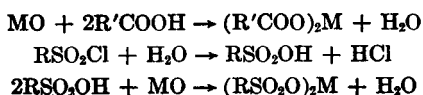# Ionic Crosslinking of Chlorosulfonated Polyethylenes

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It has long been assumed[1] that the primary mode of crosslinking in curing of elastomeric chlorosulfonated polyethylenes such as Hypalon synthetic rubber (registered trademark for du Pont's synthetic rubbers) is the formation of metal sulfonate bridges by a sequence of reactions such as the following:

$$MO + 2R'COOH \rightarrow (R'COO)_2M + H_2O$$
$$RSO_2Cl + H_2O \rightarrow RSO_2OH + HCl$$
$$2RSO_2OH + MO \rightarrow (RSO_2O)_2M + H_2O$$

where MO is the oxide of a bivalent metal, usually lead or magnesium; R'COOH is an organic acid, often rosin or a derivative; and R represents the polymer chain. Thus, four mole equivalents of metal oxide are formally required for each crosslink formed, two for formation of water, one for neutralization of HCl, and one for sulfonate formation. This idealized mechanism does not take into account inefficiency due to mixed salt formation between sulfonic and carboxylic acids, to any recycling of water formed in HCl neutralization and sulfonate formation, or, most importantly, to structural changes due to decomposition of the sulfonyl chloride structure at curing temperatures. Nevertheless, it probably represents a fair approximation of the basic mechanism of Hypalon cures.

In actual practice, it has always been found that useful cures can be achieved only in systems that include sulfur-containing curing agents, the one most often used being dipentamethylene thiuram tetrasulfide (Tetrone A, registered trademark for du Pont's rubber accelerator). The mechanism of action of a sulfur curing agent on chlorosulfonated polyethylenes has never been determined, although it is reasonable to assume that chain unsaturation resulting from thermal or free-radical degradation of sulfonyl chloride and perhaps tertiary chloride structures acts as a site for sulfur crosslinking.

In certain end uses, for example, wire insulation applied directly over bare copper, the presence of sulfur compounds is undesirable because adhesion to the copper results from the copper-sulfur interaction. Also, the excellent water resistance of compounds of Hypalon chlorosulfonated polyethylene that can be achieved with litharge-containing stocks has been unavailable in white and light-colored articles because of the interaction of lead and sulfur compounds to form black lead sulfide. For these reasons, a

study of sulfur-free curing systems for chlorosulfonated polyethylenes was
undertaken.

RESULTS AND DISCUSSION

Re-examination of the curing behavior of chlorosulfonated polyethylenes
has resulted in the discovery that excellent cures can be achieved with metal
oxides or hydroxides and organic acids in the absence of any other agent
except small concentrations of any one of a wide variety of compounds
known to inhibit free-radical reactions. Typical compounds found to be
active are listed in Table I and include nitrosoamines, nitrosohydroxyl-

TABLE I
Free-Radical Scavengers Found Active in Ionic Crosslinking of Chlorosulfonated
Polyethylene

Sodium nitrite
N,N'-Dinitrosopiperazine
N-Nitrosophenylhydroxylamine, ammonium salt (Cupferron)
N-Nitrosophenylhydroxylamine, lead salt
N-Nitrosophenylhydroxylamine, calcium salt
p-Nitrosophenol
1-Nitroso-2-naphthol
Dibenzoyl quinone dioxime
N,p-Dinitrosomethylaniline
Octene nitrosate
Cyclohexene nitrosate
m-Dinitrobenzene
2,4-Dinitrotoluene
Diphenylpicryl hydrazine
Diphenylpicryl hydrazyl
Methylene-4,4'-bis(2,6-ditertiarybutylphenol)
Galvinoxyl (2,6-Di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadiene-1-
     ylidene)-p-tolyloxy)[2]

amines, alkylene nitrosates, inorganic nitrites, hindered phenols, aromatic
nitro compounds, and certain stable free radicals.
It is our hypothesis that these free-radical scavengers intercept free-
radical chain reactions that would otherwise lead to extensive decomposition
of sulfonyl chloride groups, thus allowing efficient reaction of the latter with
metal ions. In the absence of free-radical scavengers, the same compounds
give no cure and show severe blowing due to evolution of acid gases at nor-
mal curing temperatures, i.e., 150–160°C. These scavengers are effective
in such low concentrations, e.g., at 100 ppm in the case of dinitrobenzene,
that it is clear that curing must be exclusively by formation of metal sul-
fonate crosslinks, i.e., by the idealized mechanism mentioned above.
Details of behavior of this kind of curing system are discussed in the follow-
ing sections.

TABLE II

Effect of Free-Radical Scavenger Type and Concentration on Tensile Properties of Vulcanizates of Hypalon-40[a]

Scavenger	Amt. scavenger phr	M_{100}, psi	M_{300}, psi	T_B, psi	E_B, %	Perm. set, %	Mooney scorch time, 10 pt. rise, min
Sodium nitrite	0.25	560	1870	4080	540	29	8
p-Nitrosophenol	0.25	430	1450	3550	570	41	5½
m-Dinitrobenzene	1.0	440	1620	3800	560	25	4½
"	0.1	520	1720	4130	560	26	6½
"	0.05	510	1670	3880	550	28	10
"	0.01	430	1410	3700	600	34	8
2,4-Dinitrotoluene	0.1	500	1910	4260	550	25	7
Octene nitrosate	0.25	460	1620	3620	530	25	7
Cupferron	0.1	540	2160	4580	510	25	12
Lead N-nitrosophenylhydroxylamine	0.4	780	2450	3820	440	23	8
"	0.1	600	1970	4010	520	28	7
Diphenylpicryl hydrazyl	0.5	460	1600	3640	560	29	7
Antioxidant 702[b]	0.5	420	1440	3830	570	30	—
Galvinoxyl	0.5	530	1760	4070	540	26	—

[a] Stock: 100 parts Hypalon-40, 50 phr TiO₂, 25 phr PbO, 2.5 phr Staybelite resin; cure: 30 min. at 153°C.
[b] Methylene-4,4'-bis(2,6-di-tert-butylphenol).

General Characteristics

Cures of chlorosulfonated polyethylenes based on this free radical scavenger technique show a number of characteristics that must be recognized to make effective use of this technology.

(1) Cures are independent of the nature of the free-radical scavenger used. Properties of vulcanizates and cure rate show little or no relation to the type of agent employed so long as it is an effective free radical scavenger. This is illustrated in Table II, in which 100 and 300% modulus (M_{100} and M_{300}, respectively), tensile at break (T_B), elongation at break (E_B), permanent set, and Mooney scorch time are shown.

(2) Cures are independent of concentration of free-radical scavenger so long as an adequate minimum concentration is employed. This is also illustrated in Table II, where it can be seen that some loss in tensile properties results if concentration of dinitrobenzene is reduced to 0.01 phr. This represents about one mole equivalent of dinitrobenzene per 500 sulfonyl chloride groups. On the other hand, increase in concentration made no change in cure rate or vulcanizate properties. For most agents, a concentration of 0.1–0.2 phr was found adequate.

(3) Cure rates and scorch times are a function only of the characteristics and concentration of the polymer, metal oxide, and organic acid used. A given chlorosulfonated polyethylene with constant levels of metal oxide and organic acid shows a substantially longer scorch time in an extended stock than in a lightly loaded compound. This appears to be largely a mass action effect. Hypalon-40, for example, which contains 1% sulfur as sulfonyl chloride, with 25 phr of sublimed litharge and 3–4 phr of rosin acid usually shows a time to 10 point rise in Mooney viscosity at 250°F. of 7–10 min. in a lightly loaded stock, while in a highly extended stock the same system will show a 15–20 min. scorch time. Scorch times can also be lengthened by the lubricating action of added plasticizer, where use conditions of the vulcanizate allow this.

Choice of Metal Oxide

The best all-around properties in this type of cure are achieved with litharge. For applications where the use of lead compositions is objectionable, it has been found that the hydroxides of the alkaline earth metals also give good vulcanizates. In some cases it is found best to cure these at slightly higher temperatures. Magnesium oxide stocks did not give adequate cures in free radical scavenger systems, while the corresponding hydroxide gave good cures. Typical results comparing litharge, magnesium hydroxide, and slaked lime are shown in Table III. As would be expected, water absorption is high in the magnesium hydroxide compound and low in the litharge compound.

Choice of Organic Acid

Of many acids tested in this type of cure, only the rosin acids were found practical. In fact, of all the acids tried, only the rosin acids and some

fatty acids gave any cure at all, as shown in Table IV. Scorch times were impractically short with the fatty acids. The hydrogenated or dimerized rosin acids are therefore preferred for this type of cure.

TABLE III

Dependence of Vulcanizate Properties on Metal Oxide or Hydroxide Used in Ionic Crosslinking of Hypalon-40[a]

	A	B	C
Metal oxide			
Sublimed litharge	25	—	—
Mg(OH)$_2$, N.F.	—	8	—
Slaked lime, commercial[b]	—	—	5
Properties			
M_{100}, psi	540	550	350
M_{300}, psi	2160	1460	1150
T_B, psi	4580	4120	4080
E_B, %	510	580	610
Permanent set, %	25	35	41
Volume swell, 7 days/70°C. H$_2$O, %	0.6	26	27
Yerzley resilience (25°C.), %	66	60	66
Shore A hardness (25°C.)	70	68	65
Compression set (22 hr./70°C.), %	80	72	75

[a] Stock: 100 parts Hypalon-40, 50 phr TiO$_2$, 2.5–5.0 phr Staybelite resin, 0.1–0.5 phr free radical scavenger; cure: 30 min. at 153°C.

[b] Mixture of calcium and magnesium hydroxides (Warner Co., Philadelphia, Pa.).

TABLE IV

Effectiveness of Various Organic Acids in Ionic Crosslinking of Hypalon-40[a]

Acid	100% Modulus, psi	Mooney scorch time, 10 pt. rise (250°F.), min.
Hydrogenated rosin (Staybelite)	500	7–10
Refined hydrogenated rosin (Foral)	800	13
Partially dimerized rosin (Polypale)	600	10–12
Stearic	800	2
Tall oil fatty acid (Acintol FA2)	700	1
Oleic	Poor cure	—
Lauric	Poor cure	—
Docosanoic	Poor cure	—
Benzoic	No cure	
Adipic	"	—
Suberic	"	—
Maleic	"	—
Phthalic	"	—
Chlorendic	"	—
Citric	"	—
Salicylic	"	—

[a] Stock: 100 parts Hypalon-40, 50 phr TiO$_2$, 25 phr PbO, 0.2 phr free-radical scavenger; cure: 30 min. at 153°C.

Effect of Loading

Because these ionic cures depend on the interaction of polymer with inorganic oxides, the mass action effect of dilution by inert fillers is perhaps more pronounced in this kind of cure than with those involving organic

TABLE V

Dependence of Vulcanizate Properties on Loading in Ionic Crosslinking of Hypalon-40[a]

	A	B	C	D	E	F
Filler						
Sublimed litharge, phr	20	25	25	—	—	—
Mg(OH)$_2$, phr	—	—	—	8	8	10
TiO$_2$, phr	—	50	25	—	50	25
Hard clay, phr	—	—	75	—	—	75
Dioctyl phthalate, phr	—	—	15	—	—	15
Properties						
M_{100}, psi	210	780	1610	190	400	1240
M_{300}, psi	720	2120	—	370	1540	1660
T_B, psi	5030	4450	2110	3240	3640	1660
E_B, %	540	440	250	710	590	330
Permanent set, %	16	22	18	36	32	32
Volume swell (7 days/70°C. H$_2$O), %	1.3	0.7	3.1	63	48	88
Yerzley resilience (25°C.), %	66	68	—	62	63	—
Shore A hardness	56	72	—	56	66	—
Compression set (22 hr./ 70°C.), %	90	75	—	80	68	—

[a] Stock: 100 parts Hypalon-40, 0.2–1.0 phr free-radical scavenger, 2.5–6.5 phr Staybelite resin; cure: 30 min. at 153°C.

TABLE VI

Effect of Nature of Filler on Vulcanizate Properties of Ionically Crosslinked Hypalon-40[a]

	A	B	C	D
Filler				
Litharge	25	25	—	—
Mg(OH)$_2$	—	—	10	10
Whiting	50	—	50	—
Hard clay	—	50	—	50
Properties				
M_{100}, psi	1280	2580	710	1460
M_{300}, psi	2040	—	1120	1940
T_B, psi	2770	3000	2490	2160
E_B, %	390	240	570	430
Permanent set, %	19	13	43	41
Volume swell (7 days/70°C. H$_2$O), %	14	1.0	39	29

[a] Stock: 100 parts Hypalon-40, 35 phr TiO$_2$, 0.2 phr free-radical scavenger, 4–5 phr Staybelite resin; cure: 30 min. at 153°C.

agents that can more readily migrate through the stock at curing temperatures. The range of tensile properties from gum stocks through highly loaded stocks is illustrated in Table V. Tensile properties fall off markedly at loadings over about 100 pphr.

The differences in stress–strain properties that result from changes in the nature of fillers are illustrated in Table VI. Vulcanizates with low moduli and high elongations result when a natural whiting is used, while hard clay at the same level gives high modulus, low elongation stocks. Clay also gives vulcanizates with much better water resistance. The high surface area silicas seem to interfere with this type of cure, perhaps by some adsorptive action on the free-radical scavenger.

CONCLUSIONS

A new and simple technique for curing chlorosulfonated polyethylene elastomers has been found that offers an economical means of making white and light-colored vulcanizates that do not contain sulfur compounds. This kind of stock can therefore be used directly in contact with bare copper, as in wire coverings, or with lead, as in lead press cures of hose and cables. In applications where the presence of litharge is acceptable, excellent water resistance can be developed. Aging characteristics of vulcanizates are generally comparable to those employing other curing systems, although extensive data are not now available. Because crosslinking is achieved entirely through electrostatic bonding of ion pairs, compression set values of these compounds are high, and this should be recognized in considering the applicability of this technique.

References

1. Smook, M. A., J. D. Roche, W. B. Clark, and O. G. Youngquist, *India Rubber World*, **128,** 54 (1953).
2. Bartlett, P. D., and T. Funahashi, *J. Am. Chem. Soc.*, **84,** 2596 (1962).

Synopsis

It is shown that chlorosulfonated polyethylenes heated with divalent metal oxides or hydroxides and rosin acids in the presence of trace amounts of free-radical scavengers crosslink exclusively by formation of metal–sulfonate bonds. Vulcanizate properties are independent of the nature and concentration of free-radical scavenger, and it is suggested that these agents prevent decomposition of the sulfonyl chloride crosslinking sites, thus allowing efficient reaction with the salt-forming components of the system. This technique allows the curing of chlorosulfonated polyethylenes in direct contact with copper and lead without development of the adhesion or discoloration usually encountered in sulfur-containing systems.

Résumé

On a montré que des polyéthylènes chlorosulfonés chauffés avec des oxydes ou hydroxydes de métaux divalents et des acides de colophane forment des ponts en présence de traces de capteurs de radicaux libres et ce exclusivement par la formation de liaisons métal–sulfonates. Les propriétés de vulcanisation sont indépendantes de la nature et de la concentration du capteur de radicaux libres et on a suggéré que ces agents empêchent

la décomposition du chlorure de sulfonyle formant des sites permettant ainsi une réaction efficace avec les composants du système formant du sel. Cette technique permet la vulcanisation de polyéthylènes chlorosulfonés en contact direct avec du cuivre et le plomb sans entrainer une adhésion ou décoloration habituellement encourue dans des systèmes contenant du soufre.

Zusammenfassung

Chlorsulfoniertes Polyäthylen wird beim Erhitzen mit Oxyden oder Hydroxyden zweiwertiger Metalle und Harzsäuren in Gegenwart von Spurenmengen von Abfängern für freie Radikale ausschliesslich durch Bildung von Metallsulfonatbindungen vernetzt. Die Eigenschaften des Vulkanisates sind von der Natur und Konzentration der Radikalabfänger unabhängig und es wird angenommen, dass diese Stoffe den Zerfall der Sulfonylchloride-Vernetzungstellen verhindern und so eine wirksame Reaktion mit den salzbildenden Komponenten des Systems ermöglichen. Diese Methode erlaubt eine Vernetzung von chlorsulfoniertem Polyäthylen in direktem Kontakt mit Kupfer und Blei, ohne Adhäsions- oder Verfärbungserscheinungen, wie sie gewöhnlich in schwefelhältigen Systemen auftreten.