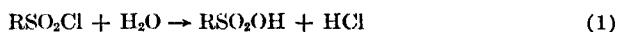# Novel Curing Systems for Chlorosulfonated Polyethylene

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Synopsis

Polyfunctional alcohols, acyclic, cyclic, and heterocyclic imines, and organotin oxides have been studied as crosslinking agents for chlorosulfonated polyethylene. Mechanisms for the crosslinking reactions involving the sulfonyl chloride moiety have been proposed. Differences in curing activity have been correlated with structural modifications of the curing agents consistent with classical chemical reactions for nonpolymeric systems. Of the curing systems examined, the polyols provide nontoxic, low cost, safe-processing formulations offering excellent physical properties which have found use in practical commercial applications.

The curing of chlorosulfonated polyethylene elastomers, commercially available as Hypalon -20, -30, and -40 (Hypalon is the registered trademark of E. I. du Pont de Nemours and Co., Inc.), to obtain optimum physical properties requires the use of both a metal oxide and a sulfur accelerator in the most commonly used systems. Metal sulfonate crosslinks are formed by hydrolysis and neutralization reactions[1] [eqs. (1), (2), and (3)]. The role of the sulfur accelerator appears to involve the formation of sulfur crosslinks through chain unsaturation arising from dehydrochlorination [eqs. (4) and (5)]. This is supported by the observation that the omission of accelerator results in inferior vulcanizates,[1] and the fact that the sulfonamide formed by the reaction of a chlorosulfonated polyethylene with a dialkyl amine can be cured with the sulfur curing systems used for butyl rubber. Since this polymeric derivative is devoid of reactive sulfonyl chloride cure sites, sulfur crosslink formation alone is probably responsible for vulcanization. The presence of labile chlorines, such as tertiary chlorines in a branched polymer or chlorines beta to the sulfonamide (or sulfonyl chloride) groups, is the most probable source of this unsaturation.[2]
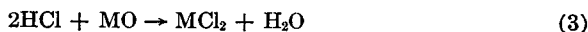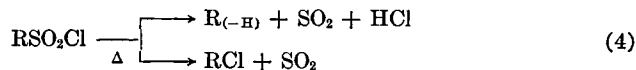
Hydrolysis:
$$RSO_2Cl + H_2O \rightarrow RSO_2OH + HCl \tag{1}$$

where R = polymer chain.

Inorganic crosslinking:
$$2RSO_2OH + MO \rightarrow (RSO_2O)_2M + H_2O \tag{2}$$

Neutralization:

$$2HCl + MO \rightarrow MCl_2 + H_2O \tag{3}$$

Decomposition:

$$RSO_2Cl \underset{\Delta}{\longrightarrow} \begin{cases} R_{(-H)} + SO_2 + HCl \\ RCl + SO_2 \end{cases} \tag{4}$$

Sulfur bonding:

$$2R_{(-H)} + Accelerator \rightarrow R_{(-H)}-S_x-R_{(-H)} \tag{5}$$

Organic crosslinking:

$$2RSO_2Cl + HX-R'-XH \rightarrow [RSO_2-X]_2R' + 2HCl \tag{6}$$
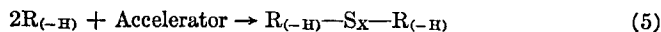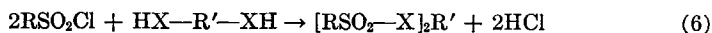
The hydrolysis reaction and the presence of labile chlorines require the use of an acid acceptor in the curing composition, as is the case with all halogen containing elastomers. In the inorganic curing systems for chlorosulfonated polyethylene, polyvalent metal oxides, such as litharge and magnesia, or lead salts, such as tribasic lead maleate,[1,3,6a] function both as crosslinking agents and as acid acceptors. Practical bifunctional or polyfunctional organic compounds to serve in either or both of these roles have long been sought, and polyalcohols, polyamines, dioximes, thioureas, and mercaptoimidazolines[4] have been recognized to show curing activity. An organic curing system based on epoxy resins[5] has been commercially used, and more recently a pentaerythritol system has achieved commercial importance.[6]

This report is concerned with the reactions of polyfunctional alcohols, imines and organotin oxides with the sulfonyl chloride groups in chlorosulfonated polyethylene polymers. The concomitant formation of sulfur crosslinks is considered to occur, although not shown in the proposed curing mechanisms.

Polyfunctional Alcohols

The reaction of sulfonyl chlorides with monofunctional alcohols in the presence of basic catalysts gives sulfonate esters. The ethyl, cyclohexyl, and phenyl sulfonate esters have been reported.[7] Similarly, solutions of chlorosulfonated polyethylene and polyfunctional alcohols, such as ethylene glycol, sorbitol, 1,4-butynediol, hydroquinone, resorcinol, and catechol, rapidly gel at room temperature in the presence of strong organic bases or inorganic hydroxides.[8] This presumably occurs because of bis-sulfonate ester network formation [eq. (6)]. The speed of this reaction renders these systems impractical for normal elastomer compounding techniques. With the less reactive bases, such as calcium and magnesium oxides, a slower esterification reaction occurs as shown by the necessity for employing longer reaction times and elevated temperatures to gel polymer solutions. This behavior suggested that practical, safe processing polyol curing systems could be developed for solid polymers.

TABLE I. Curing Action of Alcohol Additives in Chlorosulfonated Polyethylene[a]

| Vulcanizate no. | Hydroxyl curing agent | | | Vulcanizate Properties[b] | | | | | | |
	Alcohol[c]	phr	m.p., °C.	M_{100}, psi	T_B, psi	E_B, %	Compression Set, %	Hardness Shore A (25°C.)	Resilience (25°C.), %	Appearance of press-cured stock
A	None	—	—	Control: Base Formulation — Slab completely sponged, SO₂Cl decomposition						
				Group I: Primary Polyols						
B	PER	3.0	260	390	1915	320	57	65	59	Excellently molded
C	DPER	3.8	222	250	1525	440	63	60	53	Excellently molded
D	TPER	4.1	240–250	350	1600	350	65	60	56	Excellently molded
E	TME	4.5	158–194	665	1705	260	64	70	63	Excellently molded
F	TMP	4.4	134	795	1855	300	66	70	64	Excellently molded
				Group II: Secondary Polyols						
G	PVA	8.8	—	230	1060	520	89	64	48	Partially sponged-pocked
H	Sorbitol	3.3	110	250	1475	470	82	59	48	No sponginess, but pocked
				Group III: Primary Monofunctional Alcohols						
I	1-Octanol	11.4	194(b.p.)	100	845	790	63	46	50	No sponginess, but pocked
J	1-Decanol	7.9[d]	231(b.p.)	95	750	750	55	48	49	No sponginess, but pocked

[a] Compounding formulation: Hypalon-20, 100 parts; MgO (Maglite D), 2.0 phr; dipentamethylenethiuram tetrasulfide (Tetrone A), 1.5 phr; 2-benzothiazolyl disulfide (MBTS), 0.5 phr; titanium dioxide (Ti Pure R-610), 63 phr; alcohol as shown.

[b] Press-cured 30 min. at 153°C.

[c] Pentaerythritol (PER); dipentaerythritol (DPER); tripentaerythritol (TPER); trimethylolethane (TME); trimethylolpropane (TMP); poly-vinyl alcohol (PVA).
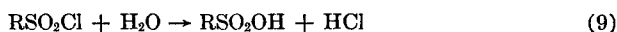
[d] Used at slightly greater than one OH equivalent per SO₂Cl.

Initial investigations in this area again demonstrated the need for including sulfur accelerators in the curing recipe to avoid spongy vulcanizates. Consideration of the free radical mechanism for the decomposition of sulfonyl chlorides[9] led to the hypothesis that these accelerators (thiuram di- or tetrasulfides) may play a dual role by: (a) supplying sulfur crosslinks with unsaturated sites generated during cure [eq. (5)], (b) functioning as free radical traps to prevent sulfonyl chloride decomposition [eq. (4)]. Polyol curing recipes, therefore, include the chlorosulfonated polymer, a polyol, a sulfur accelerator, and a metal oxide.

Comparison of chemical activity and cure data from various polyols suggested the curing mechanism involves the initial formation of a bis-sulfonate ester network. Subsequent reactions of the ester result in a final combination of metal sulfonate and ester crosslinks.

In Table I are listed representative poly- and monofunctional alcohols which were tested for curing activity at equivalent hydroxyl concentrations and at about twice the hydroxyl concentration required for stoichiometric reaction with the sulfonyl chloride groups present. The metal oxide concentration used was approximately 10% in excess of the theoretical amount needed to form salt crosslinks and to neutralize the hydrogen chloride generated from the sulfonyl chloride groups during the cure. In sharp contrast to the control stock which was badly blown, the primary polyols (group I) showed excellent curing activity. Polyols containing principally secondary hydroxyl groups (group II) gave poorly formed vulcanizates, but sorbitol, having two primary and four secondary hydroxyl groups was superior to polyvinyl alcohol. The monofunctional primary alcohols (group III) gave poorly molded vulcanizates, but there was no evidence of blowing, and the state of cure, as measured by compression set, was equivalent to the Group I polyols. The low moduli and tensiles of these stocks (Table I) resulted from the plasticizing effect of the monofunctional alcohols or their reaction products [eq. (8)].

The differences in the behavior of the three groups of alcohols are consistent with a mechanism involving esterification and subsequent metal sulfonate crosslink formation. Ester formation, the initial step of the curing reaction, is represented by eq. (7) for a monohydric alcohol. With polyols, the sulfonate ester in eq. (7) now assumes a crosslinked polyester structure. Thus, the differences in curing activity between group I and II polyols parallel the greater rate of esterification of primary over secondary alcohols.

$$2RSO_2Cl + 2R'OH + MgO \rightarrow 2RSO_2OR' + MgCl_2 + H_2O \qquad (7)$$

$$2RSO_2OR' + Mg^{++}(2Cl^-) \rightarrow (RSO_2O)_2Mg + 2R'Cl \qquad (8)$$

$$RSO_2Cl + H_2O \rightarrow RSO_2OH + HCl \qquad (9)$$

Since sulfonate esters are known to undergo attack by nucleophilic agents[10] at the carbon C atom of the C—O bond, the ultimate formation of magnesium sulfonate crosslinks most likely occurs according to reaction (8).
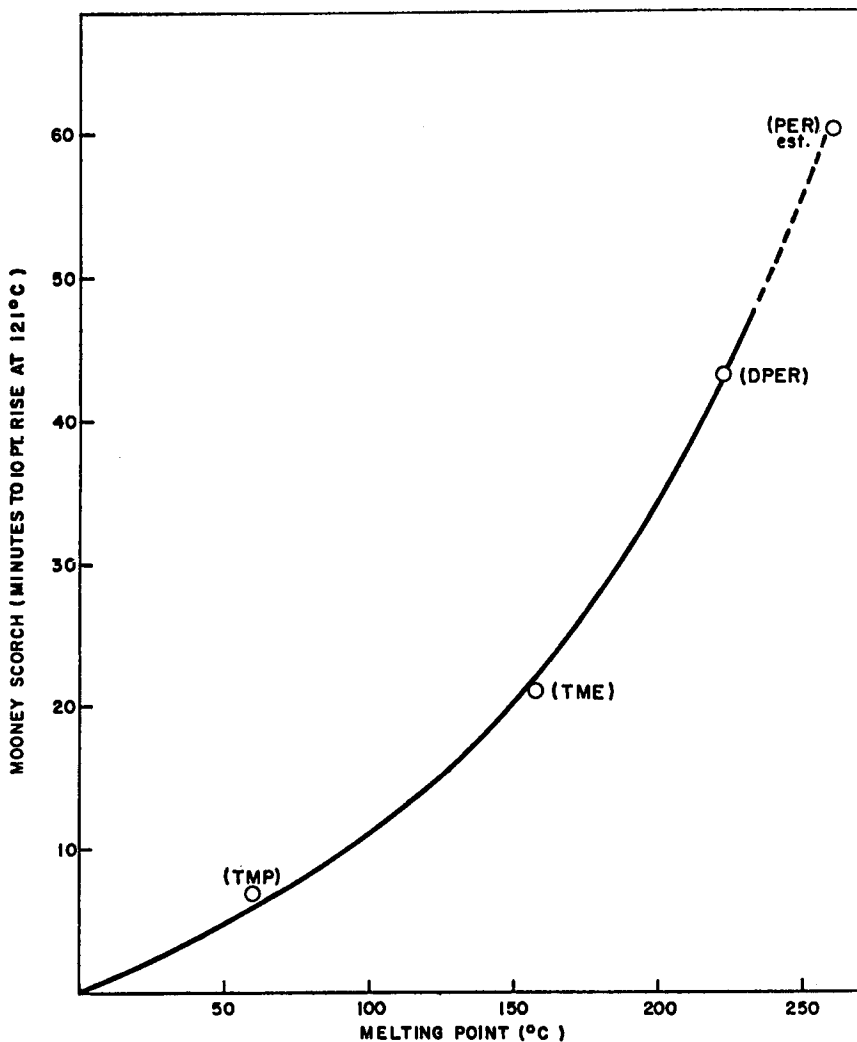
Fig. 1. Mooney scorch as a function of polyol melting point. Compounding formulation: polymer, 100 parts; TiO₂, 63 phr; MgO, 2.0 phr; Tetrone A, 1.5 phr; MBTS, 0.5 phr; polyol OH at 2× SO₂Cl equivalents.

The hydroxyl function thus serves in the role of effecting an efficient utilization of crosslinking sites.

On the basis of the overall reaction, it is apparent why primary monofunctional alcohols (group III) should produce vulcanizates with ultimate physical properties approaching those obtained with the Group I polyols. However, unlike the polyfunctional alcohols, the esterification reaction (7) with monohydric alcohols does not lead to network formation. Stocks thus do not build up back pressure in the mold during this stage of the cure and continue to flow until the second stage of the reaction occurs
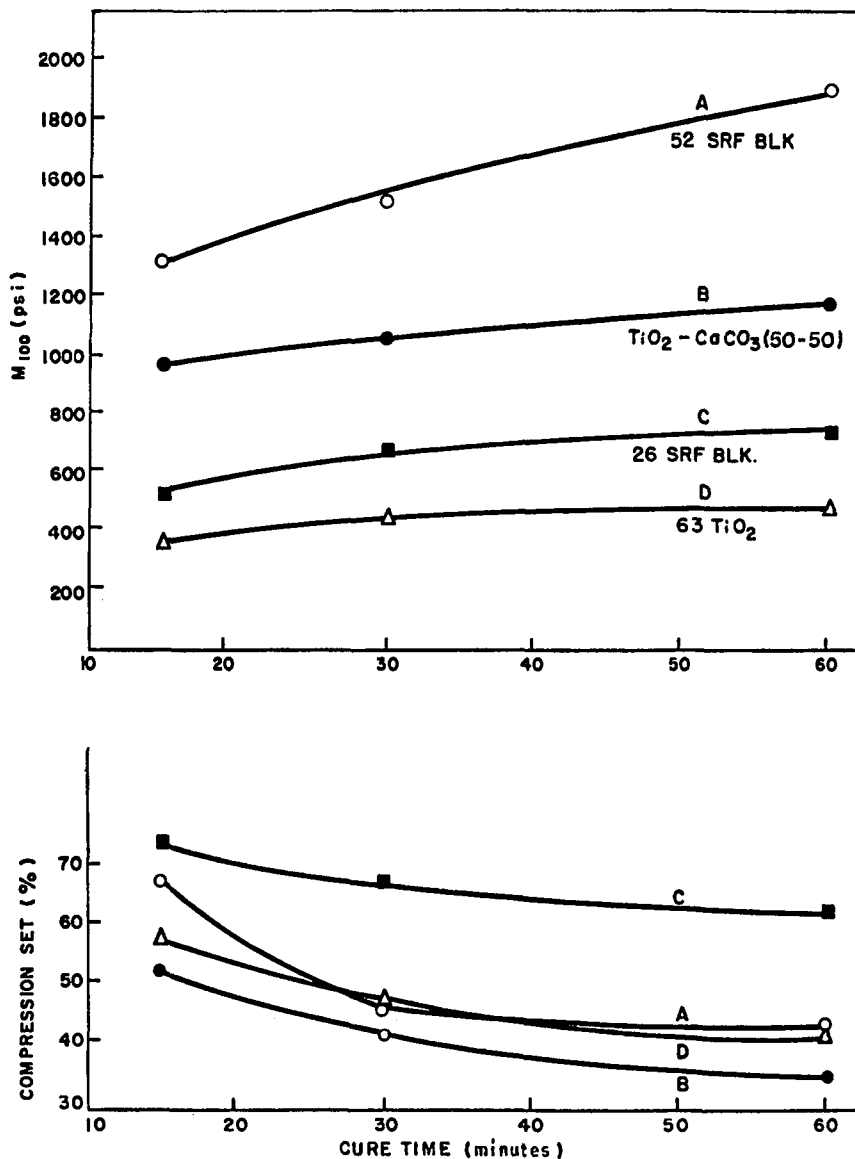
Fig. 2. Modulus and compression set of Hypalon-20 vulcanizates (2 phr MgO + 3.0 phr PER) as a function of cure time.   Accelerator levels: white stocks, 2.0 phr Tetrone A; black stocks, 2.0 phr Tetrone A and 0.5 phr MBTS.   Press-cured at 153°C.

where magnesium sulfonate crosslinks are formed.   The end result, of course, is a poorly molded but nonetheless crosslinked product.

Reaction (9) represents a competing side reaction occurring as a result of water formed in reaction (7).   This leads directly to magnesium sulfonate crosslinks,

TABLE II
Vulcanization of Hypalon Synthetic Rubber with
Magnesia-Pentaerythritol System[a]

| | Filler | |
Properties	Calcium carbonate	Suprex clay
Mooney scorch (121°C.)		
Time to 5 pt. rise, min.	21	28
Time to 10 pt. rise, min.	26	31
Original vulcanizate[b]		
M_{100}, psi	775	1400
M_{300}, psi	1325	1850
T_B, psi	2300	2350
E_B, %	465	430
Hardness, Shore A (25°C.)	72	80
Compression set, %		
22 hr./70°C.	32	41
70 hr./100°C.	77	82
Vol. increase (ASTM No. 3 oil,		
70 hr./100°C.), %	61	60
Vulcanizate aged in Weather-O-Meter (250 hr.)		
Color	White	White
M_{100}, psi	1050	1800
M_{300}, psi	1725	2150
T_B, psi	2200	2200
E_B, %	410	310
Hardness, Shore A (25°C.)	75	82
Vulcanizate aged in Florida sunlight (6 months)		
Color	White	—
M_{100}, psi	450	—
M_{300}, psi	1050	—
T_B, psi	2000	—
E_B, %	420	—
Hardness, Shore A (25°C.)	70	—
Dirt pick-up	Slight	—
Crazing (10× magnification)	None	—

[a] Compounding formulation: Hypalon-40, 100 parts; MgO (Maglite D), 2.0 phr; pentaerythritol, 3.0 phr; dipentamethylenethiuram tetrasulfide (Tetrone A), 2.0 phr; TiO_2 (Ti Pure R-610), 50 phr; Suprex clay or Atomite whiting, 50 phr.
[b] Press-cured 30 min. at 153°C.

The number of ester relative to salt crosslinks in the final vulcanizate network thus is dependent on the rate at which the sulfonate ester is attacked according to reaction (8) as well as the relative rates of esterification and the competing hydrolysis reaction (9).

The polyols of group I provide the best combination of curing activity and vulcanizate physical properties. From a processing standpoint, however, they are not all satisfactory since they exhibit wide differences in Mooney scorch behavior. Comparative data plotted in Figure 1, obtained from titanium dioxide-filled stocks, shows that processing safety as measured by a 10 point increase in Mooney viscosity is directly related to the

polyol melting point.   The faster scorch rates of the lower melting polyols probably result from both their greater mobility and increased solvation of the sulfonyl chloride groups.

For practical compounding formulations pentaerythritol affords the best balance of low cost, processing safety and vulcanizate properties.   The system performs effectively in all Hypalon stocks regardless of the filler medium, and offers a particular advantage in Hypalon formulations designed for white or light colored end products.   Pentaerythritol, magnesium oxide, and accelerator levels can be varied to optimize any desired property,[11] and recommended formulations for black or light colored compounds are readily available.[6]

Cure studies as measured by modulus at 100% elongation and compression set are shown in Figure 2 for a number of Hypalon stocks.   The results demonstrate that an excellent balance of physical properties is obtained from 30 min. cures, while for applications not requiring optimized physical properties 15–20 min. cures offer good overall results.   Table II illustrates the properties obtained from the magnesia–pentaerythritol curing system in a practical white stock formulation containing a basic filler (calcium carbonate) and an acidic filler (Suprex Clay).

Bifunctional Amines and Imines

Bifunctional amines or imines are organic curing systems for chlorosulfonated polyethylene since they combine both crosslinking and acid-accepting capabilities.   However, most of the simple aliphatic and aromatic diamines react too rapidly with sulfonyl chloride groups to be used in solid polymer compounding.   Sterically hindered amines or complexed amines give safe processing stocks but poor states of cure.   These diamines generally give vulcanizates having poor resistance to water swell.

Benzaldimines and cyclohexylketimines, derived from both aliphatic and aromatic diamines, were found to be effective curing agents but they offered no advantage in scorch characteristics or water susceptibility over their parent free amines.
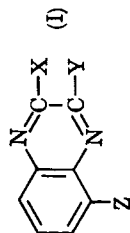
Quinoxalines

Quinoxalines (I) having unhindered alkyl substituents in the 2 and 3 positions, serve as both acid acceptors and delayed action curing agents when used in conjunction with sulfur accelerators.   Crosslinking does not occur even after 45 min. in the Mooney viscometer at 121°C., but excellent vulcanizates are obtained in 30 min. at 153°C. in the presence of sulfur accelerators.   This unusual behavior, in contrast to other amines and imines, prompted a more detailed study of this class of compounds.

Examination of the thirteen quinoxalines shown in Table III demonstrated that the delayed action curing activity is not destroyed when the alkyl substituents in the 2 and 3 positions form part of a six-membered ring (I_D) or when the nitrogens are converted to N-oxides (I_K).   Further, these properties are preserved when the aromatic ring of the quinoxaline

TABLE III. Vulcanization of Chlorosulfonated Polyethylene with Quinoxalines

$$\text{(I)}$$

Vulcanizate no.	Quinoxaline (I)			Prep-aration (lit. ref.)	Relative basicity $-E_{1/2}$, m.v.[b]	Mooney scorch time to 20 pt. rise, (121°C.), min	Vulcanizate properties[a]				
	X	Y	Z				M_{300}, psi	T_B, psi	E_B, %	Comp. set, %	Vol. increase (H$_2$O, 7 days/70°C.) %
A	H	H	H	c	320	>45	150	160	800	97	16.3
B	CH$_3$	CH$_3$	H	c	304	>45	2400	2610	320	41	21.2
C[d]	CH$_3$	CH$_3$	H	c	304	>45	2120	2490	330	39	60.3
D	CH$_2$—(CH$_2$)$_2$—CH$_2$		H	15	377	22	—	2270	230	18	15.9
E	CH$_3$	CH$_3$	CH$_3$	16	423	>45	1500	1810	340	55	—
F	CH$_3$	CH(CH$_3$)$_2$	H	17	384	>45	290	340	460	93	18.9
G	CH$_3$	C$_2$H$_5$	H	18	440	>45	490	600	350	81	13.4
H	CH$_2$CH$_3$	CH$_2$CH$_3$	H	19	390	>45	880	1100	390	91	15.3
I	C$_6$H$_5$	C$_6$H$_5$	H	20	374	>45	No cure				
J	OH	OH	H	21	—	>45	420	500	350	—	16.7
K	2,3-Dimethyl-1,4-dioxide			22	497	>45	1900	2225	400	42	55.8
L	2,3-Dimethyl-5,6,7,8-tetrabromo			23	510	>45	—	2150	150	89	53.6
M	2,3-Dimethyl-6,7-benzo-			24	346	38	—	1620	180	25	13.2
N	2,3-Diphenyl-1,2,3,4-tetrahydro-			20	289	15	2170	2170	300	26	21.9
O	o-Phenylenediamine			c	—	4	—	2550	230	40	28.4

[a] Compounding formulation: Hypalon-20, 100 parts; SRF Black, 35 phr; Sundex 53, 10 phr; Tetrone A, 2 phr; MBTS, 0.75 phr; quinoxaline, equimolar with SO$_2$Cl content of polymer. Press-cured 30 min. at 153°C.

[b] The half-wave neutralization potentials were determined by potentiometric titration of the quinoxaline in acetonitrile with 0.1N HClO$_4$ in dioxane. The more positive $E_{1/2}$ designates a stronger basicity.

[c] Obtained from Eastman Organic Chemicals Dept. and used without further purification.

[d] No rubber accelerators were used in this vulcanizate which was cured for 60 minutes at 153°C.

contains alkyl or halogen groups (I_E and I_L), or is part of a fused benzenoid ring system (I_M). The delayed action curing properties are sacrificed by the reduction of the quinoxaline to an *ortho* diamine (I_N). No correlation was observed between the basicity of the quinoxaline and its curing activity.

Although the curing mechanism is not clearly understood at this time, the established requirement for unhindered alkyl substituents in the 2 and 3 positions must be consistent with any proposed mechanism. The 2,3-dialkylquinoxalines (I), having a hydrogen on the α-carbon, can exist in tautomeric equilibria with their more basic enamine forms (II). This has been established by the ability of such compounds to react with maleic anhydride in the Diels-Alder fashion.[12] The bis-sulfonamide (III) may be the final product, as shown in the mechanism [eq. (10)] below, although aromatization and rearrangement to the more stable bis-sulfone (IV) is more probable.

Evidence that the quinoxaline can vulcanize chlorosulfonated polyethylene in the absence of sulfur accelerators is shown by I_C, where 2,3-dimethylquinoxaline is the sole crosslinking agent. The bis-sulfonamide or bis-sulfone structure is further supported by the failure of quinoxalines to cure when they are devoid of both hydrogen bearing alkyl substituents in the 2 and 3 positions as exemplified by quinoxaline and 2,3-diphenylquinoxaline or 2,3-

(10)
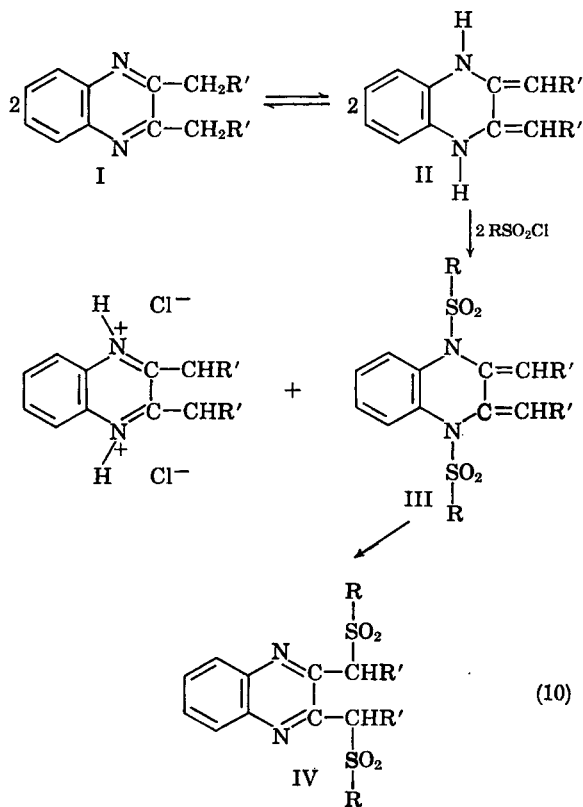
dihydroxyquinoxaline (I_A, I_I, and I_J). The removal of one of these alkyl substituents is sufficient to impair vulcanization as illustrated by the 2-methyl-3-phenyl derivative (I_G).

If one of the alkyl substituents is present as a bulky group such as in 2-methyl-3-isopropylquinoxaline (I_F), again little or no cure results. A Fisher-Taylor-Hirschfelder molecular model shows that spacial limitations just permit the tautomeric conversion of the methyl group into methylene. However, the simultaneous existence of both the methylene and isopropylidene groups is not sterically permissible. The methylene function cannot assume the required planarity due to its steric interaction with the isopropylidene group. Thus it appears that tautomerism of both groups is necessary to achieve vulcanization.

In an alternative mechanism leading to the bis-sulfone structure, the alkyl substituents of the quinoxaline may react in a fashion analogous to that of α-picoline or its oxide with acylating agents.[13,14]
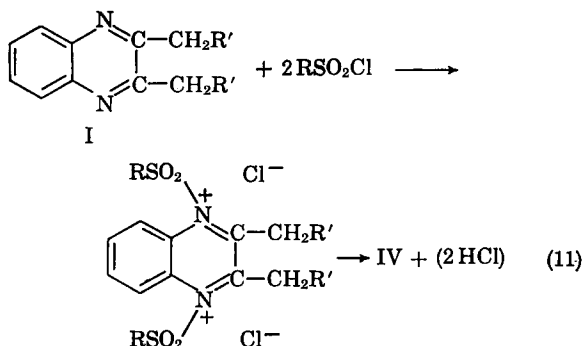
The quinoxalines offer a unique and chemically interesting curing system for chlorosulfonated polyethylenes. However, in practical formulations their sole advantage is their delayed action characteristic. All vulcanizates are subject to moderate water swell, and white stocks tend to develop a gray discoloration during cure.

Aziridines

The availability of ethylenimine has made possible the ready preparation of a number of aziridines which offer a new class of bi- and trifunctional imines (V) exhibiting both acid-accepting and crosslinking properties. Since mineral acids like HCl[25] and carboxylic acid chlorides and sulfonyl chlorides[26] are known to add across the C—N bond of aziridines, the curing reaction proceeds most probably by the route shown in eq. (12):
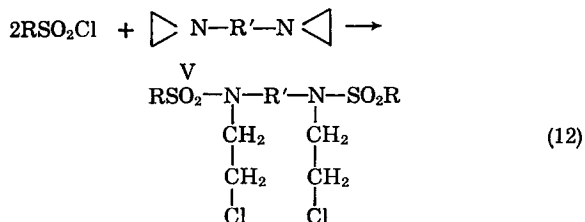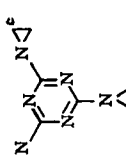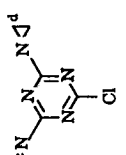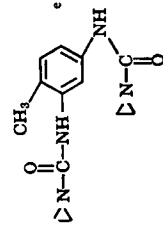
TABLE IV

Vulcanization of Chlorosulfonated Polyethylene with Polyfunctional Aziridines (V)

Vulcanizate no.	Aziridine structure	Amount of aziridine[a]	Mooney scorch time to 10 pt. rise (121°C.), min	Vulcanizate properties[a]			
				M_{300}, psi	T_B, psi	E_B, %	Comp. set, %
A		S	<2	790	1840[b]	400	80
B		S	7	—	—	—	—
C		S 2S	40 —	670 530	1470 680	900 430	76 63
D		S 2S	8 8		No cure No cure		

E	S	7	260	600	500	—
	2S	3	590	700	340	—
F	S	13	300	350	350	59
	2S	3	600	700	350	44
G	S	42	140	990	660	60
	2S	28	180	1860	690	58
H	S	7	300	1710	500	39
	2S	3	430	2600	480	47
I	S	8	220	610	610	66
	2S	7	240	750	600	65

Structures:

E: (⊳N)₃PO[f]

F: (⊳N)₂PO—⟨C₆H₅⟩[c]

G: (⊳N)₂PO—CH₂Cl[e]

H: (⊳N)₃PO[f] (CH₃ substituent)

I: (CH₃⊲CH₃)N₃PO[f]

[a] Compounding formulation: Hypalon-20, 100. Polyfunctional aziridine, S represents the stoichiometric quantity of imine function which is equimolar with the sulfonyl chloride content of the polymer. 2S represents twice the stoichiometric quantity of imine. Press-cured 30 min. at 153°C.

[b] Press-cured 30 min. at 100°C.

[c] Prepared according to the method of Wystrach et al.[28]

[d] Prepared according to the method of Schaefer, et al.[29]
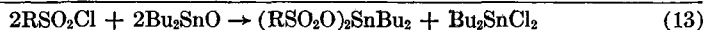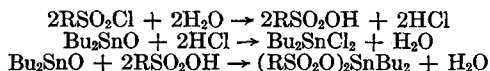
[e] Preparation given in experimental section.

[f] Obtained from Interchemical Corp. and used without further purification.

The curing activity of a number of these compounds is shown in Table IV, where the Mooney scorch can be taken as a measure of crosslinking rate. It is obvious that most of these compounds react too rapidly to be useful on a practical basis with solid rubber compounding techniques. However, it is of interest to note that the strongly electron attracting groups such as $P \rightarrow O$ deactivate the aziridinyl group, and that this effect is markedly increased when additional electron withdrawing groups are present as in V_F and V_G.

These groups decrease the basicity of the aziridinyl nitrogen rendering nucleophilic replacement on the sulfur atom more difficult. A similar inductive effect has been reported for nucleophilic displacement on carbon in the preparation of aziridinylpyrimidines.[27]

Organotin Oxides

The organotin oxides represent another class of compounds serving as both acid acceptors and crosslinking agents. The mechanism by which they operate resembles that proposed for bivalent metal oxides:[1]

$$2RSO_2Cl + 2H_2O \rightarrow 2RSO_2OH + 2HCl$$
$$Bu_2SnO + 2HCl \rightarrow Bu_2SnCl_2 + H_2O$$
$$Bu_2SnO + 2RSO_2OH \rightarrow (RSO_2O)_2SnBu_2 + H_2O$$

$$2RSO_2Cl + 2Bu_2SnO \rightarrow (RSO_2O)_2SnBu_2 + Bu_2SnCl_2 \qquad (13)$$

This reaction sequence was substantiated by a model experiment in which n-$BuSO_2Cl$ was allowed to react with n-Bu_2SnO. The highly characteristic odor of n-Bu_2SnCl_2 was detected, and $(BuSO_2O)_2SnBu_2$ was identified as one of the products.

When curing chlorosulfonated polyethylene with these agents, it is again desirable to have the usual rubber accelerators present in the composition. The data shown in Table V are representative of the properties obtained

TABLE V
Vulcanization of Chlorosulfonated Polyethylene with Organotin Oxides

	Curing agent[a]		
	(n-Bu)$_2$SnO	(n-C$_8$H$_{17}$)$_2$SnO	Ph$_2$SnO
Mooney scorch, time to 20 pt. rise (121°C.), min.	13	25	>45
Vulcanizate properties[b]			
M_{100}, psi	270	185	170
T_B, psi	2220	1550	300
E_B, %	280	380	690
Compression set, %	36	50	48
Vol. increase (H$_2$O, 7 days/70°C.), %	5.7	9.3	6.5

[a] Obtained from Metal and Thermit Corp.

[b] Compounding formulation: Hypalon-20, 100 parts; SRF Black, 35 phr; Sundex 53, 2 phr; Tetrone A, 2 phr; MBTS, 0.5 phr; curing agent, equimolar with the SO$_2$Cl content of the polymer; press-cured 30 min. at 153°C.

in practical curing formulations. The curing activity of the organotin oxides decreases as the electronegativity of the hydrocarbon substituent increases giving a less basic oxide. Thus, curing efficiency is in the order of $(n\text{-Bu})_2\text{SnO} > (n\text{-C}_8\text{H}_{12})_2\text{SnO} > (\text{C}_6\text{H}_5)_2\text{SnO}$.

The organotin oxide curing system offers no advantage over presently recommended curing systems for black stocks. Although not shown, good white stocks, using TiO_2 as the filler, can be obtained which offer better resistance to water swell than straight magnesia–TiO_2 stocks, but poorer water swell than stocks using epoxy resins as the curatives. The organotin oxide vulcanizates, however, have poor heat aging properties. This deficiency was somewhat surprising since such agents are known thermal stabilizers for polyvinyl chloride.

EXPERIMENTAL

Compounding. Stocks were mixed on a conventional rubber mill, standard Hypalon mixing procedures[3b] being used.

Test Procedures. Compression set was determined by ASTM D-395–55, Method B (22 hr. at 158°F.). Tensile tests following ASTM D-412–51T on dumbbells, die C, with an Instron tensile tester, Floor Model TT-C, were carried out with 10,000 lb. load. The tester was operated at head and chart speed of 10 in./min.; tests were at 75°F. unless otherwise designated. Evaluated were 100 and 300% modulus (M_{100} and M_{300}, respectively), tensile to break (T_B), and elongation to break (E_B).

Resilience (ASTM D-945-55) was measured with a Yerzley oscillograph. Shore hardness was determined according to ASTM D-676-55T, with a Shore Durometer, Type A.

To determine Mooney scorch, ASTM D-1077-55T was followed, a Mooney viscometer, large rotor, being used. The scorch value is given in minutes to listed point rise above the minimum reading.

Weathering tests followed ASTM D-750-55T, Tentative Method.

Methylenebis(p-phenyl-N,N-ethylene urea) (V_C). This preparation is based on the method described by Bestian.[26]

A solution of 100 g. (0.40 mole) of methylenebis(p-phenyl isocyanate) in 300 ml. of benzene containing 300 ml. of dry acetone was cooled to 0–5°C. With rapid stirring, a solution of 35.4 g. (0.80 mole) of ethylenimine in 100 ml. of dry acetone was added dropwise at such a rate that the temperature was maintained at 5–10°C. After addition, the mixture was stirred for 1 hr. at 30°C. and filtered with suction. The product filter cake was washed several times with ether and dried in a vacuum desiccator over paraffin shavings. There was obtained 132 g. (98% of theory) of white powder which decomposed at 160–165°C.

ANAL. Calcd. for $C_{19}H_{20}N_4O_4$: C, 67.8%; H, 5.99%; N, 16.7%. Found: C, 67.8%; H, 5.80%; N, 16.8%.

Toluene-2,4-bis(N,N-ethylene urea) (V_D). To 69.6 g. (0.41 mole) of 2,4-toluene diisocyanate in 350 ml. of dry acetone cooled to 0–5°C. was

added with stirring 38 g. (0.884 mole) of ethylenimine in 200 ml. of dry acetone. The mixture was maintained at 0–5°C. during addition and then stirred for 1 hr. longer at that temperature. It was filtered by suction, and the product filter cake was washed several times with ice-cold acetone. There was obtained 95.9 g. (91.5% of theory) of white product which decomposed at 162–165°C.

ANAL. Calcd. for $C_{13}H_{16}N_4O_2$: C, 60.0%; H, 6.20%; N, 21.5%. Found: C, 60.0%; H, 6.20%; N, 21.4%.

Bis(1-aziridinyl)phenylphosphine oxide (V_F). To 23.0 g. (0.535 mole) of ethylenimine and 52.5 g. (0.520 mole) of triethylamine in 300 ml. of benzene was added dropwise a solution of 49.0 g. (0.251 mole) of phenylphosphonyl dichloride in 100 ml. of benzene. The mixture was stirred during the addition and cooled to maintain the temperature at 5°C. When addition was completed, the mixture was stirred for 3 hr. at 5°C. and then filtered by suction. The $Et_3N.HCl$ filter cake was washed with three 30-ml. portions of benzene and the filtrate and wash were combined. The solvent was removed at 20 mm. pressure leaving 50.0 g. (95.8% of theory) of oily product which crystallized upon cooling and melted at 50–51°C.

ANAL. Calcd. for $C_{10}H_{13}N_2OP$: C, 57.7%; H, 6.29%; N, 13.5%. Found: C, 57.0%; H, 6.00%; N, 13.2%.

Bis(1-aziridinyl)chloromethylphosphine oxide (V_G). A solution of 70.0 g. (0.418 mole) of chloromethylphosphonyl dichloride in 100 ml. of benzene was added to 37.0 g. (0.86 mole) of ethylenimine dissolved in 300 ml. of benzene. The addition and product isolation were carried out in the manner described above for V_F. There was obtained 68.1 g. (90.2% of theory) of the product oxide melting at 50–53.5°C.

ANAL. Calcd. for $C_5H_{10}ClN_2PO$: C, 33.3%; H, 5.54%; N, 15.5%. Found: C, 32.9%; H, 5.50%; N, 15.0%.

$(C_4H_4SO_2O)_2Sn(C_4H_9)_2$. A mixture of $(n\text{-Bu})_2SnO$ (24.9 g., $0.1M$), butane-1-sulfonyl chloride (15.7 g., $0.1M$), water (0.1 ml.) and 25 ml. of benzene was refluxed for 18 hr. The hot mixture was filtered to remove the flocculent white precipitate which had separated. It was purified by stirring in hot benzene, filtered hot, and dried at 50°C. and 100 mm. Hg. There was obtained 14.8 g. (59% of theory) of white powder melting at 273–275°C. (uncorr.) with decomposition.

ANAL. Calcd. for $C_{16}H_{36}O_6S_2Sn$: C, 37.90%; H, 7.16%. Found: C, 37.9%; H, 7.00%.

Its infrared spectrum (Nujol mull) showed bands at 1415 cm.$^{-1}$ and doublet at 1750 and 1900 cm.$^{-1}$ characteristic of covalent sulfonates.[30] Monosulfonates of the type R_3SnO_3SR have been reported.[31]

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Résumé

On a étudié les alcools polyfonctionnels, des imines cycliques, acycliques et hétérocycliques, et des oxydes organostanniques comme agents de ramification pour des polyéthylènes chlorosulfonés. On a proposé des mécanismes pour les réactions de ramification impliquant des groupes chlorures de sulfonyle. Des différences dans l'activité vulcanisante sont en corrélation avec les modifications cristallines des agents vulcanisants consistant avec des réactions chimiques classiques pour des systèmes non-polymériques.

Parmi les systèmes vulcanisants examinés, les polyols fournissent des produits non toxiques, peu couteux, de technique sure et offrant d'excellentes propriétés physiques qui trouvent un emploi dans des applications commerciales pratiques.

Zusammenfassung

Polyfunktionelle Alkohole, acyklische, cyklische und heterocyklische Imine sowie Organo-Zinnoxyde wurden als Vernetzungsmittel für chlorsulfoniertes Polyäthylen untersucht. Ein Vernetzungsmechanismus unter Beteilung der Sulfonylchloridgruppe wurde aufgestellt. Unterschiede in der Vernetzungswirksamkeit wurden zu den Strukturänderungen des Vernetzungsmittels in Übereinstimmung mit den klassischen Reaktionen nichtpolymerer Systeme in Beziehung gebracht. Von den untersuchten Vernetzersystemen liefern die Polyole nichtgiftige, billige und sichere Verfahrensmöglichkeiten mit ausgezeichneten physikalischen Eigenschaften, die für die praktische technische Verwendung herangezogen wurden.