	[68555-98-6]		1.20	78–93	
methylolphenol–formaldehyde resin	[26678-93-3]	~1,000	1.05	60–70	
brominated alkylphenol formaldehyde resin	[112484-41-0]	~900	1.10	57–66	
		Mercapto compounds			
2-mercapto-1,3,4-thia-diazole-5-thiobenzoate	[51988-14-8]	254	1.46		2,500
5,5′-thiobis-1,3,4-thia-diazole-2(3*H*)thione	[7340-97-8]	266	1.90	172–177	930
trithiocyanuric acid	[638-16-4]	177	1.66	200 dec	>5,000[d]
		Diamino compounds			
hexamethylenediamine carbamate	[143-06-0]	160	1.28	152–155	2,875
N,N′-dicinnamylidene-1,6-hexanediamine	[140-73-8]	345	1.09	82–88	[d]
4,4′-methylenebis-(cyclohexylamine)carbamate	[15484-34-1]	254	1.23	145–155	1,000
4,4′-methylenedianiline	[101-77-9]	200	1.15	70–80	200[e]
		Other difunctional cross-linking agents			
hexamethylene-1,6-bis-thiosulfate, disodium salt	[5719-73-3]	322	1.39	125[f]	>5,000
1,3-bis(ditraconimido-methyl)benzene	[119462-56-5]	234	1.27	70–85	>2,000
N,N′-*meta*-phenylenebis-maleimide	[3006-93-7]	268	1.44	195–202	1,370

[a] Toxicity data are for rats unless otherwise indicated.

[b] Transition to monoclinic crystal form.

[c] Approximately 200,000 molecular weight.

[d] 4-h inhalation $LC_{50} > 5$ mg/L.

[e] Classified as IARC carcinogen.

[f] Begins to lose water of hydration.

Table 5. Properties of Activators and Retarders

Activator/retarder	CAS Registry Number	Mol wt	Density, Mg/m^3	Melting point, °C	Acute oral LD$_{50}$, mg/kg[a]
		Activators			
zinc oxide	[1314-13-2]	81	5.61	sublimes	5,400
stearic acid (octa-decanoic acid)	[57-11-4]	284	0.85	55–70	21.5 (iv)
zinc stearate	[557-05-1]	632	1.05	124–126	
lauric acid (dodeca-noic acid)	[143-07-7]	200	0.87	40–50	131 (iv)[b]
zinc laurate	[68242-42-0]	364	1.18	107–114	
zinc 2-ethylhexoate	[136-53-8]	352	1.11	liquid	3,550
		Metal oxides			
magnesium oxide	[1309-48-4]	40	3.5	2,800	
litharge (lead monoxide, PbO)	[1317-36-8]	223	9.53	888	430 (ip)[c]
red lead (lead tetroxide, Pb_3O_4)	[1314-41-6]	686	9.1	500 dec	200 (ip)[d]
synthetic hydrotalcite[e]	[12304-65-3]		2.09		
calcium oxide	[1305-78-8]	56	3.33	2,572	
zinc carbonate (hydrozincite)	[12122-17-7]	125	3.5		
		Acidic retarders			
phthalic anhydride	[85-44-9]	148	1.48	125–130	4,020
benzoic acid	[65-85-0]	122	1.32	122[f]	2,530
salicylic acid	[69-72-7]	138	1.44	157–159[g]	890
		High performance retarders			
N-(cyclohexyl-thio)phthalimide	[17796-82-6]	260	1.3	90–95	2,600
sulfonamide derivative	[2280-49-1]		1.68	110	>2,500
tetra-*iso*-butyl thiuram monosulfide		377	1.08	60–68	

[a] Toxicity data are for rats unless otherwise indicated.
[b] For mice.
[c] For rats (poisonous).
[d] For guinea pigs (poisonous).
[e] $Mg_{1-x}Al_x(OH)_2CO_2H_2O$.
[f] Begins to sublime at ~100°C.
[g] Sublimes at 76°C.

Nevertheless, some diamines are still used for food-contact applications of fluorocarbon rubbers and in zinc-free cures of halobutyl rubbers for pharmaceutical stoppers. Methylene dianiline and triethylene tetramine are cross-linking agents for ethylene–acrylic elastomers.

2.4. Other Difunctional Cross-Linking Agents

These are used in certain polymers and to provide specialized properties. Both hexamethylene-1,6-bisthiosulfate and 1,3-bis(ditraconimidomethyl)benzene are reported to provide long, flexible cross-links for good resistance to fatigue by flexing without the poorer thermal stability inherent with polysulfide cross-links. *meta*-Phenylenebismaleimide is a coagent used to increase the state of cure with peroxides. The maleimide can also contribute to cross-linking in chlorosulfonated polyethylene and provide thermal stability in sulfur cures of highly unsaturated rubbers.

3. Activators and Retarders

Table 5 shows common properties of activators and retarders.

Zinc oxide is a common activator in rubber formulations. It reacts during vulcanization with most accelerators to form the highly active zinc salt. A preceding reaction with stearic acid forms the hydrocarbon-soluble zinc stearate and liberates water before the onset of cross-linking (6). In cures at atmospheric pressure, such as continuous extrusions, the prereacted zinc stearate can be used to avoid the evolution of water that would otherwise lead to undesirable porosity. In these applications, calcium oxide is also added as a desiccant to remove water from all sources.

For increased solubility to prevent bloom, shorter-chain carboxylic acids or zinc carboxylates can be substituted. The use of chain-branched carboxylic acids reduces the tendency for the formulations to lose sulfur cross-links or revert upon prolonged heating (7). Translucent articles such as crepe soles can use a zinc carboxylate or employ zinc carbonate as a transparent zinc oxide.

Magnesium oxide is a typical acid scavenger for chlorinated rubbers. Compounds containing zinc oxide or magnesium oxide may tend to swell upon immersion in water. These inorganic salts have some water solubility and osmotic pressure causes the vulcanizates to imbibe water to equalize pressure (8, 9). As such, vulcanizates tend to swell more in fresh (distilled) water than in salt water. To minimize water swell, insoluble salts such as lead oxides can be substituted. Because of the health concerns associated with lead, there is much rubber industry interest in other acid acceptors, such as synthetic hydrotalcite.

Retarders were originally arenecarboxylic acids. These acidic materials not only delay the onset of cross-linking but also slow the cross-linking reaction itself. The acidic retarders do not function well in black-filled compounds because of the high pH of furnace blacks. Another type of retarder, *N*-nitroso diphenylamine [86-30-6], was used for many years in black-filled compounds. This product disappeared when it was recognized that it trans-nitrosated volatile amines to give a several-fold increase in airborne nitrosamines. U.S. production peaked in 1974 at about 1.6 million kg.

Modern retarders are designed to scavenge the most reactive accelerator precursors and are known as prevulcanization inhibitors. This technique delays the onset of cure without affecting the speed of the main cross-linking reaction. *N*-(Cyclohexylthio)phthalimide was the first high performance retarder to find wide acceptance (10). This retarder sells for about $11/kg and its use has grown with the switch from sulfenamides based on secondary amines to those based on primary amines which give less delayed action. The sulfonamide provides similar performance whereas the developmental thiuram monosulfide provides a modest delay in cure onset along with a reduction in cure time. All these high performance retarders function principally with sulfenamide accelerators.

4. Overview of Vulcanization Chemistry

Sulfur vulcanization leads to a variety of cross-link structures as shown in Figure 1. All the sulfur does not result in cross-links; some of it remains as pendent accelerator polysulfide groups and internal cyclic polysulfides. These alternative structures do not contribute to load bearing or strength properties and are more prevalent in unaccelerated or weakly accelerated vulcanization systems. Additional heating can also reduce the polysulfide rank of the cross-links. In some elastomers, this leads to a larger number of cross-links. However, in natural rubber or its synthetic polyisoprene equivalent, the overall result is a loss of cross-links, especially at temperatures over 160°C.

Although it has been studied since the 1950s, the exact mechanism of accelerated sulfur vulcanization remains unresolved, including whether it proceeds by a radical or ionic process. One review (11) suggests that the nature of the reaction may change, depending on the polarity of the particular polymer (solvent) and whether or not zinc oxide is present. Sulfur vulcanization employs a combination of zinc oxide, fatty acid, sulfur, and at least one accelerator. These materials react as shown in Figure 2 to form a complex (I) in which the eight-member sulfur ring has been opened (12). The complex then abstracts a hydrogen on an alpha-carbon position to the double bond in the polymer to form a rubber-bound pendent accelerator polysulfide (II),

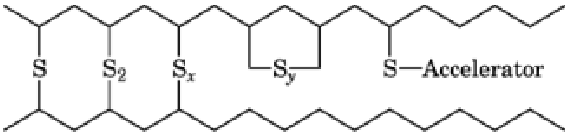


Fig. 1. Structures formed during sulfur vulcanization of elastomers.

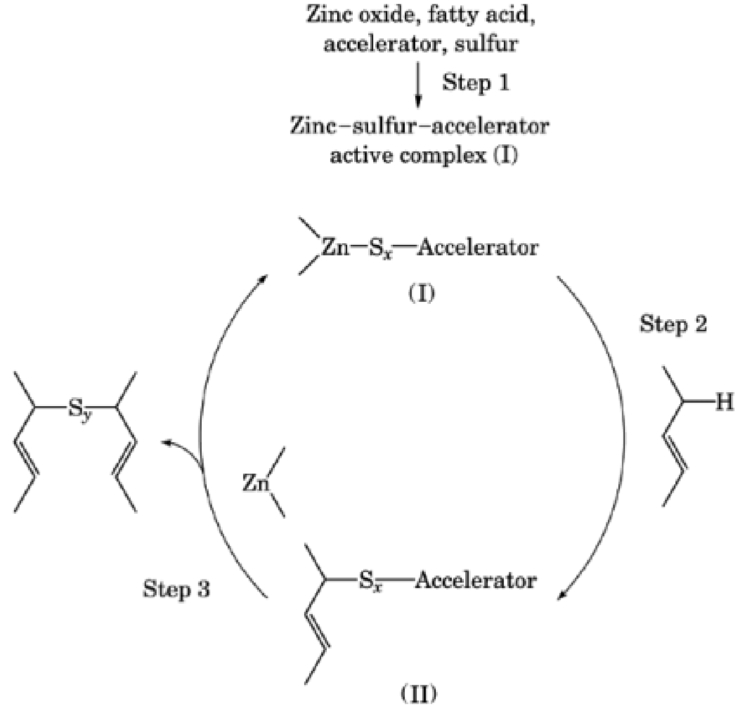
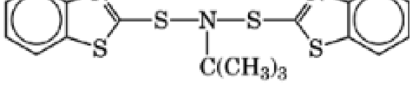


Fig. 2. Cyclic nature of vulcanization process (12).

a cross-link precursor. In Step 3, a zinc complex and an adjacent polymer chain react with the pendent polysulfide to form the polysulfide cross-link while regenerating the zinc–accelerator complex. The cycle is continued until all the sulfur is consumed.

In the absence of zinc oxide, cross-linking proceeds through an accelerator polysulfide. With TBSI **(14)** and other sulfenamides, the accelerator decomposes upon heating during the induction period (before cross-linking) as shown in Figure 2 (13).



(14)

The decomposition generates amine and MBTS. Small quantities of MBT and benzothiazyl (Bt) polysulfides form just before the onset of cross-linking. Sulfur disappears and large quantities of MBT are formed

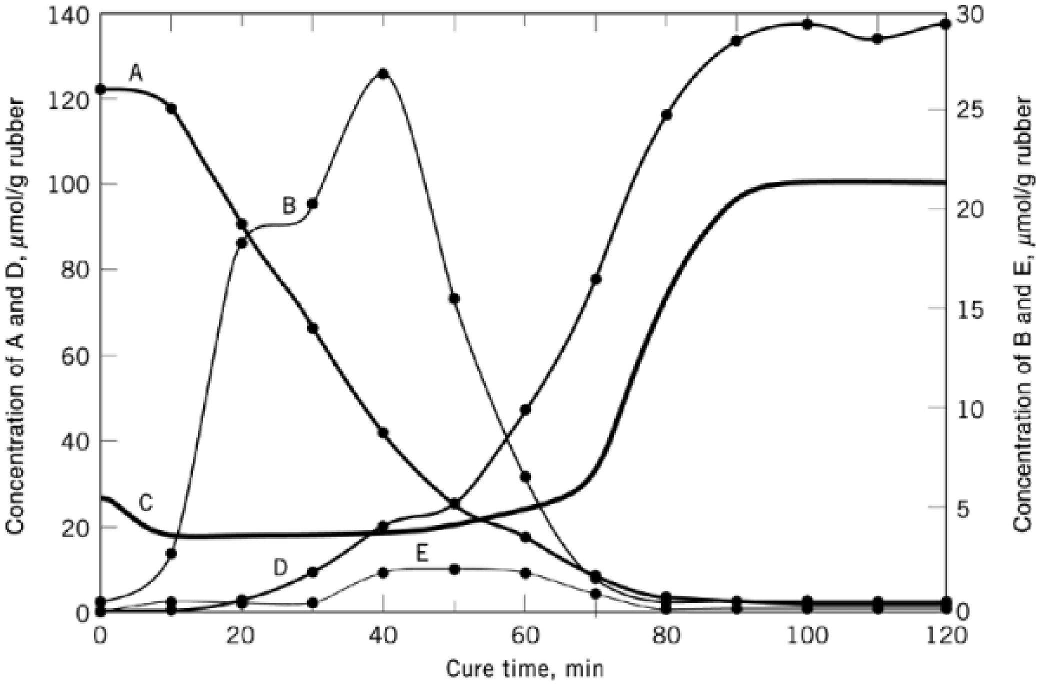
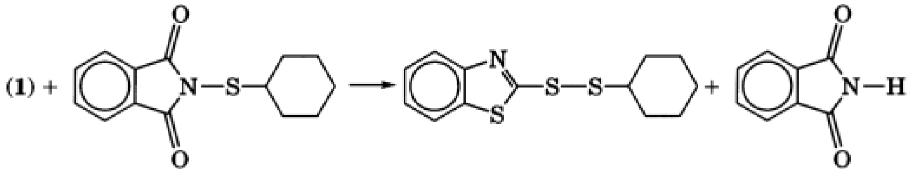


Fig. 3. Fate of accelerator components during cure, where A is TBSI; B, MBTS; C, development of cross-links (rheometer); D, MBT; and E, BtS_3Bt (13).

during the main cross-linking reaction. The development of cross-links is shown as the rheometer line (curve C) in Figure 3.

The inhibition chemistry has been extensively studied. As shown in equation **1**, the prevulcanization inhibitor (retarder) reacts with MBT **(1)** before it can form polysulfides.



(1)

For optimum cross-linking efficiency, a combination of accelerators is used. Table 6 shows the increase in load-bearing capability of vulcanizates based on different rubbers as the ratio of two accelerators is changed (14). The term 300% modulus represents the strain at 300% stress and is not a true modulus because rubber gives nonlinear stress–strain behavior. For polymers with primary allylic carbon atoms, the use of two accelerators gives significantly higher 300% modulus than either accelerator used alone. When the rubber polymer consists of secondary allylic carbon atoms, the modulus is level until the sulfenamide OBTS becomes the principle accelerator.

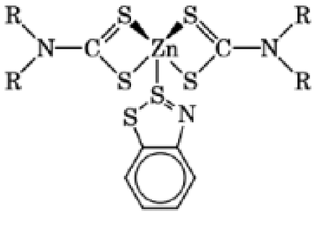
The optimum modulus occurs at about a 2:1 weight ratio of OTOS to OBTS. Similar optimums have been observed with other accelerator combinations. The examples shown in Figure 4 are calculated from regression equations developed from designed experiments in a black-filled natural rubber compound. On a

Table 6. Effect of Accelerator Ratio on 300% Modulus, MPa[a]

OTOS, % OBTS, %	100 0	67 33	50 50	0 100	Total accelerator[b]
		Rubbers based on $CH_3-C{=}C-$			
natural rubber (polyisoprene)	15.4	19.7	20.0	15.7	1.44
butyl rubber (poly-*iso*-butylene)	3.6	3.9	3.8	3.2	3.20
EPDM					
1,4-hexadiene cure site	2.9	3.6	3.9	3.1	3.0
ethylidenenorbornene cure site	4.8	4.9	4.8	4.2	2.0
		Rubbers based on $-CH_2-C{=}C-$			
EPDM, dicyclopentadiene cure site	3.0	3.1	3.0	2.2	2.0
polybutadiene	12.4	11.8	12.2	8.4	1.0
butadiene–styrene copolymer[c]	8.2	7.9	7.3	6.2	0.9
butadiene–acrylonitrile copolymer	12.0	11.5	11.2	8.4	1.25

[a] Ref. 14. To convert MPa to psi, multiply by 145.
[b] Parts per 100 parts of rubber polymer (phr).
[c] Blended with polybutadiene.

molar basis, the synergistic accelerator complex appears to consist of two dithiocarbamate ligands and one mercaptobenzothiazole moiety, as shown in structure **(15)** (14).



(15)

5. Processing Agents

Natural rubber must be reduced in viscosity in order to obtain workable compounds. Many different chemical peptizers have been employed over the years for this purpose, including arenemercaptans, arenesulfonic acids, pentachlorothiophenol [133-49-3] or its zinc salt, and dithiobisbenzanilide [135-57-9] or its zinc salt. Dithiobisbenzanilide with an activator and clay diluent is the preferred peptizing agent for natural and synthetic rubbers. The viscosity of natural rubber and synthetic polyisoprene can be reduced by mechanical shear alone, but using a peptizer makes the viscosity reduction during mixing less sensitive to variations in time and temperature, providing uniformity in viscosity from batch to batch.

Processing aids also assist flow but do so by physical rather than chemical means. Processing aids may be separated into two general categories: external and internal. External processing aids have a polar functionality at one end of the molecule and a long-chain, oleophilic tail. These materials tend to migrate to surfaces where the polar head becomes adsorbed and the oleophilic tail allows the hydrocarbon polymer to slide along the coated surface with less effort. The surface can be either the metal walls of the processing equipment or the filler particles introduced into the rubber matrix. Internal processing aids such as oils or waxes increase melt flow. They reduce the viscosity of the rubber matrix by allowing polymer chains to slide past one another with

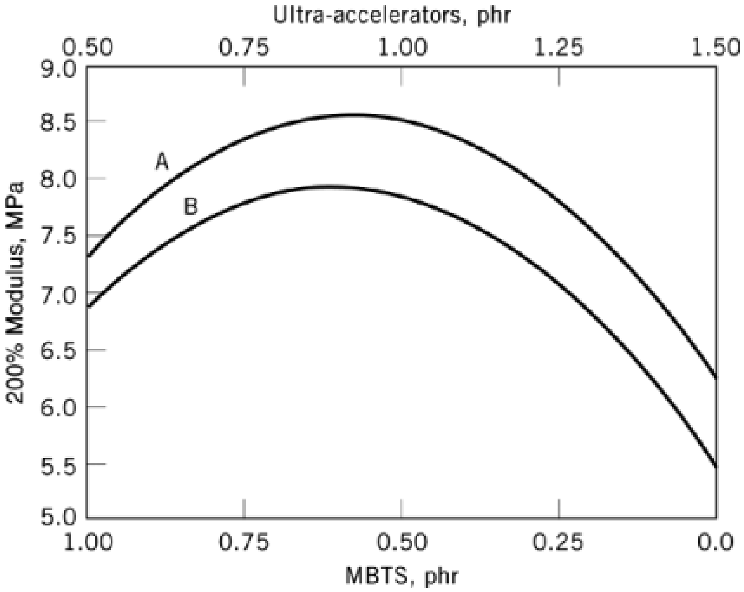


Fig. 4. Accelerator synergism where A is tetra-*iso*-butyl thiuram disulfide and B is zinc di-*iso*-butyl dithiocarbamate. To convert MPa to psi, multiply by 145.

greater ease. Many high performance processing aids are proprietary mixtures of materials with both internal and external functions.

Homogenizing agents are higher molecular weight versions of external processing aids. They are useful in polymer blends to reduce the domain size of the dispersed polymer phase. Homogenizing agents can be particularly useful in blending polymers having dissimilar solubility parameters.

Vulcanized vegetable oils are processing aids that flow under shear but not under heat. They are made by heating unsaturated soybean or rapeseed oil with either sulfur monochloride, S_2Cl_2, or elemental sulfur. The products cross-linked with S_2Cl_2 are white powders. They are used as a main component of erasers to allow greater ability to lift a pencil mark without smearing (noodling). The sulfur-vulcanized products are dark brown solids, used in soft roll compounds to help hold in liquid plasticizers and assist the grinding of the rubber-covered roller to concentricity.

Other processing aids are tackifiers or antitack agents. Tackifiers are resinous products which help a multilayered article stick together before it is vulcanized. Tackifiers may be aliphatic or aromatic materials derived from coal, petroleum, or renewable sources. A variety of additives are used to keep unvulcanized sheets of rubber from sticking together and can be applied by dusting, dipping, or spraying.

6. Other Rubber Chemicals

Blowing agents are used to create cellular products and have been reviewed (15). Closed-cell sponge is used for minimal water absorption in applications such as wet suits or automotive weather-strip. For closed-cell sponge, three nitrogen-releasing blowing agents are used: azodicarbonamide [123-77-3], *p,p′*-oxybis(benzenesulfonyl hydrazide) [80-51-3], and dinitrosopentamethylenetetramine [101-25-7]. Open-cell sponge is used for cushioning when the product must deform without much effort, eg, rug carpet underlay. The basic blowing agent for open-cell sponge is sodium bicarbonate [144-55-8]. Many other rubber chemicals in the mixed compound can affect the temperature and rate at which blowing agents decompose to release gas. Careful compound development and process control are needed to match the gas generation with the cross-linking reaction.

Adhesion promoters are used to bond rubber to brass-plated steel cord in radial tires or conveyor belting. A gradual decrease in stiffness from steel to rubber is desired. A thin layer of a harder rubber compound is applied to the steel to aid bonding. In addition to higher sulfur levels for increased cross-link density, the bonding layer contains resin-forming additives. One resin-forming component is a methylene acceptor such as resorcinol [108-46-3] or a thermoplastic resorcinol–formaldehyde condensate. The other component is formaldehyde or a methylene donor such as hexamethylenetetramine or hexamethoxymethylmelamine [3089-11-0]. Optionally, cobalt naphthenate or other salts can be included to modify the rate at which sulfur reacts with the brass coating (16).

Rubber processed in latex form accounts for about 10% of new rubber consumption. Rubber latex is a liquid, oil-in-water emulsion which is used to make foam or thin-walled rubber articles. The same accelerators and antidegradants used in dry rubber are used in latex, with longer-chain versions preferred for greater oil solubility. To prepare these and other additives for addition to latex, they must be predispersed in water and the surface of the powder or oil droplet coated with a surface-active agent to prevent destabilization (coagulation) of the latex.

Dispersing agents such as sodium salts of polymerized alkylarenesulfonates [9084-06-4] or [8061-51-6] are surface-active agents which only weakly reduce the surface tension. Wetting agents such as sodium lauryl sulfate [151-21-3] more strongly reduce surface tension. Dispersing agents are used when a large quantity of surface area must be treated with surfactant without the mixture entrapping bubbles; wetting agents are used to adjust the amount of fabric penetration or the flow of the latex mixture. Thickeners are used to prevent the settling of additives and can be organic polyelectrolytes or inorganic smectites [12199-37-0]. Colloidal stabilizers such as casein are also used but are falling into disfavor because of the desire to avoid protein which can cause anaphylactic shock in sensitive individuals. Various antifoams prevent air entrapment and preservatives help avoid growth of microbes that could create slime or odors (see Industrial antimicrobial agents). Once formulated with additives, the rubber article is formed by adding acid-generating gellants to natural rubber or calcium nitrate [10124-37-5] to polychloroprene.

Flame retardants such as α-alumina trihydrate [14762-49-3] can be added to latex-based foamed carpet backing; a combination of antimony oxide [1309-64-4] and chlorinated paraffins is used in dry rubber.

Organofunctional silanes are used to promote polymer-to-filler bonding with clay or silica fillers. Vinyl silanes are used in peroxide-cured wire insulation to promote stronger bonding with calcined clay fillers. Mercapto silanes are used to treat kaolin clay in sulfur-cured compounds.

Consumer articles often use colorants (qv), reodorants, or finishing agents. Carbon black (qv) provides the best technological properties for industrial applications, so most rubber articles are black. Red iron oxide or other inorganic pigments are used to color mineral-filled articles. Organic coloring materials provide brighter colors, although special compounding or processing may be required to maintain the color. For example, sulfur cure systems quench fluorescent pigments so peroxide cures are needed. Reodorants can be used to provide a more pleasing aroma for consumer articles. Finishing agents can be applied for a more attractive surface appearance.

BIBLIOGRAPHY

"Rubber Chemicals" in *ECT* 1st ed., Vol. 11, pp. 870–892, by R. A. Mathes and A. E. Juve, The B. F. Goodrich Research Center; in *ECT* 2nd ed., Vol. 17, pp. 509–542, by F. Shaver, The B. F. Goodrich Co.; in *ECT* 3rd ed., Vol. 20, pp. 337–364, by R. Taylor and P. N. Son, The B. F. Goodrich Co.

Cited Publications

1. *Synthetic Organic Chemicals*, United States International Trade Commission Reports, Government Printing Office, Washington, D.C., 1965–1994.
2. U.S. Pat. 3,633 (June 15, 1844), C. Goodyear.
3. G. Oenslager and Cf. W. C. Greer, *J. Ind. Eng. Chem.* **14**, 373 (1922).
4. M. A. Thomson, C. R. Green, R. B. Balodis, and co-workers, "*N*-Nitrosamines", in *Patty's Industrial Hygiene and Toxicology*, 4th ed., Vol. **2**, John Wiley & Sons, Inc., New York, 1993, Part A, Chapt. 11.
5. K. L. Chasey, *Rubber Chem. Tech.* **65**, 385 (1992).
6. A. B. Sullivan, C. J. Hann, and G. H. Kuhls, "Vulcanization Chemistry—Fate of Elemental Sulfur and Accelerator during Scorch Delay as Studied by Modern HPLC", Paper No. 9, presented at the *ACS Rubber Division Meeting, Toronto, Canada, May 21–24, 1991,* American Chemical Society, Washington, D.C., 1991.
7. J. Vander Kooi, *Rubber Plast. News*, 17–19 (May 23, 1994).
8. D. C. Edwards, *Rubber Chem. Technol.* **39**, 581 (1966).
9. A. Hallenbeck and S. W. Schmitt, *Compounding Neoprene for Water Resistance*, NP-520.1 (E-27911), E.I. du Pont de Nemours and Co., Inc., Wilmington, Del., 1987.
10. U.S. Pats. 3,427,319 (Feb. 11, 1969), 3,546,185 (Dec. 8, 1970), 3,752,824 (Aug. 14, 1973), and 3,855,262 (Dec. 17, 1974), A. Y. Coran and E. Kerwood (to Monsanto Co.).
11. M. R. Kvejsa and J. L. Koenig, *Rubber Chem. Technol.* **66**, 376 (1993).
12. R. W. Layer, *Rubber Chem. Technol.* **65**, 211 (1992).
13. C. J. Hann, A. B. Sullivan, B. C. Host, and G. H. Kuhls, Jr., *Rubber Chem. Technol.* **67**, 76 (1994).
14. R. W. Layer, *Rubber Chem. Technol.* **62**, 124 (1989).
15. D. G. Rowland, *Rubber Chem. Technol.* **66**, 463 (1993).
16. W. J. van Ooij, *Rubber Chem. Technol.* **57**, 421 (1984).

General References

17. M. Morton, ed., *Rubber Technology*, 3rd ed., Van Nostrand Reinhold, New York, 1987. An introductory textbook for novices.
18. H. Long, ed., *Basic Compounding and Processing of Rubber*, ACS Rubber Division, Washington, D.C., 1985. An intermediate-level textbook focusing on basic manufacturing processes for rubber articles.
19. F. R. Eirich, ed., *Science and Technology of Rubber*, 2nd ed., Academic Press, Inc., New York, 1994. An advanced treatise.
20. R. F. Ohm, ed., *The Vanderbilt Rubber Handbook*, 13th ed., R. T. Vanderbilt Co., Inc., Norwalk, Conn., 1990. Contains general information for novices and practical reference formulations for experienced compounders.

21. R. F. Mausser, ed., *The Vanderbilt Latex Handbook* 3rd ed., R. T. Vanderbilt Co., Inc., Norwalk, Conn., 1987. Contains introductory and reference information for people engaged in the latex branch of the rubber industry.
22. D. R. Smith, ed., *Rubber World Magazine's 1995 Blue Book*, Lippincott & Peto, Akron, Ohio, 1995. An annual compilation of materials, compounding ingredients, machinery, and services for the rubber industry. Available on CD-ROM in combination with R. F. Ohm, ed., *The Vanderbilt Rubber Handbook*, 14th ed., 1995.

Robert F. Ohm
R. T. Vanderbilt Company, Inc.

Related Articles

Rubber compounding; Rubber, natural